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**SPECTROSCOPIC AND STRUCTURAL STUDIES OF ORGANOTIN(IV)
CARBOXYLATES AND 1:1 CHLORIDE COMPLEXES**

The University of Oklahoma

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THE UNIVERSITY OF OKLAHOMA
GRADUATE COLLEGE

SPECTROSCOPIC AND STRUCTURAL STUDIES OF ORGANOTIN(IV)
CARBOXYLATES AND 1:1 CHLORIDE COMPLEXES

A DISSERTATION
SUBMITTED TO THE GRADUATE FACULTY
in partial fulfillment of the requirements for the
degree of
DOCTOR OF PHILOSOPHY

SEIK WENG NG

Norman, Oklahoma

May 1983

SPECTROSCOPIC AND STRUCTURAL STUDIES OF ORGANOTIN(IV)
CARBOXYLATES AND 1:1 CHLORIDE COMPLEXES

A DISSERTATION

APPROVED FOR THE DEPARTMENT OF CHEMISTRY

By

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ACKNOWLEDGEMENTS

In the spring of 1980, Professor J.J. Zuckerman invited me to work with him for my doctorate. This dissertation is the result of our inquiries into a selected area of organotin chemistry, and it is my very pleasant duty to thank Professor Zuckerman for his guidance and encouragement in the preparation of this manuscript. Through him, I have been a little better able to understand the philosophy of the inexact science that is known as chemistry. The discussions with his post-doctoral research associates, Drs. M.P. Bigwood, R.E. Karl, K.C. Molloy and E.R. Whipple had been enjoyable, and their assistance is also much appreciated. My gratitude extends to my fellow doctoral candidates, Mr. T.S. Dory and F.A.K. Nasser for technical assistance in the laboratory.

The X-ray crystallography course taught by Professor D. van der Helm was a fascinating experience and part of the second half of the dissertation is the collaborative effort with him and his able post-doctoral research associates on the solution of crystal structures. It is my pleasure to thank Professor van der Helm, Drs. C.L. Barnes, M.B. Hossain and D.R. Powell for much needed assistance in the structural determinations. I am also grateful to Professor A.L. Rheingold of the University of Delaware, Newark, for solution of the latter crystal

structures.

I thank Professors H.B. Abrahamson, N. Fogel, V. Litovchenko, D.F. Marten and Dr. D.L. Tomaja for serving on my dissertation committee. The technical assistance of Dr. M. Magerstädt of the Technical University of Berlin, Germany, is acknowledged. Special thanks are due to S.B. Martin for her time in typing the manuscript. The University of Oklahoma is thanked for providing computer time and the Department of Chemistry, University of Oklahoma, for permission to use the facilities in the department. I thank the Office of Naval Research, the National Science Foundation, the North Atlantic Treaty Organization and the Oklahoma Mining and Mineral Resources Institute for funding the project, and the Fulbright Commission for the award of a travel grant for me to pursue my studies in the United States of America.

A PREFACE TO THE STRUCTURAL STUDIES OF THE
1:1 ORGANOTIN(IV) CHLORIDE COMPLEXES WITH OXYGEN DONOR LIGANDS

The second section of the dissertation deals with the X-ray crystal and molecular structures of the 1:1 organotin(IV) chloride complexes with oxygen donor ligands. The initial idea for this series of investigations originated with my M.Sc. work with Professor V.G. Kumar Das of the University of Malaya, Kuala Lumpur, Malaysia, and it arose from our studies of complexes of organotin(IV) chlorides. The product isolated from the reaction of dimethyltin(IV) dichloride with diphenylcyclopropanone has a 1:1 stoichiometry. The formation of a 1:1 adduct was ascribed to the fact that the ligand was a weak base toward tin; the tin in the adduct would not be a sufficiently strong Lewis acid to complex another mole of the base. At the time of the report (1978), only one other 1:1 adduct had been structurally characterized. The Mössbauer partial quadrupole splitting of the complex with diphenylcyclopropanone suggested a trigonal bipyramidal geometry for the tin, with the oxygen atom of the ligand and one of the chloride atoms at the apical positions. A similar geometry was said to be adopted by the known salicylaldehyde complex.

In the spring of 1981, Professor van der Helm offered a course on X-ray crystallography. Data on $(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{O}=\text{CC}_2(\text{C}_6\text{H}_5)_2$ were collected by his post-doctoral research associates, Drs. C.L. Barnes and M.B.

Hossain, both of whom guided me in the actual solution of the crystal structure in a sort of an on-the-job training. Owing to my inexperience, unfortunately, the bridging Sn...Cl distance in the complex was not noticed, and after discussions with Professor van der Helm, Drs. Barnes and Hossain and Professor Zuckerman, a paper was prepared by us for publication. The structure would have had been the second structural report in the literature of a monomeric 1:1 R_2SnX_2 adduct.

Professor van der Helm was kind enough to collaborate on another structural investigation on yet another 1:1 complex, $(CH_3)_2SnCl_2 \cdot 2,6-(CH_3)_2C_5H_3NO$, later that year. Data collection was undertaken by Dr. Barnes. Since I had acquired some knowledge on X-ray crystallography, the previous method of solution, i.e., from data reduction to the manual location of peaks in the Patterson map to the building of clay models (the Ahmed method), was dispensed with, and the structure was solved, under Dr. Barnes' guidance, using the SHELX program. This method located an intermolecular Sn...Cl bridge, and the complex turned out to be dimeric. Since this structure and the previous structure was rather similar in many respects, intermolecular distances were looked for again in the diphenylcyclopropanone complex, and sure enough, the bridge was found. Dr. D.R. Powell assisted with some of the computer programs.

Curiously enough, the Mössbauer point-charge approximations that were developed by Bancroft, et. al., only predicts the carbon-tin-carbon angle in diorganotin(IV) compounds, and although the model was developed for six-coordinated compounds, the calculations could also be used for five-coordinated compounds because the contribution to the quadrupole splitting by the ligands is assumed to be zero. The application of this

model to $(C_6H_5)_2SnCl_2 \cdot 2,6-(CH_3)_2C_5H_3NO$ gave a C-Sn-C angle that was rather close to the angle that would be adopted by the two phenyl groups in the equatorial positions of a regular trigonal bipyramid. It was hoped that this C-Sn-C angle would not be opened to accommodate the chlorine atom of a neighboring molecule because of the steric bulk of the aryl groups, as is the case with the dimethyltin(IV) dichloride analogue, and that this complex would be a truly simple 1:1 adduct.

The data collection and the solution of this structure along with the structure of $(CH_3)_3SnCl \cdot 2,6-(CH_3)_2C_5H_3NO$ was undertaken by Professor A.L. Rheingold of the University of Delaware, Newark, Delaware, and was solved by him completely.

This preface therefore acknowledges the collaborators who have helped make the solution of the crystal structures that follow in this dissertation possible.

ABSTRACT

Organotin(IV) carboxylates of the formula $[(C_6H_5)_3P(CH_2)_2CO_2SnR_3]^+ X^-$ where X is a halide or pseudohalide were prepared through the nucleophilic displacement of the anions in R_3SnX compounds by the phosphonobetaine $(C_6H_5)_3P(CH_2)_2CO_2$. Double salts, $[(C_6H_5)_3P(CH_2)_2CO_2SnR_3]^+ [R_3SnX_2]^-$, were obtained by adding R_3SnX to the already formed simple salts. The products are associated materials with triphenylphosphonium cations. The non-ionic phosphinylacetates, $(C_6H_5)_2P(O)CH_2CO_2SnR_3$, were synthesized from the condensation reaction between diphenylphosphinylacetic acid and the organotin(IV) hydroxide or oxide, and they are weakly associated oligomers. The phosphinyl oxygen is coordinated to the tin. The diorganotin(IV) derivatives are six-coordinated, trans-octahedra. In the case of the related sulfinylacetates, $C_6H_5S(O)CH_2CO_2SnR_3$, coordination to the tin takes place through the sulfinyl oxygen when the R group is aliphatic and through the carboxylate oxygen when the R group is aromatic. The much less basic ketonic oxygen in the 2-benzoylbenzoates, $[2-C_6H_5C(O)C_6H_4CO_2]_n SnR_{4-n}$ ($n = 1, 2$), is not involved in coordination. The structures of all these di- and triorganotin(IV) carboxylates were probed by a number of spectroscopic techniques such as NMR, ir, Raman, mass and Mössbauer

spectroscopies. The second half of this dissertation deals with the X-ray crystal and molecular structures of the 1:1 adducts of diorganotin(IV) dichlorides with oxygen donor ligands. The dimethyltin(IV) dichloride complexes with $(C_6H_5)_2C_2C=O$ and $2,6-(CH_3)_2C_5H_3NO$ are dimeric in the solid state with trans-methyl groups. The diphenyltin(IV) dichloride complex with the latter ligand, however, is monomeric in the solid state, and is a structurally characterized example of a monomeric 1:1 R_2SnCl_2 adduct. The magnitudes of the carbon-tin-carbon angles in these diorganotin(IV) systems are found to correlate well with the values predicted by Mössbauer partial quadrupole splitting calculations. The methyl groups occupy the equatorial positions in $(CH_3)_3SnCl \cdot 2,6-(CH_3)_2C_5H_3NO$.

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CHAPTER 1

SOME RECENT DEVELOPMENTS IN THE FIELD OF ORGANOTIN CHEMISTRY

In 1950, the Organic Chemistry Institute, T.N.O., in Utrecht, the Netherlands, began a program of research in organotin chemistry in cooperation with the International Tin Research Council and the Tin Research Institute in London, England. The program called for fundamental research in the organic chemistry of tin. A search for new and novel applications of organotin compounds was also initiated. In their chemical application, organotin compounds find a very wide variety of usefulness and the origin of their versatility in such diverse fields as in fungicides, bacteriocides, insecticides, stabilizers for polyvinyl chloride, wood preservatives and antifouling agents lies in the presence of the tin-carbon bond, their most important feature. The diversity of applications of organotin compounds is probably not surpassed by any other class of organometallic compounds.

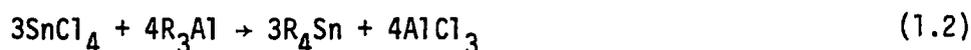
In most of the chemical and biological applications of organotins, only a small amount of the organotins is required to have the desired effect, i.e., the performance-to-weight ratio is extremely high. Furthermore, the organotin compounds are easily biodegradable by atmospheric

agents to essentially non-toxic tin oxide. Thus, it is no surprise that the organotin compounds are widely used as agricultural biocides.

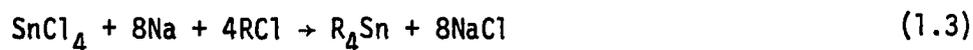
Organotin compounds of the type R_3SnX and R_2SnX_2 where R is an organic residue and X is an anion such as a halide comprise the major portion of the commercial applications of organotin compounds. The $RSnX_3$ compounds are used to a much lesser degree. The tetraorganotin compounds, R_4Sn , are generally not used, but they are the important starting materials in the synthesis of the other organotin derivatives. The classical Grignard reagents are used in the preparation of the tetraorganotins provided the substituents in the organic groups do not interact with the organomagnesium compounds:



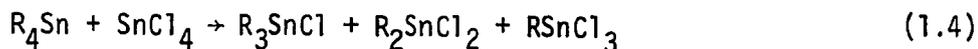
Organoaluminums are also used industrially, and a base is required to absorb the aluminum chloride that is liberated:



The Würtz process is rather inefficient because expensive sodium is lost:



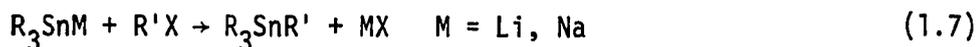
A second, disproportionation reaction, is necessary to convert the tetraorganotins to the desired triorgano-, diorgano- or monoorganotin(IV) chlorides:



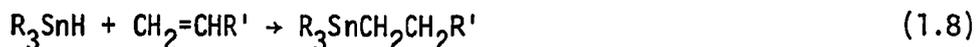
In the laboratory, the tin-carbon bond can be formed by other means. In the direct synthesis method, an alkyl halide oxidatively adds to metallic tin or a tin(II) halide:



The metal in lithium- and sodium-tin compounds can be exchanged for an organic group:



The organotin hydrides are extremely versatile reagents which can add anti-Markovnikov across carbon-carbon double and triple bonds:



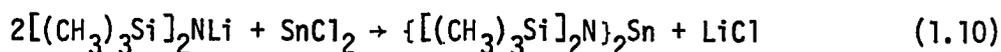
Perhaps the most intriguing synthesis is the Akzo process, to be discussed in a later section, in which transient chlorostannanes are reacted with olefins activated by substituents on the double bond.

Many advances have taken place during the past three decades. It is impossible to discuss these in any degree of depth. Many of the recent developments have already been covered in other reviews. The topics that

follow appear to be the most significant developments this one decade.

The Tin-Tin Double Bond

N,N-Bis(trimethylsilyl)aminotin(II) is a tin(II) derivative which is stable. It is prepared from the lithioamination of tin(II) chloride: 1,2



The red color of this material contrasts with the color of organotin(II) compounds, which are generally not intensely colored.^{3,4} The compound is monomeric in solution⁵ and the N-Sn-N angle as determined by electron diffraction is 96°. ⁶ The isoelectronic compound, $\{[(\text{CH}_3)_3\text{Si}]_2\text{CH}\}_2\text{Sn}$, is brick-red, and it is a dimer with a tin-tin bond distance of 2.764 Å.² This distance is intermediate between the covalent radii of singly and doubly bonded tin (2.60 and 2.80 Å) as predicted by Pauling.⁷ The dimer is thought to be formed by the pairwise overlap of the filled sp_xp_y non-bonding orbital of one monomeric unit with the empty p_z orbital of the other monomeric unit.² Although the CH group is isoelectronic with a nitrogen atom, the lone pair is absent and consequently, the origin of the color of this material cannot arise from the interaction between the electrons on carbon with the empty orbitals on tin. The bond is termed a "bent double bond".² Interestingly, the structure of tetrakis[bis(trimethylsilylmethyl)tin(IV)] is available for comparison. It is a white solid that changes to a dark yellow color on heating, and the change is reversible. The compound is a tetrameric organotin compound with tin-tin single bonds of length 2.834 and 2.839 Å.⁸

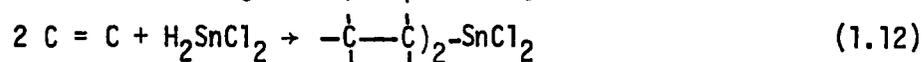
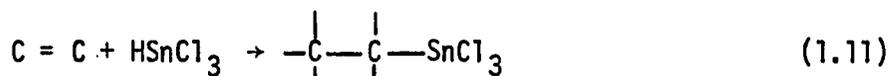
The tin-tin bond in bis[bis(trimethylsilyl)methyltin(II)] should be viewed as a true double bond in light of the recent discovery of the silicon-silicon double bond. Organosilicon chemists have been attempting to synthesize the disilenes for more than sixty years. The bond in tetrakis(mesityl)disilene is 2.17 \AA .^{9,10} The challenge of the germanium-germanium double bond is waiting to be taken up, and this type of bond is shown by spectroscopic means to be present in tetrakis(dimethylphenyl)-digermene.¹¹ Both this compound and the silicon analogue, tetrakis(2,6-dimethylphenyl)disilene, could be prepared from the hexakis(2,6-dimethylphenyl)cyclotrisilane and -germane.^{11,12} The doubly bonded organometallic derivatives of the Group IVb elements also await the synthesis of the corresponding cyclotriplumbane to complete the series of Group IVb metal-metal double bonds.

The Elusive Chlorostannanes, HSnCl_3 and H_2SnCl_2

Organotin(IV) hydrides are versatile reagents which form part of the fundamental chemistry that was developed in Utrecht. Tin-carbon bonds are formed by the reaction of the organotin hydrides R_3SnH and R_2SnH_2 with double or triple bonds, and the addition is commonly referred to as the hydrostannation reaction. This theme has been discussed in an excellent review,¹³ and similar material will not be mentioned. The chlorostannanes are most intriguing since they would theoretically be the precursors to the more desirable organotin(IV) halides in a one-step synthesis which would eliminate the need for a second disproportionation between the tetraorganotins and tin(IV) chloride.

This idea is the basis for the Azko process developed in England. The olefin must be activated by a substituent placed on the double bond.

The chlorostannanes are prepared by passing hydrogen chloride gas into an ether slurry of metallic tin or tin(II) chloride, and by this route, a number of C-2 substituted ethyltin(IV) halides have been prepared.¹³⁻¹⁷



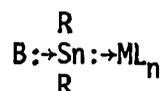
The Coordination Chemistry of the Diorganotin(II) Compounds

The R_2Sn compounds represent a class of compounds which, by the presence of the lone pair, would be expected to behave as Lewis bases. The inorganic chemistry of tin(II) derivatives has been well-developed, but there are few fully characterized diorganotin(II) derivatives. The R_2Sn formulations frequently encountered in the older literature should be reformulated as linear or cyclic oligomers, $(R_2Sn)_n$.¹⁸ The true R_2Sn compounds fall into four classes, the σ - and π -bonded types, and the phenyltin(II) derivatives whose conversion to tin(IV) compounds is inhibited by 2,6-substituents on the ring which either coordinate to the tin or prevent another tin from coming too close. In the π -bonded compounds, the bonding is similar to the pentahapto bonding interactions found in the cyclopentadienyl complexes of transition metal chemistry.

The transition metal complexes of the R_2Sn compounds are interesting from a structural point of view because of the energetically accessible empty d-orbitals of the transition metal. The bond can be envisaged as a σ -bond initially formed by donation of the lone pair of the tin to the empty d-orbital of the transition metal followed by a back donation of the filled d-orbitals of the latter to the vacant d- or

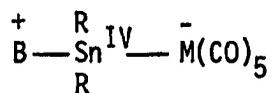
p-orbitals of the tin. The metal-tin coordinate bond possesses some double-bond character and consequently will be shorter than metal tin single bonds.^{19,20}

The organostannylene complexes can be synthesized from either the divalent R_2Sn derivatives or the tetravalent R_2SnX_2 compounds. The bonding can be compared to the analogous carbene complexes but unlike them, the vacant p-orbital on the tin is further able to accept another mole of a base:

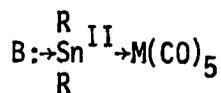


The X-ray structure of $\{[(CH_3)_3Si]_2CH\}_2Cr(CO)_5$ shows that the geometry around the tin is trigonal planar and the tin-chromium distance of 2.562 Å is taken to mean that there is a substantial degree of back donation from the chromium to the tin.¹⁹ In contrast, the complex ${}^tBu_2Sn(py):Cr(CO)_5$ is base-stabilized, and the chromium cannot participate in back bonding because the vacant p-orbital of tin is now filled by the pyridine ligand. The tin-chromium distance is now considerably longer, at 2.654 Å.²⁰

The base-adducts can be represented by two forms:



(I)



(II)

The first formulation (I) is a ylide and formulation (II) is a carbene

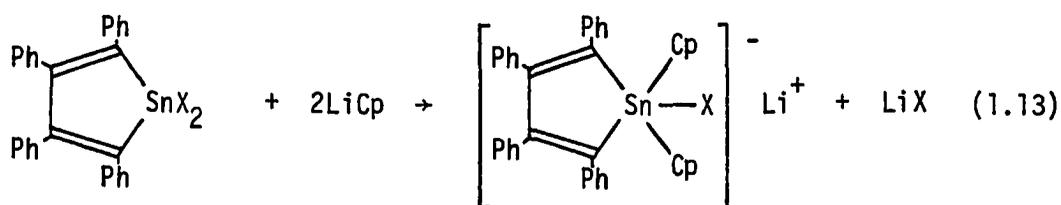
type complex. The two formulations differ in the oxidation states of the tin atom. Happily, they can be differentiated by noting the isomer shifts in the Mössbauer spectra; they fall in the range for tin(IV) compounds.²¹

The two factors that allow for the existence of stable diorganotin(II) compounds are steric and coordination factors. The simple phenyltin(II)'s are oligomeric, but the use of trifluoromethyl groups accounted for the successful isolation of bis(2,6-trifluoromethyl)tin(II), as shown by the Mössbauer data. The lithium salt of 2,4,6-trimethoxybenzene reacts with tin(II) chloride to give 2,4,6-trimethoxyphenyltin(II) chloride, and coordination by the ethereal oxygen to the tin was confirmed by a comparison of the infrared spectrum with that of the starting material.²²

Five-coordinated Tetraorganotin(IV) Compounds

The highest coordination number for triorganotin(IV) compounds is five, and although higher coordination numbers have been suggested for some of these derivatives, none has been so far authenticated structurally.^{23,24} In the case of the organotin(IV) halides, the triorganotin(IV) halides are weaker Lewis acids than the corresponding diorganotin(IV) dihalides which in turn are weaker acids compared to the monoorganotin(IV) trihalides. The R_4Sn compounds are essentially devoid of any Lewis acidity whereas the SnX_4 halides are hard Lewis acids.

The only report of a five-coordinated tetraorganotin(IV) species appears to be the lithium and thallium salts of 1,1-bis(η^1 -cyclopentadienyl)-1-bromo-2,3,4,5-tetraphenylstannole and the lithium salt of the iodo analogue. The materials could be prepared by adding cyclopentadienyllithium to the 1,1-dihalotetraphenylstannole:



The bromo derivative is reported to be a crystalline solid, but rather unfortunately, a structural investigation of this very unusual compound has not been made. The salient features of the stannoles are: they are 1:1 electrolytes and the two resonances of the cyclopentadienyl group collapse into a single peak in the NMR at elevated temperatures. The R_4SnX^- species is described as an anion with "pseudorotating axial- and equatorial-fluxional η^1 -cyclopentadienyl groups".²⁵

The preparation of the precursor, the hexaphenylstannole, is a non-trivial task and part of the reason is because the lithiation of diphenylacetylene is a free-radical reaction which is still not well-understood. The two double bonds present in the product are in a cis-, cis-conformation.²⁶ Diphenyltin(IV) dichloride is then added to give the ring compound, but the yields appear to be variable.²⁷⁻³¹ The light-yellow stannole is fluorescent.³² The bromination step to give the dibromide or diiodide is reported to be quantitative, but it is not clear what causes the cleavage process to take an alternative course to yield the open compound, $\text{Br}(\text{C}_6\text{H}_5)\text{C}=\text{C}(\text{C}_6\text{H}_5)-(\text{C}_6\text{H}_5)\text{C}=\text{C}(\text{C}_6\text{H}_5)\text{Sn}(\text{C}_6\text{H}_5)\text{Br}_2$.³³

Stable Tin(III) Radicals

Radicals that contain the Group IVb elements are of interest because their properties can be directly compared with those of the familiar

radicals of carbon compounds. The simple $R_3\text{Sn}\cdot$ radicals are not expected to be stable, but the presence of sterically bulky groups such as the trimethylsilyl group is expected to confer a degree of kinetic stability. Photolysis of $\{[(\text{CH}_3)_3\text{Si}]_2\text{CH}\}_2\text{Sn}\}_2$ results in the formation of the centered radical $\{[(\text{CH}_3)_3\text{Si}]_2\text{CH}\}_3\text{Sn}\cdot$ which is relatively long-lived.³⁴ The isoelectronic radical $\{[(\text{CH}_3)_3\text{Si}]_2\text{N}\}_3\text{Sn}\cdot$ is also prepared in the same manner.³⁵ However, the trimesitylstannyl radical is not as stable, demonstrating the fact that while steric factors prevent dimerization, electronic factors account for the thermodynamic stability of the organotin(III) radicals.³⁶

Direct Synthesis of Organotin(IV) Compounds

The direct synthesis of organotin compounds from metallic tin and the organic halide has tremendous industrial potential and in fact, the first organotin compound was prepared by heating ethyl iodide with tin metal.³⁷ The Akzo process has been mentioned earlier. In the direct synthesis, the product is the organotin(IV) halide, and, therefore, the disproportionation to the desired $R_n\text{SnX}_{4-n}$ is eliminated. Benzyl chloride and tin powder suspended in boiling water gives tribenzyltin(IV) chloride and if the reaction is carried out in boiling toluene, the product is dibenzyltin(IV) dichloride.³⁸ In general, the direct synthesis requires some sort of a catalyst. Because dioctyltin(IV) derivatives are used in the stabilization of PVC, some attention has been directed to the direct synthesis of dioctyltin(IV) dihalides. Octyl bromide reacts with tin metal in hexamethylphosphoramide catalyzed by copper(I) iodide to give the dioctyltin(IV) dibromide adduct with HMPA which can then be

hydrolyzed to the oxide. Acidification of the oxide with various acids gives the desired compounds.³⁹ Alternatively, amines can be used to catalyze the process.⁴⁰

Cyclopentadienyltin(II) Cations

The structures of two cyclopentadienyltin(II) cations are known, and their features can be contrasted with those of the π -bonded dicyclopentadienyltin(II) compounds. The gas phase electron diffraction of Cp_2Sn gives a Cp-Sn-Cp angle of 125° ,⁴¹ but this material is also monomeric in the condensed phase, in which case the centroid angles of the two independent molecules are 143.7 and 148.0° .⁴² The compound is a Lewis base. When one of the rings is removed, however, one bonding site is available and the monoorganotin(II) cation behaves as a Lewis acid, like the tetravalent organotins. Compounds of the formula $(\text{CH}_3)_5\text{C}_5\text{Sn}^+\text{X}^-$ ($\text{X}^- = \text{AlCl}_4^-, \text{BF}_4^-, \text{CF}_3\text{CO}_2^-, \text{CCl}_3\text{CO}_2^-, \text{CF}_3\text{SO}_3^-$ ⁴³⁻⁴⁵) are known. The cation is stable because the very weakly nucleophilic anions do not interact with the positive charge. Treatment of the CF_3SO_3^- derivative with pyridine yields $(\text{CH}_3)_5\text{C}_5\text{Sn}:\text{py}^+\text{CF}_3\text{SO}_3^-$.⁴⁶ The so-called "BF₃ adduct of stannacene" is a triscyclopentadienylditin cation.⁴⁷

These wonderful topics are considered to be the more significant developments in the field of organotin chemistry during this past decade. The organotin chemistry to be described in this dissertation is a continuation of the investigations in organotin chemistry that have been carried out in this laboratory. One section discusses the organotin carboxylates. Another is the result of the structural investigation of the 1:1 adducts of dimethyltin(IV) dichloride with oxygen donor ligands. The

latter chemistry arose because although the 1:1 adducts have been alluded to in the literature, none so far has been structurally characterized.

The carboxylate group is very powerful in organotin chemistry when it comes to bridging interactions. The tin-carboxylate bridges result in the formation of polymers or short-chain oligomers.^{23,24} If the bonds happen to be long, the weak bridges give rise to solids that have relatively low melting points. An interesting competition occurs when another potentially bridging or chelating substituent is placed in the carboxylate chain. The carboxylate stretching frequency of organic compounds appears in the infrared at about 1700 cm^{-1} . When the group bonds to tin, this stretch is shifted to lower energies. However, in organotin(IV) derivatives, the position of the band is also dependent on the mass effect which would further decrease the energy of the carbon-oxygen band. Interestingly, the symmetric stretch may also be seen, and the magnitude of the difference in wavenumbers between the asymmetric and symmetric stretching frequencies has been employed to decide the coordination number at tin.⁴⁸

Tricyclohexyltin(IV) acetate is a monomer that melts at 62° C . X-ray structural data could not decide the coordination number, but the ambiguity was resolved by its infrared spectrum which displayed a band at 1645 cm^{-1} .⁴⁹ The related tricyclohexyltin(IV) trifluoroacetate is described as either a distorted trigonal bipyramid or a distorted tetrahedron with a tin-oxygen contact distance of 3.11 \AA . Since a band is observed at 1690 cm^{-1} , it is more probable that the intermolecular contact is insignificant, and the compound is probably four-coordinated.⁵⁰

The 2-pyridylcarboxylato anion is potentially terdentate. However, the compound trimethyltin(IV) 2-pyridylcarboxylate monohydrate

has a unidentate carboxylate group. The water molecule is situated at the other apical position of the trigonal bipyramid and the crystal lattice is a polymer through hydrogen-bonding.⁵¹ Probably one of the best structural examples of a substituted carboxylate group is the amino-substituted glycinato group, $\text{NH}_2\text{CH}_2\text{CO}_2^-$. The trimethyltin(IV) derivative has bridging amino groups rather than bridging carboxylate groups.⁵² In the related diphenyltin(IV) glycyglycinato compound, coordination is through the carboxylate oxygen, the peptide nitrogen and the amino nitrogen as well.⁵³

In this dissertation, a number of organotin(IV) carboxylates are prepared in which a potential oxygen donor group is placed at an β - or a γ -position to allow for chelation by the substituents. Although the carboxylate is known to be a powerful bridging group, there is some evidence in the literature that another group if placed in a stereochemically significant site near the tin atom may coordinate in preference. It is, therefore, my intention to compare the relative strengths of the carboxylate bridge versus the phosphine oxide, sulfoxide and ketonic groups.

In organotin chemistry, a large array of physicochemical methods provide an important, though essentially qualitative, source of information on the structure of the organotin compounds. Of the organotin compounds, the most well studied are the methyltin(IV) derivatives because of their simplicity as model systems.^{54,55} The substitution of halide groups for the methyl groups on the tin results in a class of methyltin(IV) halides that are Lewis acids. Of the methyltin(IV) halides, the coordination chemistry of the dimethyltin(IV) dichloride system appears to be most extensively studied, and the enormous interest in this area of

organotin chemistry arises partly because the structures of these adducts can be easily probed by a number of spectroscopic techniques.

For example, the tin-methyl stretching frequency occurs in the 600-500 cm^{-1} region of the infrared. Theoretical predictions show that only the asymmetric stretch is ir-active if the C-Sn-C skeleton is linear and consequently, the presence of the symmetric stretch at lower wavenumbers implies distortion from the ideal geometry. The analysis of the tin-halogen and tin-ligand bands allows the geometries of the halogen and ligand sites to be assigned.⁵⁵ These assignments are complemented by assignments made from the Raman spectrum. Nuclear magnetic resonance spectroscopy probes the structures of the organotin compounds in solution. The magnitude of $|^2J(^{119}\text{Sn-C-}^1\text{H})|$ is determined by the coordination status at the tin atom, and the coordination number in turn can be correlated to the C-Sn-C angle. An approximately linear relationship exists between the magnitudes of $|^2J(^{119}\text{Sn-C-}^1\text{H})|$ and $|^1J(^{119}\text{Sn-}^{13}\text{C})|$ ^{55,56} and, therefore, ^1H NMR complements ^{13}C NMR coupling data.

Perhaps the most valuable tool in organotin chemistry is Mössbauer spectroscopy. In the diorganotin(IV) systems, the size of the carbon-tin-carbon angle is important. Data from the tin-119m Mössbauer quadrupole splitting (QS) values can resolve some questions on the structure of these diorganotin(IV) compounds, and a point-charge approximation model is available in which the QS values can be used to predict the angles at the tin.⁵⁷ However, in this treatment, the contribution to the magnitude of the QS is assumed to arise solely from the organic groups, and, therefore, the treatment cannot be used to differentiate between five- six- or even seven-coordinated diorganotin(IV) compounds. Alternatively, another

point-charge approach can be used in which the organic groups and ligands are placed in idealized geometries, and the contributions from all the organic and ligand groups (the ligands are assigned a partial quadrupole splitting) are summed up. The smaller the difference between the predicted and observed QS values is, the more ideal is the geometry.⁵⁸ Using this latter approach, it is possible to compare the abilities of various ligands to induce perturbation in the electric field gradient around the tin nucleus. Generally, carbonyl donors are weak bases towards tin, and at the other end of the scale, arsine oxides are extremely strong Lewis bases.

The validity of these assignments, however, must rest on the confirmation of the structures of model compounds for which both these and X-ray structural data are available. Where such information exists, the assignments from spectroscopic data have been corroborated by X-ray structural data. The technique of X-ray diffraction, unfortunately, is severely limiting in that single crystals of the compound are required, but this technique is vastly superior in that weak bridging interactions can be detected that would otherwise escape the usual spectroscopic techniques.

It is a curious fact that with certain pointed ligands in which the donor atom carries only a single attachment, i.e., is unbranched, dimethyltin(IV) dichloride forms 1:1 adducts. These less sterically demanding ligands should proceed to the ubiquitous 1:2 complexes without difficulty, but syntheses involving some thirty complexes stop at the 1:1 stage. These complexes will be commented on under the appropriate sections. These 1:1 adducts have been universally formulated as five-coordinated, trigonal-bipyramidal tin compounds. Curiously enough too,

the halide bridges are known to engage in a phenomenon called "auto-complexation" whereby the coordination number of the central tin atom is increased by the presence of a halide atom within van der Waals distance.^{55,59}

This section of the dissertation will describe the crystal structures of the 1:1 adducts of dimethyltin(IV) dichloride with two oxygen donor ligands, diphenylcyclopropanone, $(C_6H_5)_2C_2C=O$ and 2,6-dimethylpyridine (2,6-lutidine) N-oxide, $2,6-(CH_3)_2C_5H_3NO$ and the 1:1 adducts of latter ligand with diphenyltin(IV) dichloride and trimethyltin(IV) chloride. The solution of the crystal structures of these complexes will perhaps answer the question why monomeric 1:1 adducts do form, if at all, given the extraordinary capacity of tin to achieve high coordination numbers.

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CHAPTER 2

SYNTHESIS OF TRIPHENYLPHOSPHONOPROPIONBETAINE- TRIORGANOTIN(IV) SALTS BY NUCLEOPHILIC DISPLACEMENT OF ANIONS FROM TRIORGANOTINS

Introduction

Triorganotin compounds R_3SnX are of commercial interest as biocidal materials, but the nature of the X group does not have a marked effect on the biological activity.¹ Organophosphorus compounds also exhibit strong biocidal activity,² and it may be possible to confer desirable biocidal characteristics on the triorganotin compound by incorporating an organophosphorus substituent on the X group.

As a follow-up on the tin amino acids,³⁻⁶ a carboxylic acid with an organophosphorus substituent was looked for. There has been considerable interest in the structures of the triorganotin carboxylates,^{7,8} and five-coordinated, one-dimensional polymeric structures with the more electronegative oxygen groups in the axial-positions have been confirmed by X-ray studies.⁷⁻¹¹ Of the organophosphorus compounds, the tetraorganophosphonium salts are known to behave as phase-transfer catalysts, and they have the ability to alter the surface tension of water.¹² It was,

therefore, decided to prepare triorganotin derivatives of triphenyl(2-carboxyethyl)phosphonium chloride, $[(C_6H_5)_3P(CH_2)_2CO_2H]^+Cl^-$, to test the effect of this novel group.

Experimental Section

The phosphonium cation, triphenyl(2-carboxyethyl)phosphonium, is easily prepared in high yield from the reaction of 3-chloropropionic acid and triphenylphosphine. The triphenylphosphonopropionbetaine is derived in high yield from the product by treatment with sodium bicarbonate in ethanol.¹³ Triphenyltin(IV) chloride and triphenylphosphine were gifts from M & T Chemicals, Inc., and 3-chloropropionic acid was from the Aldrich Chemical Co. Other organotin derivatives were prepared from the reaction between triphenyltin(IV) chloride and the potassium salt of the halide or pseudohalide in ethanol. In this way, the following organotin(IV) salts were prepared: triphenyltin(IV) bromide, mp 115-16° C (lit. 120-21° C,¹⁴ 121.5-22.5° C¹⁵), triphenyltin(IV) iodide, mp 120-21° C (lit. 122-24° C¹⁶), triphenyltin(IV) isothiocyanate, mp 166-68° C (lit. 166-68° C,¹⁷ 171-72° C¹⁸), triphenyltin(IV) isocyanate, mp 98-100° C (lit. 98-99° C¹⁹) and triphenyltin(IV) azide, mp 114° C (lit. 117° C²⁰).

Methyldiphenyltin(IV) chloride was prepared from the cleavage of methyltriphenyltin by elemental iodine in chloroform.²¹

Diphenyltin(IV) chlorooxinate was prepared from 8-hydroxyquinoline and diphenyltin(IV) dichloride, mp 164-65° C (lit. 167-68° C^{22,23}).

Triphenyltin(IV) nitrate²⁴ was prepared and reacted in situ, as was triphenyltin(IV) tetraphenylborate.^{25,26} Triphenyltin(IV) tetracarbonylcobaltate was prepared by the reaction of triphenyltin(IV) chloride

and sodium tetracarbonylcobaltate from the sodium metal cleavage of octacarbonyldicobalt.²⁷

Triphenylphosphonopropionbetainetrimethyltin(IV) chloride, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(CH_3)_3]^+Cl^-$

Trimethyltin(IV) hydroxide (1.81 g, 10.0 mmol) and triphenyl(2-carboxyethyl)phosphonium chloride (3.71 g, 10.0 mmol) were dissolved in dry benzene (a suspected carcinogen) (150 mL) and dimethylformamide (7 mL) and heated for 30 min. in a Dean-Stark assembly to remove the water formed. The benzene was removed on a rotary evaporator and the pure compound obtained in 80% yield mp 173 - 74° C, by recrystallization from 2-propanol.

Triphenylphosphonopropionbetainetripentyltin(IV) chloride, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+Cl^-$

Tripentyltin(IV) hydroxide (3.67 g, 10.0 mmol) and triphenyl(2-carboxyethyl)phosphonium chloride (3.71 g, 10.0 mmol) were combined in dry benzene (150 mL) and dimethylformamide (7 mL). The benzene suspension was heated with magnetic stirring in a flask equipped with a Dean-Stark trap, and the theoretical amount of water was collected in ten minutes. The white precipitate was collected by suction filtration, washed with ethanol and then with ether and air-dried to give the title compound, mp 195 - 97° C, in 90% yield.

This same compound was also prepared by mixing warm ethanolic solutions of the phosphonium betaine, $(C_6H_5)_3P^+(CH_2)_2CO_2^-$ (3.34 g, 10.0

m mol), and triphenyltin(IV) chloride (3.85 g, 10.0 m mol). The white precipitate formed on cooling, was filtered, washed with ethanol and then ether; mp 194 - 95° C, yield 70%. The melting point of an intimate mixture of the two products is not depressed, and their infrared spectra are identical.

The corresponding bromide and iodide salts were prepared by the second method, and their melting points and yields are listed in Table 1.

Triphenylphosphonopropionbetainetriphenyltin(IV) isothiocyanate $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+NCS^-$

Mixing triphenyltin(IV) isothiocyanate (2.04 g, 5.00 m mol) and the phosphobetaine, $(C_6H_5)_3P^+(CH_2)_2CO_2^-$ (1.67 g, 5.00 m mol), in ethanol (50 mL) gave an immediate precipitate, mp 198 - 99° C, in 90% yield. When the amount of the organotin was doubled, the product obtained after washing with ethanol had an identical melting point and infrared spectrum.

Triphenylphosphonopropionbetainetriphenyltin(IV) acetate, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+CH_3CO_2^-$

Triphenylphosphonopropionbetainetriphenyltin chloride (2.88 g, 4.00 m mol) and lead acetate trihydrate, $Pb(CH_3CO_2)_2 \cdot 3H_2O$ (0.76 g, 2.0 m mol) were allowed to react in hot ethanol (50 mL) to give lead(II) chloride which precipitated immediately and was removed by filtration. The resulting solution was concentrated to give the product, mp 170 - 73° C, in 50% yield.

Triphenylphosphonopropionbetainetriphenyltin(IV) nitrate, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+NO_3^-$

A solution of triphenyltin chloride (3.85 g, 10.0 mmol) in acetone (50 mL) was added to a solution of silver nitrate (1.70 g, 10.0 mmol) in water (5 mL). The silver chloride which precipitated immediately was filtered. To this solution of triphenyltin(IV) nitrate was added the phosphonium betaine, $(C_6H_5)_3P^+(CH_2)_2CO_2^-$ (3.34 g, 10.0 mmol) in ethanol (10 mL), the solution concentrated and ether added to precipitate the white product, which was recrystallized from acetone, mp 162 - 64° C, in 80% yield.

Triphenylphosphonopropionbetainetriphenyltin(IV) tetraphenylborate, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+B(C_6H_5)_4^-$

Triphenyltin(IV) chloride (3.85 g, 10.0 mmol) and sodium tetraphenylborate (3.42 g, 10.0 mmol) were mixed in 2-propanol (50 mL). The resulting sodium chloride was filtered, and the solution was mixed with the phosphonium betaine, $(C_6H_5)_3P^+(CH_2)_2CO_2^-$ (3.34 g, 10.0 mmol) in 2-propanol (50 mL) to precipitate the white product, mp 190 - 92° C, in 60% yield, which was washed with ethanol and ether.

Triphenylphosphonopropionbetainetriphenyltin(IV) tetracarbonylcobaltate(I), $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+[Co(CO)_4]^-$

Triphenyltin(IV) tetracarbonylcobaltate(I)²⁷ (2.60 g, 5.00 mmol) was dissolved in acetone (20 mL) and mixed with the betaine (1.67 g, 5.00 mmol) dissolved in ethanol (20 mL). No precipitate formed immediately

but a brown solid formed on slow evaporation of the solvent. This was filtered and recrystallized from acetone, mp 107 - 08° C, in 60% yield.

Triphenylphosphonopropionbetainetriphenyltin(IV) triphenyltin(IV)di-
chloride, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+[(C_6H_5)_3SnCl_2]^-$

Triphenyltin(IV) chloride (3.85 g, 10.0 m mol) and $(C_6H_5)_3P^+(CH_2)_2CO_2^-$ (1.67 g, 5.00 m mol) were each dissolved in hot ethanol (20 mL) and then mixed. On slowly cooling the mixture, a white semi-solid was obtained. Triturating this in hot ethanol gave a precipitate, mp 188 - 90° C, which was filtered and washed with ethanol and then ether, to give the double salt in 80% yield.

Triphenylphosphonopropionbetainetriphenyltin(IV) triphenyltin(IV)di-
bromide, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+[(C_6H_5)_3SnBr_2]^-$

A similar procedure with triphenyltin(IV) bromide gave the product in 60% yield, mp 184 - 85° C.

Triphenylphosphonopropionbetainetriphenyltin(IV) triphenyltin(IV)diiso-
cyanate, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+[(C_6H_5)_3Sn(NCO)_2]^-$

Triphenyltin(IV) isocyanate (3.92 g, 10.0 m mol) reacted with tri-
phenylphosphonopropionbetaine (3.34 g, 10.0 m mol) in ethanol (50 mL) to
form the 1:2 product in 60% yield, mp 149 - 52° C.

Triphenylphosphonopropionbetainetriphenyltin(IV) triphenyltin(IV)diazide,
 $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+[(C_6H_5)_3Sn(N_3)_2]^-$

A semi-solid which formed immediately on mixing the phosphorus betaine (1.67 g, 5.00 m mol) and triphenyltin(IV) azide (3.92 g, 10 m mol) in ethanol became a powder on trituration and warming, mp 152 - 53° C, yield 80%.

