Reactivity of diorganotin(IV) and triorganotin(IV) phenoxides

Archana Thakur

Jaypee University of Information Technology, Waknaghat, Solan, Himachal Pradesh-173234, India

Abstract: The reactivity of diorganotin(IV) diphenoxides toward acetylacetone and salicylaldehyde; diorganotin(IV) chlorophenoxides towards potassium salts of benzohydroxamic acids, aluminium(III) chloride and iron(III) chloride and triorganotin(IV) phenoxides towards Hg(II) salts has been examined. The products were authenticated by physico-chemical and spectral studies. This article deals with study of cleavage of Sn-O, Sn-C bond and behaviour of the organotin(IV) phenoxides as chloride ion donors under different conditions. These reactions can be utilized as the course for the synthesis of the reaction products as these are obtained in quantitative yields.

Keywords: Reactivity of organotin phenoxides; acetylacetone; salicylaldehyde; benzohydroxamates; aluminium trichloride and iron trichloride.

Introduction

The organotin chemistry has developed into one of the significant domains of research in organometallic chemistry ascribing to their numerous applications\textsuperscript{1-10}. The full scope of usage of organotin compounds, have fascinated many researchers to look into different aspects of organotin chemistry. Among several classes of extensively studied organotin(IV) compounds, organotin(IV) phenoxides represent a category of compounds which has not been analysed considerably. The bulk of the reports available in literature focus on the synthesis and characterization of organotin phenoxides\textsuperscript{11-18} and merely a few publications on the reactions of organotin(IV) phenoxides with ethylpropiolate\textsuperscript{19}, diethylacetylenedicarboxylate\textsuperscript{20}, bis 2,2,2-trichloroethyl azodicarboxylate\textsuperscript{21}, diethyl azo dicarboxylate\textsuperscript{22}, carbon dioxide and isocynate\textsuperscript{23} etc have been described.

As a part of our ongoing work and our pursuit to look into different aspects of organotin phenoxides chemistry, we report herein the synthesis and characterization of reaction products of organotin(IV) phenoxides towards various ligands viz. acetylacetone, salicylaldehyde, p-chloro-, p-nitro-benzohydroxamic acid, iron(III) chloride and aluminium(III) chloride in order to have an insight into the stability of various bonds present in organotin(IV) phenoxides. We have already reported the synthesis and characterization of parent organotin phenoxides\textsuperscript{17,18}.

Experimental Section

Materials and Methods

Acetylacetone (Sisco) was firstly dried by refluxing over P\textsubscript{2}O\textsubscript{5} (5-6 hours) and was then distilled under reduced pressure and salicylaldehyde (Reidel) was purified by distillation. p-
chlorobenzoic acid (Merck), p-nitrobenzoic acid (Merck), Iron(III) chloride (AR), Mercuric(II) chloride (Ranbaxy), Mercuric(II) bromide (Merck) and Mercuric(II) acetate (Merck) were used as received without further purification. Anhydrous aluminium(III) chloride (BDH) was purified by subliming in an atmosphere of chlorine. All solvents are purified according to methods described in literature. p-chloro, p-nitro benzohydroxamic acids were prepared via the ethyl esters of p-chlorobenzoic acid, p-nitrobenzoic acid by a literature method.24

Tin was evaluated as SnO₂ by utilizing a mixture of concentrated H₂SO₄ and HNO₃ in 2:3 ratios (by vol.) and chlorine content was approximated by the Volhard’s method. Analysis for carbon and hydrogen elements was carried out on Elemental Vario EL III Carlo Erba 1108 analyzer. The melting points were recorded in capillary tubes using melting point apparatus. Molar conductance values of 10⁻³ mol L⁻¹ solutions of compounds in nitrobenzene were taken at 25±0.1ºC on an Elico Conductivity Bridge (type CM-82T). Rast’s camphor method was used to find the molecular weights of the complexes. FTIR spectra of the complexes were collected with Nicolet 5700 spectrophotometer.