Triphenylphosphonopropionbetainemethyldiphenyltin(IV) methyldiphenyltin(IV)dichloride, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(CH_3)(C_6H_5)_2]^+[(CH_3)(C_6H_5)_2SnCl_2]^-$

Methyldiphenyltin(IV) chloride (3.23 g, 10.0 m mol) was added dropwise to an ethanolic solution of triphenylphosphonopropionbetaine (3.34 g, 10.0 m mol) and the solution concentrated to precipitate a solid which was recrystallized from chloroform. Instead of the anticipated 1:1 product, the compound isolated analyzed as the above formulation, mp 105 - 06° C, in 30% yield.

Triphenylphosphonopropionbetainediphenyltin(IV) 8-hydroxyquinolinatochloride, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_2(C_9H_6NO)]^+Cl^-$

The betaine (0.84 g, 2.50 m mol) dissolved in ethanol (20 mL) and diphenyltin(IV) chlorooxinate (1.13 g, 2.50 m mol) dissolved in a benzene-ethanol mixture were mixed. Slow evaporation of the solvent mixture yielded the yellow product, mp 172 - 75° C, in 30% yield.

Triphenylthiophosphonopropionbetainetriphenyltin(IV) triphenyltin(IV) dichloride, $[(C_6H_5)_3PS(CH_2)_2CO_2Sn(C_6H_5)_3]^+[(C_6H_5)_3SnCl_2]^-$

Triphenylphosphonopropionbetainetriphenyltin(IV) chloride (3.60 g, 5.00 m mol) was dissolved in boiling ethanol (150 mL) and elemental sulfur

(0.16 g, 5.0 mg-at) added. The sulfur dissolved completely on stirring. A cream-colored precipitate which melted to a red liquid at 174 - 75 ° C formed on cooling.

Attempted dehydrochlorination of triphenylphosphonopropionbetainetriphenyltin(IV) chloride

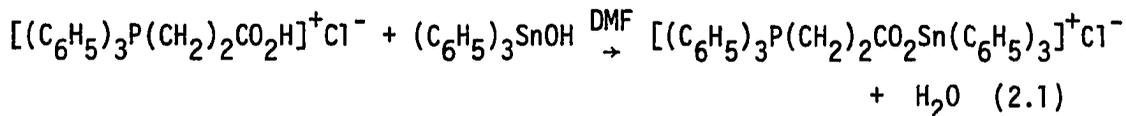
A suspension of sodium hydride in mineral oil (57% suspension, 0.42 g, 10 m mol) was washed with petroleum ether and dissolved in dimethylsulfoxide.²⁸ Triphenylphosphonopropionbetainetriphenyltin(IV) chloride (7.19 g, 10.0 m mol) in DMSO was added and the mixture stirred for 30 min. The solution was then added to water and the precipitate, mp 191 - 92° C was collected and recrystallized from ethanol. The product was identified through carbon and hydrogen analysis, melting point, infrared and mass spectroscopy to be $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3SnCl_2]^-$.

The compounds prepared, along with their mp's, yields and microanalytical data are listed in Table 1. Difficulty was experienced in obtaining correct microanalytical data for carbon on compounds 3, 4, 6-10, 12, 14 16 and 17 and for hydrogen on compounds 3, 4, 14 and 17 listed in Table 1. The tin-119m Mossbauer data are gathered in Table 2, and the infrared data in Table 3.

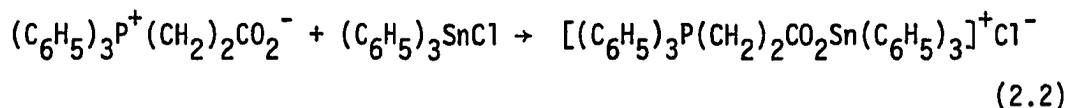
Results and Discussion

The action of triphenyltin(IV) hydroxide on triphenyl(2-carboxyethyl)phosphonium hydrochloride in benzene releases water and gives the triorganotin carboxylate in ca. 90% yield after heating in a Dean-Stark

apparatus for ten minutes with dimethylformamide (DMF) as a catalyst:

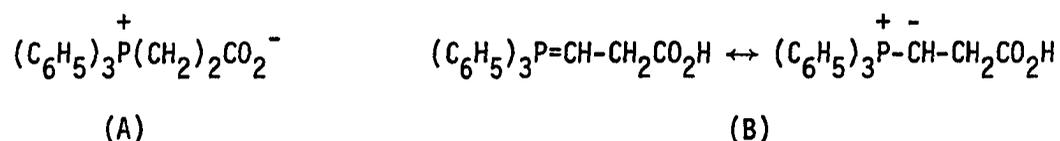


The same tin product results from the displacement of chloride ion by the phosphobetaine, $(C_6H_5)_3P^+(CH_2)_2CO_2^-$:



Other organotin carboxylates with an organophosphorus substituent are prepared by this novel nucleophilic displacement of the chloride or pseudohalide from the triorganotin(IV) moiety.

There has been controversy over the structure of the $(C_6H_5)_3P^+(CH_2)_2CO_2^-$ moiety which is called triphenylphosphonopropionbetaine in accordance with recommended nomenclature;^{29,30} but as has been pointed out, phosphorus-31 NMR measurements fail to differentiate between the phosphobetaine structure, A, and the ylide structure, B:³¹



The results indicate that the correct form is probably structure A which would lead to the formation of tin-oxygen bonds, whereas B would be expected to lead to the formation of tin-carbon bonds. The latter products would be easily identified by tin-119m Mössbauer spectroscopy, since because the tin atom is surrounded by four organic groups, simple singlet spectra with no quadrupole splitting (QS) would be expected.³²

The phosphonium hydrochloride, $[(C_6H_5)_3P(CH_2)_2CO_2H]^+Cl^-$, is prepared by reacting triphenylphosphine with 3-chloropropionic acid. Treatment of the product acid with aqueous ethanolic sodium bicarbonate gives

triphenylphosphonopropionbetaine in high yield:¹³

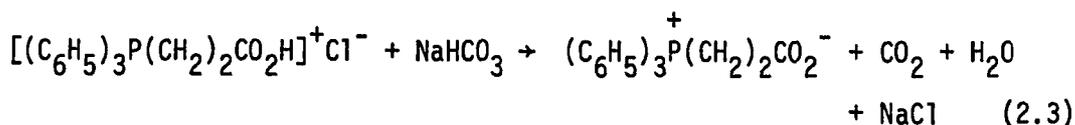
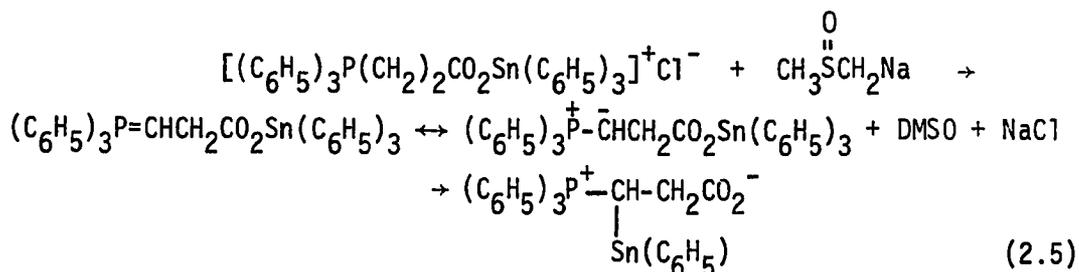


Table 1 lists the various triphenylphosphonopropionbetainetriorganotin(IV) salts that were prepared by the novel nucleophilic displacement together with their analytical data and percentage yield. Most of the triphenyltin derivatives are high melting solids (with decomposition) and the similarity of the temperatures suggests that it is the common triphenylphosphonopropionbetainetriphenyltin cation that undergoes decomposition in each case. All the compounds are white except for the tetracarbonylcobaltate and diphenyl(8-hydroxyquinolino)tin derivatives which are brown and yellow-colored solids, respectively.

Since the triphenylphosphonopropionbetainetriorganotin complexes can be prepared in good yield by reaction pathway (2.2), it seemed worthwhile to attempt further reactions on the triphenyltin(IV) chloride derivative.

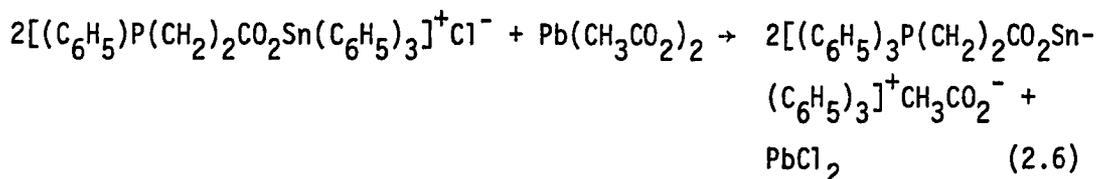
The attempt to dehydrochlorinate the phosphonium salt, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+Cl^-$, by treatment with methylsulfinyl sodium from sodium hydride in dimethylsulfoxide²⁸ gave instead the double salt, $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+[(C_6H_5)_3SnCl_2]^-$ as the only tin containing product. The formation of the ylide which would displace the triphenyltin group from the carboxylate to form a carbon-tin bond through the phosphorus ylide as has been previously reported³³ was not realized:



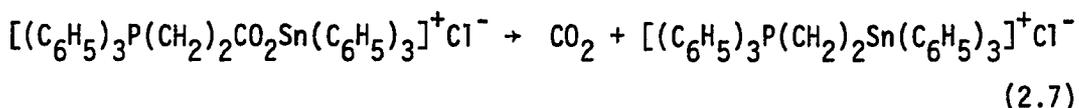


Such a compound would function as a precursor in the preparation of compounds with three tin atoms in the molecule, all in different environments. The attempt to prepare the trimethyltin(IV) double salt $[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{CH}_3)_3]^+[(\text{CH}_3)_3\text{SnCl}_2]^-$, by concentrating a solution of the ylide and organotin(IV) chloride in a 1:2 ratio gave only an oil which could not be crystallized.

The acetate derivative could be prepared through a simple metathesis reaction from lead(II) acetate:



Triphenylphosphonopropionbetainetriphenyltin(IV) chloride loses carbon dioxide at its melting point of 191° C, presumably to produce the corresponding 2-(triphenylstannyl)ethyltriphenylphosphonium chloride:



Proton NMR Data

Most of the carboxylates prepared in this study are too insoluble in common NMR solvents to give meaningful results, with the exception of the species listed in Table 5. In deuterated chloroform, the methyl signal of $[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{CH}_3)_3]^+\text{Cl}^-$ appears at $\delta = 0.64$ ppm, relative

to TMS and the $|^2J(^{119}\text{Sn-C-}^1\text{H})|$ coupling constant is 72.8 Hz. It was not possible to make the double salt $[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{CH}_3)_3]^+[(\text{CH}_3)_3\text{SnCl}_2]^-$, but a deuteriochloroform solution of $[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{CH}_3)_3]^+ \text{Cl}^-$ and $(\text{CH}_3)_3\text{SnCl}$ in a 1:1 stoichiometry displays only one methyl signal at $\delta = 0.64$ ppm, and $|^2J(^{119}\text{Sn-C-}^1\text{H})|$ is decreased to 64.5 Hz.

The compound $[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_2\text{CH}_3]^+[\text{CH}_3(\text{C}_6\text{H}_5)_2\text{SnCl}_2]^-$ shows a $|^2J(^{119}\text{Sn-C-}^1\text{H})|$ coupling constant of 76.0 Hz compared with 60.0 Hz for $(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{SnCl}$. As with the trimethyltin case, only one methyl signal is observed at $\delta = 1.00$ ppm.

Mössbauer Data

Table 2 lists the Mössbauer parameters of the compounds prepared. The IS and QS values are consistent with five-coordinated triorganotin formulations,³² with the exception of triphenylphosphonopropionbetaine-diphenyl(8-hydroxyquinolinato)tin(IV) chloride which is probably six-coordinated. Since the QS for the latter is ca. 2 mm s^{-1} , the two phenyl groups must be cis- to each other. Diaryltin compounds can adopt either a cis- or a trans-configuration in their complexes, whereas with the dialkyl analogues, the carbon-tin-carbon skeleton is almost invariably linear.^{7,8} The carbon-tin-carbon angle in the diphenyltin(IV) chloride can be calculated from a point charge approach³⁴ that assumes that the partial QS contributions from the ligands will be small compared to that from the phenyl groups, and the correlation is supported by data from compounds for which both Mössbauer and diphenyltin(IV) carbon-tin-carbon angles are available.³⁵ On this basis an angle of 109° for the diphenyltin system in the derivative is predicted.

In the series $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+X^-$ where the X group is varied from the potentially bridging halide, pseudohalide, acetate, nitrate, etc.. to the essentially non-nucleophilic tetraphenylborate anion, there appears to be not much variation in the Mössbauer parameters. Thus the X groups are probably not bonded directly to the tin atom, but exist as counterions. Hence, the compounds should be formulated as phosphonium salts in which one of the organic groups on the phosphorus atom is an organotin-containing carboxylate residue.

In the series of compounds with tin both in the cation and anion, the Mössbauer spectra are best fitted by only one symmetrical doublet, and the IS and QS values are close to the values obtained for the previous tin cation series. It seems, therefore, that either the electronic environments about the tin nuclei are identical, or that the whatever differences there are cannot be detected by tin-119m Mössbauer spectroscopy.

It is interesting to note in this connection that the compound $[(CH_3)_2SnCl_2]_2 \cdot \text{terpyridyl}$ exists as a double salt $[(CH_3)_2SnCl \cdot \text{terpyridyl}]^+ [(CH_3)_2SnCl_3]^-$ with the tin cation in an octahedral environment and the tin anion in a trigonal bipyramidal environment³⁶ but exhibits only one doublet in its Mössbauer spectrum.³⁷

Infrared Data

Tables 3 and 4 list the ir assignments, and Table 4 are the bands of the carboxylate system. The tin-carbon and tin-oxygen modes below 600 cm^{-1} cannot be unambiguously assigned because the phosphonobetaine moiety itself has a rich spectrum in this region. Triphenylphosphonopropionbetaine absorbs at 1593 cm^{-1} and 1583 cm^{-1} , and in the complexes the

asymmetric CO_2 stretch is observed near 1645 cm^{-1} for the $[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{X}^-$ compounds and 1585 cm^{-1} for the $[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+[(\text{C}_6\text{H}_5)_3\text{SnX}_2]^-$ compounds. The lowered values in the latter series would suggest that stronger association by the carboxylate oxygens is taking place there. The slightly lesser degree of association in the first series can be interpreted in terms of some steric hinderance arising from the proximity of the counterion to the tin atom rather than to the phosphorus atom. Tin(IV) is a hard acid, and although organic groups confer some degree of softness, it retains its hard character, and it is, therefore, not surprising that the counterion would be found to be within possible interaction distance of the tin atom rather than the phosphorus atom.

The compound $[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{CH}_3)_3]^+\text{Cl}^-$ exhibits an asymmetric CO_2 band at 1616 cm^{-1} . The effect of lowered mass is unlikely to predominate in this case, and it appears that because of decreased steric crowding about the tin atom, the strength of the carboxylate bridging is greater than in the triphenyltin case.

When the X group, as with the pseudohalide and $\text{Co}(\text{CO})_4$ groups, also absorbs in the infrared, it is possible to record the shift of the bands to lower energies upon complexation. Of the various anions studied, the most informative is the tetracarbonylcobaltate because the geometry of the moiety can be deduced from the absorption bands of the carbonyl group.³⁸ In the ionic form the moiety has tetrahedral symmetry and a single absorption band for $\nu(\text{CO})$ in the infrared. On the other hand, bonding the tin atom to the cobalt lowers the symmetry of that group in such compounds as $(\text{C}_6\text{H}_5)_3\text{SnCo}(\text{CO})_4$.⁷ In a polar solvent such as

acetone, however, this compound dissociates to the solvated triphenyltin cation and the tetracarbonylcobaltate anion,³⁸ the latter exhibiting a single carbonyl stretching absorption at 1890 cm^{-1} . In the complex $[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{Co}(\text{CO})_4^-$, a single carbonyl absorption band is observed at 1885 cm^{-1} in the solid state (1870 cm^{-1} in acetone solution). It appears, therefore, that the cobaltate moiety is tetrahedral and hence anionic and is not coordinated to tin.

Whereas the infrared spectra of the salts below 600 cm^{-1} do not yield significant structural information because of the strong phosphonium ligand absorptions, the Raman spectra of these $[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{X}^-$ compounds are much more informative. The Raman spectra for the $\text{X} = \text{Cl}, \text{Br}, \text{I}$ derivatives in the region 350 and 60 cm^{-1} are virtually identical as can be seen in Table 7. No substantive tin-halogen interactions are present, and the products are true salts.

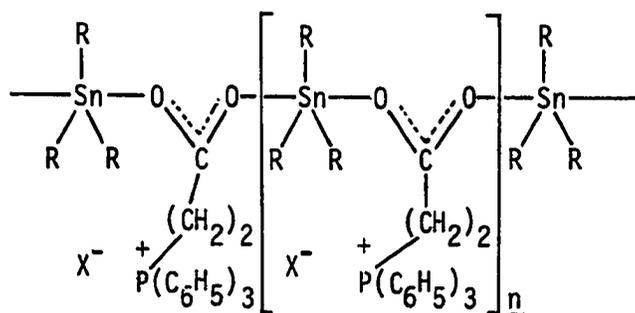
Structural Conclusions

The tin-119m Mössbauer data show that the tin atoms in the compounds are in a five-coordinated geometry in all but the 8-hydroxyquinoline complex which is probably six-coordinated and octahedral, and from the small magnitude of the QS value contains a cis-diphenyltin system.³⁵ That the spectra are doublet in nature for the others serves to rule out the possibility that the compounds are derivatives of the ylide structures, B, (vide supra), since these tetraorganotin(IV) species would give singlets only,³² and can instead be formulated as phosphobetaines with the tin groups bonding through the carboxylate oxygen atoms. The absence of ambient temperature Mössbauer spectra does not rule out bridging

rather than chelating forms, and the question of involvement of the anion group, X, arises. Interaction with groups such as the $B(C_6H_5)_4$ is ruled out, however; yet the Mössbauer data for this derivative are not different. A more decisive test involves the tetracarbonylcobaltate derivative, where the infrared spectrum of the transition metal moiety is conclusive for tetrahedral symmetry and hence no interaction with the tin atom. The identical Raman data for the halides in the low frequency region are corroboratory in this regard. Conductivity measurements in dimethylformamide for $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+Cl^-$ give a molar conductivity value, $\Lambda_m = 48 \Omega^{-1} cm^{-1} M^{-1}$, characteristic of a 1:1 electrolyte which can be compared with $65 \Omega^{-1} cm^{-1} M^{-1}$ for the known ionic complex $SnCl_4 \cdot 2 SaH-N-p-tolyl$ in the same solvent.³⁹ Thus these systems are formulated as salts.

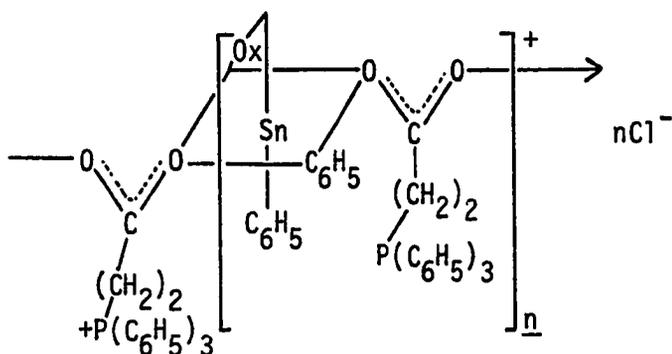
Tin bonding through the acetate group in a five-coordinated form suggests an association through oxygen atoms bridging flat trimethyltin(IV) groups in the universal, axially-most-electronegative trigonal bipyramidal configuration. Unfortunately, infrared absorption bands of the ligand obscure the $\nu(SnC_3)$ mode region, thus denying the information necessary to decide whether the trimethyltin(IV) moiety is truly planar. The lowered infrared $\nu(CO_2)$ absorption frequencies for the acetate group support the suggestion of the use of both the carboxyate oxygens in coordination to tin, most likely in the well-known bridging acetate form.^{7,8}

The structural proposal for these systems is presented in C in which a polymeric chain of bridging carboxylate groups contains dangling triphenylphosphonium cations:



(C)

The 8-hydroxyquinolatodiphenyltin(IV) derivative, on the other hand, is, from the very low IS value, six-coordinated at tin, and the magnitude of its Mössbauer QS value specifies a cis-diphenyltin configuration. The quinolinato group will chelate in a cis-fashion, too, but this does not serve to determine the connectivity of the bridging carboxylate. Structure D can be written in a cis-, cis-, trans-configuration without wishing to specify the way in which the carboxylate groups are bound:



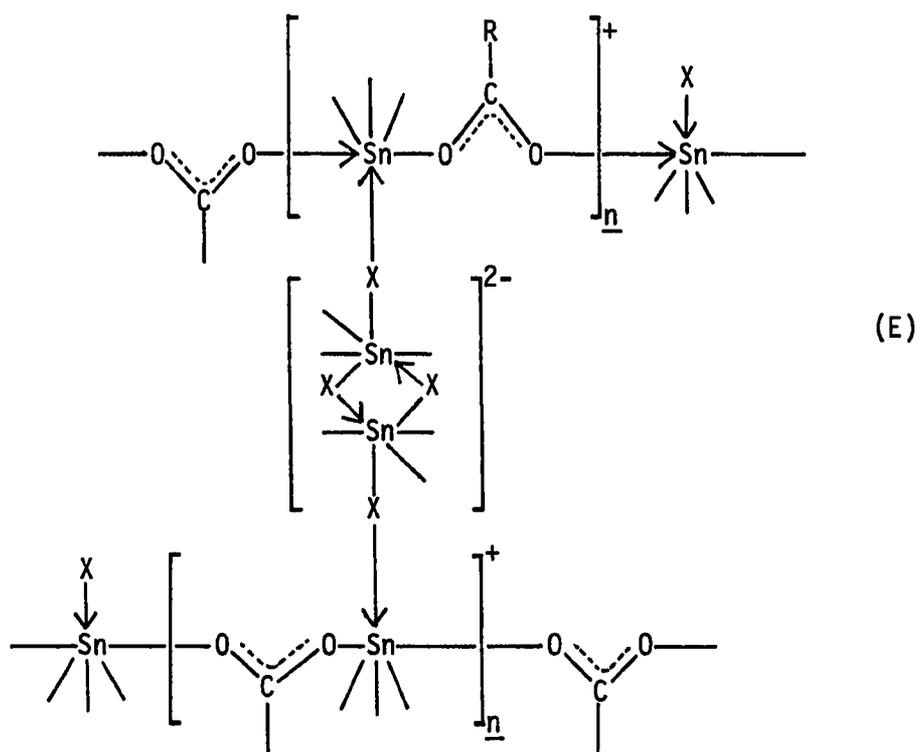
(D)

The double salts with triorganotin residues in both the anion and cation should behave in a straight forward manner structurally, with their solids composed of tin anions and cations, both trigonal bipyramidal. The $[\text{R}_3\text{SnCl}_2]^-$ anion has been characterized structurally for $\text{R} = \text{CH}_3$ in the $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_3\text{S}_4]^+$ salt,⁴⁰ and the structure of the trigonal bipyramidal $[(\text{CH}_3)_2\text{SnCl}_3]^-$ anion is known in its double salt with the $[(\text{CH}_3)_2\text{SnCl}\cdot\text{terpy}]^+$ cation,³⁶ but no double salts are known with tin in both a trigonal bipyramidal anion and cation.^{7,8}

The spectroscopic evidence, however, presents a more puzzling picture. The Mössbauer spectra of all the double salts contain only a simple doublet. This has been observed before for the double salt $[\text{R}_2\text{SnCl}\cdot\text{ter}]^+ [\text{R}_2\text{SnCl}_3]^-$ discussed above where surprisingly well-defined doublets are recorded for the bent trans-dimethyltin(IV) octahedral cation and the

trigonal bipyramidal anion combination where $R = \text{CH}_3$, $n\text{-C}_4\text{H}_9$ and C_6H_5 .³⁷ More recently, the same phenomenon has been observed for the terpyridyl adducts of the dihalotetraarylstannoles.⁴¹ The sole similarity linking the positive and negative ions in these cases which produce superimposable spectra is the number of bonds tin makes to carbon, and the nature of the attached organic groups. In the phosphonium salts studied here the differences should be less severe since both ions are five-coordinated, presumably axially-most-electronegative with a relatively planar triphenyltin(IV) system at the equator of the ion. Yet, a direct comparison of the Mössbauer data for the phosphonium cation halide or pseudohalide salt and those for the double salts as presented in Table 2 reveal a larger linewidth and a QS value somewhat higher for the latter, both being outside experimental error. The IS values for the double chloride and bromide salts are also smaller outside experimental error. These data taken together seem to indicate that the tin atoms in these double salts may be in a higher coordinated situation than in their simple precursor salts, but there is no compelling argument to account for how this could come about. Anion-cation bridging by chloride, bromide or azide groups, while certainly possible for these five-coordinated species unlike in the six-coordinated R_2Sn cations that are studied before,^{37,41} would have to be coupled to a similar bridging of the anions to bring the tin atoms in these species to a six-coordinated state as well. This situation seems to be unlikely since there is little precedence for triorganotin moieties being complexed by more than one donor atom to form R_3SnL_3 species, although the complexing moieties here bear opposite charges which would assist in their pairing. Indeed, in the

solid quinolinium trichlorodimethylstannate(IV), $[\text{C}_9\text{H}_8\text{N}]^+[(\text{CH}_3)_2\text{SnCl}_3]^-$, there is a close contact between tin and chlorine of neighboring anions at 3.486 \AA to form dimeric dianionic units containing six-coordinated tin atoms.⁴² In addition, the structure of diphenyltin(IV) dichloride⁴³ has been reinterpreted in terms of tetrameric units containing terminal, four-coordinated molecules, one of whose chlorine atoms forms a single bridge to the two central molecules which engage in four-center bridging between them to produce six-coordination at tin.⁴⁴ Triphenyltin(IV) chloride on the other hand, forms a crystal of monomers.⁴⁵ In the more favorable electrostatic situation, dimeric $[(\text{C}_6\text{H}_5)_3\text{SnX}_2]_2^{2-}$ units could cross-link the linear, carboxylate-bridged polymers by bridging the tin atoms in two chains to produce structure E in which all the tin atoms are now six-coordinated of the R_3SnXO_2 type:

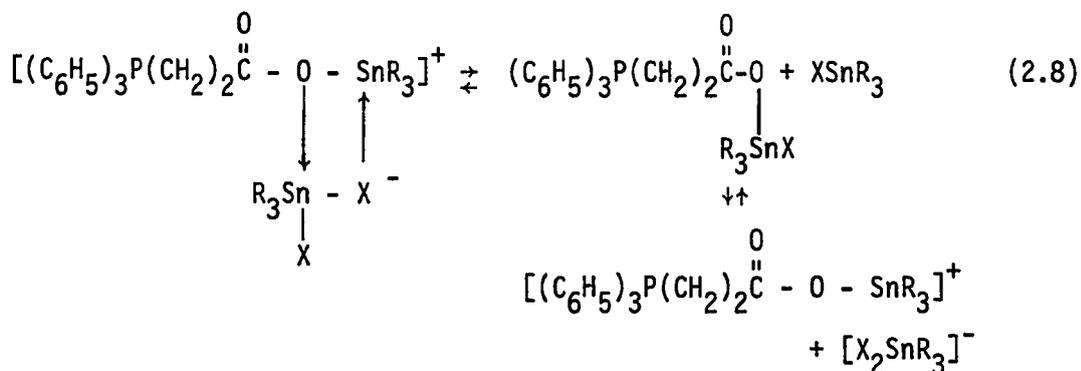


Trimethyltin(IV) chloride⁴⁶ and azide^{47,48} form singly bridged solids. The additional interactions depicted in E are not reflected in higher melting points of these double salt solids.

The NMR evidence presented in Table 5 is even more puzzling. Unfortunately, it was not possible to isolate either the double salt based on methyltin(IV) chloride or the simple salt derived from methyldiphenyltin (IV) chloride, but both mixtures of the simple salt of the former and additional trimethyltin chloride in a 1:1 ratio, or the latter double salt give single sets of sharp NMR resonances with tin-117 and 119 satellites. The chemical shifts stay relatively constant in going from the simple chloride to the phosphonium chloride salt to the double salt, but the coupling constants, which are potentially more informative about the structural situation at the tin atom, tell a confused story since in the trimethyltin case the phosphonium chloride salt value is indicative of coordination higher than four at tin, but this value drops on adding trimethyltin chloride. However, the double salt of the methyldiphenyltin derivative exhibits a coupling constant consistent with higher coordination.

The simple NMR signals observed for each of these double salts must result from either the identity of the s-electron density directed along the methyl-tin axes in the equatorial positions of the trigonal bipyramidal anion and cation or from a dynamic process which could scramble the two tin sites.⁴⁷ The former is unlikely given the sensitivity of the NMR technique to small changes, but structures such as E could serve as intermediates in a process by which chlorine and oxygen attachments are exchanged via four-centered interactions as in the equilibria involving ion

pairing in \underline{F} , followed by dissociation and chloride exchange steps:



The R_3Sn group remains intact throughout the processes described in Eq. 2.8 and thus the NMR $|^2J(^{119}\text{Sn}-^1\text{H})|$ couplings are observed in the methyl-tin case.

The variation of the tin-methyl coupling constant of trimethyltin chloride in a chloroform solution of trimethyltin chloride and triphenylphosphonopropionbetaine was recorded to probe the possibility of such interactions and the data are listed in Table 8. It is seen that the coupling constant decreases when the proportion of the organotin chloride is in excess of the 1:1 stoichiometry. Only one methyl signal is observed. The widths at half-height of these resonances are ca. 1 Hz.

Summary

Trimethyl- and triphenyltin(IV) hydroxide act on triphenyl(2-carboxyethyl)phosphonium hydrochloride, which is made from 3-chloropropionic acid and triphenylphosphine, to release water in the presence of dimethylformamide (DMF) as a catalyst. The water is azeotropically distilled to drive the reaction forward and produce triphenylphosphonopropionbetaine-trimethyl- and triphenyltin(IV) chlorides in high yield. The latter product also results from the displacement of chloride from triphenyltin(IV)

chloride by the phosphobetaine, $(C_6H_5)_3P(CH_2)_2CO_2$, which is made by treating the phosphonium hydrochloride with bicarbonate, and the compounds $[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+X^-$ where $X = Cl, Br, I, N_3, NCS, NO_3, B(C_6H_5)_4$ and $Co(CO)_4$ are made in the same way. The acetate salt results from metathesis from the chloride and lead(II) acetate. A double salt, $[C_6H_5)_3P(CH_2)_2CO_2SnR_3]^+[R_3SnX_2]^-$, is formed for $X = Cl, Br$ and N_3 by adding additional $(C_6H_5)_3SnX$ to the already-formed simple salts. Double salts are also obtained from the 1:1 reactions between the phosphobetaine and triphenyltin(IV) isocyanate and methyldiphenyltin(IV) chloride. The phosphonium chloride double salt could be converted to the thiophosphonium derivative by heating with elemental sulfur in ethanol. The products of these novel nucleophilic displacement reactions are high melting solids. Tin-119m Mössbauer data are consistent with five-coordinated, triorgano-tin(IV) formulations with the exception of the diphenyl(8-hydroxyquinolino)tin(IV) chloride salt in which the tin atom is six-coordinated, and the diphenyltin system cis-oriented. The parameters otherwise do not change with the nature of the X group, which in the tetracarbonylcobaltate derivative is tetrahedral by infrared, establishing the ionicity of the products. The chloride exhibits a molar conductivity indicative of a 1:1 electrolyte in DMF. A bridging acetate structure in the solid is consistent with the lowered $\nu(CO_2)$ frequencies. The Mössbauer spectra of the double salts give simple doublets of lowered isomer shift (IS) and raised quadrupole splitting (QS) which may arise from a cross-linking ion pairing of the polymer chains in the solid, and the NMR spectra of the two methyltin derivatives shows only a single resonance line and tin satellites which is rationalized by a dynamic exchange process. The products are

formulated as associated tin carboxylate polymers with dangling triphenylphosphonium cations.

TABLE 1

TRIPHENYLPHOSPHONOPROPIONBETAINETRIORGANOTIN(IV) SALTS^a

Compound	mp °C(decomp.)	Found (Calcd) % C	Found (Calcd) % H	Yield(%)
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(CH_3)_3]^+Cl^-$	173-74	54.19 (54.01)	5.31 (5.25)	80
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+Cl^-$	195-97	65.09 (65.07)	4.79 (4.73)	90
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+Br^-$	183-84	62.01 (61.29)	4.59 (4.45)	80
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+I^-$	183-84	60.58 (57.74)	4.61 (4.19)	70
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+NCS^-$	198-99	64.81 (64.72)	4.64 (4.58)	90
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+N_3^-$	154-55	62.79 (64.49)	4.63 (4.69)	70
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+NO_3^-$	162-64	61.39 (62.76)	4.70 (4.46)	80
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+CH_3CO_2^-$	170-73	64.55 (66.24)	4.90 (4.98)	50
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+B(C_6H_5)_4^-$	190-92	71.94 (75.41)	5.45 (5.39)	60
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+Co(CO)_4^-$	107-08	56.35 (60.38)	4.58 (4.33)	60
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+[(C_6H_5)_3SnCl_2]^-$	188-90	61.66 (61.93)	4.53 (4.44)	80
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+[(C_6H_5)_3SnBr_2]^-$	183-84	59.44 (57.32)	4.48 (4.11)	60

TABLE 1, cont'd.

Compound	mp °C(decomp)	Found (Calcd) % C	Found (Calcd) % H	Yield(%)
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+[(C_6H_5)_3Sn(N_3)_2]^-$	152-53	61.36 (61.21)	4.59 (4.39)	80
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+[(C_6H_5)_3Sn(NCO)_2]^-$	149-52	61.22 (63.36)	4.80 (4.39)	60
$[(C_6H_5)_3P(CH_2)_2CO_2SnCH_3(C_6H_5)_2]^+[CH_3(C_6H_5)_2SnCl_2]^-$	105-06	57.60 (57.52)	4.95 (4.59)	30
$[(C_6H_5)_3PS(CH_2)_2CO_2Sn(C_6H_5)_3]^+[(C_6H_5)_3SnCl_2]^-$	173-74	58.13 (60.19)	4.30 (4.31)	50
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_2(C_9H_6NO)]^+Cl^-$	172-75	62.89 (64.11)	4.07 (4.45)	30

^a Analyses performed by Galbraith Laboratories, Knoxville, Tennessee.

TABLE 2

TIN-119m MÖSSBAUER DATA FOR THE TRIPHENYLPHOSPHONOPROPIONBETAINETRIORGANOTIN(IV) SALTS AT 77K IN mm s^{-1}

	IS±0.03	QS±0.06	Γ±0.03	ρ=QS/IS
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{CH}_3)_3]^+\text{Cl}^-$	1.30	3.45	1.35	2.65
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{Cl}^-$	1.22	2.90	1.24	3.28
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{Br}^-$	1.26	3.00	1.05	2.38
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{I}^-$	1.10	2.98	1.45	2.95
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{NCS}^-$	0.96	3.05	1.28	3.18
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{N}_3^-$	1.00	3.01	1.22	3.01
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{NO}_3^-$	1.25	3.23	0.89	2.58
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{CH}_3\text{CO}_2^-$	1.19	2.90	1.32	2.44
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{B}(\text{C}_6\text{H}_5)_4^-$	0.98	3.06	1.60	3.12
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{Co}(\text{CO})_4^-$	1.21	2.96	1.17	2.45
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_2(\text{C}_9\text{H}_6\text{NO})]^+\text{Cl}^-$	0.71	2.17	2.15, 3.18	3.06
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+[(\text{C}_6\text{H}_5)_3\text{SnCl}_2]^-$	1.05	3.14	1.41	2.99

TABLE 2, cont'd.

	IS+0.03	QS+0.06	r+0.03	ρ=QS/IS
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3SnBr_2]^-$	1.09	3.16	1.21	2.90
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3Sn(N_3)_2]^-$	1.02	3.10	1.50	3.04
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3Sn(NCO)_2]^-$	0.98	2.92	1.14	2.98
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(CH_3)(C_6H_5)_2]^+ [(CH_3)(C_6H_5)_2SnCl_2]^-$	1.35	3.36	2.55	2.49
$[(C_6H_5)_3PS(CH_2)_2CO_2Sn(C_6H_5)_3]^+ [(C_6H_5)_3SnCl_2]^-$	1.28	3.15	1.02	2.45

TABLE 3

INFRARED ABSORPTIONS (cm^{-1})^{a,b}

$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{H}]^+\text{Cl}^-$	1436(s), 1418(m), 1406(m), 1357(s,br), 1278(m), 1218(s), 1190(m), 1161(m), 1112(s), 1032(m), 994(m), 947(m), 908(m), 856(m), 812(m), 750(s), 737(s), 727(s), 681(s), 533(m), 504(m), 474(s), 428(m)
$(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2$	1468(vs), 1439(vs), 1305(w), 1112(s), 996(m), 958(w), 911(m), 806(w), 706(s), 750(s), 697(s), 688(s), 514(m), 503(m), 489(m)
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{CH}_3)_3]^+\text{Cl}^-$	1587(m), 1437(vs), 1342(m), 1299(m), 1283(s), 1215(m), 1194(w), 1180(m), 1159(m), 1105(vs), 996(m), 805(s), 767(sh), 746(vs), 728(vs), 688(s), 585(w), 490(s,br), 438(w)
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{Cl}^-$	1436(s), 1375(s), 1287(s), 1192(m), 1110(s), 1167(m), 996(m), 797(w), 749(vs), 698(s), 510(m), 495(m), 442(m)
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{Br}^-$	1400(s), 1358(s), 1290(m), 1111(m), 740(s), 698(m), 510(m,br), 445(m,br)
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{I}^-$	1441(s), 1357(m), 1289(m), 1111(m), 739(m), 698(m), 687(m), 511(m,br), 498(m), 442(m)
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{NCS}^-$	1439(s), 1355(s), 1113(s), 740(s), 697(s), 689(sh), 512(w,br)
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{N}_3^-$	1439(s), 1355(w), 1068(vs), 730(s), 695(s), 498(m,br), 445(m,br)

TABLE 3, cont'd.

$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+NO_3^-$	1440(vs), 1357(s), 1300(s), 1290(s), 1275(m), 1260(m), 1113(s), 1025(m), 996(m), 737(s), 700(m), 687(m), 515(m), 445(m)
$[(C_6H_5)_3P(CH_2)CO_2Sn(C_6H_5)_3]^+CH_3CO_2^-$	1440(s), 1365(s), 1355(sh), 1315(m), 1387(m), 1108(s), 735(s), 696(s), 686(sh), 508(m), 490(sh)
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+B(C_6H_5)_4^-$	1439(s), 1355(s), 1287(m), 1111(m), 732(m), 699(m), 685(sh), 605(w,br), 510(w,br)
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+Co(CO)_4^-$	1438(s), 1362(m), 1289(m), 1111(s), 995(m), 735(s), 685(s), 545(s), 510(m,br)
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_2(C_9H_6NO)]^+Cl^-$	1495(s), 1428(s), 1326(vs), 1280(s), 1110(vs), 1073(m), 822(m), 804(m), 785(m), 728(vs), 695(vs), 500(m), 437(m)
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+[(C_6H_5)_3SnCl_2]^-$	1442(m), 1430(m), 1315(m), 748(m), 729(s), 695(s), 496(w,br), 445(w,br)
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+[(C_6H_5)_3SnBr_2]^-$	1442(m), 1309(m), 1115(m), 767(m), 727(s), 692(s), 495(w,br), 445(w,br)
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+[(C_6H_5)_3Sn(N_3)_2]^-$	1440(s), 1112(w), 729(m), 695(m), 495(w,br), 445(w,br)
$[(C_6H_5)_3P(CH_2)_2CO_2Sn(C_6H_5)_3]^+[(C_6H_5)_3Sn(NCO)_2]^-$	1428(s), 1290(m), 1112(m), 1075(m), 997(m), 912(m), 894(m), 693(vs), 500(w,br), 440(w,br)
$[(C_6H_5)_3PS(CH_2)_2CO_2Sn(C_6H_5)_3]^+[(C_6H_5)_3SnCl_2]^-$	1480(vs), 1442(vs), 1428(vs), 1114(m), 745(m), 690(vs), 492(w,br), 440(w,br)

TABLE 3, cont'd.

$[(C_6H_5)_3P(CH_2)_2CO_2Sn(CH_3)(C_6H_5)_2]^+ [(CH_3)(C_6H_5)_2SnCl_2]^-$	1442(vs), 1110(s), 730(vs), 690(vs), 500(m), 440(w,br)
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^a Recorded as Nujol Mulls on KBr plates and polystyrene film.

^b s =strong, m = medium, w = weak, v = very, sh = shoulder, br = broad.

TABLE 4

INFRARED ABSORPTIONS FOR THE CARBOXYLATE SYSTEM IN TRIPHENYLPHOSPHONOPROPIONBETAINETRIORGANOTIN SALTS
(cm^{-1})

	ν_{CO_2} (asym)	Other ν 's
$(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2$	1593,1583	
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{Sn}(\text{CH}_3)_3]^+\text{Cl}^-$	1616	
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{Cl}^-$	1643	
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{Br}^-$	1647	
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{I}^-$	1646	
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{NCS}^-$	1646	2050 (ν_{NCS}) ^a
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{N}_3^-$	1642,1586,1548	2075,2065,2045 (ν_{N_3}) ^b
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{NC}_3^-$	1648	ν_{NO_3} cannot be located
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{CH}_3\text{CO}_2^-$	1645	
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{B}(\text{C}_6\text{H}_5)_4^-$	1646	
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sb}(\text{C}_6\text{H}_5)_3]^+\text{Co}(\text{CO})_4^-$	1635,1585	1885 (ν_{CO}) ^c

TABLE 4, cont'd.

	ν_{CO_2} (asym)	Other ν 's
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_2(\text{C}_9\text{H}_6\text{NO})]^+\text{Cl}^-$	1585,1575,1560	
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+[(\text{C}_6\text{H}_5)_3\text{SnCl}_2]^-$	1600,1585,1575	
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+[(\text{C}_6\text{H}_5)_3\text{SnBr}_2]^-$	1587,1575,1557	
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+[(\text{C}_6\text{H}_5)_3\text{Sn}(\text{N}_3)_2]^-$	1587,1574,1569	2075,2065 (ν_{N_3}) ^b
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+[(\text{C}_6\text{H}_5)_3\text{Sn}(\text{NCO})_2]^-$	1645	2205 (ν_{NCO}) ^d
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{CH}_3)(\text{C}_6\text{H}_5)_2]^+[(\text{CH}_3)(\text{C}_6\text{H}_5)_3\text{SnCl}_2]^-$	1585,1575,1560	
$[(\text{C}_6\text{H}_5)_3\text{PS}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+[(\text{C}_6\text{H}_5)_3\text{SnCl}_2]^-$	1585,1575,1560	

^a The ν_{NCS} mode in $(\text{C}_6\text{H}_5)_3\text{SnNCS}$ is at 2080 cm^{-1} .

^b The ν_{N_3} mode in $(\text{C}_6\text{H}_5)_3\text{SnN}_3$ is at $2100, 2080, 2065\text{ cm}^{-1}$.

^c The ν_{CO} mode in $(\text{C}_6\text{H}_5)_3\text{SnCo}(\text{CO})_4$ is at 1890 cm^{-1} .

^d The ν_{NCO} mode in $(\text{C}_6\text{H}_5)_3\text{SnNCO}$ is at 2230 cm^{-1} .

TABLE 5

NMR DATA FOR THE METHYLTIN(IV)-CONTAINING DERIVATIVES

	δ_{CH_3} , ppm	$ ^2J(^{119}\text{Sn}-^1\text{H}) $, Hz
$(\text{CH}_3)_3\text{SnCl}$ (CDCl_3)	0.69 ^a	57.8 ^b
$[(\text{CH}_3)_3\text{SnO}_2\text{C}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_3]^+\text{Cl}^-$	0.64	72.8
" + $(\text{CH}_3)_3\text{SnCl}$ 1:1	0.64	64.5
$\text{CH}_3(\text{C}_6\text{H}_5)_2\text{SnCl}$	0.88	60.0
$[\text{CH}_3(\text{C}_6\text{H}_5)_2\text{SnO}_2\text{C}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_3]^+$		
$[\text{CH}_3(\text{C}_6\text{H}_5)_2\text{SnCl}_2]^-$	1.00	76.0

^a Ref. 50.^b Ref. 51.

TABLE 6

COMPARISON OF THE MELTING POINTS, °C., AND TIN-119m MÖSSBAUER DATA FOR THE HALIDE AND AZIDE
SIMPLE AND DOUBLE SALTS IN mm s^{-1} AT 77K

	mp	IS \pm 0.03	QS \pm 0.06	$\Gamma\pm$ 0.03
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{Cl}^-$	195-197	1.22	2.90	1.25
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+[(\text{C}_6\text{H}_5)_3\text{SnCl}_2]^-$	188-190	1.05	3.14	1.41
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{N}_3^-$	154-155	1.00	3.01	1.22
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+[(\text{C}_6\text{H}_5)_3\text{Sn}(\text{N}_3)_2]^-$	152-153	1.02	3.10	1.50
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{Br}^-$	183-184	1.26	3.00	1.05
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+[(\text{C}_6\text{H}_5)_3\text{SnBr}_2]^-$	183-184	1.09	3.16	1.21

TABLE 7

RAMAN DATA FOR THE SIMPLE HALIDE SALTS BETWEEN 350 AND 50 cm^{-1}

$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{Cl}^-$	255, 205, 70
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{Br}^-$	255, 202, 70
$[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+\text{I}^-$	255, 202, 70

TABLE 8

VARIATION OF THE NMR TIN-METHYL COUPLING CONSTANT IN
 TRIMETHYLTIN(IV) CHLORIDE IN CHLOROFORM SOLUTIONS
 OF $(C_6H_5)_3P(CH_2)_2CO_2$

$[(CH_3)_3SnCl]$	
$[(CH_3)_3SnCl] + [(C_6H_5)_3P(CH_2)_2CO_2]$	$ ^2J(^{119}Sn-C^{-1}H) $
0.299	71.8 Hz
0.442	71.8
0.483	70.4
0.646	67.8
0.680	66.6
0.710	64.8
0.783	64.4
0.814	63.8
0.834	63.8

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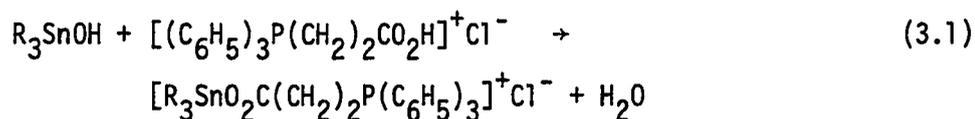
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CHAPTER 3

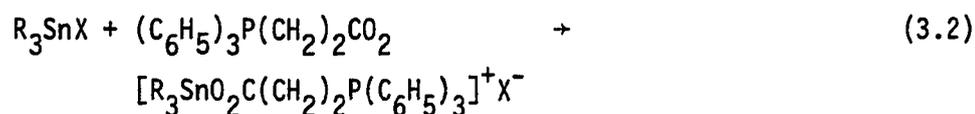
DI- AND TRIORGANOTIN(IV) DERIVATIVES OF DIPHENYLPHOSPHINYL- AND DIPHENYLTHIOPHOSPHINYL-ACETIC ACID

Introduction

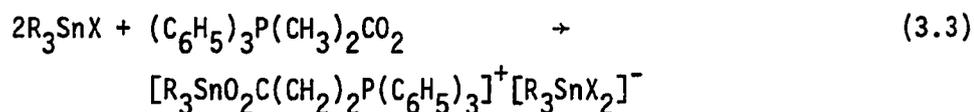
Triorganotin(IV) carboxylates in which the carboxylate moiety contains an organophosphorus substituent can be prepared from triphenyl(2-carboxyethyl)phosphonium chloride, $[(C_6H_5)_3P(CH_2)_2CO_2H]^+Cl^-$, and organostannols with the release of water:



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

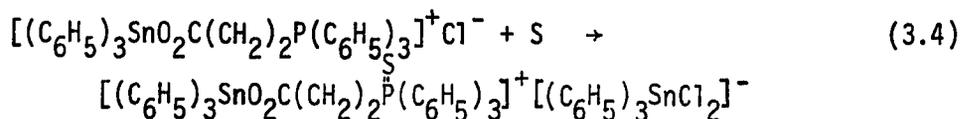


Double salts result from a 2:1 ratio of reactants:



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 triphenyl-

phosphonium cations.¹ In one case conversion to the thiophosphonium derivative was effected by the action of elemental sulfur which produced the double salt as the product:

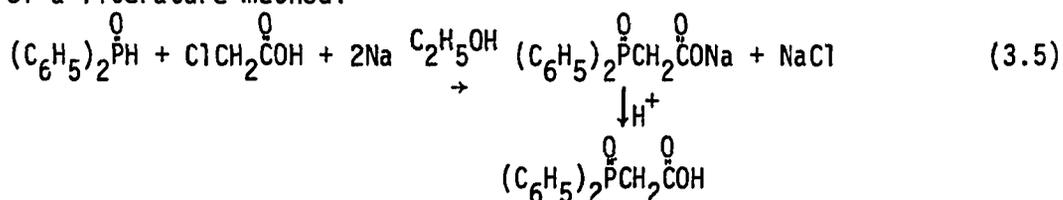


The phosphorus(V) chalcogenide atom would be expected to compete with the carboxylate oxygen as the base atom of choice for donation to tin.¹ In this present investigation the P=O function is placed on the α -carbon of the carboxylic acid. The resulting products would then be analogous to the α -amino acid derivatives.^{2,3} In trimethyltin(IV) glycinate, amino group bridging to tin is preferred⁴ to the more generally known carboxylate association.^{5,6}

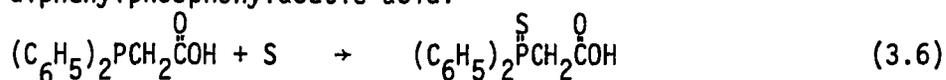
The preparation of a series of triorganotin(IV) diphenylphosphinylacetates of the form $\text{R}_3\text{SnO}\overset{\text{O}}{\text{C}}\overset{\text{O}}{\text{C}}\text{H}_2\overset{\text{O}}{\text{P}}(\text{C}_6\text{H}_5)_2$ by two methods of synthesis is described here.

Experimental Section

Diphenylphosphinylacetic acid⁷⁻¹⁰ was prepared from the sodium salt of diphenylphosphine oxide and chloroacetic acid through a modification of a literature method:⁷



and the thio derivative^{11,12} was prepared by the action of elemental sulfur on diphenylphosphonylacetic acid:¹¹



The starting organotin 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.

The ^{119m}Sn Mossbauer spectra were recorded on a Ranger Engineering constant-acceleration spectrometer equipped with a sodium iodide proportion counter. The source was $\text{Ca}^{119m}\text{SnO}_3$ (New England Nuclear Corp.) and $\text{Ca}^{119}\text{SnO}_3$ 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 circuit, and the temperature was kept at 77K 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 discs, 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 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 methods used

and their yields, melting points and microanalytical data in Table 1. Tin-119m Mössbauer data are listed in Table 2, mass spectral data in Tables 3-4, infrared data in Tables 5 and 6, and P-31 and Sn-119 NMR data in Tables 7 and 8, respectively.

Diphenylphosphinylphosphinylacetic Acid, $(C_6H_5)_2P(O)CH_2CO_2H$ ⁷⁻¹⁰

To sodium metal (5.7 g, 0.25 g-at) dissolved in absolute ethanol was added diphenylphosphine oxide (25.0 g, 0.124 mol) followed by chloroacetic acid (11.7 g, 0.124 mol). The white sodium salt precipitate was heated for 2 h, cooled, filtered, dissolved in water and the solution acidified with 1:2 sulfuric acid. The resulting diphenylphosphinylacetic 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 - 45° C (lit.⁷⁻¹⁰ 142 - 46° C).

Thallium(I) Diphenylphosphinylacetate, $(C_6H_5)_2P(O)CH_2CO_2Tl$

Diphenylphosphinylacetic acid (7.80 g, 30.0 m mol) was dissolved in absolute ethanol (50 mL) and thallium(I) ethoxide (7.48 g, 30.0 m mol) was added. The white product precipitated immediately in quantitative yield, and was filtered and washed with ethanol, mp 201 °C (d).

Diphenylthiophosphinylacetic Acid, $(C_6H_5)_2P(S)CH_2CO_2H$ ^{11,12}

This compound was prepared in quantitative yield by adding a stoichiometric amount of elemental sulfur to diphenylphosphonylacetic acid¹⁰ in acetonitrile, mp 193 - 95° C (lit.^{11,12} 190° C, 192 - 93° C).

Trimethyltin(IV) Diphenylphosphinyacetate, $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{CH}_3)_3$

Trimethyltin(IV) chloride (1.00 g, 5.00 m mol) and thallium(I) diphenylphosphinyacetate (2.32 g, 5.00 m mol) were refluxed in chloroform for 1 h, the solvent removed, and the resulting oil 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 - 65° C.

Triethyltin(IV) Diphenylphosphinyacetate, $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_2\text{H}_5)_3$

Triethyltin(IV) chloride (1.21 g, 5.00 m mol) was added to a suspension of thallium(I) diphenylphosphinyacetate (2.32 g, 5.00 m mol) in chloroform. The mixture was stirred under reflux for 2 h, cooled, the precipitated thallium(I) chloride filtered, the chloroform solvent removed on a rotary evaporator, and the resulting oil placed under vacuum. Treatment with ether gave a white solid, mp. 138 - 39° C, in 80% yield.

Tri-n-propyltin(IV) Diphenylphosphinyacetate, $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\underline{\text{n}}\text{-C}_3\text{H}_7)_3$

Bis(tri-n-propyltin) oxide (2.51 g, 5.00 m mol) and the acid (2.60 g, 10.0 m mol) were heated for 2 h in benzene (a suspected carcinogen) (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 filtered and the ether removed. The oil

solidified under vacuum to give the title compound, mp 112 - 14° C, in 70% yield.

Tri-n-butyltin(IV) Diphenylphosphinylacetate, $(C_6H_5)_2P(O)CH_2CO_2Sn(n-C_4H_9)_3$

The above-outlined procedure was used to prepare the tri-n-butyltin derivative from bis(tri-n-butyltin) oxide (2.98 g, 5.00 m mol) and diphenylphosphinylacetic acid (2.60 g, 10.0 m mol), mp 73-75° C, in 90% yield.

Tricyclohexyltin(IV) Diphenylphosphinylacetate, $(C_6H_5)_2P(O)CH_2CO_2Sn(\underline{c}-C_6H_{11})_3$

Diphenylphosphinylacetic acid (2.60 g, 10.0 m mol) and tricyclohexyltin(IV) hydroxide (3.85 g, 10.0 m mol) were dissolved in benzene (150 mL) and heated as described above. Recrystallization from chloroform gave the product mp 160 - 62° C, in 90% yield.

Triphenyltin(IV) Diphenylphosphinylacetate, $(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3$

This compound was prepared in a similar way from diphenylphosphinylacetic acid (2.60 g, 10.0 m mol) and triphenyltin(IV) hydroxide (3.67 g, 10.0 m mol), mp 180 - 83° C, in 90% yield.

Bis[triphenyltin(IV)diphenylphosphinylacetate]triphenyltin(IV) chloride, $[(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3]_2 \cdot (C_6H_5)_3SnCl$

Triphenyltin(IV) diphenylphosphinylacetate (3.05 g, 5.00 m mol)

from the preparation described above and triphenyltin(IV) chloride (1.93 g, 5.00 m mol) were dissolved in chloroform, the solution concentrated and ether added to induce crystallization of the white product, mp 177 - 180° C, in 80% yield, which 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(diphenylphosphinylacetate), $[(C_6H_5)_2P(O)CH_2CO_2]_2Sn-(CH_3)_2$

Dimethyltin(IV) oxide (0.83 g, 5.0 m mol) and diphenylphosphinylacetic acid (2.60 g, 10.0 m mol) 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%.

Diphenyltin(IV) Bis(diphenylphosphinylacetate), $[(C_6H_5)_2P(O)CH_2CO_2]_2Sn-(C_6H_5)_2$

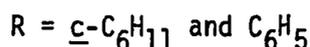
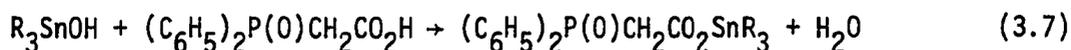
Triphenyltin(IV) chloride (1.93 g, 5.00 m mol) and sodium tetraphenylborate (1.71 g, 5.00 m mol) were dissolved in 2-propanol to precipitate sodium chloride which was filtered, and diphenylphosphinylacetic acid (1.30 g, 5.00 m mol) dissolved in the same solvent was added. A white solid slowly formed in the pink-colored solution, was filtered, and washed with chloroform, and then ether to give the product, mp 182 - 83° C, in 60% yield.

Triphenyltin(IV) Diphenylthiophosphinylacetate, $(C_6H_5)_2P(S)CH_2CO_2Sn(C_6H_5)_3$

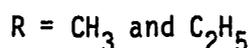
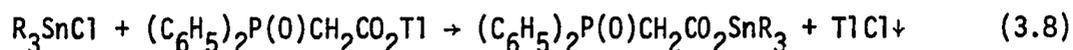
This compound was prepared from diphenylthiophosphinylacetic acid (2.60 g, 10.0 m mol) and triphenyltin(IV) hydroxide (3.67 g, 10.0 m mol) as described for diphenylphosphinylacetic acid. The crude product was recrystallized from acetonitrile to give the pure compound, mp 121 - 123.5° C, in 30% yield.

Results and Discussion

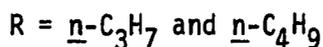
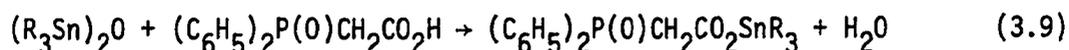
The synthesis of the triorganotin diphenylphosphinylacetates proceeds in high yield from the reaction of a triorganotin(IV) hydroxide with the diphenylphosphinylacetic acid in benzene with the reaction driven to completion by the azeotropic distillation of the water released:



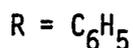
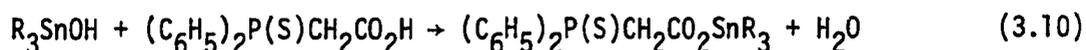
or from the action of triorganotin(IV) chloride and thallium(I) diphenylphosphinylacetate in chloroform:



or from the parent acid and the bis[trialkyltin(IV)] oxide in benzene:

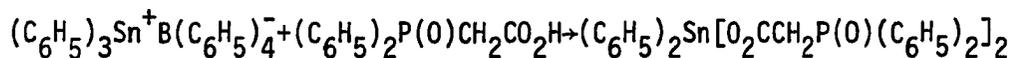


The thiophosphinylacetic acid also reacts in a similar way:

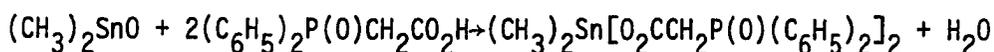


The products are white solids soluble in common organic solvents. The attempted synthesis of triphenyltin(diphenylphosphinylacetic acid)

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: (3.11)

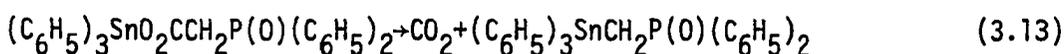


and the dimethyl derivative was synthesized from the parent acid and dimethyltin(IV) oxide: (3.12)



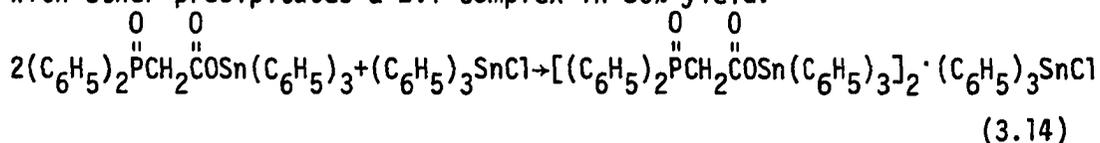
The diorganotin(IV) derivatives are white solids which are soluble in chloroform.

Heating $(\text{C}_6\text{H}_5)_3\text{SnO}_2\text{CCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)_2$ above its melting point (180 - 183° C) releases carbon dioxide which was detected as barium carbonate:



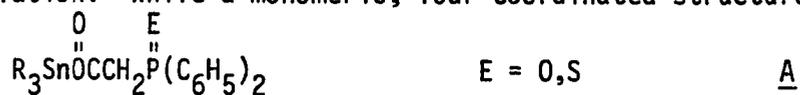
The tin-containing product has also been synthesized by organolithium and Grignard routes from triphenyltin(IV) chloride.^{10,13}

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

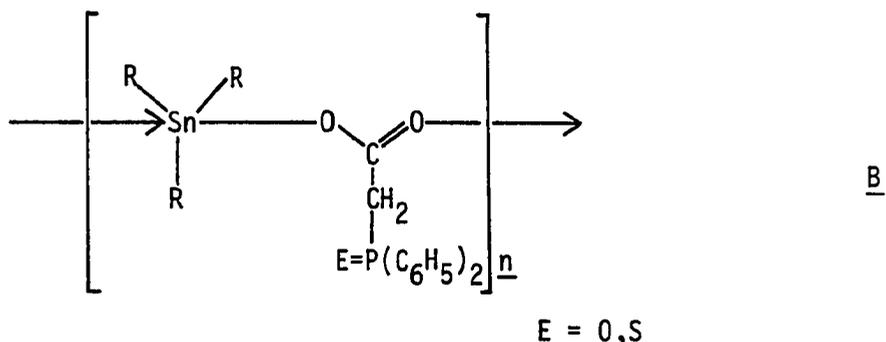


Attempts to produce representatives of the other three permutations of methyl- and phenyltin combinations in the 2:1 complexes from trimethyltin(IV) diphenylphosphinyacetate and trimethyltin(IV) chloride in addition to the above phenyltin derivatives gave only oils. Attempted replacement of the chlorine in the 2:1 product above with $\text{B}(\text{C}_6\text{H}_5)_4$ from triphenyltin(IV) tetraphenylborate also failed.

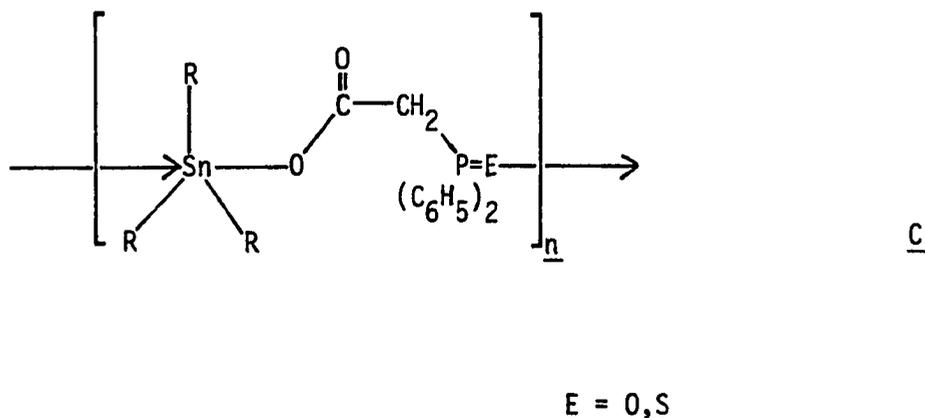
Structural discussion for these acetates must acknowledge the presence of two potential oxygen atom donor sites available for bridging or chelation. While a monomeric, four-coordinated structure, A:



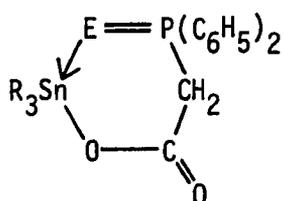
such as that discussed for tricyclohexyltin(IV) acetate^{14,15} is possible, more interesting arrangements utilize either the carboxylate oxygen atom in the bridged polymers generally found in the tin derivatives^{5,6} but ionic structure B in which the phosphorus portion of the molecule is pendant to 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:

D

E = O, S

Triphenylphosphine oxide forms a complex with triphenyltin(IV) nitrate,¹⁷ and the carbonyl-stabilized triphenylphosphoranylidene acetone ylide uses its carbonyl trimethyltin(IV) oxygen and not its carbanionic carbon in complexing trimethyltin(IV) chloride in $(C_6H_5)_3PCHC(CH_3)OSn(CH_3)_3Cl$.¹⁸ It is assumed that no six-coordinated, R_3SnL_3 forms, are possible,^{5,6} but ionic formulations as in E, need to be considered, too:



The easy solubility of these species in non-polar organic solvents makes structures B, C and E unlikely. In addition, molecular weight determinations in chloroform for the E=O; R=CH₃ and C₆H₅ derivatives give monomeric results, and the E=O, R=C₆H₅ derivative does not conduct ($\Lambda_M = 4.4 \Omega^{-1} \text{ cm}^{-1} \text{ M}^{-1}$) in DMF.

Infrared Data

Three stretching modes are important in the compounds studied, $\nu(CO_2)$, $\nu(PE)$ where E=O, S and $\nu(SnC)$, listed in the order of decreasing frequency. Assignments for the first two modes are listed in Table 5. Each can in principle yield information which can help distinguish the structural possibilities.

Trimethyltin(IV) diphenylphosphinylacetate 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 $\nu_{\text{sym}}(\text{SnC}_3)$ mode in the infrared and the $\nu_{\text{asym}}(\text{SnC}_3)$ 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,¹⁹ trimethylsilyl acetate possesses a normal ester structure in which the $\nu_{\text{asym}}(\text{CO}_2)$ frequency occurs at 1725 cm^{-1} . The corresponding absorption at 1576 cm^{-1} in trimethyltin(IV) acetate²⁰ is typical of the associated tin carboxylates.²¹ By contrast, $\nu_{\text{asym}}(\text{CO}_2)$ 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 not¹⁴ (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 the triorganotin(IV) diphenylphosphinylacetates the $\nu_{\text{asym}}(\text{CO})_2$ modes can be assigned at $1647 \pm 7 \text{ cm}^{-1}$, with $\nu_{\text{sym}}(\text{CO})_2$ at $1325 \pm 10 \text{ cm}^{-1}$. Thus strong interactions between the carboxylate carbonyl group and the tin atom as required in structure B can be ruled out. The $\nu_{\text{asym}}(\text{CO})_2$ values are almost identical to those in tricyclohexyltin(IV) acetate, and

weak interactions which probably are present in that solid cannot be excluded. By contrast, the thallium(I) derivative shows a much lowered $\nu_{\text{asym}}(\text{CO})_2$ absorption at 1575 cm^{-1} , and its higher melting point and limited solubility in non-polar organic solvents suggest a polymeric network with bridging carboxylate groups. More interesting 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 $\nu(\text{P}=\text{O})$ mode in the parent diphenylphosphinylacetic acid solid would be expected to be lowered by hydrogen bonding with the carboxylate O-H,²² 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, the former conclusion is favored, thus structure C or D.

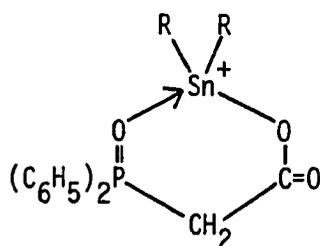
A strictly linear carbon-tin-carbon system is ruled out in $(\text{CH}_3)_2\text{Sn}[\text{O}_2\text{CCH}_2\overset{\text{O}}{\text{P}}(\text{C}_6\text{H}_5)_2]_2$ by the presence of both the ν_{asym} and $\nu_{\text{sym}}(\text{SnC}_2)$ at 565 and 545 cm^{-1} in the infrared.

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 tri-cyclohexyl derivative is a $[(C_6H_5)_2P(O)CH_2SnR_2]^+$ fragment which is derived from loss 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 $[(C_6H_5)_2P(O)CH_2SnR_2]^+$ which may also have the structure $[H_2C=P(C_6H_5)_2-O-SnR_2]^+$ if the chelated configuration is the origin of the process:



Loss of CO_2 is also observed on heating $(C_6H_5)_3SnO_2CCH_2P(O)(C_6H_5)_2$ (vide supra).

The mass spectrum of the 2:1 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) diphenylphosphinylacetate itself, except for the presence of an $[SnCl]^+$ peak. The most abundant signal arises from $[(C_6H_5)_2]^+$ at $m/e = 154$, unlike in the phosphinylacetate derivative (see Table 3).

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.²³ Thus structure A can be confidently ruled 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 acids²⁻⁴ which adopt bridged polymeric structures^{5,6} do show Mössbauer spectra at room temperature. Therefore, the absence of resolvable spectra argues against polymeric structures B and C.

For the dimethyl- and diphenyltin(IV) derivatives a treatment based upon a point charge model²⁴ can be applied 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.^{5,6,24,25} 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 $\nu_{\text{sym}}(\text{SnC}_2)$ mode in the infrared spectrum.

The Mössbauer spectrum of the 2:1 complex, $[(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]_2 \cdot (\text{C}_6\text{H}_5)_3\text{SnCl}$, is a simple doublet, implying that both types of tin atoms involved are higher than four-coordinated, since the data are nearly identical to those for the triphenyltin diphenylphosphinylacetate

derivative. While simple doublet Mössbauer spectra have been recorded for tin compounds containing tin in two different higher coordination numbers, the most famous example being the spectrum of $[(\text{CH}_3)_2\text{SnCl}\cdot\text{terpy}]^+ [(\text{CH}_3)_2\text{SnCl}_3]^-$,²⁶ the combination of four- and five-coordinated tin should be more easily distinguishable.

NMR Data

The phosphorus-31 chemical shifts for the compounds containing the $(\text{C}_6\text{H}_5)_2\text{P}(0)\text{CH}_2-$ group lie in the range 26.3 to 28.9 ppm relative to 85% phosphoric acid as shown in Table 7. This compares with similar data for the closely-related $(\text{C}_6\text{H}_5)_2\text{P}(0)\text{R}$ where $\text{R} = \text{CH}[\text{CH}_2\text{C}(0)\text{C}_6\text{H}_5]\text{C}(0)\text{C}_6\text{H}_5$ (27.5 ppm) and $\text{R} = \text{C}[\text{CH}_2\text{C}(0)\text{C}_6\text{H}_5][=\text{C}(\text{OCH}_2\text{C}_6\text{H}_5)\text{C}_6\text{H}_5]$ (28.6 ppm).²⁷ In the direct comparison of $(\text{C}_6\text{H}_5)_3\text{P}=\text{E}$ chemical shifts, with $\text{E} = \text{O}$ (23.0 - 27.0 ppm) and $\text{E} = \text{S}$ (42 ppm), the sulfur derivative is to lower field,²⁷ just as in the case of the present 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.²⁸⁻³⁰ For the monomeric triorganotin(IV) carboxylates, the tin chemical shift is found to low field of tetramethyltin(IV), while for associated species it is found to high field.³¹ Of the tin-119 NMR data, for only two compounds are the chemical shifts to low field. These are the derivatives with the smallest alkyl groups, $(\text{C}_6\text{H}_5)_2\text{P}(0)\text{CH}_2\text{CO}_2\text{SnR}_3$ where $\text{R} = \text{CH}_3$ ³² and C_2H_5 . The other compounds listed in Table 9 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 monomeric and associated species which are in a slow equilibrium on the NMR timescale. The 2:1 complex shows three resonances, all to high field, but this is puzzling since dissociation in solution can give rise to only two monomeric species.

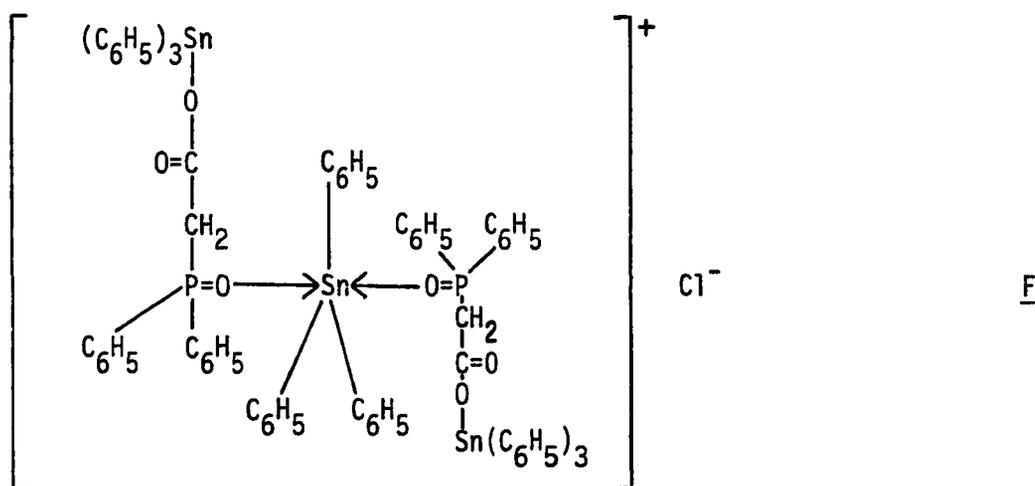
Molecular weight determinations show the trimethyl- and triphenyltin derivatives to be monomers in chloroform solution, and proton NMR data for the methyl groups [$\delta = 0.57$ ppm; $|^2J(^{119}\text{Sn-C-}^1\text{H})| = 65.6$ Hz] in the same solvent are consistent with four-coordinated tin in this phase.³³ The lack of shift of the $\nu(\text{CO}_2)$ 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 $\nu(\text{CO})_2$ 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 there is

the frequency in the strongly hydrogen bonded parent acid as a model of a coordinated system,²² and the similarity to the positions observed for the tin 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,^{5,6} but this is ruled out by infrared and Raman $\nu(Sn-C_3)$ data. Thus the most probable structure is 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 into planarity, or to hold the oligomers together in the solution or gas phases.

The structure of the 2:1 complex is more difficult to interpret. Discarding the unlikely six-coordinated, R_3SnClL_2 , form for the triphenyltin(IV) chloride forces consideration of a cationic formulation:

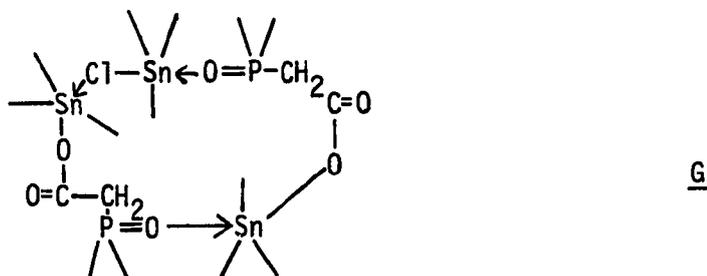


which is drawn in F with the conventional axially-most-electronegative structure. The infrared data in the carboxylate group region are like

those for the simple diphenylphosphinylaceta derivatives in ruling out carbonyl-oxygen interaction, and those for the $\nu(\text{P}=\text{O})$ are similar as well in confirming coordination to tin through this oxygen.

The difficulty with structure F lies in the fact that use of the $\text{P}=\text{O}$ moieties to coordinate the tin atom in the triphenyltin cation means denying its use to coordinate the intramolecular tin atoms, thus presumably reducing their coordination number to four. Such atoms should show a characteristic Mossbauer spectrum whose pattern would be very different from that of the five-coordinated, cationic tin.^{5,6} In addition, the chloride in the complex could not be replaced with the $\text{B}(\text{C}_6\text{H}_5)_4^-$ anion by metathesis using triphenyltin(IV) tetraphenylborate. Conductivity measurements in DMF give $18.9 \Omega^{-1} \text{ cm}^{-1} \text{ M}^{-1}$, which is a much lower value than that recorded for the analogous 1:1 ionic $[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+ \text{Cl}^-$ ($48 \Omega^{-1} \text{ cm}^{-1} \text{ M}^{-1}$) in the same solvent.¹

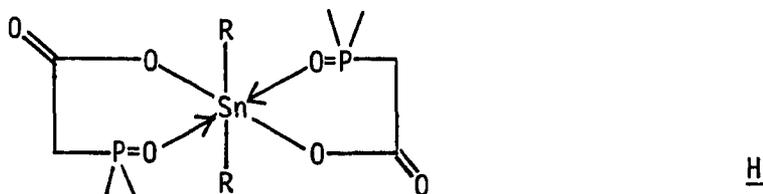
The alternative structure, G, avoids the ionic formulation of F, but introduces three different types of tin atoms, and does not provide a solution to the problem of writing a formulation with all the tin atoms higher than four-coordinated unless chlorine bridging is invoked:



Such bridging in trimethyltin(IV) chloride determines the zig-zag polymeric nature of this solid,³⁴ but triphenyltin(IV) chloride forms a crystal

of monomers.³⁵

The data for the diorganotin(IV) bisdiphenylphosphinyllacetates are easier to interpret in terms of structure. Here the high Mössbauer QS values specify open carbon-tin-carbon angles²⁴ characteristic of the ubiquitous, trans-diorganotin octahedral structures,^{5,6} and the high $|^2J(^{119}\text{Sn}-\text{C}-^1\text{H})|=98.0$ Hz coupling recorded for the dimethyltin derivative specifies that the six-coordinated structure³³ survives transfer to chloroform solution. Observation of both ν_{asym} and $\nu_{\text{sym}}(\text{SnC}_2)$ 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 one can write in the trans-, trans-, trans-form without wishing to specify the connectivity of the diphenylphosphinyllacetato ligand.

Summary

Seven triorganotin(IV) diphenylphosphinyl- and diphenylthiophosphinyl acetates, $(\text{C}_6\text{H}_5)_2\text{P}(\text{E})\text{CH}_2\text{CO}_2\text{SnR}_3$, where $\text{E} = \text{O}$ and $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \underline{n}\text{-C}_3\text{H}_7, \underline{n}\text{-C}_4\text{H}_9, \underline{c}\text{-C}_6\text{H}_{11}$ and C_6H_5 , and $\text{E} = \text{S}$ and $\text{R} = \text{C}_6\text{H}_5$ 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, $(\text{C}_6\text{H}_5)_2\text{Sn}[\text{O}_2\text{CCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)_2]_2$, 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 2:1 complex, $[(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]_2 \cdot (\text{C}_6\text{H}_5)_3\text{SnCl}$. Evidence from a battery of 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 non-planar 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. The 2:1 complex may be either a bis-complex of the triphenyltin(IV) cation, or more likely a cyclic trimer held by two $\text{P}=\text{O} \rightarrow \text{Sn}$ and one bridging $\text{Sn}-\text{Cl}-\text{Sn}$ coordinate linkages.

TABLE 1

DI- AND TRIORGANOTIN(IV) DIPHENYLPHOSPHINYL- AND THIOPHOSPHINYLCETATES

Compound	Prepn ^a	mp °C	%C Found (Calcd)	%H Found (Calcd)	Yield
$(C_6H_5)_2P(O)CH_2CO_2H$	-	144-45			70%
$(C_6H_5)_2P(O)CH_2CO_2Tl$	-	201	35.56 (35.25)	2.57 (3.02)	100%
$(C_6H_5)_2P(S)CH_2CO_2H^{10-11}$	-	193-95			100%
$(C_6H_5)_2P(O)CH_2CO_2Sn(CH_3)_3^b$	2	164-65	47.80 (48.26)	5.12 (4.97)	60%
$(C_6H_5)_2P(O)CH_2CO_2Sn(C_2H_5)_3$	2	138-39	51.72 (51.65)	5.85 (5.81)	80%
$(C_6H_5)_2P(O)CH_2CO_2Sn(\underline{n-C_3H_7})_3$	3	112-14	54.64 (54.47)	6.54 (6.51)	70%
$(C_6H_5)_2P(O)CH_2CO_2Sn(\underline{n-C_4H_9})_3$	3	73-75	57.08 (56.86)	7.02 (7.11)	90%
$(C_6H_5)_2P(O)CH_2CO_2Sn(\underline{c-C_6H_{11}})_3$	1	160-62	63.54 (61.27)	7.32 (7.18)	90%
$(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3^c$	1	180-83	61.36 (63.09)	4.40 (4.44)	90%
$(C_6H_5)_2P(S)CH_2CO_2Sn(C_6H_5)_3$	4	121-24	61.35 (61.47)	4.41 (4.32)	30%
$[(C_6H_5)_2P(O)CH_2CO_2Sn(C_6H_5)_3]_2 \cdot (C_6H_5)_3SnCl^d$	5	177-80	61.84 (61.40)	4.55 (4.31)	80%
$[(C_6H_5)_2P(O)CH_2CO_2]_2Sn(CH_3)_2$	6	75-78	55.04 (54.00)	4.72 (4.50)	30%

TABLE 1, cont'd.

Compound	Prepn ^a	mp °C	%C Found (Calcd)	%H Found (Calcd)	Yield
$[(C_6H_5)_2P(O)CH_2CO_2]_2Sn(C_6H_5)_2$	7	182-83	59.69 (60.71)	4.31 (4.30)	80%

^a Preparations 1, 2, 3, 4, 5, 6 and 7 are depicted in Eqs. 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: 1.98 (2.22)%.

TABLE 2

TIN-119m MÖSSBAUER DATA FOR THE DI- AND TRIORGANOTIN(IV) DIPHENYLPHOSPHINYL- AND
DIPHENYLTHIOPHOSPHINYLCETATES AT 77K IN mm s⁻¹ ^a

Compound	IS±0.03	QS±0.06	Γ±0.03	ρ=QS/IS
(C ₆ H ₅) ₂ P(O)CH ₂ CO ₂ Sn(CH ₃) ₃	1.33	3.71	1.31	2.79
(C ₆ H ₅) ₂ P(O)CH ₂ CO ₂ Sn(C ₂ H ₅) ₃	1.45	3.66	1.15	2.52
(C ₆ H ₅) ₂ P(O)CH ₂ CO ₂ Sn(<u>n</u> -C ₃ H ₇) ₃	1.46	3.71	1.34	2.54
(C ₆ H ₅) ₂ P(O)CH ₂ CO ₂ Sn(<u>n</u> -C ₄ H ₉) ₃	1.44	3.54	0.92	2.46
(C ₆ H ₅) ₂ P(O)CH ₂ CO ₂ Sn(<u>c</u> -C ₆ H ₁₁) ₃	1.50	3.57	1.08	2.38
(C ₆ H ₅) ₂ P(O)CH ₂ CO ₂ Sn(C ₆ H ₅) ₃	1.28	3.28	0.90	2.56
(C ₆ H ₅) ₂ P(S)CH ₂ CO ₂ Sn(C ₆ H ₅) ₃	1.34	3.47	1.56	2.59
[(C ₆ H ₅) ₂ P(O)CH ₂ CO ₂ Sn(C ₆ H ₅) ₃] ₂ ·(C ₆ H ₅) ₃ SnCl	1.28	3.31	1.00	2.59
[(C ₆ H ₅) ₂ P(O)CH ₂ CO ₂] ₂ Sn(CH ₃) ₂	1.26	3.80	1.35	3.02
[(C ₆ H ₅) ₂ P(O)CH ₂ CO ₂] ₂ Sn(C ₆ H ₅) ₂	1.28	3.27	1.08	2.55

^a Relative to Ca¹¹⁹SnO₃.

TABLE 3

MASS SPECTRAL DATA FOR THE TRIORGANOTIN(IV) DIPHENYLPHOSPHINYLCETATES^a

R	$[(C_6H_5)_2P(O)CH_2CO_2SnR_2]^+$	$[(C_6H_5)_2P(O)CH_2SnR_2]^+$	$[(C_6H_5)_2P(O)CH_2CO_2Sn]^+$	$[(C_6H_5)_2P(O)CH_2Sn]^+$	$[RSn]^+$	$[C_6H_5Sn]^+$	$[Sn]^+$
CH ₃	85	100	0	46	57	47	22
C ₂ H ₅	53	100	0	98	21	44	25
<u>n</u> -C ₃ H ₇	17	100	3	97	0	68	40
<u>n</u> -C ₄ H ₉	39	100	4	96	10	32	24
<u>c</u> -C ₆ H ₁₁	34	44	10	100	0	27	6
C ₆ H ₅	5	100	0	26	10	10	43

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

TABLE 4

MASS SPECTRAL DATA FOR THE DIORGANOTIN(IV) BIS-DIPHENYLPHOSPHINYLCETATES

	$[(C_6H_5)_2P(O)CH_2]_2SnR_2]^+$	$[(C_6H_5)_2P(O)CH_2CO_2SnR_2]^+$	$[(C_6H_5)_2P(O)CH_2SnR_2]^+$	$[(C_6H_5)_2P(O)CH_2Sn]^+$	$[SnR_3]^+$	$[Sn(C_6H_5)]^+$	$[Sn]^+$	Others
R = CH ₃	11	0	52	27	6 ^a	21	15 ^b	<u>c</u>
R = C ₆ H ₅	0	8	100	21 ^d	23	56	19	

^a $[Sn(CH_3)_2(C_6H_5)]^+$.

^b $[SnH]^+$.

^c $[(C_6H_5)_2P(O)CHSn(CH_3)_2(C_6H_5)]^+$ 5%; $[(C_6H_5)_2P(O)CH_2]^+$ 100%.

^d $[(C_6H_5)_2P(O)CHSn]^+$.