Synthesis

Reactions of R₂Sn(OAr)₂ (where OAr = OC₆H₄Bu'₂ and C₆H₃Bu'-2-Me-4) with chelating ligands viz. acetylacetone and salicylaldehyde.

In a representative reaction, to a solution of parent organotin(IV) phenoxides of composition R₂Sn(OAr)₂ in dry benzene was added bimolar number of chelating ligands under anhydrous conditions, in separate experiments. The reaction components furnished a clear solution upon mixing followed by refluxing for 8-10 hours. The solids separated during the course of reaction were filtered and dried under vacuum. The filtrate upon keeping undisturbed for 3-4 days gave phenolic crystals in case of a reaction with organotin(IV) 2-tert-butyl-4-methyl phenol. Solids were recrystallized from benzene.

Reactions of R₂SnCl(OAr) (where R = n-Bu, Me: OAr = OC₆H₄Bu'-2 and OC₆H₃Bu'-2-Me-4) with Potassium salts of p-chloro and p-nitro benzyhydroxamic acids:

To the solutions of parent organotin(IV) chloro phenoxides in methanol (30 mL) were added equimolar solutions of potassium salts of p-chloro and p-nitro benzohydroxamic acids in dry methanol (20 mL) in different experiments. The reaction mixtures were stirred for 2-3 hours at room temperature and were then refluxed for 8-10 hours. White solids separated in the course of refluxing were filtered and filtrates were vacuum concentrated. The filtrates were then kept for 3-4 days undisturbed whereupon crystalline solids separated out. These were then dried under vacuum. The solids were recrystallized from methanol.

Reactions of R₂SnCl(OAr) (where R = n-Bu, Me: OAr = OC₆H₄Bu'-2 and OC₆H₃Bu'-2-Me-4) with Lewis acids (Lewis acids = FeCl₃ and AlCl₃)

In a typical preparative scheme, to a suspension of organotin(IV) phenoxides in THF (20 mL), an equimolar quantity of FeCl₃ dissolved in the same solvent, was added. The reaction mixture was firstly stirred, followed by refluxing for 4-5 hours. It was then filtered and the filtrate was distilled off to eliminate excess of solvent. The concentrate was then treated with diethyl ether and the solid, hence attained was dried in vacuum. The resultant solids were recrystallized from THF.
Reactions of triphenyltin(IV) phenoxides with mercuric(II) salts viz. HgCl₂, HgBr₂ and Hg(ac)₂.

In a standard reaction run, to a solution of triphenyltin(IV) phenoxides in THF (25 mL), a solution of mercuric(II) salts in 1:1 molar ratios in THF, were added drop wise with continuous stirring for 5-8 hours at room temperature. The reaction mixture was concentrated under vacuum and the concentrate was treated with petroleum ether, upon which a white solid (I) resulted. The solid was removed by filtration and washed with petroleum ether. It was then treated with hot benzene and the solution was set aside overnight, which left a white crusty solid (II). The crusty white solids were recrystallized from THF.

Results and Discussion

Reactions of diorganotin(IV) phenoxides with acetylacetone and salicylaldehyde

The reactions of parent diorganotin(IV) complexes of composition R₂Sn(OAr)₂ (where R = n-Bu and Me; OAr = OC₆H₄Bu'-2 and OC₆H₄Bu'-2-Me-4) have been undertaken with the acetylacetone and salicylaldehyde in accordance with the following reaction:

\[ R₂Sn(OAr)₂ + 2 LH \xrightarrow{\text{Benzene, Reflux}} R₂Sn(L)₂ + 2 HOAr \]

(Where R = n-Bu, Me; OAr = OC₆H₄But-2, OC₆H₃But-2-Me-4; LH = acetylacetone and salicylaldehyde)

Interestingly, on varying the molar ratios of reactants, only bis-chelated diorganotin(IV) complexes have been obtained. The elemental analyses of the isolated complexes agreed well with their expected stoichiometric compositions. The complexes obtained were sharp melting, non-electrolytic and monomeric solids. The physico-chemical and IR spectral data has been presented in Table 1.