TABLE 5

INFRARED $\nu(\text{CO}_2)$ AND $\nu(\text{P}=\text{O})$ ASSIGNMENTS FOR THE DI- AND TRIORGANOTIN(IV) DIPHENYLPHOSPHINYLCETATES

	$\nu_{\text{asym}}(\text{CO}_2)$	$\nu_{\text{sym}}(\text{CO}_2)$	$\nu(\text{P}=\text{O})$
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{H}$	1733(vs) 1708(vs)		1214(m), 1157(vs), 1145(vs), 1128(vs), 1096(vs), 1070(s)
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{CH}_3)_3$	1648(vs)	1332(vs)	1217(m), 1174(vs), 1118(s), 1106(s), 1070(m)
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_2\text{H}_5)_3$	1640(vs)	1335(vs)	1200(m), 1173(vs), 1150(vs), 1126(s), 1100(s)
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\underline{\text{n}}\text{-C}_3\text{H}_7)_3$	1642(vs)	1335(vs)	1199(m), 1178(vs), 1124(s), 1107(s), 1068(m)
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\underline{\text{n}}\text{-C}_4\text{H}_9)_3$	1654(vs)	1328(vs)	1190(s), 1180(vs), 1122(s), 1102(m), 1074(w)
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\underline{\text{c}}\text{-C}_6\text{H}_{11})_3$	1645(vs)	1327(vs) 1315(vs)	1201(s), 1157(vs), 1128(s), 1102(m), 1082(m)
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3$	1645(vs)	1335(vs) 1318(sh)	1216(s), 1147(vs), 1129(vs), 1098(vs), 1073(s)
$[(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]_2 \cdot (\text{C}_6\text{H}_5)_3\text{SnCl}$	1642(vs)	1335(vs) 1322(sh)	1216(m), 1147(vs), 1131(vs), 1097(s), 1080(m)
$[(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2]_2\text{Sn}(\text{CH}_3)_2$	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)

TABLE 5, cont'd.

	$\nu_{\text{asym}}(\text{CO})_2$	$\nu_{\text{sym}}(\text{CO}_2)$	$\nu(\text{P}=\text{O})$
$[(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2]_2\text{Sn}(\text{C}_6\text{H}_5)_2$	1645(vs)	1335(vs) 1320(sh)	1216(m), 1148(vs), 1131(vs), 1098(s); 1082(m)
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Tl}$	1575(s) 1567(vs)	1348(vs)	1201(m), 1167(vs), 1123(s), 1098(m); 1073(m)
$(\text{C}_6\text{H}_5)_2\text{P}(\text{S})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3$	1575(vs)	1308(m)	

TABLE 6

 INFRARED DATA FOR THE DI- AND TRIORGANOTIN(IV) DERIVATIVES
 BELOW 1500 cm^{-1}

$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{H}$	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)
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{CH}_3)_3$	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)
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_2\text{H}_5)_3$	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)
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\underline{n}\text{-C}_3\text{H}_7)_3$	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)
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\underline{n}\text{-C}_4\text{H}_9)_3$	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)
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\underline{c}\text{-C}_6\text{H}_{11})_3$	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)
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3$	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)
$[(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]_2 \cdot$ $(\text{C}_6\text{H}_5)_3\text{SnCl}$	1436(m), 1431(m), 1025(w), 996(w), 851(w), 818(w), 693(s), 596(w), 506(w), 442(m), 408(m,br)
$[(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2]_2\text{Sn}(\text{CH}_3)_2$	1436(s), 997(w), 932(w), 852(m), 796(m), 745(s), 692(s), 600(m,br), 580(sh), 521(s), 501(s)

TABLE 6, cont'd.

$[(C_6H_5)_2P(O)CH_2CO_2]_2Sn(C_6H_5)_2$	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 7

^{31}P NMR DATA FOR THE ORGANOTIN DIPHENYLPHOSPHINYLCETATES IN
DEUTERATED CHLOROFORM^a

$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{CH}_3)_3$	28.9 ppm
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_2\text{H}_5)_3$	26.9
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{n-C}_3\text{H}_7)_3$	26.3
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{n-C}_4\text{H}_9)_3$	26.9
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{c-C}_6\text{H}_{11})_3$	26.0
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3$	27.0
$[(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]_2 \cdot (\text{C}_6\text{H}_5)_3\text{SnCl}$	27.2
$[(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2]_2\text{Sn}(\text{C}_6\text{H}_5)_2$	26.9
$(\text{C}_6\text{H}_5)_2\text{P}(\text{S})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3$	37.4

^a Relative to 85% phosphoric acid. Positive values downfield.

TABLE 8

 ^{119}Sn NMR DATA FOR THE ORGANOTIN DIPHENYLPHOSPHINYLCETATES
 IN DEUTERATED CHLOROFORM^a

$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{CH}_3)_3$	+66 ppm
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_2\text{H}_5)_3$	+108
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\underline{n}\text{-C}_3\text{H}_7)_3$	-62
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\underline{n}\text{-C}_4\text{H}_9)_3$	-60
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3$	-120
$[(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]_2 \cdot (\text{C}_6\text{H}_5)_3\text{SnCl}$	-116, -143, -158
$(\text{C}_6\text{H}_5)_2\text{P}(\text{S})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3$	-97, +11

^a Relative to tetramethylstannane. Positive values downfield.

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CHAPTER 4

ORGANOTIN(IV) PHENYLSULFINYLACETATES

Introduction

In the bidentate ionic ligand $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2^-$, the phosphinyl oxygen coordinates to the tin in preference to the carboxylate oxygen, despite carboxylate being an unusually strong bridging group in organotin(IV) chemistry.¹ Mössbauer partial quadrupole splitting predictions show that the sulfoxide group is a slightly weaker base towards tin,² and it is, therefore, possible to form complexes of tin(IV) of the type $\text{C}_6\text{H}_5\text{S}(\text{O})\text{CH}_2\text{CO}_2\text{SnR}_3$, with the possibility of the sulfinyl oxygen engaging in coordination to give a six-membered ring. The resulting phenylsulfinylacetates would be expected to possess solid-state structures similar to those of the phosphinylacetates. On the other hand, ketones are generally extremely weak bases towards tin, and ketone-tin complexes can result only if the ligand has the ability to disperse charge.³ In the analogous series of 2-benzoylbenzoates, $2\text{-C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2\text{SnR}_3$, the ketonic oxygen does not engage in bridging,⁴ whereas in the aminoacetate derivatives, the lone pair on the amino nitrogen interacts with the tin atom.^{5,6} The present study extends the series of substituted carboxylates of organotin(IV).

Experimental Section

Thiophenoxyacetic acid, $C_6H_5SCH_2CO_2H$, was purchased from the Aldrich Chemical Company, Inc. Oxidation by hydrogen peroxide⁷⁻¹⁰ was found to be too tedious, and the sulfoxide, $C_6H_5S(O)CH_2CO_2H$, was instead prepared by the periodate oxidation of thiophenoxyacetic acid in water,¹¹ mp 119.5° C.

Trimethyltin(IV) Phenylsulfinylacetate, $C_6H_5S(O)CH_2CO_2Sn(CH_3)_3$

Trimethyltin(IV) acetate (2.33 g, 10.0 m mol) and phenylsulfinylacetic acid (1.84 g, 10.0 m mol) were dissolved in toluene (250 mL). The solvent was removed to half its volume by distillation, and the distillate, which had a faint odor of acetic acid, was discarded. The organotin solution was filtered and then evaporated to dryness to yield an oil. Addition of ether gave a cream-colored product, mp 142 - 44° C, in 70% yield. The mass spectrum showed peaks at m/e (intensity) values of 348 (16.2), M^+ ; 333 (93.7), $[C_6H_5S(O)CH_2CO_2Sn(CH_3)_2]^+$; 289 (10.1), $[C_6H_5(O)CH_2Sn(CH_3)_2]^+$; 275 (4.8), $[C_6H_5S(O)CH_2SnCH_3]^+$; 259 (17.3), $[C_6H_5S(O)CH_2Sn]^+$; 165 (100), $[(CH_3)_3Sn]^+$ and 120 (0.2) Sn^+ . In deuterated chloroform, the $|^2J(^{119}Sn-C-^1H)|$ value is 66.1 Hz.

Tricyclohexyltin(IV) Phenylsulfinylacetate, $C_6H_5S(O)CH_2CO_2Sn(C_6H_{11})_3$

The compound was prepared from tricyclohexyltin(IV) hydroxide (3.86 g, 10.0 m mol) and phenylacetic acid (1.84 g, 10.0 m mol) by refluxing the reagents in toluene in a Dean-Stark water separator for 1 h. The solution was filtered hot, and evaporation of half the volume of the

toluene followed by cooling gave the white product in 60% yield, mp 165 - 67° C. The mass spectrum displayed tin-bearing fragments at m/e (intensity) values of 469 (100), $[\text{C}_6\text{H}_5\text{S}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_{11})_2]^+$; 425 (55.7), $[\text{C}_6\text{H}_5\text{S}(\text{O})\text{CH}_2\text{Sn}(\text{C}_6\text{H}_{11})_2]^+$; 395 (19.3), $[\text{C}_6\text{H}_5\text{SSn}(\text{C}_6\text{H}_{11})_2]^+$ and 321 (6.5), unassigned. A ditin fragment at m/e 613 (1.9), unassigned, is also observed.

Triphenyltin(IV) Phenylsulfinylacetate, $\text{C}_6\text{H}_5\text{S}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3$

Triphenyltin(IV) hydroxide (3.67 g, 10.0 m mol) and phenylsulfinylacetic acid (1.84 g, 10.0 m mol) were refluxed in toluene (150 mL) in a Dean-Stark apparatus for 1 h. The solution was filtered and the solvent removed under vacuum to give an oil. Addition of ether gave the white compound in 60% yield, mp 151 - 53° C. The mass spectrum showed fragments at m/e (intensity) values of 457 (27.9), $[\text{C}_6\text{H}_5\text{S}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_2]^+$; 413 (28.5), $[\text{C}_6\text{H}_5\text{S}(\text{O})\text{CH}_2\text{Sn}(\text{C}_6\text{H}_5)_2]^+$; 365 (20.6), $[\text{C}_6\text{H}_5\text{CH}_2\text{Sn}(\text{C}_6\text{H}_5)_2]^+$; 351 (100), $[(\text{C}_6\text{H}_5)_3\text{Sn}]^+$; 274 (5.2), $[(\text{C}_6\text{H}_5)_2\text{Sn}]^+$ and 120 (1.5) Sn^+ . No m/e fragments greater than the parent ion were observed.

Attempted Preparations of the Phenylacetates of $(\text{C}_2\text{H}_5)_3\text{Sn}$, $(\text{CH}_3)_2\text{Sn}$ and $(\text{C}_6\text{H}_5)_2\text{Sn}$

The attempted preparations of the triethyltin(IV) derivative from triethyltin(IV) chloride and sodium phenylsulfinylacetate in ethanol returned the starting materials. Refluxing R_2SnO ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) and the acid in benzene or toluene followed by the removal of the solvent resulted in a brown oil which was not amenable to crystallization.

Results and Discussion

The band at 1008 cm^{-1} in the infrared spectrum of phenylsulfinylacetic acid is assigned to the S=O stretching frequency,⁹ and this band is not shifted to lower wavenumbers in the trimethyl- and tricyclohexyltin(IV) compounds, but is shifted by 36 cm^{-1} in the triphenyltin(IV) derivative. Thus, it appears that coordination does not take place via the sulfinyl oxygen in the first two cases, but does in the last. Further support of this comes from the position of the asymmetric CO_2 stretch of the aryl derivative, which at 1682 cm^{-1} is not indicative of coordination through the carboxylate oxygen. The carbonyl band appears at about 1650 cm^{-1} in the two alkyl compounds and in the trimethyltin(IV) derivative, only one Sn-C band is observed, thus establishing the planarity of the $(\text{CH}_3)_3\text{Sn}$ skeleton.

Higher than four coordination for the trimethyltin(IV) compound is also dictated by the coupling constant of 66.1 Hz in chloroform. However, molecular weight measurements in the same solvent were not able to detect the presence of oligomers, although ditin fragments were observed in the mass spectrum at 12 eV. Such fragments were not observed for triphenyltin(IV) phenylsulfinylacetate, and this is negative evidence for a monomeric formulation.

The sulfoxide group is not expected to be as strong a donor as compared to, for example, DMSO, because of the presence of the electron-withdrawing carboxylate group. Thus, in the NMR spectrum of a 1:2 chloroform mixture of $(\text{CH}_3)_2\text{SnCl}_2:\text{C}_6\text{H}_5\text{S}(\text{O})\text{CH}_2\text{CO}_2\text{H}$, the value of 78.3 Hz recorded for the coupling constant suggests that only one ligand is able to be coordinated to the tin.

TABLE 1

ANALYTICAL DATA FOR THE TRIORGANOTIN(IV) PHENYLSULFINYLACETATES

Compound	%C Found (Calcd.)	%H Found (Calcd.)	Mol. wt. (in CHCl ₃)
$C_6H_5S(O)CH_2CO_2Sn(CH_3)_3$	38.20 (38.07)	4.79 (4.61)	360
$C_6H_5S(O)CH_2CO_2Sn(c-C_6H_{11})_3$	56.76 (56.66)	7.33 (7.26)	
$C_6H_5S(O)CH_2CO_2Sn(C_6H_5)_3$	58.43 (58.57)	4.15 (4.13)	

TABLE 2

INFRARED DATA FROM 2000 TO 400 cm^{-1} FOR THE TRIORGANOTIN(IV)
 PHENYLSULFINYLACETATES IN NUJOL

$\text{C}_6\text{H}_5\text{S}(\text{O})\text{CH}_2\text{CO}_2\text{H}$	1725(vs,b), 1240(s,b), 1191(m), 1122(s), 1085(s), 1008(vs,b), 984(vs), 887(s), 746(s), 682(s), 651(m), 565(m), 493(s)
$\text{C}_6\text{H}_5\text{S}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{CH}_3)_3$	1651(sh), 1639(vs), 1357(vs), 1330(vs), 1209(m), 1197(m), 1085(m), 1005(vs), 995(vs), 927(m), 780(s), 737(s), 702(m), 687(s), 543(s), 513(sh), 501(s), 486(s)
$\text{C}_6\text{H}_5\text{S}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\underline{\text{C}}\text{-C}_6\text{H}_{11})_3$	1649(vs), 1450(vs), 1357(vs), 1204(s), 1176(s), 1081(s), 1010(vs), 996(vs), 926(s), 905(s), 881(m), 842(m), 751(vs), 688(vs), 663(m), 505(s), 471(m)
$\text{C}_6\text{H}_5\text{S}(\text{O})\text{CH}_2\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3$	1682(vs), 1486(vs), 1430(vs), 1322(vs,b), 1200(m), 1109(m), 1092(m), 1080(vs), 1026(m), 1000(m), 972(vs), 913(s), 808(s), 749(s), 734(vs), 699(vs), 686(vs), 603(w), 498(m), 475(w), 450(vs)

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CHAPTER 5

DI- AND TRIORGANOTIN(IV) DERIVATIVES OF 2-BENZOYLBenZOIC ACID

Introduction

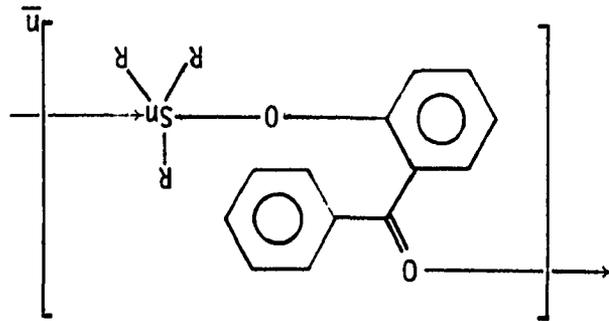
2-Benzoylbenzoic acid is an example of a non-enolizable carbonyl compound which exists in a ring-chain tautomeric equilibrium in solution. The relative amounts of the keto-acid (I) and the lactol (II) in solution can be varied depending upon the substitution pattern and the solvent polarity. For example, while the parent acid exists in the open form (I) in the solid state and dissolved in non-polar solvents, 2-benzoyl-3,4,5,6-tetrachlorobenzoic acid exists as the lactol (II) in the solid state and in very polar solvents.¹ Pseudo and normal esters can be formed from these tautomers, and infrared $\nu(\text{C}=\text{O})$ frequencies can be used to distinguish the two forms (pseudo ester 1765, normal ester 1715 and 1663 cm^{-1}).^{1,2}

The synthesis of a series of organotin(IV) carboxylates in which the organic acid moiety contains a diorganophosphine oxide substituent α -to the acetate group has been reported.³ These tin(IV) diphenylphosphinylacetate derivatives, $[(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CO}_2]_n\text{SnR}_{4-n}$ ($n = 1, 2$), contain tin atoms with coordination numbers greater than four, but it is the phosphinyl oxygen atom that binds in each case in preference to the more

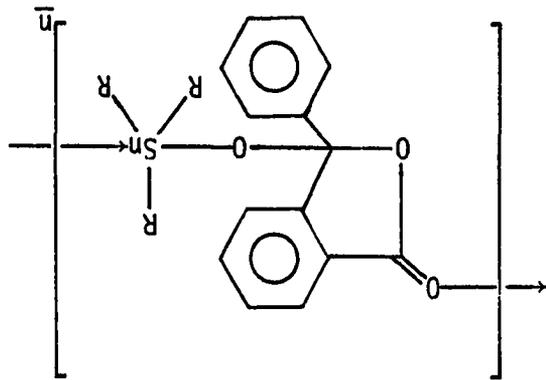
conventional carboxylate bridging.^{4,5} Carboxylate bridging is also not the preferred form in the α -amino acid derivatives, $\text{NH}_2\text{CHR}\text{CO}_2\text{SnR}_3$, in which the amino nitrogen coordinates to the tin atom intermolecularly,^{6,7} but the triphenylphosphonopropionbetainetriorganotin(IV) salts, $[(\text{C}_6\text{H}_5)_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{SnR}_3]^+\text{X}^-$, are associated tin carboxylate linear polymers with dangling triphenylphosphonium cations.⁸

Organotin(IV) esters of the 2-benzoylbenzoic acids should be particularly interesting. The product deriving from the open-keto acid form, (I), would be an organotin carboxylate ester with a ketonic carbonyl group in the γ -position potentially capable of intramolecularly coordinating to the tin atom to form a seven-membered heterocyclic system, (III), or intermolecularly coordinating to form an associated, carboxylate-bridged polymer with dangling benzophenone groups, (V). The product from the lactol form, (II), would be an ester whose uncoordinated form, (IV), is depicted in equilibrium with the monomeric carboxylate ester product, (III). Both polymeric (VI) and monomeric coordinated forms are possible for the product from the lactol (II), but model studies favor the former, since the latter would necessitate rather severe distortions of the valence angles to produce the axial-carbonyl binding to the tin atom. The monomeric, intramolecularly-coordinated product, (III), from the open form would contain both axial- and equatorial-oxygen atoms rather than the preferred axially-most-electronegative configuration with equatorial-triorganotin groups.

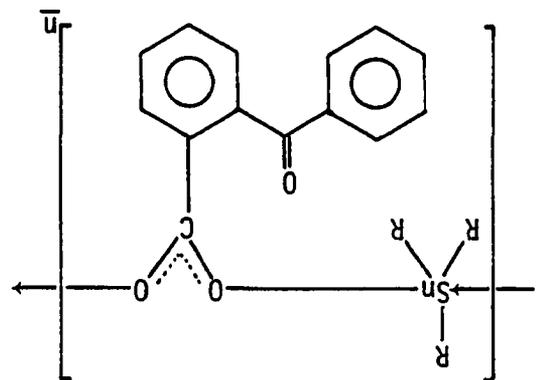
(VII)



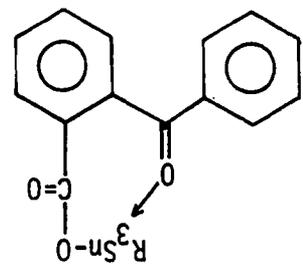
(VI)



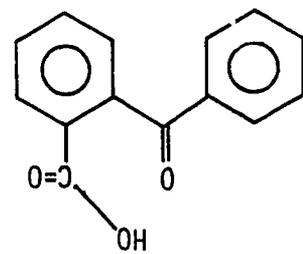
(V)



(IV)

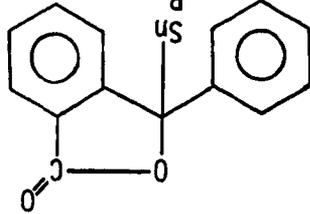


(I)

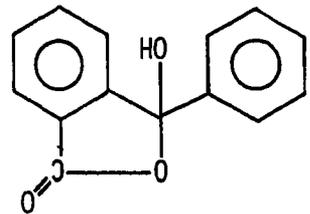


105

(III)



(ii)



(5.2)

(5.1)

Ketones are generally weak donors toward tin, and isolable complexes usually involve the capacity for charge dispersal. However, the 1:1 adduct of dimethyltin(IV) dichloride with diphenylcyclopropenone, $[(CH_3)_2SnCl_2 \cdot O=CC_2(C_6H_5)_2]_2$, is a dimer in the solid state with tin-chlorine bridges.⁹

In this section the synthesis and spectroscopic study of a series of di- and triorganotin(IV) 2-benzoylbenzoates are reported. Di-n-butyltin bis-2-benzoylbenzoate has been claimed in a patent.¹⁰

Experimental Section

The starting organotin compounds were gifts from M & T Chemicals, Inc., and were used without further purification. 2-Benzoylbenzoic acid (Eastman) was recrystallized from ethanol or chloroform before use and 2-benzoyl-3,4,5,6-tetrachlorobenzoic acid was prepared from a Friedel-Crafts reaction between tetrachlorophthalic anhydride and benzene. The acid chloride of the latter acid, mp 183° C, and the pseudo-methyl ester of 2-benzoylbenzoic acid, mp 90° C, were prepared by literature procedures.¹ Other reagents were articles of commerce.

The ^{119m}Sn Mössbauer spectra were recorded on a Ranger Engineering, constant-acceleration spectrometer equipped with an NaI proportion 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 natural iron foils. The Ranger Engineering variable-temperature liquid nitrogen dewar and controller were regulated by a variable-bridge, silicon-controlled-rectifier circuit, and the measurements were done at 77K. The data were

stored in 512 channels the Tracor Northern Model TN-1314 multichannel analyzer and the resultant spectra fitted using standard least-squares techniques assuming a Lorentzian shape.

Infrared spectra were recorded on a Beckman 4250 spectrometer as Nujol mulls on CsI discs, and the spectra were calibrated with polystyrene. Mass spectra were recorded on a Hewlett-Packard 5985B GC/MS system at 70 eV. Proton and carbon-13 NMR data were obtained on Varian T-60 and IBM NR-80 instruments. The tin-119 NMR spectra were recorded by M. Magerstädt at the Technical University of Berlin, Germany, on a Bruker SXP-109 instrument. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

The compounds prepared, their microanalytical data, melting points and synthetic methods are listed in Table 1. The tin-119m Mössbauer parameters are found in Table 2, and the infrared data below 2000 cm^{-1} are found in Table 3. Table 4 compares the carbonyl stretching frequencies for various organometallic(IV) esters of 2-benzoylbenzoic acid. The tin-119 NMR data are found in Table 5. Table 6 lists the carbon-13 data for 2-benzoylbenzoic acid and selected organotin(IV) 2-benzoylbenzoates. Mass spectral data are listed in Table 7.

Trimethyltin(IV) 2-benzoylbenzoate, $2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn(CH}_3)_3$

To a solution of sodium (0.23 g, 10 mg-at) dissolved in ethanol (100 mL) was added 2-benzoylbenzoic acid (2.26 g, 10.0 mmol) followed by trimethyltin(IV) chloride (1.99 g, 10.0 mmol). The mixture was stirred for one h, and the precipitated sodium chloride was removed by filtration. The solvent was then evaporated, and the crude product was

purified by reprecipitation from ethanol by ether. The compound melted sharply at 162 - 63° C, yield 80%.

Triethyltin(IV) 2-benzoylbenzoate, $2\text{-C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2\text{Sn}(\text{C}_2\text{H}_5)_3$

To a solution of sodium (0.23 g, 10 mg-at) in ethanol (100 mL) was added 2-benzoylbenzoic acid (2.26 g, 10.0 m mol), and the sodium salt of the acid precipitated. To the suspension was added triethyltin(IV) chloride (2.41 g, 10.0 m mol) and the mixture was stirred for one h. The precipitated sodium chloride was filtered, and the solvent removed under vacuum. Ether was added to precipitate the product, mp 111 - 12° C, in 50% yield.

Tri-n-propyltin(IV) 2-benzoylbenzoate, $2\text{-C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2\text{Sn}(\underline{n}\text{-C}_3\text{H}_7)_3$

Bis-tri-n-propyltin(IV) oxide (2.56 g, 5.00 m mol) and 2-benzoylbenzoic acid (2.26 g, 10.0 m mol) were heated in benzene (a suspected carcinogen) for two h. The solvent was then removed under vacuum to give a solid which was soluble in common organic solvents. This product was subjected to high vacuum for one day to remove traces of the organotin starting material. The yield was quantitative, mp 49 - 50° C.

Tri-n-butyltin(IV) 2-benzoylbenzoate, $2\text{-C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2\text{Sn}(\underline{n}\text{-C}_4\text{H}_9)_3$

Bis-tri-n-butyltin(IV) oxide (2.98 g, 10.0 m mol) and 2-benzoylbenzoic acid (2.26 g, 10.0 m mol) were reacted as before. The benzene was removed under vacuum to give 4.90 g of a cream-colored solid with a wide melting range. The pure product was obtained by heating under

vacuum overnight, yield 90%, mp 60 - 61° C.

Tricyclohexyltin(IV) 2-benzoylbenzoate, $2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn}(\underline{\text{C-C}_6\text{H}_{11}})_3$

Tricyclohexyltin(IV) hydroxide (3.85 g, 10 m mol) and 2-benzoylbenzoic acid (2.26 g, 10.0 m mol) were refluxed in benzene in a Dean-Stark apparatus for two h. Then the solvent was removed on a rotary evaporator. Addition of ether to the resulting solid gave the product in 70% yield, mp 140 - 41° C, after washing with more ether.

Triphenyltin(IV) 2-benzoylbenzoate, $2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3$

Triphenyltin(IV) hydroxide (3.67 g, 10.0 m mol) and 2-benzoylbenzoic acid (2.26 g, 10.0 m mol) were heated in benzene in a Dean-Stark apparatus. The solvent was removed on a rotary evaporator, and traces of benzene were removed under vacuum. The crude product was recrystallized from ether to give the compound, mp 106 - 07° C, in 50% yield.

Trimethyltin(IV) 2-benzoyl-3,4,5,6-tetrachlorobenzoate, $2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{Cl}_4\text{-CO}_2\text{Sn}(\text{CH}_3)_3$

To sodium (0.23 g, 10 mg-at) in absolute ethanol (100 mL) was added 2-benzoyl-3,4,5,6-tetrachlorobenzoic acid (3.64 g, 10.0 m mol). Sodium chloride precipitated immediately when solid trimethyltin(IV) chloride (1.99 g, 10.0 m mol) was then added. The mixture was refluxed for one h, cooled and the sodium chloride removed by filtration. The ethanol was evaporated and the last traces removed under vacuum. The

title compound was recrystallized from ether in 50% yield. The compound shrinks at ca. 100° C before finally melting sharply at 200° C. The product can also be recrystallized from chloroform. The mass spectrum showed peaks at m/e (intensity) 512 (82.3) $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{Cl}_4\text{CO}_2\text{Sn}(\text{CH}_3)_2]^+$; 467 (100) $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{Cl}_4\text{Sn}(\text{CH}_3)_2]^+$; 437 (23.9) $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{Cl}_4\text{Sn}]^+$; 401 (9.2) $[\overline{\text{CH}=\text{HC}(\text{O})\text{C}_6\text{Cl}_4}\text{SnCH}_3]^+$; 165 (44.4) $[(\text{CH}_3)_3\text{Sn}]^+$; 155 (83.2) $[\text{SnCl}]^+$; 135 (58.2) $[\text{CH}_3\text{Sn}]^+$ and 120 $[\text{Sn}]^+$. At 12 eV, the only fragments are $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{Cl}_4\text{CO}_2\text{Sn}(\text{CH}_3)_2]^+$ (37.0) and $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{Cl}_4\text{Sn}(\text{CH}_3)_2]^+$ (100).

Triphenyltin(IV) 2-benzoyl-3,4,5,6-tetrachlorobenzoate, $2\text{-C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{Cl}_4\text{-CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3$

This compound was obtained in a similar manner from sodium (0.23 g, 10 mg-at), 2-benzoyl-3,4,5,6-tetrachlorobenzoic acid (3.64 g, 10.0 m mol) and triphenyltin(IV) chloride (3.86 g, 10.0 m mol) in 70% yield, mp 55 - 59° C. The same compound was obtained from the condensation between the acid (3.64 g, 10.0 m mol) and triphenyltin(IV) hydroxide (3.67 g, 10.0 m mol) in benzene. The mass spectrum showed peaks at m/e (intensity) 712 (2.6) $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{Cl}_4\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3]^+$; 677 (5.9) $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{Cl}_4\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3\text{-Cl}]^+$; 635 (32.0) $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{Cl}_4\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_2]^+$; 591 (35.4) $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{Cl}_4\text{Sn}(\text{C}_6\text{H}_5)_2]^+$; 437 (16.8) $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{Cl}_4\text{Sn}]^+$; 351 (22.4) $[(\text{C}_6\text{H}_5)_3\text{Sn}]^+$; 309 (32.4) $[(\text{C}_6\text{H}_5)_2\text{SnCCH}]^+$; 197 (67.7) $[\text{C}_6\text{H}_5\text{Sn}]^+$; 155 (64.8) $[\text{SnCl}]^+$ and 120 (43.9) $[\text{Sn}]^+$.

Attempted preparation of the pseudo ester isomer of triphenyltin(IV) 2-benzoyl-3,4,5,6-tetrachlorobenzoate, $\overline{\text{OC}(\text{O})\text{C}_6\text{Cl}_4(\text{C}_6\text{H}_5)\text{COSn}(\text{C}_6\text{H}_5)_3}$

Triphenyltin(IV) hydroxide (3.67 g, 10.0 m mol) and 2-benzoyl-3,4,5,6-tetrachlorobenzoic acid (3.64 g, 10.0 m mol) were refluxed for one h in nitromethane (100 mL). The solvent was then removed, and ether added. The cloudy solution was then filtered to remove undissolved solids, and the ether removed. The resulting solid, yield 90%, had an infrared spectrum identical with that of $2\text{-C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{Cl}_4\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_3$.

Dimethyltin(IV) bis-2-benzoylbenzoate, $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2]_2\text{Sn}(\text{CH}_3)_2$

Dimethyltin(IV) oxide (1.66 g, 10.0 m mol) and 2-benzoylbenzoic acid (4.52 g, 20.0 m mol) were reacted in benzene as above. After refluxing for two h, the benzene was removed under vacuum. Ether was added to the resulting oil. The pure product was obtained by washing the precipitate with more ether, yield 80%, mp 178 - 80° C. The mass spectrum displayed peaks at m/e (intensity) values of 585 (31) $\{[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2]_2\text{SnCH}_3\}^+$; 541 (50) $\{[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2][\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4]\text{SnCH}_3\}^+$; 497 (19.2) $\{[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4]\}_2\text{Sn}^+$; 375 (45.2) $\{[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2\text{Sn}(\text{CH}_3)_2\}^+$; 331 (64.1) $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{Sn}(\text{CH}_3)]^+$; 301 (85.9) $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{Sn}]^+$; 135 (17.7) $[\text{CH}_3\text{Sn}]^+$; 120 (15.3) $[\text{Sn}]^+$ and 105 (100) $[\text{C}_6\text{H}_5\text{CO}]^+$. At 12 eV, the only fragments are $\{[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2]\text{SnCH}_3\}^+$ (84.6) and $\{[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2][\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4]\text{SnCH}_3\}^+$ (100).

Diphenyltin(IV) 2-benzoylbenzoate, $2\text{-C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2\text{Sn}(\text{C}_6\text{H}_5)_2$

Diphenyltin(IV) oxide (2.89 g, 10.0 m mol) and 2-benzoylbenzoic acid (4.52 g, 20.0 m mol) were heated in 150 mL benzene for two h. The benzene solution was filtered and then concentrated to a third of its original volume. The resulting precipitate was filtered and washed with

ether to give the title compound in 50% yield, mp 210 - 12° C. The mass spectrum showed peaks a m/e (intensity) 647 (10.5) $\{[C_6H_5C(O)C_6H_4CO_2]_2 SnC_6H_5\}^+$; 559 (5.1) $\{[C_6H_5C(O)C_6H_4CO_2][C_6H_5C(O)C_6H_4]SnC_6H_5\}^+$; 499 (100) $[C_6H_5C(O)C_6H_4CO_2Sn(C_6H_5)_2]^+$; 455 (91.7) $[C_6H_5C(O)C_6H_4Sn(C_6H_5)_2]^+$; 301 (69.2) $[C_6H_5C(O)C_6H_4Sn]^+$; 197 $[C_6H_5Sn]^+$ and 120 (19.3) $[Sn]^+$.

Trimethylsilyl 2-benzoylbenzoate, 2-C₆H₅C(O)C₆H₄CO₂Si(CH₃)₃

Hexamethyldisilazane (1.61 g, 10.0 m mol) and 2-benzoylbenzoic acid (4.52 g, 20.0 m mol) were refluxed in a 1:1 mixture of benzene/hexane (150 mL) under a nitrogen atmosphere. The acid was only partly soluble in the hot solvent, but after five h, most of the solid had dissolved. Heating was continued for another twelve h, after which the solution was filtered hot to remove any insolubles. The solvent was then removed, and ether (100 mL) was added. The solution was again filtered, and the ether removed under vacuum. A cream-colored oil was obtained, $n_D^{25} = 1.5531$.

Triethylgermyl 2-benzoylbenzoate, 2-C₆H₅C(O)C₆H₄CO₂Ge(C₂H₅)₃

The sodium 2-benzoylbenzoate prepared from sodium (2.3 g, 10 mg-at) and 2-benzoylbenzoic acid (2.26 g, 10.0 m mol) was reacted with triethylchlorogermane (1.95 g, 10.0 m mol) in ethanol. The sodium chloride was removed and the solvent evaporated. Traces of ethanol were removed under vacuum to give an oil which could not be crystallized; $n_D^{25} = 1.5615$.

Triphenyllead(IV) 2-benzoylbenzoate, 2-C₆H₅C(O)C₆H₄CO₂Pb(C₆H₅)₃

In a similar manner, sodium (0.23 g, 10 mg-at), 2-benzoylbenzoic acid (2.26 g, 10.0 m mol) and triphenyllead(IV) chloride (4.74 g, 10.0 m mol) were reacted in ethanol to give the title compound in 80% yield, mp 183 - 85° C (decomp.).

Sodium 2-benzoylbenzoate, $2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2^-\text{Na}^+$

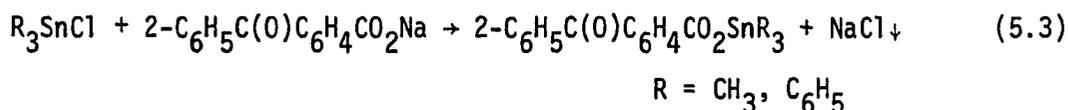
This salt was prepared from sodium metal (0.23 g, 10.0 m mol) and 2-benzoylbenzoic acid (2.26 g, 10.0 m mol) in ethanol (50 mL). Ether was added to the solid which was then filtered. The salt was washed with more ether and air-dried. It showed no signs of decomposition below 250°. Yield 90%. The formulation of this compound was assumed.

Sodium 2-benzoyl-3,4,5,6-tetrachlorobenzoate, $2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{Cl}_4\text{CO}_2^-\text{Na}^+$

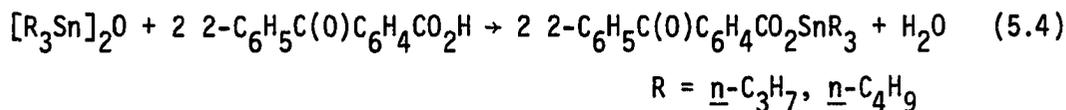
This salt was prepared from sodium metal (0.23 g, 10.0 m mol) and 2-benzoyl-3,4,5,6-tetrachlorobenzoic acid (3.64 g, 10.0 m mol) in ethanol (50 mL). The solvent was removed and ether added. The white solid was collected by filtration and washed repeatedly with more ether, giving the compound in 90% yield, mp above 250°. The formulation was also assumed.

Results and Discussion

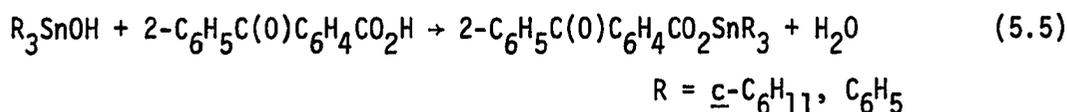
The synthesis of the triorganotin(IV) 2-benzoylbenzoates proceeds in good yield from the metathesis of the corresponding triorganotin(IV) chloride and the sodium salt of the acid in absolute ethanol, the reaction being driven to completion by the precipitation of sodium chloride:



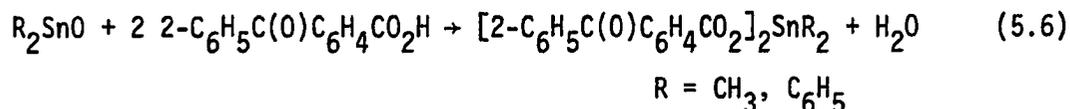
or from the reaction of the corresponding bis-triorganotin(IV) oxide with the parent acid, with the reaction driven to completion by the azeotropic distillation of the water released:



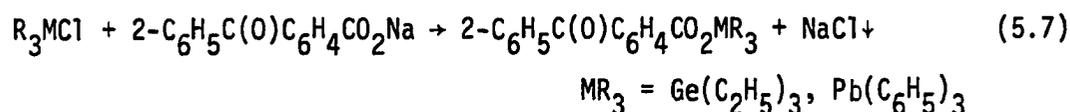
or from the analogous condensation reaction using the corresponding triorganotin(IV) hydroxide:



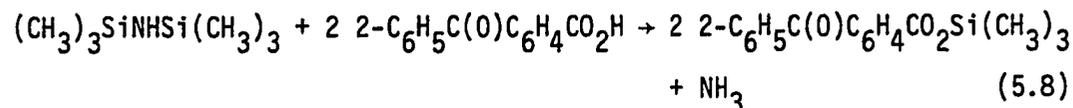
The diorganotin(IV) derivatives are synthesized in high yield from condensation reactions, starting from the diorganotin(IV) oxides in refluxing benzene:



The other organometallic esters of 2-benzoylbenzoic acid were prepared by the sodium salt route



but the organosilyl compound was prepared by the condensation of hexamethyldisilazane with 2-benzoylbenzoic acid, in a method used for synthesizing trimethylsilyl carboxylates:¹¹



Mössbauer Data

The Mössbauer spectra for all the organotin compounds studied are well-resolved doublets whose isomer shifts (IS) specify tetravalent tin and whose quadrupole splittings (QS) and ρ (QS/IS) values (3.04 - 3.54 mm s^{-1} and 2.16 - 2.70, respectively) dictate higher than four-coordination at the tin atom.¹² Structure (IV) can thus be confidently ruled out. The failure of the trimethyl- and triphenyltin and dimethyl- and diphenyltin derivatives to give ambient temperature Mössbauer spectra argues against a highly associated polymeric lattice. The aliphatic compounds uniformly show a larger QS than the corresponding aromatic analogues.

For the dimethyl- and diphenyltin(IV) bis-2-benzoylbenzoates, the point-charge approximations to relate the observed QS to the carbon-tin-carbon angles can be applied.¹³ These results correlate with the known X-ray data^{4,5} for the dimethyl-¹³⁻¹⁵ and diphenyltin(IV)¹⁴ systems. Assuming that the partial quadrupole splitting of the ligand groups can be neglected, the carbon-tin-carbon angle in the dimethyltin compound is 154° and in the diphenyltin compound is 136° . These two derivatives hence adopt a trans- $R_2\text{Sn}$ geometry.

Triorganotin compounds with a trigonal bipyramidal geometry at the tin atom are known to have small quadrupole splittings if one of the three organic groups is at an apical position.¹⁶ Six-coordinated triorganotin compounds are not known,^{4,5} and since the QS values for the benzoylbenzoates are in the range 3.45 - 3.99 mm s^{-1} for the trialiphatic tin(IV) compounds and 3.07 - 3.16 mm s^{-1} for the triphenyltin (IV) derivatives, the $C_3\text{Sn}$ girdle is equatorial and rather flat in these systems.

Vibrational Data

The stretching frequencies that are most important in these organotin derivatives are the ketonic C=O, the carboxyl CO₂ and the Sn-C bands. Table 3 lists the prominent bands for all the derivatives prepared.

In the $\nu(\text{Sn-C})$ region, only one band is observed in the infrared for the $2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{X}_4\text{CO}_2\text{Sn}(\text{CH}_3)_3$ derivatives ($X = \text{H, Cl}$) at 546 cm^{-1} , and in the Raman spectrum only one band is seen at lower frequencies ($X = \text{H, } 521; X = \text{Cl, } 519\text{ cm}^{-1}$). These absorptions in the infrared and Raman spectra are assigned to ν_{asym} and $\nu_{\text{sym}}(\text{Sn-C})$, respectively, and the C₃Sn skeleton is planar in the solid state. In chloroform solution, however, a weak band is seen in the infrared at 511 cm^{-1} , thus ruling out strict planarity in this medium.

For the dimethyltin(IV) derivative, there are two weak bands in the $\nu(\text{Sn-C})$ region at 574 and 542 cm^{-1} in the infrared and at $589(\text{w})$ and $528(\text{vs})$ in the Raman spectrum. The observation of both ν_{asym} and $\nu_{\text{sym}}(\text{Sn-C})$ rules out a strictly linear C₂Sn skeleton, and this conclusion is supported by calculations based upon Mössbauer QS data (vide supra). Bands at 575 and 555 cm^{-1} are seen in the infrared of a chloroform solution.

In the ir, the normal methyl ester of 2-benzoylbenzoic acid exhibits two $\nu(\text{C-O})$ bands, while the pseudo-ester of the lactol (II) exhibits only one.^{1,2} However, there will be a severe lowering of the carboxylate stretching frequency owing to a mass effect if form (I) is adopted, in addition to any lowering of frequency arising from coordination to the tin atom as in forms (III), (V), (VI) and (VII). Thus it would be hazardous to use the position and number of these C-O stretching frequencies

as a criterion for distinguishing between the ester and lactol configurations as well as whether coordination through the ketonic or carboxylate oxygens.

To assist the assignments, the 2-benzoylbenzoate derivatives, $2\text{-C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2\text{MR}_3$, were synthesized where M = Si, Ge and Pb, and Table 4 compares the carbon-oxygen stretching frequencies. Trimethylsilyl acetate possesses a normal ester structure with the carbonyl stretching frequency at 1725 cm^{-1} . The $\nu_{\text{asym}}(\text{CO}_2)$ is found at 1635 cm^{-1} in trimethyltin(IV) alaninate which does not contain a coordinated carboxylate group, and at 1600 cm^{-1} in tricyclohexyltin(IV) alaninate which does.⁶ The band at 1663 cm^{-1} in the normal ester, $2\text{-C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2\text{CH}_3$, would be expected to be shifted to lower energy in the corresponding organotin(IV) derivatives whether by a mass effect or if the ketonic oxygen does engage in coordination. Thus the two sets of bands at ca. 1650 and 1600 cm^{-1} can be assigned to the ketonic and carboxylate stretching frequencies, respectively, in the organotin(IV) derivatives. Using this logic, the data in Table 4 can be rationalized. Triethylgermyl 2-benzoylbenzoate with bands at 1728 and 1617 cm^{-1} is a four-coordinated, normal ester. The bands at ca. 1650 in the organotin(IV) derivatives are relatively independent of the nature of the organic groups at tin. Coordination by a weakly basic ketonic oxygen would be expected to be sensitively affected by the steric bulk at tin. Thus the ketonic oxygen is not coordinated to tin in these derivatives.

NMR Data

The coupling constants, $|^2J(^{119}\text{Sn-C-}^1\text{H})|$, for the trimethyltin(IV)

derivatives, $2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{X}_4\text{CO}_2\text{Sn(CH}_3)_3$, where X = H and Cl are 70.0 and 67.5 Hz, respectively. Thus the five-coordinated structure persists in solution.¹⁷ The coupling constant for the dimethyltin(IV) derivative is 82.0 Hz, also consistent with a higher than four-coordinated structure in solution, perhaps with a non-linear C_2Sn skeleton as predicted from the Mössbauer QS value (vide supra).

Raising the coordination number at tin moves the tin-119 NMR chemical shift upfield of tetramethyltin, while substitution of electro-negative groups moves the resonance downfield.¹⁸⁻²⁰ For the organotin (IV) 2-benzoylbenzoates, the tin chemical shift (see Table 5) is at lower field than tetramethyltin for the aliphatic derivatives and to higher field for the triphenyl- and all the diorganotin(IV) derivatives measured. In all cases only one resonance is observed. Thus if both normal ester and lactol forms exist, they must be interconverting rapidly with respect to the NMR time scale through equilibria such as that depicted in Eq. (2).

In the parent 2-benzoylbenzoic acid the carbon-13 NMR (see Table 6) of the ketonic carbon is found at 196 ppm, while that of the carboxylate carbon is at 171 ppm relative to tetramethylsilane. The lactone from the acid chloride of the tetrachloro derivative, on the other hand, exhibits a resonance at 162 for the carboxylate carbon, but the ketal carbon now appears at 99 ppm. The carboxylate carbon of the methyl ester of the lactol (II) resonates at 168 ppm and the ketal carbon at 109 ppm. The data for four of the organotin(IV) derivatives sufficiently soluble for study are close to those for the open-form and not the lactol, thus ruling out the lactol forms (IV) and (VI) for the tin products. The

resonances of the carboxylate carbons in the tetrachloro and the pseudo-ester derivatives are found at somewhat lower field.

Mass Spectral Data

For the triorganotin(IV) derivatives (see Table 7) a parent molecular ion is only seen for the triphenyl derivatives, but no fragments higher than the parent and no dimer or other combinations of atoms which would arise from oligomers are seen. The most intense peak, except in the trimethyltin case, is the fragment $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2\text{SnR}_2]^+$ which subsequently loses a molecule of carbon dioxide. Heating the compounds themselves, however, fails to liberate CO_2 . For the trimethyl derivative, the base peak at 70 eV is the $[(\text{CH}_3)_3\text{Sn}]^+$ fragment, and the $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2\text{Sn}(\text{CH}_3)_2]^+$ ion is also found in high abundance. The latter ion is the base peak at 12 eV.

The mass spectrum of the parent, 2-benzoylbenzoic acid (I), which exists in the open form in the solid state,²¹ is different from that of the tetrachloro derivative which may be in the lactol form (II) in the solid. The prominent fragments for (I) are: $[\text{M}-\text{C}_6\text{H}_5]^+$ (43.4%), $[\text{M}-\text{CO}_2\text{H}]^+$ (26.4%) and $[\text{C}_6\text{H}_5\text{CO}]^+$ (100%) (M = molecular ion) and for the tetrachloro derivative are: M^+ (39.8%), $[\text{M}-\text{CO}_2\text{H}]^+$ (11.6%) $[\text{C}_6\text{Cl}_4\text{C}(\text{O})\text{C}_2\text{H}_2\text{OH}]^+$ (75.5%) and $[\text{C}_6\text{H}_5\text{CO}]^+$ (100%) (M = molecular ion).

Structural Conclusions

From the Mössbauer QS data the tin atoms are all higher than four-coordinated and this is corroborated by $|^2J(^{119}\text{Sn}-^1\text{H})|$ values in the proton NMR and tin-119 chemical shifts. From carbon-13 NMR chemical

shift evidence the open form and not the lactol is the one adopted. From vibrational stretching frequencies for the carbon-oxygen bonds it is clear that the ketonic carbonyl group is not involved in coordination to the tin atom. This combination of evidence rules out forms (III), (IV), (VI) and (VII), leaving only the carboxylate-bridged (V). Presumably, a six-coordinated, trans-R₂Sn octahedral form is adopted by the diorganotin(IV) derivatives.

This conclusion is supported by the structure of bis(2-benzoylbenzoato)copper(II)-4-iodoaniline which contains open-form 2-benzoylbenzoato moieties which act as bidentate bridging ligands. The ketonic carbonyl groups are not involved in coordinating to the copper center.²²

Bridging carboxylate groups are ubiquitous in organotin(IV) structural chemistry.^{4,5} The title compounds are associated solids in which the ketonic carbonyl groups are not involved in coordination to the tin atoms. The triorganotin(IV) derivatives contain equatorial-R₃Sn groups, while the diorganotin(IV) derivatives contain trans-R₂Sn groups.

Summary

Six triorganotin(IV) 2-benzoylbenzoates, 2-C₆H₅C(O)C₆H₄CO₂SnR₃, where R = CH₃, C₂H₅, n-C₃H₇, n-C₄H₉, c-C₆H₁₁ and C₆H₅, two 2-benzoyl-3,4,5,6-tetrachlorobenzoates, 2-C₆H₅C(O)C₆Cl₄CO₂SnR₃, where R = CH₃ and C₆H₅ and two diorganotin(IV) bis-2-benzoylbenzoates, [C₆H₅C(O)C₆H₄CO₂]₂SnR₂, where R = CH₃ and C₆H₅, are prepared by metathesis between the organotin(IV) chloride and the sodium salt of the acid in ethanol, by azeotropically distilling water from benzene solutions of the bis-triorganotin(IV) oxide and the parent acid, or from a triorganotin(IV)

hydroxide and the parent acid. The products are solids, and, except for the trimethyltin(IV) derivatives, are soluble in common organic solvents. Other Group IV ester derivatives of 2-benzoylbenzoic acid, $2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{MR}_3$ [$\text{MR}_3 = \text{Si}(\text{CH}_3)_3$, $\text{Ge}(\text{C}_2\text{H}_5)_3$ and $\text{Pb}(\text{C}_6\text{H}_5)_3$], were also synthesized. Tin-119m Mössbauer isomer shift (IS) values confirm the tin(IV) oxidation states and the quadrupole splittings (QS) ($3.04 - 3.54 \text{ mm s}^{-1}$) and ρ (QS/IS) values ($2.16 - 2.70$) specify higher than four coordination at tin in the solid state. From the QS values of the diorganotin(IV) derivatives a point-charge model is used to calculate the carbon-tin-carbon angles. The magnitudes of these angles show that these derivatives adopt a trans-configuration in the solid, and that the triorganotin(IV) derivatives have equatorial R_3Sn groups which are approximately planar. Absence of a $\nu_{\text{asm}}(\text{Sn-C})$ mode in the infrared and a $\nu_{\text{asym}}(\text{Sn-C})$ mode in the Raman specifies the planarity of the $(\text{CH}_3)_3\text{Sn}$ group in its solid derivative, but not in solution. Both bands appear for the $(\text{CH}_3)_2\text{Sn}$ derivative, ruling out a strictly linear array. The ketonic and carboxylate carbon-oxygen stretching frequencies are assigned at ca. 1650 and 1600 cm^{-1} , respectively, and it is concluded that the ketone group is not coordinated to the tin atom. The high values for the carbonyl stretching frequencies of the organosilyl- and germyl derivatives reflect four-coordination. NMR coupling constants, $|^2J(^{119}\text{Sn-C-}^1\text{H})|$, reflect higher than four-coordination for the tri- and dimethyltin(IV) derivatives in solution. Tin-119 NMR chemical shifts are to lower field than tetramethyltin for the aliphatic derivatives, reflecting low coordination, in contrast to the triphenyl- and diorganotin(IV) derivatives. Only one resonance is observed, so the open and lactol forms, if both are present, must be in

rapid equilibrium. Carbon-13 resonances for the keto- and carboxylate carbons of the organotin derivatives resemble those of the open and not the lactol forms of the parent materials. No ditin or other fragments characteristic of the oligomer are seen in the mass spectrum at 70 eV. The evidence specifies an associated solid with bridging carboxylate groups from the open-form of 2-benzoylbenzoate in which the ketonic carbonyl group is not involved in coordination to the tin atom. The triorganotin(IV) derivatives contain equatorial- R_3Sn groups, and the diorganotin(IV) derivatives contain trans- R_2Sn groups.

TABLE 1

DI- AND TRIORGANO-GROUP IV 2-BENZOYL BENZOATES

Compound	mp (°C)	%C [Found(Calcd)]	%H [Found(Calcd)]	Yield(%)	Route
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn(CH}_3)_3$	162-63	52.10 (52.48)	4.83 (4.63)	80	1 ^a
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn(C}_2\text{H}_5)_3$	111-12	54.52 (55.72)	5.57 (5.57)	50	1
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn}(\underline{n}\text{-C}_3\text{H}_7)_3$	49-50	58.41 (58.39)	6.59 (6.35)	100	2 ^b
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn}(\underline{n}\text{-C}_4\text{H}_9)_3$	60-61	60.95 (60.62)	7.15 (6.99)	90	2
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn}(\underline{c}\text{-C}_6\text{H}_{11})_3$	140-41	64.64 (64.79)	7.14 (7.09)	70	3 ^c
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn(C}_6\text{H}_5)_3$	106-07	66.96 (66.70)	4.42 (4.17)	50	3
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{Cl}_4\text{CO}_2\text{Sn(CH}_3)_3$	200	38.40 (38.73)	3.05 (2.66)	50	1
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{Cl}_4\text{CO}_2\text{Sn(C}_6\text{H}_5)_3$	55-59	54.14 (53.88)	3.07 (2.81)	70	1,3
$[2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2]_2\text{Sn(CH}_3)_2$	178-80	59.93 (60.13)	4.34 (4.01)	80	4 ^d
$[2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2]_2\text{Sn(C}_6\text{H}_5)_2$	210-12	66.27 (66.42)	3.94 (3.87)	50	4
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Si(CH}_3)_3$	-	68.69 (68.46)	6.01 (6.04)	100	5 ^e
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Ge(C}_2\text{H}_5)_3$	-	63.21 (62.40)	6.25 (6.24)	100	1

TABLE 1, cont'd.

Compound	mp (°C)	%C [Found(Calcd)]	%H [Found(Calcd)]	Yield(%)	Route
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Pb(C}_6\text{H}_5)_3$	183-85	57.69 (57.90)	3.76 (3.62)	80	1

a Triorganometal(IV) chloride + sodium salt.

b Bis-triorganotin(IV) oxide + acid.

c Triorganotin(IV) hydroxide + acid.

d Diorganotin(IV) oxide + acid.

e Hexamethyldisilazane + acid.

TABLE 2

TIN-119m MÖSSBAUER DATA FOR THE DI- AND TRIORGANOTIN(IV) 2-BENZOYL BENZOATES IN mm s⁻¹ AT 77K

Compound	IS _{±0.03}	QS _{±0.06}	Γ _{1±0.03}	Γ _{2±0.03}	ρ=QS/IS
2-C ₆ H ₅ C(O)C ₆ H ₄ CO ₂ Sn(CH ₃) ₃	1.28	3.45	0.94	0.92	2.70
2-C ₆ H ₅ C(O)C ₆ H ₅ CO ₂ Sn(C ₂ H ₅) ₃	1.47	3.51	1.06	1.04	2.39
2-C ₆ H ₅ C(O)C ₆ H ₄ CO ₂ Sn(<u>n</u> -C ₃ H ₇) ₃	1.46	3.54	1.23	1.25	2.42
2-C ₆ H ₅ C(O)C ₆ H ₄ CO ₂ Sn(<u>n</u> -C ₄ H ₉) ₃	1.46	3.50	0.99	0.95	2.40
2-C ₆ H ₅ C(O)C ₆ H ₄ CO ₂ Sn(<u>c</u> -C ₆ H ₁₁) ₃	1.55	3.46	1.05	1.01	2.24
2-C ₆ H ₅ C(O)C ₆ H ₄ CO ₂ Sn(C ₆ H ₅) ₃	1.31	3.16	1.10	1.10	2.42
2-C ₆ H ₅ C(O)C ₆ Cl ₄ CO ₂ Sn(CH ₃) ₃	1.44	3.99	1.80	1.80	2.77
2-C ₆ H ₅ C(O)C ₆ Cl ₄ CO ₂ Sn(C ₆ H ₅) ₃	1.42	3.07	1.62	1.57	2.16
[2-C ₆ H ₅ C(O)C ₆ H ₄ CO ₂] ₂ Sn(CH ₃) ₂	1.30	3.82	1.11	1.24	2.85
[2-C ₆ H ₅ C(O)C ₆ H ₄ CO ₂] ₂ Sn(C ₆ H ₅) ₂	1.24	3.04	1.51	1.46	2.46

TABLE 3

 INFRARED DATA FOR THE DI- AND TRIORGANOMETALLIC(IV)
 2-BENZOYL BENZOATES IN NUJOL FROM 2000 TO 400 cm^{-1}

$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{H}^{\text{a}}$	1692(sh), 1678(vs), 1595(w), 1574(m), 1428(m), 1312(m), 1306(m), 1292(m), 1277(m), 1257(m), 933(m), 767(m), 701(m)
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{Cl}_4\text{CO}_2\text{H}^{\text{b}}$	1755(vs), 1372(vs), 1280(s), 1260(s), 1227(vs), 1149(vs), 967(s), 795(s), 782(s), 732(s), 725(vs), 695(s), 670(s), 590(m,br), 505(m)
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn(CH}_3)_3^{\text{c}}$	1652(vs), 1639(vs), 1629(vs), 1610(s), 1594(vs), 1581(s), 1570(s), 1449(s), 1342(vs), 1315(vs), 1288(vs), 1255(m), 1169(m), 1145(s), 936(s), 928(s), 850(s), 814(m), 799(s), 774(vs), 734(s), 700(s), 685(s), 670(s), 634(m), 582(m), 546(s), 509(m), 454(s)
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn(C}_2\text{H}_5)_3$	1649(vs), 1594(s), 1578(s), 1339(vs), 1320(vs), 1292(vs), 1256(s), 1149(m), 1085(m), 938(m), 771(s), 698(m), 686(m), 675(s), 561(w), 514(m), 467(m)
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn(n-C}_3\text{H}_7)_3$	1660(vs), 1652(vs), 1595(m), 1578(m), 1332(vs), 1282(s), 1247(m), 1143(m), 1067(m), 992(m), 932(m), 765(s), 728(s), 715(s), 700(s), 666(m), 450(w)
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn(n-C}_4\text{H}_9)_3$	1664(vs), 1597(s), 1578(s), 1336(vs), 1279(s), 1146(m), 933(m), 764(s), 729(m), 705(vs), 671(s), 450(w)
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn(c-C}_6\text{H}_{11})$	1652(s), 1639(m), 1623(m), 1595(m), 1577(w), 1365(s), 1350(s), 1314(m), 1279(m), 932(m), 765(m), 729(m), 705(m), 450(w)
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn(C}_6\text{H}_5)_3$	1648(vs), 1594(s), 1576(s), 1334(vs), 1314(s), 1276(s), 1142(m), 1077(m), 933(m), 763(m), 729(vs), 709(s), 692(vs), 556(w), 440(m)
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{Cl}_4\text{CO}_2\text{Sn(CH}_3)_3^{\text{d}}$	1679(s), 1614(vs), 1333(vs), 1263(vs), 985(m), 780(m), 762(m), 683(m), 652(m), 586(m), 546(m)

TABLE 3, cont'd.

$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{Cl}_4\text{CO}_2\text{Sn(C}_6\text{H}_5)_3$	1677(vs,br), 1598(m), 1581(m), 1482(m), 1432(vs), 1300(vs,br), 1260(vs), 1177(m), 1130(m), 1077(m), 997(m), 981(m), 728(vs), 695(vs), 683(s), 660(s), 596(m)
$[2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2]_2\text{Sn(CH}_3)_2^e$	1670(s), 1663(s), 1584(s), 1578(s), 1560(m), 1540(m), 1316(m), 1284(m), 934(m), 798(m), 766(s), 729(s), 700(m), 686(m), 679(m), 574(w), 542(w), 450(m)
$[2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2]_2\text{Sn(C}_6\text{H}_5)_2^f$	1677(vs,br), 1598(m), 1581(m), 1482(m), 1432(vs), 1300(vs,br), 1260(vs), 1177(m), 1130(m), 1077(m), 997(m), 981(m), 728(vs), 695(vs), 683(s), 660(s), 596(m)
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Si(CH}_3)_3^g$	1775(w), 1702(vs), 1676(vs), 1598(s), 1582(m), 1450(s), 1302(vs), 1255(vs), 1135(s), 1081(m), 933(s), 868(s), 850(vs), 830(s), 765(s), 732(m), 730(s), 710(s), 696(s), 660(m), 630(w)
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Ge(C}_2\text{H}_5)_3^g$	1728(m), 1677(vs), 1600(s), 1584(s), 1462(sh), 1452(s), 1315(s,br), 1283(sh), 1139(s), 1084(m), 1012(m), 932(s), 842(m), 798(m), 768(s), 730(s), 712(s), 687(s), 637(m), 612(m), 590(m), 540(w), 470(w)
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Pb(C}_6\text{H}_5)_3$	1669(s), 1660(s), 1631(m), 1614(s), 1589(s), 1560(s), 1476(s), 1450(s), 1435(m), 1431(m), 1398(s), 1345(s), 1316(s), 1296(m), 1284(s), 1250(w), 1146(m), 1016(m), 984(m), 937(s), 844(m), 769(s), 737(s), 729(s), 725(s), 715(s), 696(s), 683(m), 670(m), 440(w)

^a In the sodium salt, $\nu(\text{CO})=1668$, $\nu_{\text{asym}}(\text{CO}_2)=1609$, 1588 and $\nu_{\text{sym}}(\text{CO}_2)=1393 \text{ cm}^{-1}$.

^b In the sodium salt, $\nu(\text{CO})=1674$, $\nu_{\text{asym}}(\text{CO}_2)=1600$ and $\nu_{\text{sym}}(\text{CO}_2)=1396 \text{ cm}^{-1}$.

^c In the Raman, $\nu_{\text{asym}}(\text{Sn-C})=521 \text{ cm}^{-1}$.

^d In the Raman, $\nu_{\text{asym}}(\text{Sn-C})=519 \text{ cm}^{-1}$.

^e In the Raman, $\nu_{\text{asym}}(\text{Sn-C})=589$, $\nu_{\text{sym}}(\text{Sn-C})=528 \text{ cm}^{-1}$. These two bands are found at 575 and 555 cm^{-1} in the infrared of a chloroform solution.

TABLE 3, cont'd.

In hexachlorobutadiene, the CO and CO₂ bands are found at 1680(m), 1665(m), 1614(vs) cm⁻¹.

^f In hexachlorobutadiene, the CO and CO₂ bands are found at 1680(m), 1636(s) and 1615(vs) cm⁻¹.

^g Neat liquid.

TABLE 4

COMPARISON OF THE CARBONYL STRETCHING FREQUENCIES OF THE
 2-BENZOYL BENZOATE ESTERS $[2-C_6H_5C(O)C_6H_4CO_2]_{4-n}MR_n$
 ($n = 1, 2$; $M = C, Si, Ge, Sn, Pb$) IN NUJOL

Ester	$\nu(CO) \text{ cm}^{-1}$
$2-C_6H_5C(O)C_6H_4CO_2CH_3$ (normal-ester) ^a	1715, 1663
$2-C_6H_5C(O)C_6H_4CO_2CH_3$ (pseudo-ester) ^a	1765
$2-C_6H_5C(O)C_6H_4CO_2Si(CH_3)_3$	1702, 1676
$2-C_6H_5C(O)C_6H_4CO_2Ge(C_2H_5)_3$	1728, 1677
$2-C_6H_5C(O)C_6H_4CO_2Sn(C_6H_5)_3$	1648, 1594, 1576
$2-C_6H_5C(O)C_6H_4CO_2Pb(C_6H_5)_3$	1669, 1660, 1631, 1614, 1589
$C_6H_5COC_6Cl_4C=O$	1785 ^b
$[2-C_6H_5C(O)C_6H_4CO_2]_2Sn(CH_3)_2$	1670, 1663, 1584, 1578 1680, ^c 1665, ^c 1614 ^c
$[2-C_6H_5C(O)C_6H_4CO_2]_2Sn(C_6H_5)_2$	1677, 1598, 1581 1680, ^c 1636, ^c 1615 ^c

^a Ref. 2. The band at 1715 cm^{-1} was assigned to the ester function, and the 1663 cm^{-1} band to the aromatic ketonic stretch.

^b Ref. 1.

^c In hexachlorobutadiene.

TABLE 5

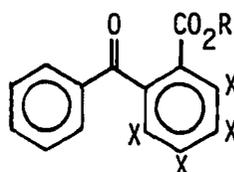
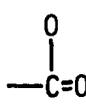
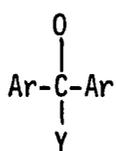
TIN-119 NMR DATA FOR THE DI- AND TRIORGANOTIN(IV) 2-BENZOYL BENZOATES

Compound	δ ppm ^a
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn(CH}_3)_3$	33.8 ^b
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn(C}_2\text{H}_5)_3$	125.1 ^b
$3\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn}(\underline{n}\text{-C}_3\text{H}_7)_3$	125.5 ^b
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn}(\underline{n}\text{-C}_4\text{H}_9)_3$	149.1 ^b
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn}(\underline{c}\text{-C}_6\text{H}_{11})_3$	29.8 ^b
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2\text{Sn(C}_6\text{H}_5)_3$	-97.8 ^b
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{Cl}_4\text{CO}_2\text{Sn(CH}_3)_3$	27.7 ^c
$2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{Cl}_4\text{CO}_2\text{Sn(C}_6\text{H}_5)_3$	-215.0 ^c
$[2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2]_2\text{Sn(CH}_3)_2$	-107.7 ^b
$[2\text{-C}_6\text{H}_5\text{C(O)C}_6\text{H}_4\text{CO}_2]_2\text{Sn(C}_6\text{H}_5)_2$	-287.4 ^b

^a Relative to tetramethylstannane. Positive values downfield.^b In CDCl_3 .^c In CD_3OD .

TABLE 6

CARBON-13 NMR DATA FOR 2-BENZOYLBENZOIC ACID AND
SELECTED ORGANOTIN(IV) DERIVATIVES^a

			C-Sn	
R = X = H	196	171	-	-
R = (CH ₃) ₃ Sn; X = Cl ^b	194	169	-3	-
R = (c-C ₆ H ₁₁) ₃ Sn; X=H	197	170		
R = (C ₆ H ₅) ₃ Sn; X = Cl	191	168	-	-
R = (CH ₃) ₂ Sn; X = H	197	175	4	-
R = CH ₃ ; X = H; Y = O	-	168	-	109
(pseudo-ester)				
C ₆ H ₅ COClC ₆ H ₄ ClC=O	-	162	-	99

^a In ppm vs. tetramethylsilane in deuteriochloroform-d₁.^b In deuteromethanol-d₄.

TABLE 7

MASS SPECTRAL DATA FOR THE TRIORGANOTIN(IV) 2-BENZOYL BENZOATES AT 70 eV^a

R	$[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2\text{SnR}_3]^+$	$[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2\text{SnR}_2]^+$	$[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{SnR}_2]^+$	$[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{Sn}]^+$	$[\text{R}_3\text{Sn}]^+$	$[\text{R}_2\text{Sn}]^+$	$[\text{RSn}]^+$	$[\text{Sn}]^+$
CH ₃	-	61.4 (100 ^b)	69.9 (35.0 ^b)	51.1	100 ^c	23.2 ^c	-	37.3
C ₂ H ₅	-	100	68.4	96.8	-	-	19.3	29.4
<u>n</u> -C ₃ H ₇	-	100	26.9	63.4	-	-	17.9	30.7
<u>n</u> -C ₄ H ₉	-	100	20.1	60.8	-	-	26.9	28.1 ^d
<u>c</u> -C ₆ H ₁₁	-	100	52.2 ^e	62.8	-	-	-	7.7 ^d
C ₆ H ₅ ^b	62.6	100	5.1	-	19.4	21.1	-	7.7

^a Based upon masses ¹H, ¹²C, ¹⁶O and ¹²⁰Sn.^e $[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{SnH}_2]^+$.^b Recorded at 12 eV.^c Peaks overlapped.^d $[\text{HSn}]^+$.

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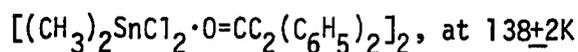
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CHAPTER 6

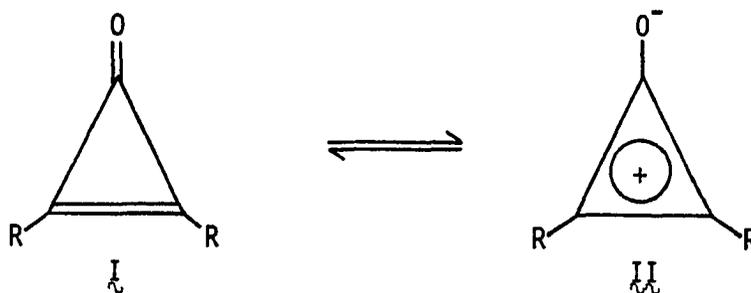
THE X-RAY CRYSTAL AND MOLECULAR STRUCTURE OF THE DIMERIC 1:1 ADDUCT OF DIMETHYLTIN(IV) DICHLORIDE WITH DIPHENYLCYCLOPROPENONE



(This structure was solved in collaboration with Professor D. van der Helm and Drs. C.L. Barnes and M.B. Hossain. See Preface.)

Introduction

Cyclopropenones,¹ of which to date only the diphenyl derivative has been extensively studied, are much more basic than other ketones, even than other α -, β -unsaturated ketones, owing to the availability of resonance forms which place negative charge on the oxygen:



This gives rise to an enhanced dipole moment ($\mu = 5.08\text{D}^2$ vs. 2.85D for acetone³), and the formation of a stable solid monohydrate, mp 87.5°C ,⁴ not generally formed by aromatic ketones. The molecular structure of the

anhydrous solid is known from X-ray studies⁵ and the gas-phase species from microwave.⁶ Independent X-ray determinations of the structure of the hydrate show half the molecules in the crystal hydrogen bonded to one, and half to two water molecules, but disagree on the details of the ring dimensions.^{7,8} Another X-ray study of di(4-chlorophenyl)cyclopropanone⁹ has been criticized as giving erroneous results.⁸

It would be expected that the contribution of II would be successively enhanced by hydrogen bonding of the carbonyl oxygen atom to one and then two water molecules. Structure II would also be expected to predominate in complexes with metal centers of which derivatives with divalent zinc, cobalt, nickel, copper, ruthenium, palladium and platinum halides,¹⁰ rhodium(III) halides,¹⁰ cobalt and platinum carbonyls¹¹ and antimony pentachloride¹² are known. All are coordinated through oxygen from infrared evidence, but no structural data have hitherto been available.

Mixing chloroform solutions of diphenylcyclopropanone and dimethyltin(IV) dichloride yields a 1:1 adduct, $(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{O}=\text{CC}_2(\text{C}_6\text{H}_5)_2$, mp 111°C(d) .¹³ Lowering of the infrared band at 1640 cm^{-1} ¹⁴ in the free ligand reflects bonding through the carbonyl, and the NMR $|^2J(^{119}\text{Sn}-\text{C}-^1\text{H})| = 77.7 \text{ Hz}$ in chloroform reflects the higher coordination number produced at the tin atom.¹³ The tin-119m Mössbauer parameters [isomer shift (IS) = 1.41; quadrupole splitting (QS) = 3.52 mm s^{-1}] were interpreted in terms of a five-coordinated, trigonal bipyramidal geometry at tin in which the ligand is axially positioned, opposite one chlorine, based upon the additivity of electric field gradients.¹⁵

Aldehydes and ketones are generally weak donors toward tin, and

the isolable complexes usually involve ligands with the capacity for charge dispersal. Diorganotin(IV) dihalides can form either 1:1 or 1:2 adducts with donor molecules. The choice depends upon the interplay of a complex mix of discernable factors, inter alia, the basicity of the coordinating atom or steric effects which may originate on the tin moiety or the donor molecule. In the latter, whether the donor atom is terminally-attached as part of a pointed group, as in the carbonyl group of an aldehyde or ketone or in a $\begin{array}{c} \diagup \\ \text{C}=\text{S} \\ \diagdown \end{array}$, $\begin{array}{c} \diagup \\ \text{S}=\text{O} \\ \diagdown \end{array}$, $\begin{array}{c} \diagup \\ \text{P}=\text{O} \\ \diagdown \end{array}$ or $\begin{array}{c} \diagup \\ \text{N}=\text{O} \\ \diagdown \end{array}$ containing ligand is apparently important,¹⁶ as is the possibility for chelation. The generation of ionic charges or strong dipoles in the resulting product must also play a role. Of course, the stoichiometry of the reactants and the conditions of the synthesis will have an influence, but it is surprising that the variation of these parameters is not more often determining. Using current knowledge it is not possible to predict whether a 1:1 or 1:2 complex will form under any given set of circumstances. Known adducts, even disregarding ancient claims, present a confused picture. For example, triphenylphosphine oxide, a strongly basic, pointed ligand forms 1:2 adducts with dimethyl-, methylphenyl- and dibenzyltin(IV) dichloride, but only a 1:1 complex with divinyltin(IV) dichloride.¹³ Both 1:1 and 1:2 adducts are isolated with diphenyltin(IV) dichloride.^{17,18} The presumably less basic, also pointed ligand, diphenylcyclopropanone, on the other hand, forms a 1:1 adduct with divinyltin(IV) dichloride.¹³ It is curious that the sterically undemanding pointed ligands which should allow complexation to proceed to the 1:2 products are the ones which form the 1:1 complexes instead.

One structure report is available for a 1:1 complex of dimethyltin

(IV) dichloride,¹⁹ and the ligand is described as being attached through a CH=O group. Although the salicylaldehyde donor is capable of chelation through the phenolic OH, this group hydrogen bonds to its aldehydic oxygen neighbor. The geometry about the tin center is interpreted as a badly distorted trigonal bipyramid with the ligand oxygen axial with one of the chlorines, and the two methyl groups and second chlorine atom equatorial.²⁰ In the 1:1 adduct of dimethyltin(IV) dichloride with pyridine N-oxide, infrared and Raman evidence was used to suggest an equatorial-position for the ligand in a trigonal bipyramidal geometry.^{21,22}

The structure of the 1:1 adduct of diphenylcyclopropanone with dimethyltin(IV) dichloride is described in this chapter. A preliminary report, describing inter alia this result has been communicated.²⁴

Experimental Section

Synthesis of the Dimethyltin(IV) Dichloride-Diphenylcyclopropanone Dimer,
 $[(CH_3)_2SnCl_2 \cdot O=CC_2(C_6H_5)_2]_2$ ¹³

Diphenylcyclopropanone was synthesized by the method of Breslow and Posner.²⁵ Concentration of a chloroform solution of dimethyltin(IV) dichloride (2.20 g, 0.01 mol) and diphenylcyclopropanone (4.12 g, 0.02 mol) gave a white precipitate which was recrystallized from chloroform to give the 1:1 adduct, mp 109-111° C, in 70% yield. Single crystals of the compound which melted sharply at 111° C were obtained by slow evaporation of a chloroform solution. Upon exposure to air for a few h, however, a white powder formed on the surfaces of the crystals which made them unsuitable for collecting data. The compound is soluble in the common, dense organic solvents, and its exact density, as a consequence, could

not be determined.

Crystal Data

Data were obtained at 138±2K with an Enraf-Nonius CAD/4 automatic counter diffractometer controlled by a PDP-8/e computer and fitted with a low-temperature apparatus. Crystal data are listed in Table 1.

Details of the diffractometer, and methods of data reduction have been outlined previously.²⁶ Specific parameters pertaining to the collection of this data set are summarized in Table 2. The structure factors for each reflection were assigned weights based upon counting statistics.²⁶

Structure Determination and Refinement

Systematic absences gave two possible space groups, C2/c and Cc, and since a distinction could be made from the Patterson map, the structure was refined in the former. The positions of the tin and chlorine atoms were determined from a three-dimensional Patterson map. Structure factors calculated with Sn and Cl parameters gave an R factor ($R = \frac{\sum ||kF_o| - |F_c||}{\sum |kF_o|}$) which was refined to 0.260 and a difference Fourier map was then calculated. From the difference map, all non-hydrogen atoms were located. These atoms were refined isotropically and then anisotropically to an R factor of 0.0351 for 4251 reflections by using a block-diagonal least-squares program.²⁷ A difference Fourier map calculated at this stage revealed all hydrogen positions. Hydrogen atoms were refined isotropically. The effect of anomalous dispersion by the tin and chlorine atoms was included in F_o by using $\Delta f'$ and $\Delta f''$ from ref. 28. Refinement

was discontinued when the maximum parameter shift for all the atoms was less than one-sixth of the corresponding standard deviation. The final R factor is 0.0296 for the 4251 reflections that were included in the least-squares calculations and is 0.0391 for all 4890 reflections. The final difference Fourier map was essentially featureless except around the tin atom where peak heights up to $1.3 \text{ e } \text{\AA}^{-3}$ still persisted. These residual peaks are ascribed to ripples originating from the tin atom.

The scattering factors used were for neutral atoms and were taken from refs. 28 (Sn, Cl, O, and C) and 27 (H).

Final atomic parameters (positional and thermal) are given in Tables 3 and 4, respectively, and final interatomic distances and angles are given in Tables 5 and 6, respectively. Hydrogen parameters are given in Table 7, and carbon and hydrogen distances and angles are listed in Table 8. The asymmetric unit (with atom numbering scheme) is shown in Figure 1, and the arrangement of molecules within the unit cell in Figure 2. The equations of the least squares planes and the deviations from these planes are listed in Table 9.

Description and Discussion of the Structure

The 1:1 nature of the complex is confirmed in the structure depicted in Figure 1, but the adduct molecules are seen to form a dimer through intermolecular chlorine bridging. At the center of the dimer is an almost planar Sn_2Cl_2 ring formed by longer $[d(\text{Sn}-\text{Cl}(1')) = 3.5607(7)]$, and shorter $[d(\text{Sn}-\text{Cl}(1)) = 2.4745(7) \text{ \AA}]$ tin-chlorine bonds. The shortest connection is made to a terminal chlorine atom $[d(\text{Sn}-\text{Cl}(2)) = 2.3713(6) \text{ \AA}]$ which lies roughly trans- to the chlorine atom $[\text{Cl}(1')]$

bridging from the second molecule at $166.10(2)^\circ$. The angle made by the methyl groups is opened to $142.2(1)^\circ$, but the largest angle at tin is formed by the Cl(1)-Sn-O system at $172.32(5)^\circ$. Each monomeric unit is related to its other half by a two-fold axis. The angles at the tins are acute [$77.26(2)^\circ$] in the Sn_2Cl_2 ring, while the angles at the chlorines are open [$102.71(2)^\circ$]. The entire diphenylcyclopropanone system is almost flat, and space is filled by packing the complexes in parallel planes with tin atoms on the same side in each layer as shown in Figure 2. This direction is reversed in alternate layers. Such packing allows the tin atom to adopt the conventional octahedral geometry for six-coordination with the carbonyl oxygen trans- to one chlorine atom.

For the cyclopropanone system sufficient structural data are now available to measure the onset of the effect of the utilization of the carbonyl oxygen atom lone pairs of electrons on the C=O distance and the ring dimensions. The four points of comparison are the anhydrous diphenylcyclopropanone, the two differently hydrogen-bonded molecules in its monohydrate which are bound by one and two waters, and the title organotin complex. The structural data should reflect a change from form I to form II with involvement of the oxygen lone pairs in donation, especially a lengthening of the carbonyl C=O and ring C=C distances and a shortening of the ring C-C distance; i.e., the ring should take on a more symmetrical form. The salient ligand parameters for the family of known structures are listed in Table 10.

Inspection of these data reveals a trend in the intraring and C=O distances on involvement of the oxygen in hydrogen bonding and donation. The anhydrous free ligand shows generally the shortest double

bond $d(\text{C}=\text{O})$ and $d(\text{C}=\text{C})$ distances and the longest single bond $d(\text{C}-\text{C})$,⁵ with all three distances in the gas-phase parent cyclopropenone somewhat smaller.⁹ The carbonyl $d(\text{C}=\text{O})$ generally increases on forming one and then two hydrogen bonds with the tin complex resembling the doubly hydrogen-bonded molecule in the hydrate. Likewise, the $d(\text{C}=\text{C})$ distance increases in length generally in progressing to the tin complex, while the average $d(\text{C}-\text{C})$ distance decreases. Attempts at exact comparison are confused by the disagreement between the two X-ray structures for the monohydrate; for example, the data in ref. 8 do not show the changes in the expected direction in going from the singly to the doubly hydrogen-bonded molecules observed in ref. 7. However, it is apparent that complexation to tin works the largest lengthening effect on the carbonyl and ring double bonds and in symmetrizing the ring shape. The difference between the single- and double-bond distances in the ring, $\Delta [d(\text{C}-\text{C}) - d(\text{C}=\text{C})]$, decreases from 0.068 in the free ligand to 0.024 Å in the tin complex, and the intraring angle $\angle \text{C}-\text{C}(\text{O})-\text{C}$ increases from 56.9° to 58.9 (2)°. The slight shortening of the connections to the phenyl groups is also in the direction expected from a larger contribution of form II .

The intraring internuclear distances would not be expected to be precisely equal, even in the ideal structure II , because of the basic asymmetry of the ring. In addition, the $d(\text{C}-\text{C})_{\text{av}}$ in triphenylcyclopropenium perchlorate³⁷ of 1.373 Å, cited frequently as the standard length of a completely delocalized cyclopropenium connection,¹ is not very different from the 1.392 Å average of the three intraring carbon-carbon distances in the tin complex. It is thus likely on this evidence that the

ligand trapped as the tin adduct is close to that represented by structure II , although something of the shorter, π character is retained in the C(4)-C(5) distance [1.376(3) Å], and the angles at these carbon atoms are also relatively more open [60.7(2) and 60.4(2)°, respectively] compared with the angle at C(3) [58.9(2)°].

The magnitude of the $\text{O} \rightarrow \text{Sn}$ distance is another test of whether structure II has been trapped in the title complex, since this linkage should be expected to be more ester-like in the C-O-Sn linkage from form II than in the donor $\text{C}=\text{O} \rightarrow \text{Sn}$ linkage from form I . The former $d(\text{Sn}-\text{O})$ should be the shorter of the two. There are ten structures known in which carbonyl groups are linked to tin(IV), six inorganic and four organotin, of which eight are part of chelated systems.¹⁹ Seven different ligand systems have been studied, the N-benzoyl, N-phenyl-O-hydroxylamino-^{38,39} oxalato-⁴⁰, acac [1,3-diphenylpropane-1,3-dionato-(dibenzoyl-methano-),⁴¹ and 2,4-pentanedionato-⁴²], acetoacetic ethyl ester,⁴³ triphenylphosphoranylideneacetone-⁴⁴, salicylaldehyde²⁰ and tropolonato-⁴⁵. The last named ligand is related to the cyclopropanone system in the ability of its ring system to delocalize positive charge, but only the tris-inorganic complexes have been studied in which the tin atom is seven-coordinated.⁴⁵ The first named^{38,39} and the $(\text{C}_6\text{H}_5)_3\text{P}-\ddot{\text{C}}\text{H}-\overset{\text{O}}{\text{C}}\text{CH}_3$ ⁴⁴ ligands also enjoy enhanced basicity because of the lone pair of electrons on the atom α - to the carbonyl group, but the former forms chelates as do the acac,^{41,42} β -ketoester and oxalato⁴⁰ derivatives. Selected data for these systems are listed in Table 11.

The most direct available comparison to the complex is the 1:1 adduct of dimethyltin(IV) dichloride with salicylaldehyde, whose struc-

ture should be reinterpreted. The ligand does not chelate the tin atom but is instead bonded intermolecularly as well through a bridging phenolic oxygen atom rather than through chlorine as in the title compound. The aldehydic donor oxygen in this ligand is also engaged in hydrogen bonding with its ortho-phenolic neighbor, and is thus trifurcatedly coordinated. Examination of the unit cell reveals a close contact at 3.366 Å to the phenolic oxygen (also thus trifurcated) of an adjacent molecule.⁴⁶ The system is thus better described as an associated solid of six-coordinated tin moieties.

The data in Table 11 allow systematics to be derived in which the longest C=O distances are found contiguous to the shortest O → Sn distances and vice versa, as in the dichlorotin(IV) derivatives of the β-keto-ester where the keto $d(\text{C}=\text{O}) = 1.322$ is paired with a $d(\text{O} \rightarrow \text{Sn}) = 2.066$ Å,⁴³ or with acac where the $d(\text{C}=\text{O}) = 1.290$ is paired with a $d(\text{O} \rightarrow \text{Sn}) = 2.051$ Å,⁴² or with N-benzoyl-N-phenyl-O-hydroxylamine where the $d(\text{C}=\text{O}) = 1.30$ is paired with a $d(\text{O} \rightarrow \text{Sn}) = 2.180$ Å.^{39,47} These examples are undoubtedly closest to the ester system C=O-Sn. The dimethyltin(IV) dichloride salicylaldehyde complex with the shortest distance $d(\text{C}=\text{O}) = 1.23$ and the longest distance $d(\text{O} \rightarrow \text{Sn}) = 2.680$ Å,²⁰ on the other hand, represents the situation closest to the carbonyl donor system C=O → Sn currently available from structural studies. In this logic the diphenylcyclopropanone ligand in the tin complex with $d(\text{C}=\text{O}) = 1.239(3)$ and $d(\text{O} \rightarrow \text{Sn}) = 2.380(2)$ Å behaves very much as a conventional carbonyl donor system of structure I, and not as the ester system expected from structure II.