Table 1. Analytical data and principal IR bands of chelate complexes of dibutyltin(IV) and dimethyltin(IV) with acetylacetone and salicylaldehyde

<table>
<thead>
<tr>
<th>Parent Complex</th>
<th>Ligand</th>
<th>Main Product</th>
<th>Side Product</th>
<th>Colour</th>
<th>M.Pt (°C)</th>
<th>Elemental analysis</th>
<th>IR Bands (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>% Found (calc.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bu₃Sn(OC₆H₄Bu'-2)₂</td>
<td>acac</td>
<td>Bu₃Sn (acac)₂</td>
<td>HOCl₄Bu'-2</td>
<td>Light Yellow</td>
<td>33</td>
<td>27.4 (27.6)</td>
<td>1600-1580, 1370-1350</td>
</tr>
<tr>
<td>Me₃Sn(OC₆H₄Bu'-2)₂</td>
<td>acac</td>
<td>Me₃Sn (acac)₂</td>
<td>HOCl₄Bu'-2</td>
<td>Light Yellow</td>
<td>77</td>
<td>34.4 (34.2)</td>
<td>1565 - 1325</td>
</tr>
<tr>
<td>Bu₃Sn(OC₆H₄Bu'-2-Me-4)₂</td>
<td>acac</td>
<td>Bu₃Sn (acac)₂</td>
<td>HOCl₄Bu'-2-Me-4</td>
<td>Light Yellow</td>
<td>33</td>
<td>7.4 (27.6)</td>
<td>1561 - 1335</td>
</tr>
<tr>
<td>Me₃Sn(OC₆H₄Bu'-2-Me-4)₂</td>
<td>acac</td>
<td>Me₃Sn (acac)₂</td>
<td>HOCl₄Bu'-2-Me-4</td>
<td>Light Yellow</td>
<td>77</td>
<td>34.5 (34.2)</td>
<td>1565 - 1328</td>
</tr>
<tr>
<td>Bu₃Sn(OC₆H₄Bu'-2)₂</td>
<td>Sal</td>
<td>Bu₃Sn (sal)₂</td>
<td>HOCl₄Bu'-2</td>
<td>Light Yellow</td>
<td>142</td>
<td>27.7 (27.6)</td>
<td>1628 - 1218</td>
</tr>
<tr>
<td>Me₃Sn(OC₆H₄Bu'-2)₂</td>
<td>Sal</td>
<td>Me₃Sn (sal)₂</td>
<td>HOCl₄Bu'-2</td>
<td>Light Yellow</td>
<td>126</td>
<td>33.9 (34.2)</td>
<td>1625 - 1215</td>
</tr>
<tr>
<td>Bu₃Sn(OC₆H₄Bu'-2-Me-4)₂</td>
<td>Sal</td>
<td>Bu₃Sn (sal)₂</td>
<td>HOCl₄Bu'-2-Me-4</td>
<td>Light Yellow</td>
<td>142</td>
<td>27.8 (27.6)</td>
<td>1628 - 1218</td>
</tr>
<tr>
<td>Me₃Sn(OC₆H₄Bu'-2-Me-4)₂</td>
<td>Sal</td>
<td>Me₃Sn (sal)₂</td>
<td>HOCl₄Bu'-2-Me-4</td>
<td>Light Yellow</td>
<td>126</td>
<td>33.9 (34.2)</td>
<td>1625 - 1215</td>
</tr>
</tbody>
</table>
The IR spectra of the complexes scanned in the 4000-200 cm\(^{-1}\) region and have provided useful information for the formation of the complexes. The absence of bands at 3333 cm\(^{-1}\) and 3180 cm\(^{-1}\) due to simple hydrogen bonded OH group in case of acetylacetone and salicylaldehyde respectively has indicated deprotonation and is further affirmed by the separation of respective phenols during the course of the reactions. The sharp bands known to occur in 1600-1580 cm\(^{-1}\) and 1370-1350 cm\(^{-1}\) regions due to \(\nu_{as}(C=O)\) and \(\nu_{s}(C=O)\) stretching frequencies in the enolic form of acetylacetone and at 1660 cm\(^{-1}\) in case of the free salicylaldehyde ligand have been found to move to lower wave numbers by 20-30 cm\(^{-1}\) in the complexes suggesting thereby the coordination of carbonyl oxygen to tin metal. In addition, sharp bands observed at 1535-1530 cm\(^{-1}\) and at 1200 cm\(^{-1}\) in uncoordinated acetylacetone and salicylaldehyde respectively assignable to \(\nu(C=C)\) mode have been found to move to higher wave numbers on complexation. The complete absence of important bands that could be attributed to the coordinated phenoxide anion has confirmed the formation of the complex by the substitution of phenoxide ligand by salicylaldehyde ligand in accordance with the reaction mentioned above. The coordination through oxygen of the ligand to tin has been further confirmed by the appearance of new bands in 490-460 cm\(^{-1}\) region has been assigned to \(\nu(Sn-O)\) mode\(^{15}\).