In the structure the carbonyl group vector makes a C=O→Sn angle of 132.7(2)° at oxygen, while the corresponding angle in the salicylaldehyde

analogue is $134(1)^\circ$.⁴⁶ The only other non-chelated example for comparison is the phosphoranylacetone complex with trimethyltin(IV) chloride for which the angle is 134.3° .⁴⁴ Thus the hybridization at the oxygen atom may be described as somewhat opened (more s-character) from sp^2 (two lone pairs plus the C-O bonding pair) with the third lone pair in a p-orbital available for π -interaction with the aromatic system of the cyclopropanone ring as in canonical form I_c . If this π -interaction were important, then the planes of the C=O-Sn system and the ligand ring should be coincident since the electron-donating, lone pair orbital would lie in the ligand ring plane. The angle between these planes is only $11.7(2)^\circ$ in the title complex, and this result could be interpreted in terms of a donor carbonyl unit. Forcing the two planes into exact coincidence would maximize the steric interference of one of the ligand phenyl rings attachments which are also in the ligand ring plane (see below) with the other substituents on the tin atom. As it is the ortho-hydrogen on one of the phenyl rings makes a short contact with the bridging chlorine atom (see below).

The distortion from perfect octahedral geometry at tin is seen in the trans-angle made by the Cl-Sn-O atoms [$172.32(5)^\circ$] (vs. 177.44° for the salicylaldehyde structure^{20,46}). The distortion can also be seen in the \angle C-Sn-C in the trans-dimethyltin system [$142.2(1)^\circ$] (vs. 131.4° in the salicylaldehyde complex^{20,46}). The angle in solid dimethyltin(IV) dichloride itself of 124° is attributed to weak association in this phase.⁴⁸ In all three dimethyltin(IV) dichloride analogues a bridging atom of an adjacent molecule binds at a point between the two carbon-tin vectors, enhancing the opening of the angles. Some incipient angle opening

derives from the unequal distribution of s -character in the girdle of the molecule with the tin atom exerting a bonding orbital with much more p -character toward the more electronegative chlorine atoms, leaving the methyl groups held by orbitals with relatively high s -orbital hybridization, with the concomitant angle opening. The tin atom lies 0.0266 \AA out of the plane formed by its two methyl groups, its terminally-bonded chlorine [Cl(2)] and the chlorine atom bridged to it [Cl(1')], in the direction of the Sn-Cl(1) vector. The shortest bond is made to the terminal chlorine [$d(\text{Sn}-\text{Cl}(2)) = 2.3713(6)$] and the next shortest to the chlorine atom which bridges [$d(\text{Sn}-\text{Cl}(1)) = 2.4745 \text{ \AA}$]. The chlorine atoms in the salicylaldehyde analogue which do not engage in bridging are found at 2.347 and 2.403 \AA .^{20.46}

The central Sn_2Cl_2 ring is bent through the torsional angles Sn-Cl(1)-Sn'-Cl(1') and Cl(1)-Sn-Cl(1')-Sn' which are coincidentally identical at $2.25(3)^\circ$. The dihedral angle between the planes defined by the Sn-Cl(1)-Sn' and Sn-Cl(1')-Sn' atoms is $3.01(2)^\circ$ and that between Cl(1)-Sn-Cl(1') and Cl(1)-Sn-Cl(1') is 2.44° . This gives a ring in which the interior distances are $d(\text{Sn}---\text{Sn}') = 4.7623(2)$ and $d(\text{Cl}(1)---\text{Cl}(1')) = 3.8621(10) \text{ \AA}$. The sum of the interior angles is 359.94° .

The bridging chlorine, Cl(1'), makes a short intra-dimer contact with an ortho-carbon of one of the ligand phenyls and its attached hydrogen, $d[\text{Cl}(1')---\text{H}(7)] = 2.79(3) \text{ \AA}$. Another close contact occurs between this chlorine and a hydrogen on one of the methyl groups, $d[\text{Cl}(1')---\text{H}(1)] = 2.93(3) \text{ \AA}$.

The ligand is relatively flat, occupying the least square planes listed in Table 9. The phenyl rings are tilted at 2.5° and 8.4° from the

plane of the cyclopropanone.

The 1:1 adduct of dimethyltin(IV) dichloride with 2,6-dimethylpyridine (2,6-lutidine) N-oxide also forms dimers in the solid through bridging chlorine atoms.⁴⁹

Summary

Dimethyltin(IV) dichloride-diphenylcyclopropanone, $C_{34}H_{32}Cl_4O_2Sn_2$, forms colorless crystals, mp 111° C, in the monoclinic space group $C2/c$ with $a = 17.049(16) \text{ \AA}$, $b = 10.027(10) \text{ \AA}$, $c = 19.834(16) \text{ \AA}$, $\beta = 96.00(6)^\circ$, $V = 3372 \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.678 \text{ g cm}^{-3}$. The structure was determined by the heavy atom method from 4890 reflections measured at 138±2K on an Enraf-Nonius CAD/4 automatic diffractometer using zirconium-filtered, monochromatic Mo $K\alpha$ radiation to a final R value of 0.0296 for the 4251 reflections included in the least-squares sums. The dimeric molecule contains six-coordinated tin with the oxygen atom of the ligand and one chlorine atom in a trans-position making a Cl(1)-Sn-O angle of 172.32(5)°. The angle made by the methyl groups is opened to 142.2(1)°, and the octahedron is completed by a roughly trans-Cl(2)-Sn-Cl(1') angle of 166.10(2)°. The Sn_2Cl_2 ring is formed by bonded [$d(Sn-Cl(1)) = 2.4745(7)$] and bridging [$d(Sn-Cl(1')) = 3.5607(7) \text{ \AA}$] connections. The tin atom lies 0.0266(2) \AA above the plane formed by the carbons of its two methyl groups, its terminally-bonded chlorine [Cl(2)] and the chlorine atom bridged to it [Cl(1')], in the direction of the Cl(1) atom. The shortest bond is made to the terminal chlorine [$d(Sn-Cl(2)) = 2.3713(6) \text{ \AA}$]. The distances in the $Sn-O=C$ system [2.380(2) and 1.239(3) \AA], respectively, reflect a normal carbonyl unit, but the intra-ring distances, $d(C=C)$ and $d(C-C)$

[1.376(3) and 1.397(3), 1.402(3) Å, respectively] and C-C-C angle [58.9(2)°] reflect a more delocalized situation than in the free diphenylcyclopropanone. The ligand system is relatively flat with the phenyl rings tilted out of the plane of the cyclopropanone system by 2.5° and 8.4°. The angle formed by the ligand oxygen and three carbon ring and the plane containing the C=O→Sn system is 11.7(2)°. The Sn₂Cl₂ ring is almost flat, being bent through dihedral angles of 2.25(3)°. The sum of the internal angles is 359.94°, with acute angles at the tin atoms 77.26(2) and open angles at the chlorines 102.72(2). Each monomeric unit is related to its other half by a two-fold axis.

TABLE 1

CRYSTAL DATA FOR $[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{O}=\text{CC}_2(\text{C}_6\text{H}_5)_2]_2$

formula	$\text{C}_{34}\text{H}_{32}\text{Cl}_4\text{O}_2\text{Sn}_2$
fw	831.84
cryst system	monoclinic
a , Å	17.049(16)
b , Å	10.027(10)
c , Å	19.834(16)
β , deg ^a	96.00(6)
V , Å ³	3372
space group	$\underline{C2/c}^b$
Z	4
$F(000)$	1680
ρ (calcd), gm cm ⁻³	1.678
μ , cm ⁻¹	18.34
dimens of data crystal, mm	0.18 x 0.33 x 0.48
$T_{\text{max}}/T_{\text{min}}$	0.72/0.41

^a From $\pm 2\theta$ values of reflections with the use of Mo $K\alpha_1$ radiation ($\lambda = 0.70926$ Å).

^b Based upon systematic absences: $\underline{h} \underline{k} \underline{l}$: $\underline{h} + \underline{k} = 2n + 1$; $\underline{h} \underline{0} \underline{l}$: $\underline{l} = 2n + 1$

TABLE 2

DATA COLLECTION PARAMETERS FOR $[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{O}=\text{CC}_2(\text{C}_6\text{H}_5)_2]_2$

diffractometer	Enraf-Nonius CAD/4
radiation	MoK α ($\lambda = 0.71069 \text{ \AA}$)
temp, K	138 \pm 2 $^\circ$
scan technique	θ - 2θ
2 θ limit, deg	0 $<$ 2 θ $<$ 60 $^\circ$
max scan time, s	50
scan angle	0.8 + 0.2 tan θ
aperture width	3.5 + 0.86 tan θ
aperture height, mm	6
aperture dist, mm	173
monitor reflctn	3
intens monitor s	3
max fluctuation in monitor	<3.0%
orientation monitors	200 reflections ^a
no of unique data	4890
no of observed data	4251
corrections	Lorentz-polarization anomalous dispersion

^a New orientation matrix if angular change $>0.1^\circ$. Orientation matrix based upon 17 reflections.

^b $I > 2\sigma(I)$

TABLE 3

FINAL POSITIONAL PARAMETERS FOR THE DIMETHYLTIN(IV) DICHLORIDE-
DIPHENYLCYCLOPROPENONE DIMER ($\times 10^4$)^a

Atoms	x	y	z
Sn	1351.3(1)	2113.5(2)	2294.6(1)
Cl(1)	100.9(4)	2160.7(8)	1539.3(4)
Cl(2)	2099.0(4)	1727.1(7)	1370.5(3)
O	2639(1)	2136(2)	2889(1)
C(1)	1254(2)	213(3)	2742(2)
C(2)	1305(2)	4172(3)	2508(2)
C(3)	2916(1)	2673(2)	3424(1)
C(4)	2849(1)	3336(2)	4035(1)
C(5)	3586(1)	3017(2)	3860(1)
C(6)	2369(1)	3916(2)	4521(1)
C(7)	1550(1)	3854(3)	4388(1)
C(8)	1071(1)	4425(3)	4834(1)
C(9)	1405(2)	5062(3)	5412(1)
C(10)	2218(2)	5113(3)	5553(1)
C(11)	2703(1)	4549(3)	5112(1)
C(12)	4429(1)	2961(2)	4003(1)
C(13)	4870(2)	2434(3)	3508(1)
C(14)	5682(2)	2305(3)	3642(1)
C(15)	6051(1)	2677(3)	4271(2)
C(16)	5615(1)	3199(3)	4765(1)
C(17)	4807(1)	3355(3)	4634(1)

^a Estimated standard deviations in parentheses.

TABLE 4

THERMAL PARAMETERS FOR THE DIMETHYLTIN(IV) DICHLORIDE-DIPHENYLCYCLOPROPENONE DIMER^a

Atoms	$B_{11} \times 10^4$	$B_{22} \times 10^4$	$B_{33} \times 10^4$	$B_{23} \times 10^4$	$B_{13} \times 10^4$	$B_{12} \times 10^4$
Sn	11.4(1)	42.2(1)	8.9(1)	0.4(1)	2.5(1)	3.4(1)
Cl(1)	14.1(2)	102.9(9)	12.9(2)	5.2(6)	-0.8(3)	8.2(6)
Cl(2)	16.7(2)	65.7(6)	11.9(1)	-2.0(5)	9.0(3)	2.3(6)
O	16(1)	72(2)	15(1)	-23(2)	-8(1)	10(2)
C(1)	19(1)	59(3)	19(1)	12(2)	7(1)	5(2)
C(2)	25(1)	54(3)	16(1)	0(2)	11(1)	4(3)
C(3)	12(1)	43(2)	14(1)	-6(2)	-1(1)	3(2)
C(4)	12(1)	43(2)	11(1)	2(2)	-2(1)	-2(2)
C(5)	13(1)	45(2)	11(1)	2(2)	1(1)	-3(2)
C(6)	14(1)	37(2)	12(1)	6(2)	5(1)	-2(2)
C(7)	16(1)	50(2)	13(1)	3(2)	3(1)	-2(2)
C(8)	13(1)	64(3)	16(1)	10(2)	8(1)	4(2)
C(9)	21(1)	54(3)	14(1)	10(2)	13(1)	10(2)
C(10)	22(1)	50(2)	13(1)	-1(2)	5(1)	-5(2)
C(11)	15(1)	47(2)	13(1)	2(2)	3(1)	-7(2)
C(12)	12(1)	43(2)	11(1)	1(2)	2(1)	-4(2)
C(13)	17(1)	55(2)	11(1)	-4(2)	3(1)	-2(2)
C(14)	16(1)	56(3)	15(1)	1(2)	8(1)	7(2)
C(15)	12(1)	50(2)	17(1)	10(2)	4(1)	0(2)
C(16)	14(1)	58(2)	12(1)	-2(2)	-1(1)	-9(2)
C(17)	15(1)	53(2)	10(1)	-3(2)	2(1)	-7(2)

^a Estimated standard deviations in parentheses.

TABLE 5

INTRAMOLECULAR DISTANCES (IN Å) IN $[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{O}=\text{CC}_2(\text{C}_6\text{H}_5)_2]_2^{\text{a}}$

<u>Sn - heteroatom distances</u>	
Sn - Cl(1)	2.4745(7)
Sn - Cl(2)	2.3713(6)
Sn - C(1)	2.116(3)
Sn - C(2)	2.111(3)
Sn - O	2.380(2)
Sn - Cl(1')	3.5607(7)
<u>C - C distances in the cyclopropenone ring</u>	
C(3) - C(4)	1.397(3)
C(3) - C(5)	1.402(3)
C(4) - C(5)	1.376(3)
<u>Other distances</u>	
O - C(3)	1.239(3)
C(4) - C(6)	1.450(3)
C(5) - C(12)	1.436(3)

^a Estimated standard deviations in parentheses.

TABLE 6

INTRAMOLECULAR ANGLES (DEG) IN $[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{O}=\text{CC}_2(\text{C}_6\text{H}_5)_2]_2^{\text{a}}$

C1(1) - Sn - C1(2)	91.94(2)
C1(1) - Sn - O	172.32(5)
C1(1) - Sn - C(1)	99.81(8)
C1(1) - Sn - C(2)	93.16(6)
C1(2) - Sn - O	80.92(5)
C1(2) - Sn - C(1)	104.43(8)
C1(2) - Sn - C(2)	110.46(8)
O - Sn - C(1)	84.82(9)
O - Sn - C(2)	86.75(9)
C(1) - Sn - C(2)	142.2(1)
Sn - O - C(3)	132.7(2)
C(4) - C(3) - C(5)	58.9(2)
C(3) - C(4) - C(5)	60.7(2)
C(3) - C(5) - C(4)	60.4(2)
C1(1') - Sn - C1(1)	77.26(2)
C1(1') - Sn - C1(2)	166.10(2)
C1(1') - Sn - O	110.23(5)
C1(1') - Sn - C(1)	69.45(7)
C1(1') - Sn - C(2)	79.25(8)
Sn - C1 - Sn'	102.71(2)

^a Estimated standard deviations in parentheses.

TABLE 7

HYDROGEN PARAMETERS FOR THE DIMETHYL TIN(IV) DICHLORIDE-
DIPHENYLCYCLOPROPENONE DIMER ^a

Atom	x x 10 ³	y x 10 ³	z x 10 ³	B _{iso}
H(1)	119(2)	36(3)	319(2)	3.4(8)
H(2)	83(2)	-13(4)	256(2)	5.4(10)
H(3)	169(2)	-28(4)	270(2)	3.8(8)
H(4)	85(2)	427(5)	268(2)	6.3(11)
H(5)	170(2)	438(4)	283(2)	5.0(9)
H(6)	130(2)	460(5)	212(2)	6.1(11)
H(7)	131(2)	336(3)	399(2)	2.3(6)
H(8)	51(2)	441(4)	471(2)	3.6(8)
H(9)	108(2)	545(3)	571(2)	3.2(7)
H(10)	243(2)	556(3)	594(2)	3.0(7)
H(11)	325(2)	460(3)	521(1)	1.7(6)
H(12)	468(2)	216(3)	309(2)	2.7(7)
H(13)	599(2)	198(2)	334(1)	1.1(5)
H(14)	660(2)	251(3)	440(2)	2.5(6)
H(15)	584(2)	344(3)	516(2)	2.3(6)
H(16)	449(2)	369(3)	497(1)	1.7(5)

^a Estimated standard deviations in parentheses.

TABLE 8

CARBON AND HYDROGEN DISTANCES (IN Å) AND ANGLES (IN DEG)
 $[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{O}=\overset{\circ}{\text{C}}\text{C}_2(\text{C}_6\text{H}_5)_2]_2^{\text{a}}$

C - C distances in the phenyl rings

C(6)-C(7)	1.395(3)
C(7)-C(8)	1.388(4)
C(8)-C(9)	1.382(4)
C(9)-C(10)	1.386(4)
C(10)-C(11)	1.386(4)
C(11)-C(6)	1.401(3)
C(12)-C(13)	1.402(3)
C(13)-C(14)	1.389(4)
C(14)-C(15)	1.389(4)
C(15)-C(16)	1.393(4)
C(16)-C(17)	1.384(3)
C(17)-C(12)	1.402(3)

C - C angles in the phenyl rings

C(11)-C(6)-C(7)	119.3(2)
C(6)-C(7)-C(8)	120.4(2)
C(7)-C(8)-C(9)	120.0(2)
C(8)-C(9)-C(10)	120.1(2)
C(9)-C(10)-C(11)	120.5(2)
C(10)-C(11)-C(6)	119.7(2)
C(17)-C(12)-C(13)	120.1(2)
C(12)-C(13)-C(14)	119.9(2)
C(13)-C(14)-C(15)	119.7(2)
C(14)-C(15)-C(16)	120.6(2)
C(15)-C(16)-C(17)	120.3(2)
C(16)-C(17)-C(12)	119.5(2)

TABLE 8, cont'd.

<u>Hydrogen distances</u>	
C(1)-H(1)	0.92(3)
C(1)-H(2)	0.85(4)
C(1)-H(3)	0.90(3)
C(2)-H(4)	0.89(4)
C(2)-H(5)	0.91(4)
C(2)-H(6)	0.88(4)
C(7)-H(7)	0.98(3)
C(8)-H(8)	0.96(3)
C(9)-H(9)	0.94(3)
C(10)-H(10)	0.93(3)
C(11)-H(11)	0.94(3)
C(13)-H(12)	0.90(3)
C(14)-H(13)	0.90(3)
C(15)-H(14)	0.96(3)
C(16)-H(15)	0.87(3)
C(17)-H(16)	0.96(3)

^a Estimated standard deviations in parentheses.

TABLE 9

LEAST SQUARES PLANES IN DIMETHYL TIN(IV) DICHLORIDE-DIPHENYLCYCLOPROPENONE
 Orthonormal Equation: $m_1x + m_2y + m_3z + d = 0$

Plane Through Atoms	m_1	m_2	m_3	d	Plane P	Dihedral Angle Between Planes [P, P']	R.M.S. of atoms Defining Plane
C1(2), C1(1'), C(1), C(2)	-0.7739	-0.0408	-0.6320	4.6102	1 ^a		0.3054
Sn, Sn', C1(1), C1(1')	-0.0000	-1.0000	0.0000	-2.1427	2	87.66°[1,2]	0.0237
C(3), C(4), C(5), O	0.0420	0.8770	-0.4786	0.4488	3	76.46°[1,3]	0.0033
C(6), C(7), C(8)	0.0095	0.8642	-0.5031	0.8730	4	2.45°[3,4]	0.0043
C(9), C(10), C(11)							
C(12), C(13), C(14)	0.1275	0.9212	-0.3675	-1.0681	5	8.43°[3,5]	0.0056
C(15), C(16), C(17)							
C(3), C(4), C(5), C(6)	0.0797	0.8884	-0.4522	0.0583	6	79.18°[1,6]	0.0854
C(7), C(8), C(9), C(10)							
C(11), C(12), C(13)							
C(14), C(15), C(16)							
C(17), O							
Sn, O, C(1)	0.3648	-0.4250	-0.8285	3.6353	<u>b</u>		0
Sn, O, C(2)	0.3890	0.2029	-0.8986	2.5520	<u>b</u>		0
Sn, O, C(3)	0.2259	0.8122	-0.5379	0.0798	<u>b</u>		0

TABLE 9, cont'd.

-
- ^a Distance of the tin atom from this plane is 0.0266(2) Å in the direction of the Sn-C1(1) vector.
- ^b The O-C(3) vector makes an angle of 79.46° with the Sn-C(1) vector and 42.60° with the Sn-C(2) vector when viewed along the Sn-O axis.

TABLE 10

COMPARISON MOLECULAR STRUCTURE DATA FOR CYCLOPROPENONES

Compound	$d(\text{C}=\text{O}), \text{\AA}$	$d(\text{C}=\text{C}), \text{\AA}$	$d(\text{C}-\text{C})_{\text{av.}}, \text{\AA}$	$d(\text{C}-\text{C}_{6\text{H}_5})_{\text{av.}}, \text{\AA}$	$\angle \text{C}-\overset{\text{O}}{\text{C}}-\text{C}, \text{deg.}$	$\Delta[d(\text{C}-\text{C})-d(\text{C}=\text{C})], \text{\AA}$
$(\text{CH}_3)_2\text{C}=\text{O}$, mw^{a}	1.212	---	1.519	---	116.2	---
ed^{b}	1.211	---	1.517	---		
 , mw^{c}	1.191	---	1.475	---	64.6	---
 , ed^{d}	---	1.28	1.52	---	49.9	0.24
ed^{e}	---	1.304	1.519	---	$\underline{\text{g}}$	0.215
mw^{f}	---	1.300	1.515	---	$\underline{\text{g}}$	0.215
 , mw^{h}	1.212	1.302	1.412	---	54.9 $\underline{\text{i}}$	0.110
 , $\text{X-ray}^{\text{j,k}}$	1.225	1.348	1.416	1.447	56.9	0.068

TABLE 10, cont'd.

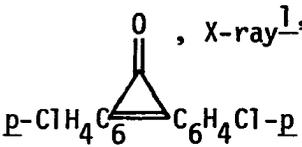
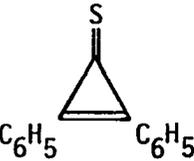
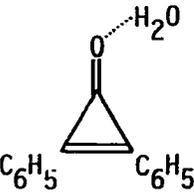
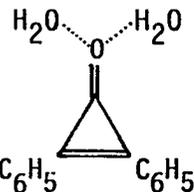
Compound	$d(\text{C}=\text{O}), \text{\AA}$	$d(\text{C}=\text{C}), \text{\AA}$	$d(\text{C}-\text{C})_{\text{av.}}, \text{\AA}$	$d(\text{C}-\text{C}_{\text{6H}_5})_{\text{av.}}, \text{\AA}$	$\angle \text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}, \text{deg.}$	$\Delta[d(\text{C}-\text{C})-d(\text{C}=\text{C})], \text{\AA}$
 $p\text{-ClH}_4\text{C}_6\text{C}_6\text{H}_4\text{Cl-p}$, X-ray ^{l,m} 1.30	1.48	1.42	1.37	62.2	0.06
 C_6H_5	, X-ray ⁿ 1.630	1.338	1.403	1.440	57.0	0.065
 C_6H_5	, X-ray ^{k,o} 1.238	1.365	1.405	1.439	58.1	0.040
	X-ray ^p 1.222	1.356	1.409	1.451	57.5	0.053
 C_6H_5	, X-ray ^{k,q} 1.245	1.376	1.389	1.441	59.4	0.013
	X-ray ^r 1.230	1.352	1.410	1.454	57.5	0.058

TABLE 10, cont'd.

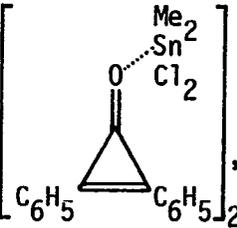
Compound	$d(\text{C}=\text{O}), \text{\AA}$	$d(\text{C}=\text{C}), \text{\AA}$	$d(\text{C}-\text{C})_{\text{av.}}, \text{\AA}$	$d(\text{C}-\text{C}_{6\text{H}_5})_{\text{av.}}, \text{\AA}$	$\overset{\text{O}}{\parallel} <\text{C}-\text{C}-\text{C}, \text{deg.}$	$\Delta[d(\text{C}-\text{C})-d(\text{C}=\text{C})], \text{\AA}$	
 $\left[\text{C}_6\text{H}_5 \text{---} \text{C}(\text{C}_6\text{H}_5)_2 \text{---} \text{C}(\text{O}) \text{---} \text{Sn}(\text{Me}_2)_2 \text{Cl}_2 \right]_2$	X-ray ^s	1.239(3)	1.376(3)	1.400(3)	1.443(3)	58.9(2)	0.024
^a Reference 30.							
^b Reference 31.							
^c Reference 32.							
^d Reference 33.							
^e Reference 34.							
^f Reference 35.							
^g Not given.							
^h Reference 6.							
ⁱ Not given in ref. 6; calculated assuming the two other interior angles are equal.							
^j Reference 5.							
					^k Calculated from the final atomic coordinates. [H. Shimanouchi, private communication, 1981]		
					^l Reference 9.		
					^m Criticized in ref. 8 as listing erroneous dimensions.		
					ⁿ Reference 36.		
					^o There are two crystallographically independent formula units per asymmetric unit, one hydrogen bonded to one water molecule, whose dimensions are listed here.		
					^p Reference 7.		
					^q There are two crystallographically independent formula units per asymmetric unit, one hydrogen bonded to two water molecules.		

TABLE 10, cont'd.

r Reference 8.

s This work.

TABLE 11

 COMPARISON MOLECULAR STRUCTURE DATA FOR SYSTEMS CONTAINING
 CARBONYL OXYGEN TO TIN(IV) COORDINATION

Compound	d(C=O→Sn), Å		<C=O→Sn, deg.
(C ₆ H ₅) ₃ Sn(1,3-diphenylpropane-1,3-dionato) ^a	1.290	2.094	135.3
	1.260	2.276	132.1
Cl ₂ Sn(2,4-pentanedionato) ₂ ^b	1.290	2.051	124.5
	1.275	2.064	125.0
Cl ₂ Sn(ethyl 3-oxobutanato) ₂ ^c	1.322	2.066	126.5
	1.293	2.101	123.1
(C ₆ H ₅) ₃ Sn(N-benzoyl-N-phenyl-O-hydroxylaminato) ^d	1.265	2.308	112.1
Cl ₂ Sn(N-benzoyl-N-phenyl-O-hydroxylaminato) ₂ ^e	1.30	2.180	111
Sn(C ₇ H ₅ O ₂) ₃ Cl·CHCl ₃ ^f	1.290 ^g	2.103 ^g	117.6 ^g
	1.284 ^g	2.156 ^g	116.5 ^g
Sn(C ₇ H ₅ O ₂) ₃ OH ^f	1.299 ^g	2.110 ^g	118.6 ^g
	1.271 ^g	2.183 ^g	117.2 ^g
(CH ₃) ₃ SnCl·triphenylphosphoranylideneacetone ^h	1.268	2.332	134.3
(CH ₃) ₂ SnCl ₂ ·salicylaldehyde ⁱ	1.23	2.680	134 ^j
[(CH ₃) ₂ SnCl ₂ ·O=CC ₂ (C ₆ H ₅) ₂] ₂ ^k	1.239(3)2.380(2) 132.7(2)		

^a Reference 38.^b Reference 42.^c Reference 43.^d Reference 38.^e Reference 39.^f Reference 45.^g Averaged for the three ligands in the molecule.^h Reference 44.ⁱ Reference 20.^j Reference 46.^k This work.

FIGURE 1

THE ASYMMETRIC UNIT OF $[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{O}=\text{CC}_2(\text{C}_6\text{H}_5)_2]_2$ SHOWING THE ATOM NUMBERING

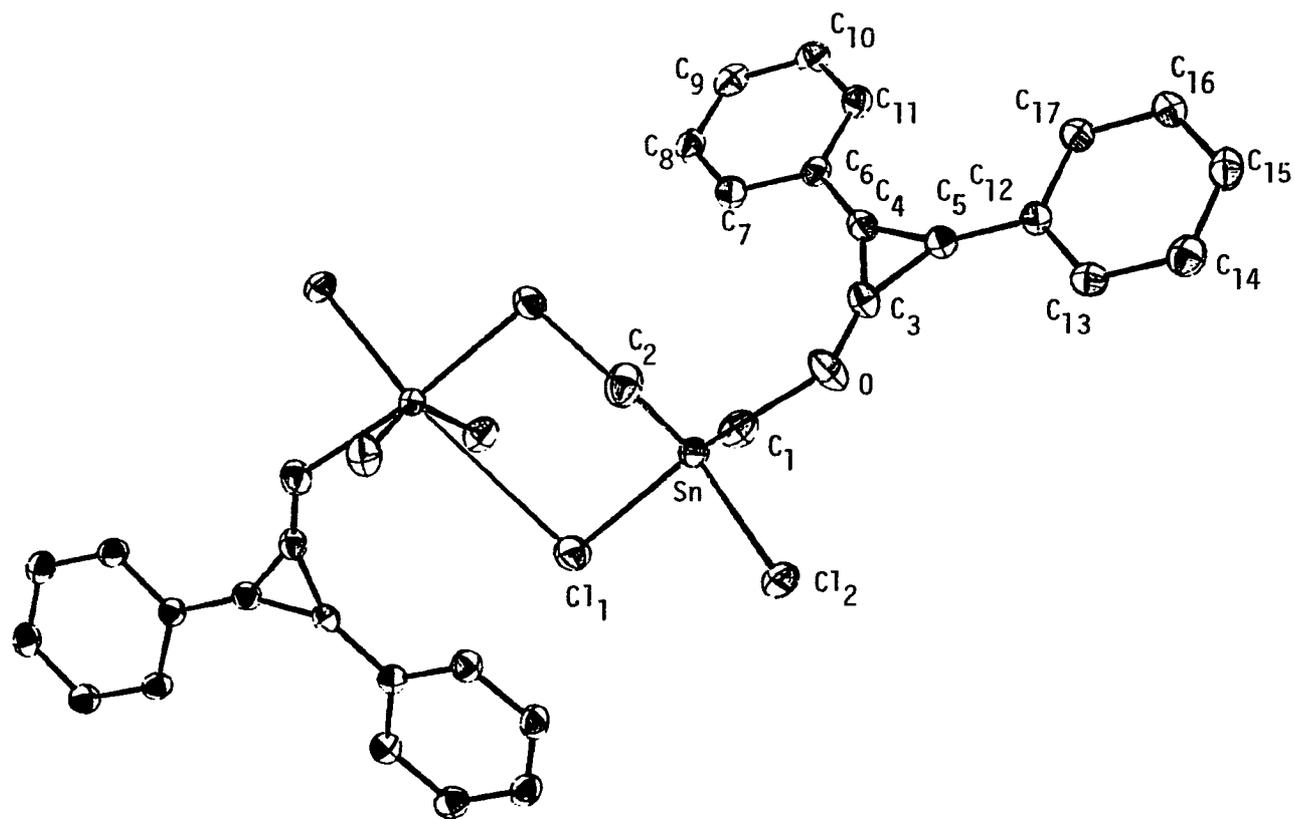
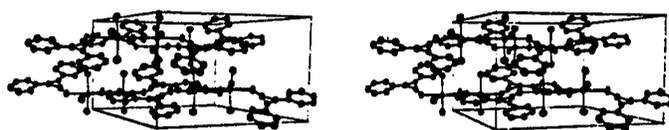


FIGURE 2

THE UNIT CELL CONTENTS OF $[(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{O}=\text{CC}_2(\text{C}_6\text{H}_5)_2]_2$



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CHAPTER 7

THE X-RAY CRYSTAL AND MOLECULAR STRUCTURE OF THE DIMERIC 1:1 ADDUCT OF
DIMETHYLTIN(IV) DICHLORIDE WITH 2,6-DIMETHYLPYRIDINE (2,6-LUTIDINE)
N-OXIDE, $[(\text{CH}_3)_2\text{SnCl}_2 \cdot 2,6-(\text{CH}_3)_2\text{C}_5\text{H}_3\text{NO}]_2$, AT $138 \pm 2\text{K}$

(This structure was solved in collaboration with Professor D. van der Helm and Dr. C.L. Barnes. See Preface.)

Introduction

Diorganotin(IV) dihalides, and more particularly dimethyltin(IV) dichloride, form the well-known 1:2 adducts with Lewis bases.¹ However, with certain pointed ligands in which the donor atom carries only one attachment (unbranched) in a $\diagdown \text{C}=\text{O}$,²⁻⁴ $\diagdown \text{C}=\text{S}$,³ $\diagdown \text{S}=\text{O}$,^{5,6} $\diagdown \text{N}=\text{O}$ ^{6,7} or $\diagdown \text{P}=\text{O}$ ⁸ system,⁹ 1:1 adducts with dimethyltin(IV) dichloride are also known. The detailed molecular structure data are largely lacking,¹² but the formation of the 1:1 systems is curious since the pointed ligands should be less, not more sterically demanding and allow the syntheses of the complexes to proceed to the 1:2 formations without difficulty. It must be remembered that dimethyltin(IV) dichloride itself forms an associated solid through double, unsymmetrical chlorine-tin bridges,¹³ and chlorine bridging may help complete the tin coordination sphere in these systems. Disregarding ancient claims, examples of these 1:1 adducts number fewer than thirty species and include as ligands several dialkylsulfoxides,⁵⁻⁶

DMF,^{2,6} hexamethylphosphoramide,⁸ N,N-dimethylpicolinamide, -nicotinamide, -isonicotinamide and their thio derivatives,³ salicylaldehyde,¹⁴ diphenylcyclopropenone^{15,16} and variously-substituted pyridine N-oxides.^{6,7,17} In certain cases both 1:1 and 1:2 complexes of dimethyltin (IV) dichloride with the same ligand have been isolated, for example, with methylbenzylsulfoxide,⁶ tetramethylurea,⁴ 3,5-dimethylpyrazole,¹⁰ N,N-dimethylnicotinamide, -isonicotinamide and -thionicotinamide³ and pyridine N-oxide.^{6,19,20} The basicity of the donor atom, the acidity of the tin atom, steric effects originating on the tin or donor moieties and the creation of strong dipoles or ionic charges in the resulting adducts must play a role in the choice of the structure of the product.²⁴ Surprisingly, neither the stoichiometry of the reactants nor the reaction conditions appear to exert much influence.

Until recently only one published structure report was available for a 1:1 adduct of a diorganotin(IV) dihalide, that of the dimethyltin (IV) dichloride complex of salicylaldehyde,²⁶ a potentially chelating donor. However, the phenolic OH group of this ligand intramolecularly hydrogen bonds to the adjacent aldehydic oxygen held at the ortho-position rather than chelate the tin atom. The aldehydic oxygen is attached to the tin atom through an angle of 174.7° with one of the tin-chlorine vectors, and 79.9° with the other. The methyl-tin-methyl angle is opened to 131.4°. The phenolic oxygen makes a short intermolecular contact to the tin atom of an adjacent molecule in the cell of 3.36 Å and at an angle of 163.1° to one of the chlorine-tin vectors and 68.4° to the other.²⁷ The structure is described, however, as a trigonal bipyramid with the two methyl groups and one chlorine atom equatorial with the aldehydic oxygen

of the ligand and the second chlorine atom axial.²⁶

The 1:1 adduct of dimethyltin(IV) dichloride with diphenylcyclopropenone, whose crystal structure has been solved,²⁸ can also be described as a trigonal bipyramid with axial-ligand and chlorine attachments, but here again, there is a short intermolecular contact, this time with the axial-chlorine atom of an adjacent molecule of 3.561 Å. This attachment is made along an equatorial chlorine-tin vector at an angle of 166.1°.²⁸

Data from tin-119m Mössbauer quadrupole splittings (QS) can potentially throw light upon the question of which is the correct coordination number of the tin atom in the 1:1 complexes. In general QS values for diorganotin(IV) systems increase with increasing carbon-tin-carbon angle.²⁹ For octahedral systems of the formula $R_2SnX_nL_{4-n}$, a treatment can be applied based upon a point-charge model in which the QS values can be used to predict these angles at tin,³⁰ and excellent results have been obtained for the dimethyl-^{30,31} and diphenyltin(IV)^{30,32} derivatives where structural data are available.¹² An analogous additivity model for five-coordinated diorganotin compounds has also been proposed. According to the latter treatment, a system of the type $(CH_3)_2SnX_{3-n}L_n$ should exhibit a QS of $3.00^{33} - 3.25^{16} \text{ mm s}^{-1}$. The QS of the 1:1 complex of dimethyltin(IV) dichloride with salicylaldehyde has a QS = 3.33,^{14,26} and of diphenylcyclopropenone 3.52 mm s^{-1} .¹⁶ Using these values in the treatment mentioned above for six-coordination yields predictions of methyl-tin-methyl angles of 137.2° and 143.1°, respectively, vs. 131.4°²⁷ and 142.2°²⁸ actually found.

However, in this treatment the magnitude of the QS is assumed to

arise only as a result of the nature of the two organic attachments and the angle they make with the tin atom. Neither the nature of the ligands nor their number is assumed to make any difference in the electric field gradient at tin. Hence, the magnitude of the QS in this treatment cannot be used to distinguish between five- and six-coordination, since it is assumed that, for example, trans- O_h and axial-trigonal bipyramidal geometries (180°) would give rise to the same values, as would cis- O_h and axial-, equatorial-trigonal bipyramidal geometries (90°). It is also true, however, that while the trans- R_2SnL_4 geometry is ubiquitous for six-coordinated complexes, the analogous axial- R_2SnL_3 is rare for the five-coordinated complexes which prefer the equally ubiquitous axial-most-electronegative geometry with equatorial-organic groups. Thus \angle 's C-Sn-C above 120° (QS $> 2.5 \text{ mm s}^{-1}$) are likely to correspond to six-coordination, as do those in the 1:1 adducts of dimethyltin(IV) dichloride with salicylaldehyde^{14,26,27} and diphenylcyclopropanone.^{16,28}

The 1:1 complex of dimethyltin(IV) dichloride with pyridine N-oxide is said to adopt a trigonal bipyramidal structure in which the ligand binds equatorially with the two methyl groups on the basis of infrared and Raman evidence.⁶ However, the QS value is 3.97 mm s^{-1} ⁶ for a predicted angle of 162.0° using the point-charge model. The 1:2 complex exhibits a QS of 4.02 mm s^{-1} ,⁶ and the structure shows the tin atom located on a crystallographic center of symmetry to give the \angle C-Sn-C = 180° .³⁴ The availability of this structure report prompted this structural study of the potentially six-coordinated diorganotin(IV) dihalides to the pyridine N-oxide series. The sterically-crowded 2,6-dimethylpyridine (2,6-lutidine) N-oxide ligand was chosen to test the effect of the possibly

severe nonbonded repulsions arising from the 2,6-substituents on the formation of a genuinely five-coordinated 1:1 adduct.

Experimental Section

Synthesis of Dimethyltin(IV) Dichloride·2,6-Dimethylpyridine N-Oxide

Dimethyltin(IV) dichloride was a gift from M & T Chemicals. 2,6-Dimethylpyridine N-oxide (Aldrich Chemicals) was used without further purification. Concentration of a chloroform solution of dimethyltin(IV) dichloride (2.20 g, 0.01 mol) and 2,6-dimethylpyridine N-oxide (1.23 g, 0.01 mol) gave a cream-colored solid which was recrystallized twice from chloroform to yield a white product. Single crystals of the adduct which melt sharply at 147° C were obtained by slow evaporation of a chloroform solution of the adduct. Dimethyltin(IV) dichloride 2,6-dimethylpyridine N-oxide is stable in air. Its Sn-119 NMR chemical shift is -13.24 ppm relative to tetramethyltin.

Crystal Data

Data were obtained on an Enraf-Nonius CAD/4 automatic counter diffractometer at 138±2K controlled by a PDP-8/e computer and fitted with a low-temperature apparatus. Crystal data are listed in Table 1.

Details of the experimental apparatus, and methods of data reduction have been outlined previously.³⁵ Specific parameters relating to the collection of this data set are listed in Table 2. The structure factors for each reflection were assigned weights based upon counting statistics.³⁵ No absorption correction was applied. The minimum and maximum transmission factors are 0.37 and 0.72, respectively.

Structure and Refinement

Systematic absences gave two possible space groups, Cc and C2/c. The position of the tin atom was found on solving the Patterson map. The averaged, normalized structure factor, E , suggested that the space group could be noncentrosymmetric. The structure factors calculated assuming a noncentrosymmetric space group gave an R factor ($R = \frac{\sum ||kF_o| - |F_c||}{\sum |kF_o|}$) of 0.489 after 2 cycles of refinement. A difference Fourier map was then calculated. From the difference map, all the non-hydrogen atoms were located. Two molecules per asymmetric unit were found, and they were observed to be approximately related by a 2-fold axis of rotation. The atoms were then refined using the SHELX program³⁶ in the C2/c space group isotropically. When the R factor was a minimum, a difference map was calculated from which the hydrogen positions were located. The hydrogens were then refined isotropically, whereas the other atoms were refined anisotropically to a final R value of 0.0364.

The scattering factors used were for neutral atoms and were taken from ref. 37 (Sn, Cl, O and C).

Final atomic parameters are given in Table 3 and final intramolecular distances and angles in Tables 4 and 5, respectively. Least-squares planes are given in Table 6.

The asymmetric unit showing the atomic numbering is depicted in Figure 1. Hydrogen atoms are numbered with respect to the carbon atom to which they are attached (all hydrogens are C-H), e.g., H(Cl). Where methyl carbons hold more than one hydrogen atom these are labeled, e.g., as H(Cl)A, H(Cl)B, H(Cl)C. The unit cell contents are shown in Figure 2. Figure 3 is a view of the monomer unit down the trans-chlorine(1)-tin-oxygen vector.

Results

For the adduct the NMR tin-proton coupling constant, $|^2J(^{119}\text{Sn-C-}^1\text{H})| = 80.4$ Hz as measured in deuteriochloroform. The corresponding value in the related 1:1 adduct with 2,4,6-trimethylpyridine N-oxide is reported as 80 Hz.⁷

The ν_{asym} and ν_{sym} (Sn-CH₃) modes appear in the infrared spectrum at 564(m) and 518(m), and in the Raman at 572(w) and 514(s) cm⁻¹, respectively. In addition, bands at 538(w) and 525(m) appear in the infrared and Raman spectra, respectively. The corresponding $\nu(\text{Sn-CH}_3)$ bands for the 1:1 adduct with pyridine N-oxide are reported at 570 and 508 in the infrared and at 566 and 506 cm⁻¹ in the Raman, respectively.⁶ These bands are found at 566 and 512 cm⁻¹ in the infrared of the 1:1 adduct with 2,4,6-trimethylpyridine N-oxide.⁷ In the $\nu(\text{N-O})$ region, bands are seen at 1212, 1197, 1172 compared with the 1246 cm⁻¹ band in the free ligand.³⁸ The corresponding 1:1 complex with tin(II) chloride has $\nu(\text{N-O}) = 1181$ cm⁻¹ ($\Delta\nu = 65$ cm⁻¹).²² The more strongly Lewis acidic tin(IV) derivative should exhibit a larger $\nu(\text{N-O})$ shift, and hence the $\nu(\text{N-O})$ mode in the adduct is assigned at 1172 cm⁻¹ ($\Delta\nu = 74$ cm⁻¹) on this basis.