**Reactions of diorganotin(IV) chloro phenoxides with benzohydroxamic acids**

The reactivity of complexes of composition \(R_2SnCl(OAr)\) (where \(R = n\text{-Bu, and Me; OA}r = OC_6H_4Bu'\text{-2 and OC}_6H_3Bu'\text{-2-Me-4})\) has been studied towards potassium salts of hydroxamic acids with an aim to achieve the replacement of chloride ion by hydroxamate ion. These reactions may be represented as:

\[
R_2SnCl(OAr) + KO-NH-CO-C_6H_4-X \xrightarrow{\text{Me}anol \text{ React} \text{Flux}} R_2SnCl(O-NH-CO-C_6H_4-X)^+ + KOAr
\]

(Where \(R = n\text{-Bu, Me; OA}r = OC_6H_4Bu'\text{-2, OC}_6H_3Bu'\text{-2-Me-4; } X = \text{Cl, NO}_2\))

Surprisingly, formation of KCl was not observed in these reactions instead a quantitative amount of respective potassium salt of the respective phenols separated out. More interestingly, the potassium salt of \(p\)-nitro benzohydroxamic acid has been found to be more responsive than the \(p\)-chloro benzohydroxamic acid towards parent phenoxides, as apparent from the separation of white solid (identified as KOAr) during the stirring of reactants. Nevertheless, the separation of white solid resulted only after refluxing in case of reaction with potassium salt of \(p\)-chloro benzohydroxamic acid. The organotin(IV) hydroxamic acid complexes are moisture sensitive, sharp melting, non-electrolytic, monomeric solids and are soluble in common organic solvents. The physico-chemical data and IR spectral data has been presented in Table 2.

IR spectra of the complexes scanned in the 4000-200 cm\(^{-1}\) region and IR spectra of \(Bu_2SnCl(O-NH-CO-C_6H_4-Cl)\) is given in Figure 1.

In the IR spectra, important ligation frequencies of the hydroxamate ion are due to \(\nu(C=O)\), \(\nu(C-N)\), \(\nu(N-O)\) and \(\nu(N-H)\) modes undergo shifts on complexation. The absorption bands due to \(\nu(C=O)\) vibration in potassium salts of \(p\)-chloro and \(p\)-nitro benzohydroxamic acids are known to occur at 1590 and 1600 cm\(^{-1}\) respectively.
The occurrence of these bands at almost same wave numbers in the IR spectra of complexes studied herein has suggested the non-participation of carbonyl oxygen in coordination. The v(C-N) mode which appears at 1320 and 1315 cm\(^{-1}\) in case of respective potassium salts of \(p\)-chloro and \(p\)-nitro benzohydroxamic acids, has been found to shift to higher wave numbers (1395-1345 cm\(^{-1}\)) upon complexation.

![Figure 1. IR Spectra of Me\(_2\) Sn(acac)\(_2\)](image-url)
The absorption band due to \( \nu(N-O) \), known to occur in 945-910 cm\(^{-1}\) region in potassium salts of \( p \)-chloro and \( p \)-nitro benzoxydrazides, appeared in 1015-960 cm\(^{-1}\) region in organotin(IV) hydroxamates. These positive shifts in \( \nu(C-N) \) and \( \nu(N-O) \) modes are suggestive of coordination through hydroxylamine oxygen with tin metal, indicating bonding of the type N-O-Sn.

The separation of the KOAr during the course of these reactions supplemented the IR spectral observations. A strong and distinct band at \( \sim 3250 \text{ cm}^{-1} \) due to \( \nu(N-H) \) mode in potassium salts of benzoxydrazides has remained nearly unchanged in organotin(IV) derivatives except for a slight reduction in the intensity of this band, indicative of the fact that in present study hydroxamate ligand is coordinating as monodentate ligand. The appearance of new and important \( \nu(Sn-O) \) mode in 490-448 cm\(^{-1}\) region has further supported bonding through hydroxylamine oxygen\(^{15}\). The \( \nu(Sn-O) \) mode depends on the precise environment of the \( \nu(Sn-O) \) in the molecule. The \( \nu(Sn-Cl) \) mode in these complexes has been observed at 366-360 cm\(^{-1}\) region\(^{11}\).

**Figure 2.** Conductance composition curves of Bu\(_2\)SnCl(OAr) and Me\(_2\)SnCl(OAr) vs. FeCl\(_3\)  

**Figure 3.** Conductance composition curves of Bu\(_2\)SnCl(OAr) and Me\(_2\)SnCl(OAr) vs. AlCl\(_3\)

**Reactions of diorganotin(IV) chlorophenoxides with Lewis acids (FeCl\(_3\) and AlCl\(_3\))**

The reactivity of diorganotin(IV) phenoxides of composition R\(_2\)SnCl(OAr) (where R = n-Bu, and Me; OAr= OC\(_6\)H\(_4\)Bu\(_t\)-2 and OC\(_6\)H\(_3\)Bu\(_t\)-2-Me-4) towards Lewis acids such as FeCl\(_3\) and AlCl\(_3\) has been studied. The conductometric titrations between parent diorganotin(IV) chloro phenoxides and Lewis acids have been carried out in dry nitrobenzene at 25\(\pm\)0.1°C. The conductance values of parent diorganotin(IV) chloro phenoxides in nitrobenzene are very low. However, the addition of solutions of FeCl\(_3\) and AlCl\(_3\) in nitrobenzene results in a significant rise in the conductance of the parent organotin(IV) phenoxides. The conductance composition (acid/base) curves (Figure 2 and 3) have revealed sharp breaks at 1:1 molar ratios {Lewis acid/R\(_2\)SnCl(OAr)}; suggesting thereby the possibility of formation of compounds with 1:1 stoichiometry (Table 3).
Table 3. Analytical data and principal IR bands of organotin(IV) chloro phenoxides and AlCl₃ and FeCl₃