The Mössbauer spectrum is a well-separated doublet with isomer shift (IS) of 1.44±0.03, quadrupole splitting (QS) of 3.80±0.06 [$\rho = \text{QS}/\text{IS} = 2.64$] and $\Gamma_1 = 1.38$ and $\Gamma_2 = 1.32 \pm 0.03$ mm s⁻¹. For the corresponding 1:1 pyridine N-oxide adduct, IS = 1.33, QS = 3.97 mm s⁻¹ [$\rho = 2.98$].⁶

Description and Discussion of the Structure

From Figure 1 it is seen that the 1:1 nature of the title complex arises because the sixth coordination position at tin is taken up by a

chlorine donor atom from a second molecule to form an unsymmetrical, double-bridged Sn_2Cl_2 ring system whose dimensions include a short [$\text{Sn} - \text{Cl}(1) = 2.528(1) \text{ \AA}$] and a long [$\text{Sn} - \text{Cl}(1') = 3.399(1) \text{ \AA}$] tin-chlorine distance. One chlorine atom in each molecule is terminal at [$\text{Sn} - \text{Cl}(2) = 2.400(1) \text{ \AA}$]. The resulting geometry about the tin atom is thus distorted octahedral with trans-dimethyl groups [$\angle \text{C}(1) - \text{Sn} - \text{C}(2) = 145.3(2)^\circ$]. The bridging chlorine from the second molecule approaches along the $\text{Sn} - \text{Cl}(2)$ vector to create a trans-dichlorotin system [$\angle \text{Cl}(1') - \text{Sn} - \text{Cl}(2) = 168.79(3)^\circ$]. The chlorine atom trans- to the N-oxide ligand [$\angle \text{O} - \text{Sn} - \text{Cl}(1) = 177.44(7)^\circ$] forms the bridge. The planar Sn_2Cl_2 ring is located on a crystallographic center of symmetry as seen in the unit cell diagram shown in Figure 2. This dimerization went undetected in the tin-119m Mössbauer spectroscopic study of the related pyridine N-oxide complex, where the IS (1.33) and QS (3.97) are not very different from the 1:2 complex (1.35 and 4.02 mm s^{-1} , respectively).⁶ Other 1:1 complexes are also reported to exhibit large QS's,^{6,8,15,16} and are probably six-coordinated in the solid through chlorine bridging. The ability to complete the coordination sphere through oligomerization or polymeric association may lie at the root of why 1:1 complexes form at all, and may explain why they are found almost exclusively⁹ with pointed >C=O , >C=S , >S=O , $\text{>N}\rightarrow\text{O}$ or >P=O ligands.

Dimethyltin(IV) dichloride itself forms an associated solid in which the distortion from tetrahedral geometry is very severe. The molecular units align themselves so that double chlorine bridges can form to give Sn_2Cl_2 planes with tin-chlorine distances of 2.40 and 3.54 \AA and methyl groups projecting above and below ($\angle \text{C-Sn-C} = 123.5^\circ$).¹³ A similar

arrangement is adopted by the two central, six-coordinated diphenyltin(IV) dichloride molecules in that tetrameric chain structure³⁹ which contains tin-chlorine distances of 2.357 and 3.77 Å, but rather closed carbon-tin-carbon angles of 125.5°. ⁴⁰ A more symmetrical polymer of this type is formed by the difluoride analogue,^{41,42} and trimethyltin(IV) chloride also crystallizes as an infinite, chlorine-bridged polymer.⁴³ A different arrangement in which both chlorine atoms from one molecule chelate the same tin atom of a neighboring molecule is found in the bis(chloromethyl) tin(IV) dichloride structure. The tin-chlorine distances here are 2.37 and 3.71 Å, and the carbon-tin-carbon angle is opened to 135°. ³⁹ In the title adduct there is no possibility for further association unless higher than six-coordination is utilized, and the bridging mode chosen to form the dimer most strongly resembles that found in dimethyltin(IV) dichloride itself, except that the dimethyltin angle is more open [123.5°¹³ vs. 145.3(2)°]. Comparison data for dimethyltin(IV) dichloride and its two pyridine N-oxide complexes are displayed in Table 7.

Close reexamination of the structural data for the related 1:1 complex of salicylaldehyde^{26,27} reveals that the short contact between the phenolic oxygen of one molecule and the tin atom of the next (3.36 Å) is directed along an Sn-Cl vector.²⁷ This is suggestive of an octahedral geometry at the tin atom with one intramolecular trans-Cl-Sn-O system formed with the donor aldehydic oxygen and a second trans-Cl-Sn-O formed intermolecularly with the phenolic oxygen atom of an adjacent molecule. This phenol group also engages in internal hydrogen bonding with the ortho-aldehyde, consistent with infrared evidence. The dimethyltin angle is opened to 131.4° to complete the distorted trans-, trans-, trans-

arrangement.

In the 1:1 complex with diphenylcyclopropenone, the dimethyltin angle is opened even farther to 142.2° , and the nearest non-bonded chlorine is found at 3.561 \AA in a position suggestive of coordination.²⁸

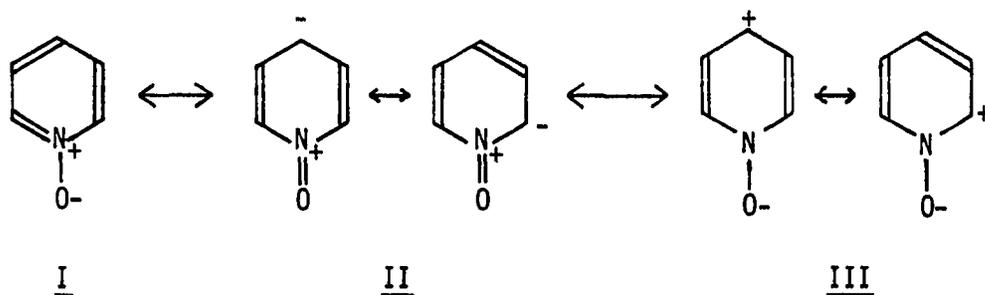
Observation of both ν_{asym} and ν_{sym} (Sn-C) modes in the infrared and Raman spectra corroborates the non-linear dimethyltin system found, and the application of a treatment based upon a point charge model³⁰ links the observed Mossbauer QS value to a predicted carbon-tin-carbon angle in octahedral complexes. The results of the calculation, which is based upon the assumption that the partial QS of the chlorine and ligand groups are negligible, are listed in Table 8. Data for the 1:1 complex of pyridine N-oxide⁶ are included on the assumption that this complex will also be found to be dimeric in the solid.

Thus the most direct comparison with the structure of the title compound is with the octahedral 1:2 complex of dimethyltin(IV) dichloride with the unsubstituted pyridine N-oxide.³⁴ and with its five-coordinated, 1:1 complex with triphenyltin(IV) nitrate which has been solved in both its mono-⁴⁴ and triclinic modifications,⁴⁵ but there are available published reports of the structures of a wide variety of transition metal complexes of pyridine N-oxide⁴⁶⁻⁴⁹ which encompass copper(II),⁵⁰⁻⁶⁶ zinc(II),^{62,64,67} nickel(II),⁶⁸⁻⁷⁰ cobalt(II),^{63,70-72} iron(II),⁶³ platinum(II)⁷³ and mercury(II)^{74,75} in three-,⁷⁴ four-,^{50,51,53-55,58,59,65,67,73} five-^{52,56,59-61,65,71} and six-coordination^{57,62-4,68,69,72,75} in neutral^{50-52,55-61,65,66,70,71} and cationic^{53,54,57,62-65,69-72,75} species. Data for some thirty transition metal complexes are available, and these are listed in Table 9. The structures of the parent pyridine N-oxide

ligand are known in the solid⁷⁶ as well as the gas phase (electron diffraction),⁷⁷ along with those of the solid 4-nitro-,⁷⁸ 4,4-trans-azo-⁷⁹ and N-oxyphenazine⁸⁰ derivatives. In addition, the structures of the hydrochloride,⁸¹ the hydrogen-bonded semiperchlorate⁸² and trichloroacetic acid⁸³ complexes are known. These data are listed in Table 10. There are structures which utilize 2-^{52,68} and 4-^{58,64} methyl-(picoline), 4-phenyl-,⁵⁹ 2,6-dimethyl-(lutidine),^{55,65} 4-nitro-,⁵⁷ 3-⁶⁵ and 4-^{66,67} carboxylate, 4-methoxy-⁷³ and 3,5-dibromo⁷⁴ substituents on the pyridine N-oxide ligands. Thus sufficient structural data are available at this time for meaningful comparison, and to resolve such questions as:

- (i) does the ligand N-O distance lengthen on coordination to an acceptor atom?
- (ii) does electron releasing methyl 2- or 2,6-substitution in picoline and lutidine ligands weaken the coordinative interaction?
- (iii) what is the nature of the bond between the oxygen atom and the acceptor in pyridine N-oxide complexes?

The electronic situation in the pyridine N-oxide ligand can be represented as:



which are said to have equal weights.⁴⁶ Canonical forms II should be favored by electron withdrawing groups, and the shorter N-O distance

(1.260 Å) in the 4-nitro-derivative⁷⁸ is usually attributed to the enhanced double-bond character of the N-O bond in this compound.⁸⁴ Electron releasing substituents such as methyl should, on the other hand, favor forms I and III, which should be better donor ligands. Coordination should lengthen the N-O distance, but the evidence, taking the X-ray structure of pyridine N-oxide as the basis, is very mixed. This arises in part from the fact that the pyridine N-oxide crystal itself contains two independent molecules whose N-O distances (1.33 and 1.37 Å) differ by 0.04 Å⁷⁶ and encompass a large part of the range represented by the known data for the complexes.^{47,49} In the simplest systems, the formation of the hydrochloride⁸¹ and the strong hydrogen bond to trichloroacetic acid⁸³ produces N-O distances of 1.37 and 1.39 Å, respectively. The d(N-O) data for the transition metal complexes range from 1.26 for one of the 2-picoline ligands in $[(2\text{-CH}_3\text{pyNO})_5\text{Co}]^{2+}(\text{ClO}_4^-)_2$ ⁷¹ to 1.362 Å for one of the pyNO ligands in $[(\text{pyNO})_2\text{Cu}]^{2+}(\text{NO}_3^-)_2$.⁵⁶ Another particularly short N-O distance is reported for the mercury(II) complex, 3,5-Br₂pyNO·HgCl₂ (1.27 Å)⁷⁴ in which the ligand carries two electron-withdrawing substituents which apparently enhance the contribution of canonical forms II. However, in the comparison among the three related copper(II) chloride complexes (4-CH₃pyNO)₂CuCl₂,⁵⁸ [2,6-(CH₃)₂pyNO]₂CuCl₂⁵⁵ and (4-NO₂pyNO)₂CuCl₂·2H₂O,⁵⁷ the last of which is six-coordinated and octahedral, while the first two are four-coordinated and tetrahedral, the N-O distances are 1.34,⁵⁸ 1.31 and 1.36 (av. = 1.34)⁵⁵ and 1.325 Å,⁵⁷ respectively. Thus the electron releasing and withdrawing substituents do not seem to register any measurable effect on d(N-O) in complexed pyridine N-oxides.

It is concluded that where data are available for comparison, there is no systematic change to the expected longer N-O distances on coordination of the pyridine N-oxide ligands to acceptors, nor do the data support a convincing shortening or lengthening of $d(\text{N-O})$ on substitution by electron withdrawing and releasing ligands on the pyridine ring in complexes. The observed changes in the frequencies of bands assigned to $\nu(\text{N-O})$ must arise from other origins, such as the orientation of the pyridine ring in the molecule,³⁴ or the assigned bands must be highly coupled to other modes.⁸⁵

In most examples the pyridine N-oxide ligand coordinates with metal atoms so as to make an angle M-O-N of roughly 120° , suggesting sp^2 -hybridization at the oxygen atom (two lone pairs plus the N-O bond pair) with the third lone pair in a pure p-orbital available for π -interaction with the aromatic system of the pyridine ring as in canonical forms II. If this π -interaction were important, then the planes of the M-O-N and pyridine rings should be coincident, but this is not the case for the complexes listed in Table 9, nor for pyridine N-oxide hydrochloride,⁸¹ nor for the structure of the title compound where it is $87.17(6)^\circ$. Thus a description based upon a distortion from sp^3 -hybridization at oxygen (canonical forms I and III) would appear to be more valid, with minimum contribution from form II, and angular coordination to acceptor atoms. Forcing the M-O-N and pyridine ring planes into coincidence would maximize the steric interference of the aromatic ring with the other ligands on the metal atom, which is probably why it is not chosen. Delocalization of the second lone pair at oxygen into the aromatic ring (an alternative way to achieve canonical forms II) is probably not favored because

of the somewhat disadvantageous geometry of this orbital, its high s-character and the low energy of the oxygen orbitals. Lack of contribution from canonical forms II probably lies at the root of the absence of N-O bond lengthening on coordination to metal atoms, since changes in this distance from forms I and III would be expected to be minimal. Overlap of the second lone pair orbital with the acceptor orbital of the metal atom is probably somewhat poor energetically since a plus charge on the nitrogen (in canonical form I) would reduce electron flow from oxygen. Both lone pairs of electrons on oxygen are utilized in coordination in the dimeric copper(II) halide complexes $[\mu\text{-pyNOCuCl}_2]_2$,^{50,51} $[\mu\text{-pyNO(pyNO)CuBr}_2]_2$,⁶⁰ $[\mu\text{-4-phenylpyNOCuCl}_2]_2$,⁵⁹ $[\mu\text{-4-phenylpyNOCuCl}_2 \cdot 2\text{H}_2\text{O}]_2$ ⁵⁹ and $(\mu\text{-2-CH}_3\text{pyNO})_2\text{Cu}_3\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ ⁵² in which bridging oxygen atoms from the pyNO ligands are found. The $\mu\text{-N-O}$ distances are 1.24⁵⁰ or 1.346,⁵¹ 1.366 (average of two dimer molecules),⁶⁰ 1.371,⁵⁹ 1.347⁵⁹ and 1.36 Å,⁵² respectively. A particularly interesting comparison is available for $[(\mu\text{-pyNO})_2\text{CuBr}_2]_2$ in which both terminal and bridging ligands are found at 1.346 and 1.366 Å, respectively,⁶⁰ which gives rise to the observation of two infrared $\nu(\text{N-O})$ stretching frequencies.⁸⁶ The orientation of the bridging pyridine rings in the two dimers is virtually the same, but the angle about the Cu-O bond is ca. 60° different for the terminal ligands in the two dimers. Unfortunately, the angles between the planes made by the Cu-O-N bonds and the pyridine rings are not listed.

Against this background the structural data for the title complex can be better understood. It is seldom that data for two such closely-related materials as the 1:2 and 1:1 pyridine N-oxide complexes of dimethyltin(IV) dichloride are available,¹² and the structure of the parent

dimethyltin(IV) dichloride which is somewhat associated in the solid state to a very distorted octahedral geometry about the central tin atom¹³ is also known. In the comparison of the data in Table 7 it is seen that the bonds that the tin atom forms to the chlorine atoms and methyl groups are longer in the more regular coordination sphere of the six-coordinated, 1:2-complex in which the tin atom occupies a crystallographic center of symmetry giving rise to a perfect trans-, trans-, trans-octahedron. However, the distance to the oxygen atom of the ligand in the title complex is longer. Thus, the expected enhancement of donor bond strength by the electron-releasing methyl groups may, in this case, as with the analogous complexes with tin(II) chloride,^{24,25} be offset by steric interference of these 2,6-substituents with the tin attachments, giving a net weakening of the tin-ligand bond.

The octahedral geometry about the tin atoms in the dimer is rather irregular. While the trans- bonds holding the ligand are almost linear [$\angle \text{Cl}(1) - \text{Sn} - \text{O} = 177.4(1)^\circ$], the dimethyltin system is quite bent [$\angle \text{C}(1) - \text{Sn} - \text{C}(2) = 145.3(2)^\circ$]. In the 1:1 complex with salicylaldehyde²⁶ in which contact with a non-bonded phenolic oxygen atom of an adjacent molecule²⁷ raises the coordination number at the tin atom to six, the dimethyltin(IV) dichloride itself, this angle is 123.5° .¹³ In the six-coordinated 1:1 complex with diphenylcyclopropanone, this angle is 142.2° .²⁸

Pairs of $(\text{CH}_3)_2\text{SnCl}_3^-$ anions also form dimeric units through axial-chlorine bridging to tin at $d(\text{Sn} \cdots \text{Cl}) = 3.486 \text{ \AA}$ in its quinolinium salt.⁸⁷ The unfavorable electrostatic situation must be balanced by a countervailing gain in overall stability of the crystal.

Viewing the molecule down the trans-oxygen-tin-chlorine(1) vector as in Figure 3, the O-N bond is seen to lie within 9.20° of eclipsing the tin-carbon(1) bond, between it and the second [C(2)] methyltin bond. The pyridine ring bends away from the plane formed by the two methyl groups [C(1) and C(2)] and the chlorine [Cl(2)] and bridging chlorine [Cl(1')] atoms, with the Sn-O-N angle = $123.0(2)^\circ$. If the plane of the pyridine ring were coincident with the plane formed by the Sn-O-N system, then the non-bonded distance to the methyl-substituent on the pyridine ring, (C(1)···C(8)), would be quite close. To alleviate this situation, the pyridine ring is rotated to bring the side of the ring holding the C(9) methyl-substituent to a position between the two methyltin groups so that the two planes intersect at $87.17(6)^\circ$. The shortest non-bonded contact distances adopted are thus C(1)···C(8) = 3.819 and C(2)···C(9) = 3.858 Å. This conformation apparently minimizes the potentially severe nonbonded interactions within the 1:1 complex. From inspection of the unit cell diagram for the corresponding 1:2 complex,³⁴ it appears that the two trans-pyridine N-oxide ligands also take positions that nearly eclipse the tin-methyl vectors.

The central Sn₂Cl₂ ring is flat since the two halves of the asymmetric unit are related by an inversion point at the center of the ring. The interior angles and distances are $\angle \text{Sn-Cl(1)-Sn}' = 100.54(3)$ and $\angle \text{Cl(1)-Sn-Cl(1')} = 79.46(3)^\circ$, and $d(\text{Sn} \cdots \text{Sn}') = 4.5918(4)$ and $d[\text{Cl(1)} \cdots \text{Cl(1')}] = 3.8468(13)$ Å. The tin atom lies 0.03 Å above the plane formed by the two trans-methyl groups [C(1) and C(2)] and the chlorine atoms [Cl(2) and Cl(1')] toward the oxygen atom.

In the dimer, the bridging chlorine Cl(1') makes a short intra-

dimer contact with a hydrogen on the tin methyl and with another hydrogen on the pyridine methyl [$d(\text{Cl}(1') - \text{H}(\text{C}2)\text{C}) = 2.78$; $d(\text{Cl}(1') - \text{H}(\text{C}9)\text{C}) = 2.71 \text{ \AA}$]. The non-bridging chlorine, $\text{Cl}(2)$, makes a short contact with a hydrogen on the methyl group of the ligand [$d(\text{Cl}(2) - \text{H}(\text{C}8)\text{B}) = 2.99 \text{ \AA}$]. The dimeric units are densely packed in the lattice. There are short interdimer contacts at $\text{Cl}(1) - \text{H}(\text{C}6)$, $\text{Cl}(1) - \text{H}(\text{C}8)\text{A}$ and $\text{Cl}(2) - \text{H}(\text{C}6)$ [2.91 , 2.88 and 2.96 \AA , respectively.].

Summary

Dimethyltin(IV) dichloride 2,6-dimethylpyridine N-oxide, $\text{C}_{18}\text{H}_{30}\text{Cl}_4\text{N}_2\text{O}_2\text{Sn}_2$, forms colorless crystals, mp 147°C , in the monoclinic space group C2/c with $a = 15.581(4) \text{ \AA}$, $b = 12.781(4) \text{ \AA}$, $c = 13.098(4) \text{ \AA}$ and $\beta = 102.26(3)^\circ$, $V = 2549 \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.787 \text{ g cm}^{-3}$. The structure was determined by direct methods from 1880 reflections measured at $138 \pm 2 \text{ K}$ on an Enraf-Nonius CAD/4 diffractometer using monochromatized $\text{Mo K}\alpha$ -radiation, and refined to a final R value of 0.0364 for the 1820 reflections included in the least-squares sums. The dimeric molecule contains six-coordinated, octahedral tin with the oxygen atom of the ligand and one chlorine atom in a trans-position making an O-Sn-Cl angle of $177.44(7)^\circ$. The tin atom lies 0.03 \AA above the plane formed by the two trans-methyl groups [$\text{C}(1)$ and $\text{C}(2)$] and the chlorine atoms [$\text{Cl}(2)$ and $\text{Cl}(1')$] toward the oxygen atom to which it makes a bond of $2.289(2) \text{ \AA}$. The angle made by the methyl groups is $145.3(2)^\circ$. The angle formed by the Sn-O-N system and the pyridine N-oxide ring is $87.17(6)^\circ$. One of the ligand methyl groups makes a short, non-bonded contact to one of the tin methyl groups. The center of the planar Sn_2Cl_2 ring of the dimer is lo-

cated on a crystallographic center of symmetry. The geometry of the octahedron at each tin atom is best described as trans-, trans-, trans-.

TABLE 1

CRYSTAL DATA FOR DIMETHYL TIN(IV) DICHLORIDE · 2,6-DIMETHYLPYRIDINE
N-OXIDE

formula	$C_{18}H_{30}Cl_4N_2O_2Sn_2$
fw	685.66
\underline{a} , Å	15.581(4)
\underline{b} , Å	12.781(4)
\underline{c} , Å	13.098(4)
β , deg ^a	102.26(3)
\underline{V} , Å ³	2549
space group ^b	$\underline{C2/c}$
\underline{Z}	4
$\underline{F}(000)$	1344
ρ_{calcd} , g cm ⁻³	1.787
μ , cm ⁻¹	22.16
dimensions of data crystal, mm	0.15 x 0.40 x 0.45

^a From $\pm 2\theta$ values of 48 reflections with the use of Mo $K\alpha_1$ radiation ($\lambda = 0.70926$ Å).

^b Based upon systematic absences: $\underline{h} \underline{k} \underline{l}$: $\underline{h} + \underline{k} = 2n + 1$; $\underline{h} \underline{0} \underline{l}$: $\underline{l} = 2n + 1$.

TABLE 2

DATA COLLECTION PARAMETERS FOR DIMETHYL TIN(IV) DICHLORIDE ·
2,6-DIMETHYLPYRIDINE N-OXIDE

diffractometer	Enraf-Nonius CAD/4
radiation	Mo $K\alpha_1$ ($\lambda = 0.70296 \text{ \AA}$)
temp, K	138 \pm 2
scan technique	θ - 2θ
2θ limit, deg	$0 < 2\theta < 47$
max scan time, s	60
scan angle	$0.9 + 0.2 \tan \theta$
aperture width	$3.5 + 0.86 \tan \theta$
aperture height, mm	6
aperture distance, mm	173
intensity monitors	3
max fluctuation	<3.0%
orientation monitors ^a	3
no. of unique data	1880
no. of observed data ^b	1820
corrections	Lorentz-polarization

^a New orientation matrix if angular change $> 0.1^\circ$. Orientation matrix based upon 24 reflections.

^b $I > 2\sigma(I)$.

TABLE 3

ATOMIC COORDINATES FOR DIMETHYLTIN(IV) DICHLORIDE·
2,6-DIMETHYLPYRIDINE N-OXIDE^a ($\times 10^4$)

Atom	x/a	y/b	z/c
Sn	667.3(2)	1539.1(2)	632.6(2)
Cl(1)	-916.5(6)	949.1(8)	173.0(8)
Cl(2)	191.6(6)	3237.5(8)	1065.9(8)
O	2080(2)	2147(2)	1061(2)
N	2702(2)	1719(2)	1825(3)
C(1)	976(3)	584(4)	1975(4)
C(2)	792(4)	1726(4)	-932(3)
C(3)	3190(2)	910(3)	1575(3)
C(4)	3815(3)	478(3)	2352(4)
C(5)	3970(3)	863(3)	3354(4)
C(6)	3473(3)	1707(3)	3577(4)
C(7)	2828(3)	2136(3)	2796(3)
C(8)	2279(3)	3036(4)	2969(4)
C(9)	3012(3)	552(3)	459(3)

^a Estimated standard deviations are in parentheses.

TABLE 4

INTRAMOLECULAR DISTANCES (IN Å) IN DIMETHYL^oTIN(IV) DICHLORIDE·
2,6-DIMETHYLPYRIDINE N-OXIDE^a

Sn-Cl(1)	2.528(1)
Sn-Cl(2)	2.400(1)
Sn-C(1)	2.110(4)
Sn-C(2)	2.113(4)
Sn-O	2.289(2)
O-N	1.352(4)
N-C(3)	1.365(5)
C(3)-C(4)	1.367(5)
C(4)-C(5)	1.374(6)
C(5)-C(6)	1.394(6)
C(6)-C(7)	1.387(6)
C(7)-N	1.354(5)
C(7)-C(8)	1.479(6)
C(3)-C(9)	1.499(6)
Sn-Cl(1') ^b	3.399(1)
Sn-Sn'	4.5918(4)
Cl(1)-Cl(1')	3.8468(13)

^a Estimated standard deviations are in parentheses.

^b Cl(1') is the bridging atom.

TABLE 5

INTRAMOLECULAR ANGLES (IN DEG) IN DIMETHYL TIN(IV) DICHLORIDE-
2,6-DIMETHYLPYRIDINE N-OXIDE^a

C1(1)-Sn-C1(2)	89.50(3)
C1(1)-Sn-O	177.44(7)
C1(1)-Sn-C(1)	93.7(1)
C1(1)-Sn-C(2)	95.1(1)
C1(2)-Sn-O	87.95(7)
C1(2)-Sn-C(1)	110.7(1)
C1(2)-Sn-C(2)	102.9(1)
C(1)-Sn-C(2)	145.3(2)
O-Sn-C(1)	87.4(1)
O-Sn-C(2)	85.3(2)
Sn-O-N	123.0(2)
C(3)-N-C(7)	123.2(3)
N-C(3)-C(4)	118.2(3)
C(3)-C(4)-C(5)	121.3(4)
C(4)-C(5)-C(6)	119.0(4)
C(5)-C(6)-C(7)	120.0(4)
C(6)-C(7)-N	118.4(3)
C1(1')-Sn-C1(1)	79.46(3)
C1(1')-Sn-C1(2)	168.79(3)
C1(1')-Sn-C(1)	72.3(1)
C1(1')-Sn-C(2)	76.4(1)
C1(1')-Sn-O	103.09(7)

^a Estimated standard deviations are in parentheses.

TABLE 6

LEAST-SQUARES PLANES IN DIMETHYLTIN(IV) DICHLORIDE·2,6-DIMETHYLPYRIDINE N-OXIDE

Planes through Atoms	Orthonormal Equation: $M_1x + M_2y + M_3z + d = 0$				Plane P	Dihedral Angle Between [P,P']	R.M.S.
	M_1	M_2	M_3	d			
Cl(2), C(1), C(2), Cl(1)'	-0.9791	-0.2031	-0.0047	1.3720	1 ^a		0.2472
Sn(1), Cl(1), Sn(1)', Cl(1)'	-0.0722	0.3283	-0.9418	0	2	89.51 [1,2]	
O, N, C(3), C(4), C(5), C(6), C(7)	0.6719	0.6393	-0.3740	-3.6183	3	-38.19 [1,3] 59.10 [2,3]	0.0064
Sn, O, N	0.2579	-0.0248	-0.7370	1.4150	4 ^b	87.17 [3,4]	0
Sn, O, C(1)	0.2904	-0.7291	-0.6197	1.5159	5 ^b	9.20 [4,5]	0

^a The tin atom is 0.0252(3) Å from this plane in the direction of the Sn-O vector.

^b The Sn-C(1) and O-N vectors make an angle of 9.20° when viewed along the Sn-O axis.

TABLE 7

COMPARISON DATA FOR DIMETHYLTIN(IV) DICHLORIDE AND ITS PYRIDINE
N-OXIDE COMPLEXES

$(\text{CH}_3)_2\text{SnCl}_2 \cdot n\text{R}_2\text{C}_5\text{H}_3\text{NO}$	$n=1^{\text{a}}$	$n=2^{\text{b}}$	$n=0^{\text{c}}$
$d(\text{Sn}-\text{Cl}), \text{Å}$	2.400(1), 2.528(1)	2.584	2.41, 3.54
$d(\text{Sn}-\text{O}), \text{Å}$	2.289(2)	2.251	--
$d(\text{Sn}-\text{C}), \text{Å}$	2.112(4), 2.110(4)	2.225	2.21
$d(\text{O}-\text{N}), \text{Å}$	1.352(4)	1.37	--
$d(\text{N}-\text{C})_{\text{av}}, \text{Å}$	1.364(5)	1.35	--
$\angle \text{C}-\text{Sn}-\text{C}, \text{deg}$	145.3(2)	180	123.5
$\angle \text{Cl}-\text{Sn}-\text{Cl}, \text{deg}$	89.50(3)	180	93.0
$\angle \text{Cl}-\text{Sn}-\text{O}, \text{deg}$	87.95(7), 177.44(7)	89.5, 90.5	--
$\angle \text{C}-\text{Sn}-\text{O}, \text{deg}$	87.4(1), 85.3(2)	95.6, 84.4	--
$\angle \text{Sn}-\text{O}-\text{N}, \text{deg}$	123.0(2)	117	--
$\angle \text{Cl}-\text{Sn}-\text{C}, \text{deg}$	$93.7(1)_{\text{ax}}, 95.1(1)_{\text{ax}},$ $102.9(1)_{\text{eq}}, 110.7(2)_{\text{eq}}$	89.5, 90.5	109.0
$\angle \text{O}-\text{Sn}-\text{O}, \text{deg}$	--	180	--
$\angle \text{pyNO ring and Sn-O-N plane}, \text{deg}$	87.17(6)	83	--

^a This work. Estimated deviations are in parentheses.

^b Ref. 34.

^c Ref. 13.

TABLE 8

COMPARISON DATA AND PREDICTED METHYL-TIN-METHYL ANGLES FROM
MÖSSBAUER QUADRUPOLE SPLITTINGS (QS) FOR
DIMETHYLTIN(IV) DERIVATIVES

Compound	QS, mm s ⁻¹	d(Sn-C), Å	<(C-Sn-C): Found	Pre- dicted ^a	Ref.
(CH ₃) ₂ SnCl ₂	3.55 ^b , 3.60 ^c	2.16 2.21	123.5°		13
1:2-pyNO	4.02 ^c	2.225	180.0°		34
1:1-pyNO	3.97	--	--	162.0°	
1:1-2,6-lutNO	3.80±0.06	2.110(4) 2.112(4)	145.3(2)°	153.0°	<u>d</u>
1:1-salicyl- aldehyde	3.33	2.098 2.107	131.4°	137.2°	<u>e</u>
1:1-diphenyl- cyclopropanone	3.52	2.111 2.116	142.2°	143.1°	<u>f</u>

^a From the point-charge model of ref. 30.

^b Ref. 13.

^c Ref. 6.

^d This work. Estimated standard deviations are in parentheses.

TABLE 9

THE PYRIDINE N-OXIDE LIGAND IN METAL COMPLEXES^a

Complex	CN and Geom.	d(N-O), Å	d(M-O), Å	∠M-O-N, deg.	d(C-N) _{av} , Å	pyNO Plane Orientation	Ref.
[μ-pyNOCuCl ₂] ₂	4 T _d	1.24	1.99 2.10	-	1.35	-	50
	4 Sq. pl. B _h	1.346	1.979 2.036	123.5 127.8	1.341	70.0	51
Niacac ₂ (pyNO) ₂	6 O _h	1.321 1.337	2.088 2.105	119.2 122.4	1.339	48.4 67.5	66
(2-CH ₃ pyNO) ₂ Cu ₃ Cl ₆ · 2H ₂ O	5 Sq. py.	1.36	1.98 2.01	121.6 127.1	1.36	88.8	52
[2,6-(CH ₃) ₂ pyNO] ₂ ZnCl ₂	4 T _d	1.38	2.01	118.6	1.39	-	65
3,5-Br ₂ pyNOHgCl ₂	3 "T" shaped	1.27	2.51	125.7	1.37	-	71
[(pyNO) ₄ Cu] ²⁺ (ClO ₄) ₂	4 T _d	1.33	1.92	116.7	1.34	88.7	53
[(pyNO) ₄ Cu] ²⁺ (BF ₄) ₂	4 Sq. pl.	1.31 1.36	1.93 1.91	116.7 118.6	1.34	89.9 78.9	54

TABLE 9, cont'd.

Complex	CN and Geom.	d(N-O), Å	d(M-O), Å	∠M-O-N, deg.	d(C-N) _{av} , Å	pyNO Plane Orientation	Ref.
$[(2,6-(\text{CH}_3)_2\text{pyNO})_2\text{CuCl}_2]$	4 T _d to cis-sq.pl.	1.31 1.36	1.97 1.93	118.6 121.6	1.38	-	55
$(4\text{-NO}_2\text{py})_2\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	6 O _h	1.325	2.635	109.9	1.354	-	57
$[(\text{pyNO})_2\text{Cu}]^{2+}$ $(\text{NO}_3)_2$	5 Distort- ed tetra. py.	1.362 1.361	1.968 1.951	118.6 119.4	1.346	64.0	56
$[(2\text{-CH}_3\text{pyNO})_5\text{Co}]^{2+}$ $(\text{ClO}_4)_2$	5 tbp	1.275(av)	2.098 _{ax} (av) 1.975 _{eq} (av)	124.2(av) (120-134)	- -	41-84	68
$[\mu\text{-(pyNO)}_2\text{CuBr}_2]_2$	5 Sq.py.	1.345,1.347 (terminal) 1.365,1.366 (bridging)	1.944,1.949 (terminal) 2.162,1.975, 2.240,1.976 (bridging)	119.7,119.5 (terminal) 121.2,123.6, 125.3,121.3 (bridging)	1.342(terminal) 1.341(bridging)	-	60
$4\text{-CH}_3\text{pyNOPt}(\text{CO})\text{Cl}_2$	4 Sq.pl.	1.35	1.99	120.0	1.35	87.5	70
$(4\text{-CH}_3\text{pyNO})_2\text{CuCl}_2$ (green modification)	4 T _d	1.34	1.949	122.0	1.34	93.9	58
$[\mu\text{-pyNOCuBr}_2]_2$	5 Sq.py.	1.381	1.965 1.994	125.9 123.8	1.355	83.0	61

TABLE 9, cont'd.

Complex	CN and Geom.	d(N-O), Å	d(M-O), Å	∠M-O-N, deg.	d(C-N) _{av} , Å	pyNO Plane Orientation	Ref.
[μ-4-PhpyNOCuCl ₂] ₂	4 Sq.pl.	1.371	1.978 1.986	123.0	1.343	85.1	59
[μ-4-PhpyNOCuCl ₂ · 2H ₂ O] ₂	5 Sq.py.	1.347	1.980 2.040	124.5	1.330	79.7	59
(pyNO) ₆ Hg ²⁺ (ClO ₄ ⁻) ₂	6 O _h	1.32	2.35	114.3	1.36	72.9	72
[(pyNO) ₆ Ni] ²⁺ (BF ₄ ⁻) ₂	6 O _h	1.332	2.060	119.0	1.41	71.4	67
[(pyNO) ₆ Co] ²⁺ (ClO ₄ ⁻) ₂	6 O _h	1.334	2.088	119.5	1.337	72.2	69
[(pyNO) ₆ Cu] ²⁺ (ClO ₄ ⁻) ₂	6 O _h	1.324	2.086	118.7	1.340	-	62
[(pyNO) ₆ Cu] ²⁺ (BF ₄ ⁻) ₂	6 O _h	1.333	2.088	118.75	1.335	-	62
[(pyNO) ₆ Zn] ²⁺ (ClO ₄ ⁻) ₂	6 O _h	1.330	2.102	119.25	1.341	-	62
[(pyNO) ₆ Zn] ²⁺ (BF ₄ ⁻) ₂	6 O _h	1.326	2.102	119.2	1.341	-	62
[(pyNO) ₆ Cu] ²⁺ (ClO ₄ ⁻) ₂	6 O _h	1.332	2.076	119.1	1.333	72.8	63
[(pyNO) ₆ Co] ²⁺ (ClO ₄ ⁻) ₂	6 O _h	1.331	2.090	119.3	1.341	72.7	63
[(pyNO) ₆ Fe] ²⁺ (ClO ₄ ⁻) ₂	6 O _h	1.331	2.112	119.7	1.338	71.8	63

TABLE 9, cont'd.

Complex	CN and Geom.	d(N-O), Å	d(M-O), Å	∠M-O-N, deg.	d(C-N) _{av} , Å	pyNO Plane Orientation	Ref.
$[(4\text{-CH}_3\text{pyNO})_6\text{Cu}]^{2+}$ (ClO ₄) ₂	6 O _h	1.326 1.312 1.326	1.965 2.008 2.385	120.2 119.4 116.1	1.350	-	64
$[(4\text{-CH}_3\text{pyNO})\text{Zn}]^{2+}$	6 O _h	1.352 1.309 1.344	2.068 2.113 2.160	119.0 119.5 116.5	1.358	-	64
$[(2\text{-CO}_2\text{pyNO})_4\text{Cu}_3(\text{OH})_2\text{H}_2\text{O}]_n^{2+}$ 2 ₄ Sq.pl. 1.327 5 Sq.py.		1.327	2.426	-	1.336	-	65
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ [4-CO ₂ pyNO] ₂ ⁻	<u>d</u>	1.324	<u>d</u>	<u>d</u>	1.343	<u>d</u>	70
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ [4-CO ₂ pyNO] ₂ ⁻	<u>d</u>	1.319	<u>d</u>	<u>d</u>	1.350	<u>d</u>	70
$[(4\text{-CO}_2\text{pyNO})\text{Cu}]_4\text{SO}_4$ (OH) ₂ ·2H ₂ O	<u>d</u>	1.30	<u>d</u>	<u>d</u>	1.37	<u>d</u>	66
(C ₆ H ₅) ₃ SnNO ₃ ·pyNO (monoclinic)	5 tbp	1.34	2.227	120.4	1.34	78.9	44
(triclinic)	5 tbp	-	2.299 2.238	-	-	-	45
(CH ₃) ₂ SnCl ₂ ·2pyNO	6 O _h	1.37	2.251	117.0	1.36	83	34

TABLE 9, cont'd.

Complex	CN and Geom.	d(N-O), Å	d(M-O), Å	∠M-O-N, deg.	d(C-N) _{av} , Å	pyNO Plane Orientation	Ref.
[(CH ₃) ₂ SnCl ₂ ·2,6- (CH ₃) ₂ pyNO] ₂	6 O _h	1.352(4)	2.289(2)	123.0(2)	1.359(5)	87.17(6)	<u>e</u>

^a The complexes are listed in the chronological order of the study being submitted for publication, with the transition metal derivatives first.

^b Reinterpreted as five-coordinate with square-pyramidal geometry at copper [Sager, F.S.; Williams, R.J.; Watson, W.H. Inorg. Chem. 1969, 8, 694].

^c The 4-NO₂pyNO ligand is held predominantly by hydrogen bonding.

^d The pyNO ligand is not bonded to M.

^e This work. Estimated standard deviations are in parenthesis.

TABLE 10

STRUCTURAL DATA FOR PYRIDINE N-OXIDE

	d(N-O), Å	d(C-N), Å	Ref.
4-NO ₂ pyNO	1.260	1.382 1.384	75
4,4- <u>trans</u> -azo-pyNO	1.283	1.351 1.364	76
<u>N</u> -oxyphenazine	1.24	1.35	77
pyNO·HCl	1.37	1.31 1.36	78
pyNO (X-ray)	1.33 1.37	1.34 1.34	73
pyNO (gas phase electron diffraction)	1.290	1.384	74
pyNO trichloroacetic acid	1.39	--	80
pyNO semiperchlorate	1.34	1.38	79

TABLE 11

ANISOTROPIC TEMPERATURE FACTORS ($\times 10^4$) FOR DIMETHYLTIN(IV)
DICHLORIDE · 2,6-DIMETHYLPYRIDINE N-OXIDE^a

$U_{11} \times 10^4$	$U_{22} \times 10^4$	$U_{33} \times 10^4$	$U_{23} \times 10^4$	$U_{13} \times 10^4$	$U_{12} \times 10^4$
135(2)	141(2)	147(2)	21(1)	-25(1)	-39(1)
158(5)	278(6)	296(6)	70(4)	-66(4)	-75(4)
210(5)	231(5)	302(6)	-68(4)	-43(4)	27(4)
105(13)	184(14)	236(14)	84(11)	-59(11)	-11(10)
103(16)	144(14)	251(18)	41(14)	-4(14)	-50(13)
205(24)	281(24)	215(23)	47(20)	-1(19)	-94(20)
283(26)	263(24)	164(22)	26(18)	25(20)	-56(21)
124(18)	139(18)	280(21)	1(16)	44(16)	-64(15)
158(21)	134(20)	399(26)	3(19)	68(19)	16(18)
177(21)	217(22)	314(24)	37(19)	-37(19)	10(17)
180(22)	193(20)	302(24)	3(18)	-63(19)	11(17)
165(19)	190(20)	256(21)	-45(17)	-12(16)	-42(16)
219(25)	202(24)	348(26)	-49(21)	-105(19)	57(19)
224(22)	255(23)	253(21)	-10(19)	39(17)	-30(19)

^a Estimated standard deviations are in parentheses.

TABLE 12

 HYDROGEN PARAMETERS FOR DIMETHYL TIN(IV) DICHLORIDE ·
 2,6-DIMETHYLPYRIDINE N-OXIDE^a

Atom	$x/a \times 10^3$	$y/b \times 10^3$	$z/c \times 10^3$	$U_{iso} \times 10^2$
H(C1)A	91(3)	90(4)	244(4)	3.4(16)
H(C1)B	53(4)	2(4)	190(4)	4.5(14)
H(C1)C	152(3)	25(3)	196(3)	2.1(11)
H(C2)A	135(5)	189(6)	-95(5)	8.0(22)
H(C2)B	47(5)	208(7)	-116(7)	9.5(31)
H(C2)C	88(4)	102(5)	-108(4)	4.9(16)
H(C4)	408(3)	4(4)	223(4)	2.0(13)
H(C5)	435(3)	59(3)	388(3)	1.7(10)
H(C6)	365(4)	198(5)	431(5)	5.5(16)
H(C8)A	249(4)	330(5)	384(6)	7.7(22)
H(C8)B	166(4)	286(5)	291(5)	7.0(19)
H(C8)C	229(3)	347(4)	251(4)	2.4(14)
H(C9)A	347(4)	-2(4)	39(4)	4.7(14)
H(C9)B	306(3)	116(4)	0(4)	3.7(13)
H(C9)C	245(4)	13(4)	26(4)	5.8(17)

^a Estimated standard deviations are in parentheses.