<table>
<thead>
<tr>
<th>Parent Complex</th>
<th>Ligand</th>
<th>Reaction product</th>
<th>Colour</th>
<th>Elemental analysis % found (calc.)</th>
<th>Molar conductance in PhNO₂ (Ohm⁻¹ cm² mol⁻¹)</th>
<th>IR data (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu₃SnCl(OC₆H₄Bu⁻-2)</td>
<td>FeCl₃</td>
<td>Bu₃Sn(OC₆H₄Bu⁻-2)⁺ FeCl₃</td>
<td>Brownish yellow</td>
<td>20.2 (20.5) 24.7 (24.5)</td>
<td>12.1 377</td>
<td></td>
</tr>
<tr>
<td>Me₂SnCl(OC₆H₄Bu⁻-2)</td>
<td>FeCl₃</td>
<td>Me₂Sn(OC₆H₄Bu⁻-2)⁺ FeCl₃</td>
<td>Dark brown</td>
<td>21.2 (21.6) 26.0 (25.8)</td>
<td>11.2 379</td>
<td></td>
</tr>
<tr>
<td>Bu₃SnCl(OC₆H₄Bu⁻-2Me-4)</td>
<td>FeCl₃</td>
<td>Bu₃Sn(OC₆H₄Bu⁻-2Me-4)⁺ FeCl₃</td>
<td>Brown</td>
<td>23.9 (24.0) 28.4 (28.6)</td>
<td>13.0 381</td>
<td></td>
</tr>
<tr>
<td>Me₂SnCl(OC₆H₄Bu⁻-2Me-4)</td>
<td>FeCl₃</td>
<td>Me₂Sn(OC₆H₄Bu⁻-2Me-4)⁺ FeCl₃</td>
<td>Brownish yellow</td>
<td>25.5 (25.5) 30.1 (30.4)</td>
<td>10.4 383</td>
<td></td>
</tr>
<tr>
<td>Bu₃SnCl(OC₆H₄Bu⁻-2)</td>
<td>AlCl₃</td>
<td>Bu₃Sn(OC₆H₄Bu⁻-2)⁺ AlCl₃</td>
<td>Brown</td>
<td>19.7 (20.0) 23.9 (23.9)</td>
<td>11.7 482</td>
<td></td>
</tr>
<tr>
<td>Me₂SnCl(OC₆H₄Bu⁻-2)</td>
<td>AlCl₃</td>
<td>Me₂Sn(OC₆H₄Bu⁻-2)⁺ AlCl₃</td>
<td>Brownish yellow</td>
<td>20.8 (21.0) 24.8 (25.1)</td>
<td>12.9 486</td>
<td></td>
</tr>
<tr>
<td>Bu₃SnCl(OC₆H₄Bu⁻-2Me-4)</td>
<td>AlCl₃</td>
<td>Bu₃Sn(OC₆H₄Bu⁻-2Me-4)⁺ AlCl₃</td>
<td>Brown</td>
<td>23.4 (23.3) 27.8 (27.8)</td>
<td>10.6 480</td>
<td></td>
</tr>
<tr>
<td>Me₂SnCl(OC₆H₄Bu⁻-2Me-4)</td>
<td>AlCl₃</td>
<td>Me₂Sn(OC₆H₄Bu⁻-2Me-4)⁺ AlCl₃</td>
<td>Brown</td>
<td>24.7 (24.7) 29.6 (29.5)</td>
<td>12.5 485</td>
<td></td>
</tr>
</tbody>
</table>

The observed continuous increase in the conductance of the solutions may be ascribed to the formation of ions in solutions as:

\[
{\text{R}_2\text{SnCl(OC}_6\text{H}_4\text{Bu}^-_2) + \text{MCl}_3 \rightarrow [\text{R}_2\text{SnCl(OC}_6\text{H}_4\text{Bu}^-_2).\text{MCl}_3] \rightarrow [\text{R}_2\text{Sn(OC}_6\text{H}_4\text{Bu}^-_2)^+.]\text{MCl}_4^-}
\]

\{Where \( R = n\text{-Bu, Me; OAr = OC}_6\text{H}_4\text{Bu}^-_2, OC}_6\text{H}_4\text{Bu}^-_2-2\text{-Me-4; M = Fe(III), Al(III)} \}\n
Substantiated from the conductance-composition curves, the compounds have actually been isolated in separate experiments by reacting the parent organotin(V) chloro phenoxides with FeCl₃ and AlCl₃ in predetermined 1:1 molar ratios in benzene. The elemental analyses of the isolated complexes supported their stoichiometric formulations as the compounds of composition \([\text{R}_2\text{Sn(OC}_6\text{H}_4\text{Bu}^-_2)]^+\cdot\text{MCl}_4^- \). The molar conductance values of milli-molar solutions of these complexes in dry nitrobenzene have been found to close to 1:1 electrolytes suggesting their electrolytic nature in nitrobenzene. The IR spectra of the compounds scanned in the 4000-200 cm⁻¹ have further substantiated their formation. Interestingly, the bands at ~360 cm⁻¹ due to \( \nu(\text{Sn-Cl}) \) modes in parent phenoxides have found to be missing in these compounds. The appearance of very sharp bands at 380 cm⁻¹ and ~485 cm⁻¹ may be assigned to \( \nu(\text{Fe-Cl}) \) and \( \nu(\text{Al-Cl}) \) modes respectively in tetrahedral anions in these complexes. It has thus been inferred that organotin(IV) chloro phenoxides behave as chloride ion donors in the presence of strong chloride ions acceptors resulting in the formation of stable ionic complexes of the type \([\text{R}_2\text{Sn(OC}_6\text{H}_4\text{Bu}^-_2)]^+\cdot\text{FeCl}_4^- \) and \([\text{R}_2\text{Sn(OC}_6\text{H}_4\text{Bu}^-_2)]^+\cdot\text{AlCl}_4^- \) in accordance with earlier eports²⁵,²⁶.

Reactions of triphenyltin(IV) phenoxides with Hg(II) salts such as chloride, bromide and acetate

The reactivity of triphenyltin(IV) phenoxides of composition Ph₃Sn(OC₆H₄Bu⁻-2) and Ph₃Sn(OC₆H₄Bu⁻-2Me-4) with mercuric(II) salts such as chloride, bromide and acetate, has been attempted, in order to investigate, the nature of the ultimate reaction product formed. The products thus obtained have been evaluated for their stoichiometric formulations (Table 4).
Table 4. Analytical and IR data of reaction products of triphenyltin(IV) phenoxides with HgCl₂/HgBr₂/Hg(ac)₂

<table>
<thead>
<tr>
<th>Parent complex</th>
<th>Hg(II) Salts</th>
<th>Product</th>
<th>Color</th>
<th>Elemental Analysis % found (Calcd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₃Sn(O₆H₄Bu'-2)</td>
<td>HgCl₂</td>
<td>Ph₃SnCl(OC₆H₄Bu'-2)</td>
<td>White</td>
<td>Sn 26.2 (26.0)  Cl 7.6 (7.8)  C 57.9 (57.8)  H 4.8 (5.0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ph₃Sn(O₆H₄Bu'-2)</td>
<td>Shining white</td>
<td></td>
</tr>
<tr>
<td>Ph₃Sn(O₆H₃Bu'-2)</td>
<td>HgBr₂</td>
<td>Ph₃SnBr(OC₆H₃Bu'-2)</td>
<td>White</td>
<td>23.7 (23.7)  Cl 67.5 (67.2)  C 6.6 (6.8)  H 4.3 (4.6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ph₃Sn(O₆H₃Bu'-2)</td>
<td>Shining white</td>
<td></td>
</tr>
<tr>
<td>Ph₃Sn(O₆H₃Bu'-2)</td>
<td>Hg(ac)₂</td>
<td>Ph₃Sn(ac)(OC₆H₃Bu'-2)</td>
<td>Off-White</td>
<td>24.5 (24.7)  Cl 60.1 (59.9)  C 5.2 (5.4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ph₃Sn(O₆H₃Bu'-2)</td>
<td>Shining white</td>
<td></td>
</tr>
<tr>
<td>Ph₃Sn(O₆H₃Bu'-2-Me-4)</td>
<td>HgCl₂</td>
<td>Ph₃SnCl(OC₆H₃Bu'-2-Me-4)</td>
<td>White</td>
<td>25.4 (25.2)  Cl 6.9 (7.2)  C 58.7 (58.5)  H 5.3 (5.3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ph₃Sn(O₆H₃Bu'-2-Me-4)</td>
<td>Shining white</td>
<td></td>
</tr>
<tr>
<td>Ph₃Sn(O₆H₃Bu'-2-Me-4)</td>
<td>HgBr₂</td>
<td>Ph₃SnBr(OC₆H₃Bu'-2-Me-4)</td>
<td>White</td>
<td>17.5 (17.4)  Cl 63.4 (63.1)  C 7.1 (7.3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ph₃Sn(O₆H₃Bu'-2-Me-4)</td>
<td>Shining white</td>
<td></td>
</tr>
<tr>
<td>Ph₃Sn(O₆H₃Bu'-2-Me-4)</td>
<td>Hg(ac)₂</td>
<td>Ph₃Sn(ac)(OC₆H₃Bu'-2-Me-4)</td>
<td>Off-White</td>
<td>24.2 (24.0)  Cl 60.4 (60.6)  C 5.5 (5.6)</td>
</tr>
</tbody>
</table>