TABLE 13

HYDROGEN DISTANCES (IN Å) IN DIMETHYL^oTIN(IV) DICHLORIDE ·
2,6-DIMETHYLPYRIDINE N-OXIDE^a

C(1)-H(C1)A	0.76(6)
C(1)-H(C1)B	0.99(6)
C(1)-H(C1)C	0.95(5)
C(2)-H(C2)A	0.90(8)
C(2)-H(C2)B	0.70(8)
C(2)-H(C2)C	0.94(6)
C(4)-H(C4)	0.73(5)
C(5)-H(C5)	0.88(4)
C(6)-H(C6)	1.00(6)
C(8)-H(C8)A	1.17(8)
C(8)-H(C8)B	0.97(7)
C(8)-H(C8)C	0.82(5)
C(9)-H(C9)A	1.04(6)
C(9)-H(C9)B	0.99(5)
C(9)-H(C9)C	1.02(6)

^a Estimated standard deviations are in parentheses.

FIGURE 1

THE DIMETHYL TIN(IV) DICHLORIDE · 2,6-DIMETHYLPYRIDINE N-OXIDE DIMER
SHOWING THE ATOMIC NUMBERING

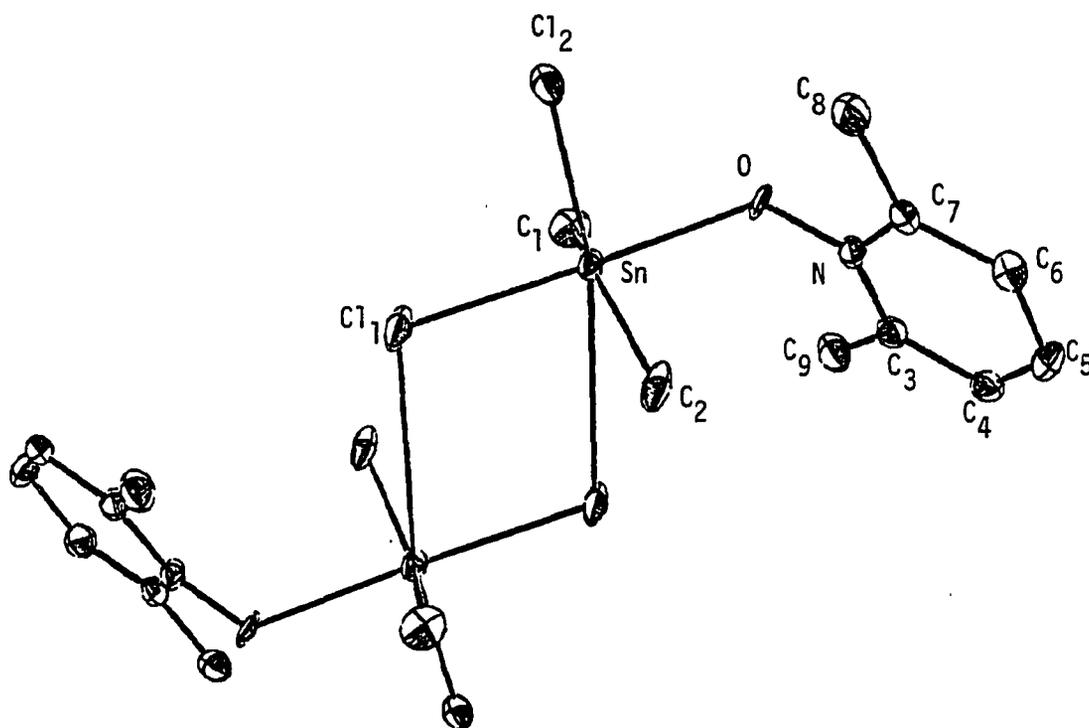


FIGURE 2

THE UNIT CELL CONTENTS OF THE DIMETHYL TIN(IV) DICHLORIDE · 2,6-DIMETHYLPYRIDINE N-OXIDE DIMER

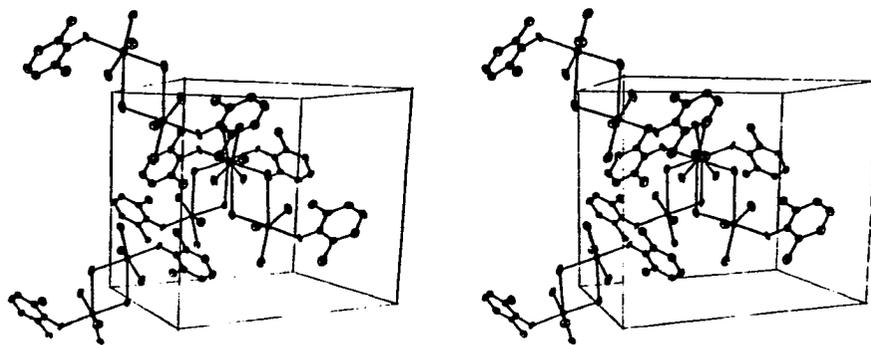
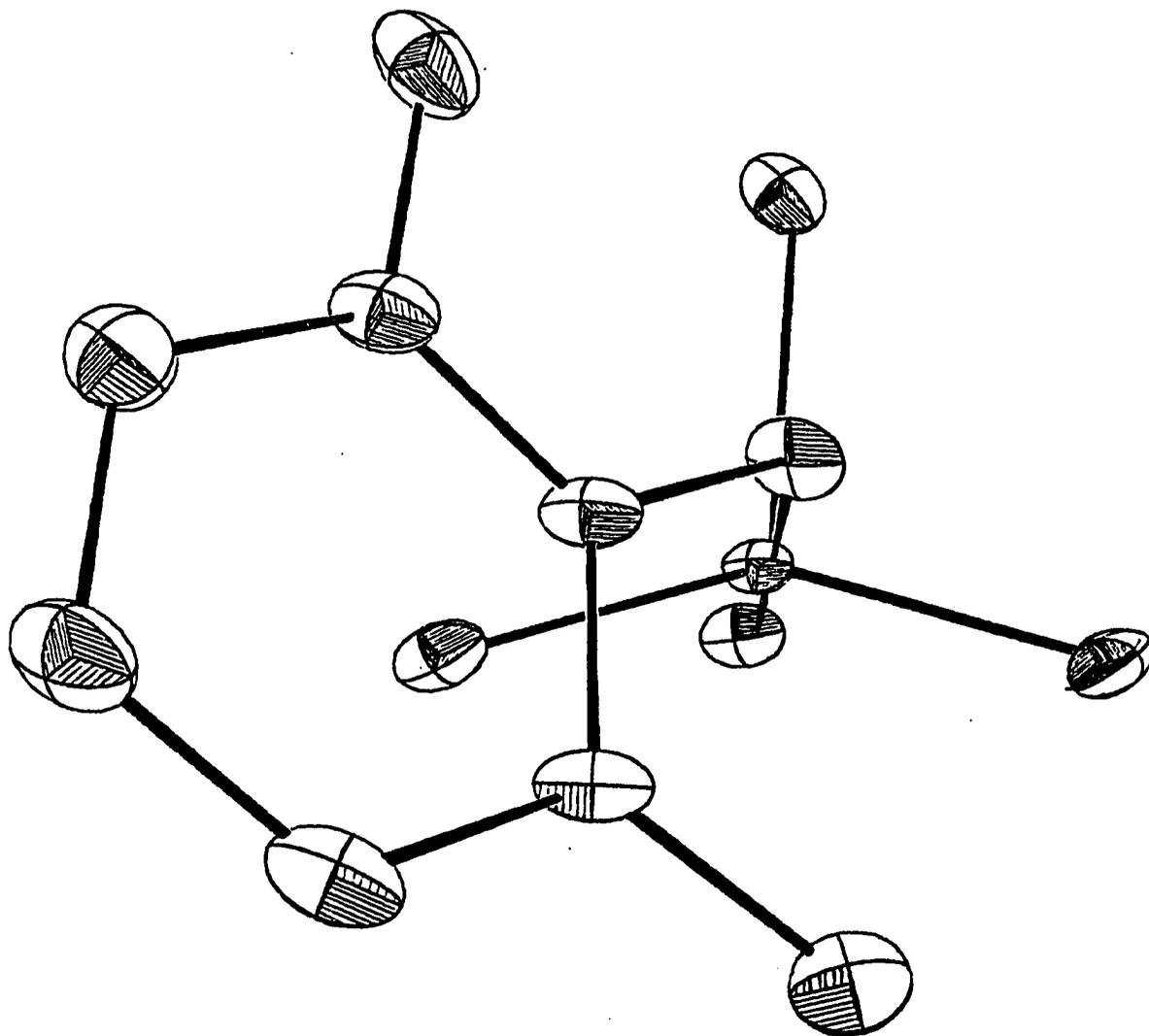


FIGURE 3

THE MONOMERIC UNIT VIEWED DOWN THE TRANS-CHLORINE(1)-TIN-OXYGEN VECTOR



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CHAPTER 8

THE X-RAY CRYSTAL AND MOLECULAR STRUCTURES OF THE MONOMERIC 1:1 ADDUCTS OF DIPHENYLTIN(IV) DICHLORIDE AND TRIMETHYLTIN(IV) CHLORIDE WITH 2,6-DIMETHYLPYRIDINE (2,6-LUTIDINE) N-OXIDE. AN AUTHENTIC EXAMPLE OF A TRULY FIVE-COORDINATED 1:1 R_2SnCl_2 COMPLEX

(These structures were solved by Professor A.L. Rheingold of the University of Delaware. See Preface.)

Introduction

The 1:1 adducts formed by diorganotin(IV) dihalides with certain pointed ligands containing the >C=O , >C=S , >S=O , >N=O or >P=O grouping are in fact six-coordinated.¹ The structures of the 1:1 dimethyltin(IV) dichloride complexes with diphenylcyclopropanone² and with 2,6-dimethylpyridine (2,6-lutidine) N-oxide³ reveal dimer formation through bridging chlorine atoms, and the structure of the 1:1 salicylaldehyde adduct^{4,5} can be reinterpreted in similar terms as an associated solid with bridging phenolic oxygen atoms.

Di-⁶ and trimethyltin(IV)⁷ chlorides are themselves associated in the solid state through bridging chlorine atoms, but triphenyltin(IV) chloride is a monomer,⁸ and the diphenyl analogue crystallizes in a complex structure which contains both four- and six-coordinated tin atoms. The structure was originally interpreted in terms of discrete molecules,⁹ and in any case the association must be weak.¹⁰

Tin-119m Mössbauer data was used to choose a complex which might be 1:1 and monomeric. The quadrupole splitting (QS) values increase with carbon-tin-carbon angles in diorganotin(IV) systems.¹¹ A treatment based upon a point-charge model has been successful in predicting these angles in diphenyltin(IV) systems^{12,13} where structural data are available.¹⁴ Since the trans-R₂SnX₂ octahedral configuration is ubiquitous for six-coordinated adducts and axially-most-electronegative, trigonal-bipyramidal configurations for five-coordinated adducts,¹⁴ the QS values can specify for the 1:1 R₂SnX₂·L complexes whether they are monomeric (equatorial-R₂Sn grouping, angle C-Sn-C=120°) or bridged (trans-R₂Sn grouping, angle C-Sn-C=180°). For the 2,6-dimethylpyridine (2,6-lutidine) N-oxide complex of diphenyltin(IV) dichloride (I), the isomer shift (IS) is 1.34±0.03 mm s⁻¹; the QS of 2.84±0.06 mm s⁻¹ corresponds to a C-Sn-C angle of 130°. Therefore, the structural determination of this complex was carried out.

The structure of the analogous 1:1 trimethyltin(IV) chloride adduct (II) was determined to complete the series, (CH₃)_nSnCl_{4-n}·xR₂C₅H₃NO, for which the n=2, x=0,⁶ 1,³ and 2¹⁵ and the n=3, x=0⁷ members have already been studied.

Experimental Section

Preparation of Diphenyltin(IV) Dichloride-2,6-Dimethylpyridine (2,6-Lutidine) N-Oxide (C₆H₅)₂SnCl₂·2,6-(CH₃)₂C₅H₃NO and Trimethyltin(IV) Chloride-2,6-Dimethylpyridine (2,6-Lutidine) N-Oxide (CH₃)₃SnCl·2,6-(CH₃)₂C₅H₃NO

The adducts were prepared by mixing stoichiometric amounts of the

organotin(IV) chloride [diphenyltin(IV) dichloride 3.44 g, 10.0 mmol; trimethyltin(IV) chloride 1.99 g, 10.0 mmol] and 2,6-dimethylpyridine (2,6-lutidine) *N*-oxide (1.23 g, 10.0 mmol) in chloroform. The organotins were gifts from M & T Chemicals and the ligand was an Aldrich product. Single crystals were obtained from the slow evaporation of chloroform solutions of the complexes which were isolated in ca. 70% yield; (I) mp 159° C; (II) mp 106° C.

The crystal data and data collection parameters, positional and thermal parameters for the nonhydrogen atoms, selected bond distances and angle, and the ORTEP drawings for the two complexes are given in Appendices 2 - 7. Appendix 1 describes the data collection, solution and refinement. The Appendices are provided by Professor A.L. Rheingold (see Preface).

Description of Structures and Discussion

An examination of the unit cell contents reveal no intermolecular contacts less than 4 Å. Thus the title compounds are indeed monomeric, and (I) is an authenticated example of a 1:1, five-coordinated, diorganotin(IV) dihalide complex.¹⁴

The Structure of (I)

In the analogous 1:1 dimethyltin(IV) dichloride complex the methyl-tin-methyl angle is opened from 123.5° in (CH₃)₂SnCl₂⁶ to 145.3° in the trans-, trans-, trans-octahedral chlorine-bridged dimer.³ With the weaker Lewis acid the angles involving the bulkier phenyl groups change from 123.9° and 127.0° in (C₆H₅)₂SnCl₂^{9,10} to 124.1(1)° in (I). The first-listed angle corresponds to a diphenyltin(IV) dichloride molecule one of

whose chlorine atoms bridge to an adjacent tin atom at 3.78 \AA .¹⁰ Its tin atom is four-coordinated in a distorted tetrahedral environment. The tin atom in (I), on the other hand, is five-coordinated in a trigonal bipyramidal arrangement. The two phenyl groups and one chlorine atom are equatorial, while the ligand oxygen and the other chlorine atom are axial [angle O-Sn-Cl(2)= $172.8(1)^\circ$]. The sum of the angles in the trigonal girdle of the complex is $359.0(3)^\circ$. The axial tin-chlorine bond [$d(\text{Sn-Cl}(2)) = 2.471(1) \text{ \AA}$] is longer than the equatorial [$d(\text{Sn-Cl}(1)) = 2.366(1) \text{ \AA}$] by $0.105(1) \text{ \AA}$.

Structure of (II)

The chlorine occupies one apical site while the oxygen atom of the ligand occupies the other at an O-Sn-Cl angle of $177.4(1)^\circ$. The sum of the angles made by the three equatorial-methyl groups at the central tin atom is $358.9(3)^\circ$, but the tin atom is displaced out of this plane toward the chlorine atom by $0.2357(2) \text{ \AA}$. That the girdle of this complex is not flat is suggested by the observation of two bands in the $\nu(\text{Sn-C})$ region of both the infrared (538,520) and Raman ($561,530 \text{ cm}^{-1}$) in the expected reversed intensity ratios using solid samples in both instances.

Bonding in the Pyridine N-Oxide Complexes

A number of molecular structure parameters reflect the bonding situation in pyridine N-oxide complexes. These include the N→O and the Sn-O distances, the angle Sn-O-N and that made between the planes containing the Sn-O-N system and the pyridine ring which intersect at the

nitrogen atom.

It would seem obvious that coordination of the oxygen would lengthen the N→O distance over that of the ligand, but a survey of the structures of over 30 complexes of variously substituted pyridine N-oxides fails to confirm this expectation.³ The claimed correlations between the frequencies assigned to $\nu(N\rightarrow O)$ modes and complexation must, therefore, arise from other origins. The structure of 2,6-dimethylpyridine (2,6-lutidine) is unknown, so no direct comparison can be made.

The structure of four organotin(IV) complexes with pyridine N-oxide ligands are available for comparison at this writing, but any conclusion based on these Sn-O bond distances would involve cross-comparing different tin coordination numbers and different organic substituents at the tin and on the ligand. The $d(\text{Sn}-\text{O})$ data are listed, inter alia, in Table 1.

The angles M-O-N in pyridine N-oxide metal (M) complexes are generally close to 120° reflecting sp^2 -hybridization at the coordinated oxygen atom.³ These values for the M=Sn complexes are listed in Table 4, and are 125.7(2) and 130.6(2)° for (I) and (II), respectively. The sp^2 -hybridization would leave one lone pair of electrons in a pure p-orbital which would be available for π -overlap with the aromatic pyridine system. The extent of this interaction would be dependent upon the angle between the Sn-O-N plane and the plane of the aromatic ring, and would maximize when the two were coincident. However, the survey reveals that the two planes are in general nearly perpendicular, the smallest interplane angle being 41° in $[(2\text{-CH}_3\text{pyNO})_5\text{Co}]^{2+}(\text{ClO}_4^-)_2$.¹⁶ The angles in the organotin complexes are listed in Table 1 with the values being 86.98(4)° and

84.75(16)° for (I) and (II), respectively. Thus a description based upon distortion from sp^3 -hybridization at oxygen is to be preferred. Forcing the Sn-O-N and pyridine ring into the same plane would give rise to severe steric repulsions between the 2,6-dimethyl groups and the substituents on the tin atom.

Summary

Diphenyltin(IV) dichloride-2,6-dimethylpyridine N-oxide, (I), $C_{19}H_{19}Cl_2NOSn$, forms colorless crystals, mp 159° C, in the space triclinic group $P\bar{1}$ with $a = 9.359(2)$, $b = 10.534(2)$, $c = 10.996(3)$ Å, $\alpha = 97.46(2)$, $\beta = 114.74(2)$, $\gamma = 93.26(2)^\circ$, $V = 968.8(3)$ Å³, $Z = 2$, $\rho = 1.60$ g cm⁻³. The structure was determined from 3609 reflections collected on a Nicolet R3 diffractometer with monochromatic MoK α radiation and refined to a final R_w value of 0.0228 for the 3102 reflections included in the least-squares sums. The monomeric complex contains five-coordinated, trigonal bipyramidal tin with the phenyl rings forming an angle of 124.1(1)° in the equatorial plane. The ligand oxygen and one of the chlorine atoms occupy the apical positions at an angle of 172.8(1)°. The sum of the angles subtended at the tin atom in the trigonal plane is 359.0(3)°. The tin atom is displaced from this plane by 0.1279(2) Å in the direction of the chlorine atom. The Sn-Cl_{eq.} bond [2.366(1) Å] is shorter than the Sn-Cl_{ax.} bond [2.471(1) Å]. The Sn-O distance is 2.296(2) Å, and the two Sn-C bond distances are approximately equal [2.119(3) and 2.128(4) Å]. Trimethyltin(IV) chloride-2,6-dimethylpyridine N-oxide, (II), $C_{10}H_{18}ClNOSn$, mp 106° C, also crystallizes as colorless crystals in the same space group with $a = 8.174(2)$, $b = 9.599(2)$, $c =$

9.895(3) Å, $\alpha = 115.33(2)$, $\beta = 105.50(2)$, $\gamma = 81.45(2)^\circ$, $V = 675.7(2)$ Å³, $Z = 2$, $\rho = 1.58$ g cm⁻³. This structure was solved from 2437 reflections and refined to a final R_w value of 0.0313 for the 2207 reflections that were used in the least-squares sums. The molecule has the tin atom in a trigonal bipyramidal geometry with the methyl carbons in the trigonal plane. The Sn-C bond distances are 2.119(5), 2.120(4) and 2.125(6) Å and the C-Sn-C angles are 114.1(2), 121.8(3) and 123.1(2)°, giving a sum of 358.9(3)°. The apical Cl-Sn-O angle is 177.4(1)°, the tin atom is displaced from the trigonal plane by 0.2357(2) Å toward the chlorine atom. Both the Sn-Cl and Sn-O distances are larger than those found in structure (I) [2.533(1) and 2.400(2) Å, respectively]. The angle at the oxygen atom is 125.7(2) in (I) and 130.6(2)° in (II), and the angle formed by the Sn-O-N system and the pyridine N-oxide ring is 86.98(4) in (I) and 84.75(16)° in (II). The N-O distances are 1.346(4) in (I) and 1.326(4) Å in (II).

TABLE 1

COMPARISON MOLECULAR DATA FOR ORGANOTIN(IV) CHLORIDES AND THEIR PYRIDINE N-OXIDE COMPLEXES

	$(\text{CH}_3)_3\text{SnCl} \cdot n2,6\text{-R}_2\text{C}_5\text{H}_3\text{NO}$		$(\text{CH}_3)_2\text{SnCl}_2 \cdot n2,6\text{-R}_2\text{C}_5\text{H}_3\text{NO}$			$(\text{C}_6\text{H}_5)_2\text{SnCl}_2 \cdot n2,6\text{-R}_2\text{C}_5\text{H}_3\text{NO}$		
	$n=1; \text{R}=\text{CH}_3 \text{ (II)}^a$	$n=0^b$	$n=2; \text{R}=\text{H}^c$	$n=1; \text{R}=\text{CH}_3^d$	$n=0^e$	$n=1; \text{R}=\text{CH}_3 \text{ (I)}^a$	$n=0^f$	
d(Sn-Cl), Å	2.533(1)	2.430	2.584	2.400	2.40	2.366(1)	2.336	2.336
d(Sn-O), Å	2.400(2)	3.269	2.251	2.528	3.54	2.471(1)	2.353	2.357
d(Sn-C), Å	2.119(5)	2.109	2.225	2.289	2.21	2.296(2)		
	2.120(4)	2.121		2.110		2.119(3)	2.105	2.112
	2.125(6)	2.216		2.112		2.128(4)	2.119	2.118
d(O-N), Å	1.326(4)		1.37	1.352		1.346(4)		
d(N-C) _{av} , Å	1.367(4)		1.35	1.364		1.360(3)		
C-Sn-C, deg	114.1(2)	115.2	180	145.3	123.5	124.1(1)	123.9	127.0
	121.8(3)	116.3						
	123.1(2)	119.8						
Cl-Sn-Cl, deg		176.85	180	79.46	93.0	88.92(4)	101.7	97.8
				89.50				
				168.79				
Cl-Sn-O, deg	177.4(1)		89.5	87.95		83.9(1)		
			90.5	103.09		172.8(1)		
				177.44				
C-Sn-O, deg	85.7(1)		84.4	85.3		87.8(1)		
	86.0(2)		95.6	87.4		88.8(1)		
	88.1(1)							
Sn-O-N, deg	130.6(2)		117	123.0		125.7(2)		

TABLE 1, cont'd.

	$(\text{CH}_3)_3\text{SnCl} \cdot n2,6\text{-R}_2\text{C}_5\text{H}_3\text{NO}$		$(\text{CH}_3)_2\text{SnCl}_2 \cdot n2,6\text{-R}_2\text{C}_5\text{H}_3\text{NO}$			$(\text{C}_6\text{H}_5)_2\text{SnCl}_2 \cdot n2,6\text{-R}_2\text{C}_5\text{H}_3\text{NO}$		
	$n=1; \text{R}=\text{CH}_3(\text{II})^{\text{a}}$	$n=0^{\text{b}}$	$n=2; \text{R}=\text{H}^{\text{c}}$	$n=1; \text{R}=\text{CH}_3^{\text{d}}$	$n=0^{\text{e}}$	$n=1; \text{R}=\text{CH}_3(\text{I})^{\text{a}}$	$n=0^{\text{f}}$	
Cl-Sn-C, deg	91.7(1)	82.6	89.5	72.3	109.0	94.9(1)	106.0	
	93.7(1)	79.6	90.5	76.4		96.0(1)	106.5	
	94.9(1)	78.0		93.7		114.7(1)	107.8	107
		99.1		95.1		120.2(1)	108.8	110
		100.1		102.9				
		100.6		110.7				
O-Sn-O, deg			180					
pyNO ring and Sn-O-N plane, deg	84.75		83	87.17		86.98(4)		

^a This work.^b Ref. 7.^c Ref. 15.^d Ref. 3.^e Ref. 6.^f Ref. 9 and 10. There are two crystallographically independent molecules in the unit cell.

TABLE 2

LEAST SQUARES PLANES IN DIPHENYLTIN(IV) DICHLORIDE·2,6-DIMETHYLPYRIDINE N-OXIDE(I) AND
 TRIMETHYLTIN(IV) CHLORIDE-2,6-DIMETHYLPYRIDINE N-OXIDE(II)

Plane Through Atoms	Orthonormal Equation $M_1x + M_2y + M_3z + d = 0$				rms	Plane P	Dihedral angle be- tween [P,P']
	M_1	M_2	M_3	d			
<u>$(C_6H_5)_2SnCl_2 \cdot 2,6-(CH_3)_2C_5H_3NO$</u>							
C1(1), C(11), C(21)	-0.5514	0.7838	-0.2857	-0.2232	0	1 ^a	
Sn, O, N	-0.0527	-0.3675	-0.9285	2.7408	0	2	
O, N, C(2), C(3), C(4), C(5)	-0.9183	0.3932	-0.0468	2.4347	0.0117	3	86.98 [2,3]
C(11), C(12), C(13), C(14), C(15), C(16)	-0.4502	-0.8740	-0.1830	2.9120	0.0011	4	67.39 [1,4]
C(21), C(22), C(23), C(24), C(25), C(26)	0.1215	0.8101	-0.5736	-0.8842	0.0063	5	42.96 [1,5] 48.87 [4,5]
<u>$(CH_3)_3SnCl \cdot 2,6-(CH_3)_2C_5H_3NO$</u>							
C(1), C(2), C(3)	-0.4127	-0.4401	-0.7975	1.1956	0	6 ^b	
Sn, O, N	-0.8455	0.1747	-0.5046	-2.2318	0	7	
O, N, C(4), C(5), C(6), C(7), C(8)	-0.1155	-0.9349	-0.3357	3.6317	0.0324	8	84.75 [7,8]

^a The tin atom is 0.1279(2) Å from this plane in the direction of the Sn-Cl(2) vector.

^b The tin atom is 0.1257(2) Å from this plane in the direction of the Sn-Cl vector.

TABLE 3

COMPARISON INFRARED DATA FOR THE 1:1 ADDUCTS OF 2,6-DIMETHYLPYRIDINE
N-OXIDE WITH TIN(II) AND TIN(IV) CHLORIDES (IN cm^{-1})

	$\nu(\text{N-O})$	$\nu(\text{Sn-C})$
$2,6-(\text{CH}_3)_2\text{C}_5\text{H}_3\text{NO}$	1246 ^a	
$\text{SnCl}_2 \cdot 2,6-(\text{CH}_3)_2\text{C}_5\text{H}_3\text{NO}$	1181 ^b	
$[(\text{CH}_3)_2\text{SnCl}_2 \cdot 2,6-(\text{CH}_3)_2\text{C}_5\text{H}_3\text{NO}]_2$	1172	546, 518 ^c
$(\text{C}_6\text{H}_5)_2\text{SnCl}_2 \cdot 2,6-(\text{CH}_3)_2\text{C}_5\text{H}_3\text{NO}$	1205 ^d	
$(\text{CH}_3)_3\text{SnCl} \cdot 2,6-(\text{CH}_3)_2\text{C}_5\text{H}_3\text{NO}$	1200	538 ^d
$(\text{C}_6\text{H}_5)_3\text{SnCl} \cdot 2,6-(\text{CH}_3)_2\text{C}_5\text{H}_3\text{NO}$	1210 ^e	

^a Ref. 17.

^b Ref. 18.

^c Ref. 3.

^d This work.

^e Unpublished results.

APPENDIX 1

X-ray Data Collection

Crystals of (I) and (II) were trimmed with a razor blade to nearly spherical shapes [rad.: (I) 0.17 mm; (II) 0.14 mm] and mounted in nitrogen-flushed, thin-walled capillary tubes. Crystal parameters and some details of data collection are provided in Appendix 2. Final unit-cell dimensions were obtained from the angular settings of 25 well-centered reflections, including Friedel pairs, in the range $30^\circ < 2\theta < 36^\circ$. Intensity data were corrected for Lp effects and decay but not for absorption. Redundant data were averaged with less than 1.5% disagreement.

Solution and Refinement of the Structure

The positions of the tin, chlorine and oxygen atoms were obtained from a sharpened Patterson map. Subsequent difference Fourier syntheses revealed the locations of all atoms, including hydrogen, for (I), and all nonhydrogen atoms for (II). In the final refinement cycles, all nonhydrogen atoms were refined with anisotropic thermal parameters. In (I), the found hydrogen atoms were refined isotropically, and in (II), the hydrogen atoms were placed in idealized locations [$d(\text{C-H}) = 0.96 \text{ \AA}$], but not refined. In both cases an initial assumption of the centrosymmetric, triclinic space group $P\bar{1}$ was shown to be correct by the successful and chemically reasonable structural solutions ultimately obtained.

All calculations were performed using a Data General Nova 4 computer with programs contained in the Nicolet libraries P3, XP and SHELXTL.

APPENDIX 2

CRYSTAL DATA AND DATA COLLECTION PARAMETERS FOR $(C_6H_5)_2SnCl_2 \cdot$
 $2,6-(CH_3)_2C_5H_3NO$ (I), AND $(CH_3)_3SnCl \cdot 2,6-$
 $(CH_3)_2C_5H_3NO$ (II) AT 23° C

	(I)	(II)
Formula	$C_{19}H_{19}Cl_2NOSn$	$C_{10}H_{18}ClNOSn$
Space Group	$P\bar{1}$	$P\bar{1}$
a , Å	9.359(2)	8.174(2)
b , Å	10.534(2)	9.599(2)
c , Å	10.996(3)	9.895(3)
α , deg.	97.46(2)	115.33(2)
β , deg.	114.74(2)	105.50(2)
γ , deg.	93.26(2)	81.45(2)
V , Å ³	968.8(3)	675.7(2)
Z	2	2
density (calcd), g cm ⁻³	1.60	1.58
μ , cm ⁻¹ (MoK α)	16.1	20.7
2 θ scan range, deg.	4-50	4-50
diffractometer	Nicolet R3	Nicolet R3
data collected	$\pm h \pm k + l$	$\pm h \pm k + l$
unique data measd	3414 (3609 collected)	2298 (2437 collected)
unique data used	3102	2207
$[I < 3\sigma(I)]$		
std. rflns	3/97 (7% decay)	3/97 (8% decay)
R_F , %	2.53	2.83
$R_W F$, %	2.28	3.13
GOF	1.61	1.21
highest peak, final diff map e Å ⁻³	0.44	0.82

APPENDIX 2, cont'd.

	(I)	(II)
mean shift/max esd, final cycle	0.08	0.04
data/parameters, final cycle	10.6/1	17.2/1

APPENDIX 3

ATOMIC COORDINATES AND ISOTROPIC THERMAL PARAMETERS FOR (I) AND (II)^a

Atom	x	y	z	U, Å ²
		(I)		
Sn	0.18251(2)	0.23379(2)	0.27358(2)	0.0380(1)
C1(1)	-0.04265(9)	0.08661(8)	0.22456(8)	0.0536(3)
C1(2)	0.0034(1)	0.39252(8)	0.17062(9)	0.0585(4)
O	0.3205(2)	0.0694(2)	0.3633(2)	0.0407(8)
N	0.2564(4)	-0.0457(3)	0.3698(3)	0.039(1)
C(1)	0.2116(3)	-0.1430(3)	0.2621(3)	0.043(1)
C(2)	0.1519(4)	-0.2614(4)	0.2728(4)	0.051(2)
C(3)	0.1349(5)	-0.2802(4)	0.3860(5)	0.061(2)
C(4)	0.1805(5)	-0.1786(4)	0.4936(4)	0.057(2)
C(5)	0.2413(4)	-0.0597(3)	0.4852(3)	0.045(1)
C(6)	0.2926(6)	0.0532(4)	0.5959(4)	0.062(2)
C(7)	0.2299(5)	-0.1166(3)	0.1405(3)	0.057(2)
C(11)	0.2924(3)	0.2252(3)	0.1385(3)	0.041(1)
C(12)	0.4395(4)	0.1815(3)	0.1742(3)	0.054(1)
C(13)	0.5135(5)	0.1830(4)	0.0879(5)	0.068(2)
C(14)	0.4427(5)	0.2274(4)	-0.0320(4)	0.074(2)
C(15)	0.2979(6)	0.2708(6)	-0.0683(4)	0.080(2)
C(16)	0.2234(4)	0.2698(4)	0.0176(3)	0.062(2)
C(21)	0.2845(3)	0.3434(3)	0.4722(3)	0.039(1)
C(22)	0.1922(4)	0.4046(3)	0.5259(4)	0.049(2)
C(23)	0.2593(5)	0.4747(4)	0.6559(4)	0.059(2)
C(24)	0.4189(5)	0.4853(3)	0.7326(4)	0.059(2)
C(25)	0.5135(5)	0.4270(4)	0.6813(4)	0.064(2)
C(26)	0.4467(4)	0.3559(4)	0.5515(4)	0.056(2)

APPENDIX 3, cont'd.

Atom	x	y	z	U, Å ²
		(II)		
Sn	0.22184(3)	0.24047(3)	0.07284(2)	0.0470(1)
Cl	0.0951(2)	0.1091(2)	-0.2125(1)	0.0785(6)
O	0.3430(3)	0.3538(3)	0.3438(3)	0.052(1)
N	0.4322(4)	0.2899(3)	0.4374(3)	0.045(1)
C(1)	0.3854(6)	0.3744(5)	0.0455(5)	0.066(2)
C(2)	-0.0076(6)	0.3585(7)	0.1284(6)	0.083(3)
C(3)	0.2991(6)	0.0255(4)	0.0875(5)	0.065(2)
C(4)	0.6043(4)	0.2694(4)	0.4528(4)	0.051(2)
C(5)	0.6967(5)	0.2156(5)	0.5591(5)	0.068(2)
C(6)	0.6208(6)	0.1819(5)	0.6478(5)	0.072(2)
C(7)	0.4485(6)	0.2003(5)	0.6276(5)	0.070(2)
C(8)	0.3514(5)	0.2521(4)	0.5209(4)	0.054(2)
C(9)	0.6794(5)	0.3075(5)	0.3537(5)	0.065(2)
C(10)	0.1633(6)	0.2739(6)	0.4904(6)	0.076(2)

^a Estimated standard deviations for the last digit in parentheses.

APPENDIX 4

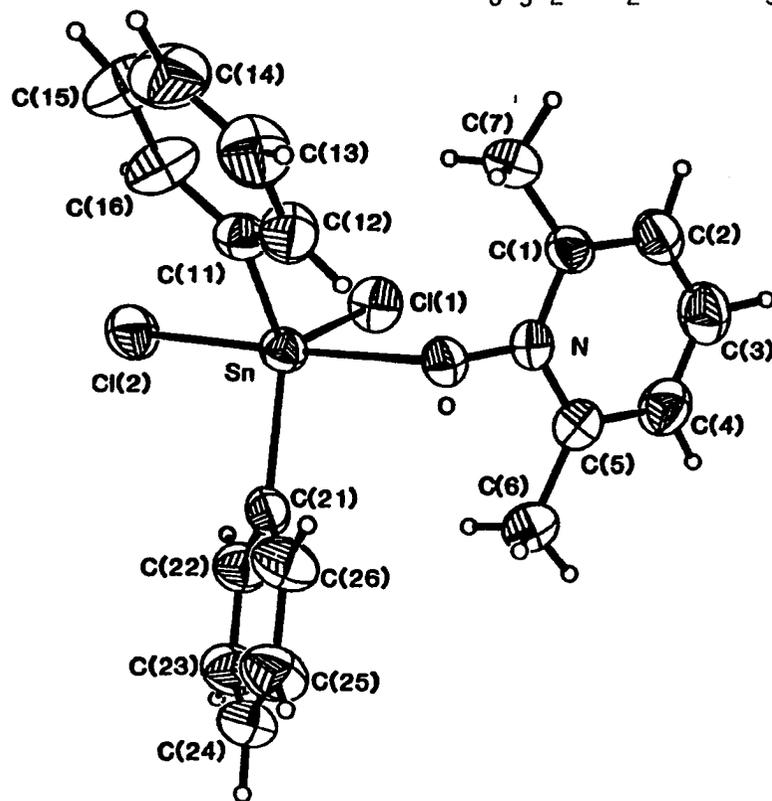
SELECTED BOND DISTANCES AND ANGLES IN (I) AND (II)^a

(I)		(II)	
(a) Bond Distances (Å)			
Sn-C1(1)	2.366(1)	Sn-C1	2.533(1)
Sn-C1(2)	2.471(1)	Sn-O	2.400(2)
Sn-O	2.296(2)	Sn-C(1)	2.125(6)
Sn-C(11)	2.218(4)	Sn-C(2)	2.119(5)
Sn-C(21)	2.119(3)	Sn-C(3)	2.120(4)
O-N	1.346(4)	O-N	1.326(4)
(b) Bond Angles (deg)			
Sn-O-N	125.7(2)	Sn-O-N	130.6(2)
O-Sn-C1(2)	172.8(1)	O-Sn-C1	177.4(1)
O-Sn-C1(1)	83.9(1)	O-Sn-C(1)	88.1(1)
O-Sn-C(11)	87.8(1)	O-Sn-C(2)	86.0(2)
O-Sn-C(21)	88.1(1)	O-Sn-C(3)	85.7(1)
C1(2)-Sn-C1(1)	88.92(4)	C1-Sn-C(1)	93.7(1)
C1(2)-Sn-C(11)	96.0(1)	C1-Sn-C(2)	94.9(1)
C1(2)-Sn-C(21)	94.9(1)	C1-Sn-C(3)	91.7(1)
C1(1)-Sn-C(11)	120.2(1)	C(1)-Sn-C(2)	114.1(2)
C1(1)-Sn-C(21)	114.7(1)	C(1)-Sn-C(3)	123.1(2)
C(11)-Sn-C(21)	124.1(1)	C(2)-Sn-C(3)	121.8(3)

^a Estimated standard deviations for the last digit in parentheses.

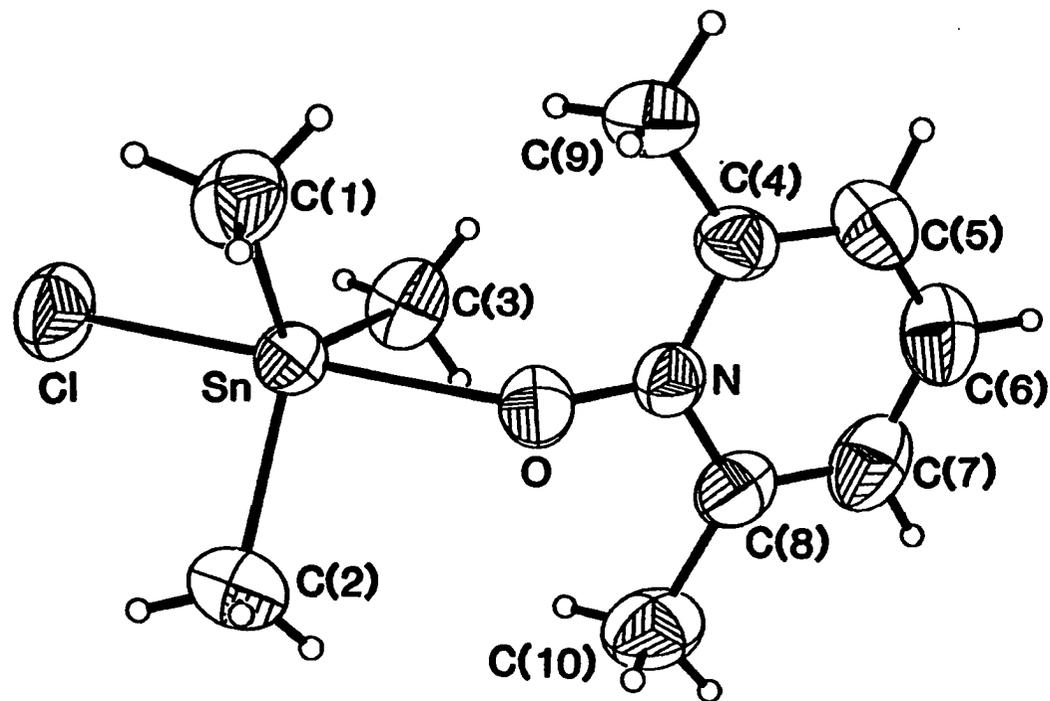
APPENDIX 5

MOLECULAR GEOMETRY AND LABELLING DIAGRAM FOR $(C_6H_5)_2SnCl_2 \cdot 2,6-(CH_3)_2C_5H_3NO$ (I)



APPENDIX 6

MOLECULAR GEOMETRY AND LABELLING DIAGRAM FOR $(\text{CH}_3)_3\text{SnCl} \cdot 2,6\text{-(CH}_3)_2\text{C}_5\text{H}_3\text{NO}$ (II)



APPENDIX 7

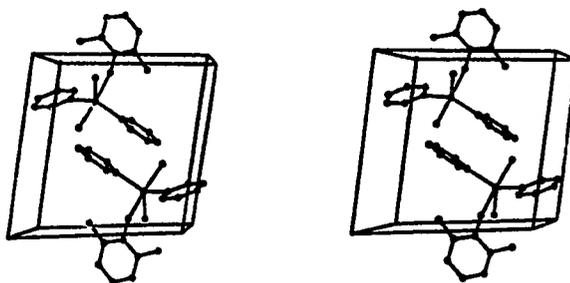
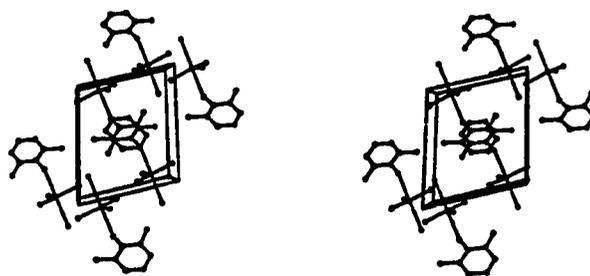
UNIT CELL PACKING DIAGRAM FOR (I) AS VIEWED ALONG THE a-AXIS

FIGURE 4

UNIT CELL PACKING DIAGRAM FOR (II) AS VIEWED ALONG THE b-AXIS

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