The elemental analyses of the two isolated compounds from each reaction substantiated the compositions as Ph₂SnX(OAr) (I) and Ph₃Sn(OAr)₃ (II) (X = Cl, Br, ac; OAr = OC₆H₄Bu'-2 and OC₆H₃Bu'-2-Me-4). The following sequence of reactions may be suggested to account for the reaction products:

\[
\text{Ph}_3\text{Sn(OAr)} + \text{HgX}_2 \rightarrow \text{Ph}_2\text{SnX(OAr)} + \text{PhHgX}
\]

\[
\text{Ph}_2\text{SnX(OAr)} + \text{Ph}_3\text{Sn(OAr)} \rightarrow \text{Ph}_2\text{Sn(OAr)}_2 + \text{Ph}_3\text{SnX}
\]

\[
\text{Ph}_2\text{Sn(OAr)}_2 + \text{HgX}_2 \rightarrow \text{PhSnX(OAr)}_2 + \text{PhHgX}
\]

\[
\text{PhSnX(OAr)}_2 + \text{Ph}_3\text{Sn(OAr)} \rightarrow \text{PhSn(OAr)}_3 + \text{Ph}_3\text{SnX}
\]

\[
3\text{Ph}_3\text{Sn(OAr)} + 2\text{HgX}_2 \rightarrow \text{PhSn(OAr)}_3 + 2\text{PhHgX} + 3\text{PhSnX}
\]

{Where OAr = OC₆H₄Bu'-2, OC₆H₃Bu'-2-Me-4; X = Cl, Br, OOCCH₃}

These reactions indicate an electrophilic substitution at carbon atom bonded to tin. The nucleophilic assistance either by chlorine or phenoxy groups cannot be ruled out. The isolated products are high melting (> 250 °C) solids. The IR spectra of the compounds scanned in
region have shown the characteristic absorption bands due to phenoxide ion, tin-chlorine, tin-oxygen and tin-carbon modes. In case of compounds of composition \( \text{Ph}_2\text{Sn(ac)(OAr)} \), the appearance of bands at \( \sim 1575 \text{ cm}^{-1} \) has been ascribed to the chelated \( \nu(\text{OCO}) \) mode. It can be resolved from the present studies, that the reactions of triphenyltin(IV) phenoxides with mercuric(II) salts under present experimental conditions have led to the replacement of two phenyl groups only, thereby suggesting incomplete demetallation.

**Conclusion**

The reactivity of organotin(IV) phenoxides has been illustrated in this report. The reactions with different ligands have signified polarity of different bonds. Reactions of parent complexes with chelating ligands like acetylacetone / salicylaldehyde and potassium salts of benzohydroxamic acids have demonstrated substitution of phenoxides ion from the parent complexes. In the reactions with Lewis acids, the organotin(IV) complexes have revealed chloride ion acceptor behaviour. In contrast, reactions of organotin(IV) phenoxides with Hg(II) salts have preferentially cleaved Sn-C bond. Such studies are required to elucidate the stability of different bonds of organotin(IV) phenoxides.

**References**

12- N. Sharma and V. Kumar, Phosphorous, Sulphur and Silicon, **2011**, 186(10), 2071-2085.