

REACTION OF BUTYLTIN TRICHLORIDE WITH
SALHEXEN(TBU) [SALHEN(TBU) = N,N'-(HEXYLENE)BIS(3,5-DI-
TERT-BUTYL)SALICYLIDENEIMINE] AND SALHEPTEN(TBU)
[SALPEN(TBU) = N,N'-(HEPTYLENE)BIS(3,5-DI-TERT-
BUTYL)SALICYLIDENEIMINE]

Burl Yearwood*

Abstract:

Butyltin trichloride was reacted with **Salhexen(tBu)** [Salhen(tBu) = N,N'-(hexylene)bis(3,5-di-tert-butyl)salicylideneimine] and **Salhepten(tBu)** [Salpen(tBu) = N,N'-(heptylene)bis(3,5-di-tert-butyl)salicylideneimine]. The products of the reaction were analyzed by FT-IR, melting point, and elemental analysis. The structure of the final products was determined from the analytical results. It is proposed that the metal binds to the oxygen and nitrogen of the ligands.

Keywords: Salen, Tin, Butyltin trichloride, Salhexen, Salhepten

* Department of Natural Sciences, LaGuardia Community College, City University of New York, 31-10 Thomson Avenue, Long Island City, NY, USA 11101

Introduction

Experimental

Schiff bases are very useful reagents in organic and organometallic chemistry. Their properties can be tuned by modifying the organic backbone between the nitrogens. The complexes between Schiff bases and metals have been shown to act as catalysts, as biocidal and anti-tumor agents, and as models for biological studies (Atwood et al. 2000; Yearwood et al. 2002; Saxena and Huber, 1995). Our research looks at the complexes formed between Group 13, Group 14 metals and Salen type ligands [‘Salen’ is the name that has historically been used to describe the entire class of such ligands possessing various diamino backbones. However, it is also the specific name of the ethyl derivative, Salen = N,N’-ethylene-bis(salicylideneimine)].

Chemicals were of reagent grade. Butyltin trichloride (Aldrich) was used as received. Triethylamine (Aldrich) was dried over molecular sieves. The reagent 3,5-di-tert-butyl-2-hydroxybenzaldehyde was prepared according to the literature (Casiraghi et al, 1980). The ligands used in this study were prepared by the condensation reaction between the hydroxybenzaldehyde and the corresponding diamine. Infrared spectra were recorded on a Perkin-Elmer RX1 infrared spectrometer from 4000-200 cm^{-1} as KBr discs and were calibrated with respect to the 1601 cm^{-1} band of a polystyrene film. NMR data were obtained on a JEOL GX-400. Carbon, hydrogen, nitrogen, and tin analysis were carried out by Gailbraith Laboratories, Knoxville, TN. Melting points were determined in open capillaries and are uncorrected.

Preparation of Butyltin trichloride Salhexen(tBu) complexes:

In a round bottom flask, fitted with a reflux condenser, triethylamine (0.98 ml, 7.04 mmol) was added to a solution of $\text{H}_2\text{Salhexen(tBu)}$ (x.xx g, 3.00 mmol) in toluene (40 mL). A solution of butyltin trichloride (0.xxx g, 3.00 mmol) in 20mL of toluene was then added slowly to the round bottom flask. The solution turned red. After addition of butyltin trichloride, the mixture was refluxed. The suspension was allowed to cool to room temperature, and the precipitated triethylamine hydrochloride was filtered off. The final product was analyzed. The butyltin derivative of $\text{H}_2\text{Salhepten(tBu)}$ was synthesized in a similar procedure to that described above. The pertinent data for the compounds are listed below:

(Bu)Sn(Salhexen(tBu))Cl (**1**):

1 was prepared from 1.65 g (3.0 mmol) of H₂Salhexen(tBu) and 0.846 g (3.00 mmol) of BuSnCl₃. Yield 81 %. M.p. 167-168 °C. Red solid.

Elemental Analysis: Anal % (Calc %) for C₃₆H₅₄N₂O₂SnCl₂: C, 58.76 (58.71), H, 7.40 (7.39), N, 3.78 (3.80), Sn, 16.10 (16.12).

IR Data: 2938(s), 2860(s), 1650(vs), 1610(vs), 1624(vs), 1540(s), 1455(m), 1405(m), 1380(s), 1345(m), 1335(m), 1280(s), 1260(vs), 1235(s), 1200(s), 1162(s), 1240(s), 1200(s), 1165 (m), 1100(s), 1030(s), 975(m), 928(w), 870(w), 795(s), 600(w), 547(m), 490(m), 300(m)

(Bu)Sn(Salhepten(tBu))Cl (**2**):

2 was prepared from 1.69 g (3.0 mmol) of H₂Salhepten(tBu) and 0.846 g (3.00 mmol) of BuSnCl₃. Yield 81 %. M.p. 167-168 °C. Red solid.

Elemental Analysis: Anal % (Calc %) for C₃₇H₅₆N₂O₂SnCl₂: C, 59.25 (59.22), H, 7.50 (7.52), N, 3.69 (3.73), Sn, 15.80 (15.82).

IR Data: 2940(s), 2860(s), 1651(vs), 1615(vs), 1650(vs), 1540(s), 1457(m), 1400(m), 1380(s), 1345(m), 1330(m), 1282(s), 1260(vs), 1231(s), 1200(s), 1164(s), 1240(s), 1200(s), 1166 (m), 1103(s), 1031(s), 973(m), 930(w), 871(w), 795(s), 602(w), 545(m), 495(m), 301(m)

The reaction between the organotin trichloride and the Salen type ligand is an elimination reaction. In complexes **1** and **2**, tin binds to the nitrogen and the oxygen of the Schiff base, as shown in Figure 1.

The IR spectra of **1** and **2** were recorded along with those of the starting reagents. A very significant feature in the spectra of **1** and **2** is the absence of $\nu(\text{OH})$ bands of the phenolic OH groups expected in the region 3000 - 3700 cm⁻¹ that is present in the IR of the Salen ligand starting material. This indicates oxygen bonding to the metal after replacement of the phenolic hydrogen. The infrared spectrum of the ligands show a HC=N stretching vibration at 1618 and 1690 cm⁻¹ for Salhexen and Salhepten respectively. In **1** and **2** this mode is shifted to lower frequencies, 1610 cm⁻¹ (**1**) and 1650 cm⁻¹ respectively indicating the coordination of the azomethine nitrogen atoms to the organotin(IV) moiety.

Further evidence for coordination in the complexes is seen in the new Sn-O bands at 547 (**1**) and 545 (**2**) cm⁻¹. The $\nu(\text{Sn-O})$ modes are reported to be at 515–613 cm⁻¹ for different organotin(IV)

complexes of Schiff bases, at 540-560 cm^{-1} organotin salicylideneimine ligands (Yearwood et al, 2002), and at 490-510 cm^{-1} for some methyltin(IV) complexes (Teoh et al, 1997).

The IR spectra also shows Sn-N bands at 490 (1) and 495 (2) cm^{-1} . Frequencies for $\nu(\text{Sn-N})$ have been reported at 450-500 cm^{-1} for organotin salicylideneimine ligands (Yearwood et al, 2002; Garnovskii et al, 1993). Absorptions for Sn-Cl are observed at 300 cm^{-1} for **1** and at 301 cm^{-1} for **2**.

Further evidence for the structures proposed in Figure 1 is provided by the elemental analysis results which agree with the calculated formula.

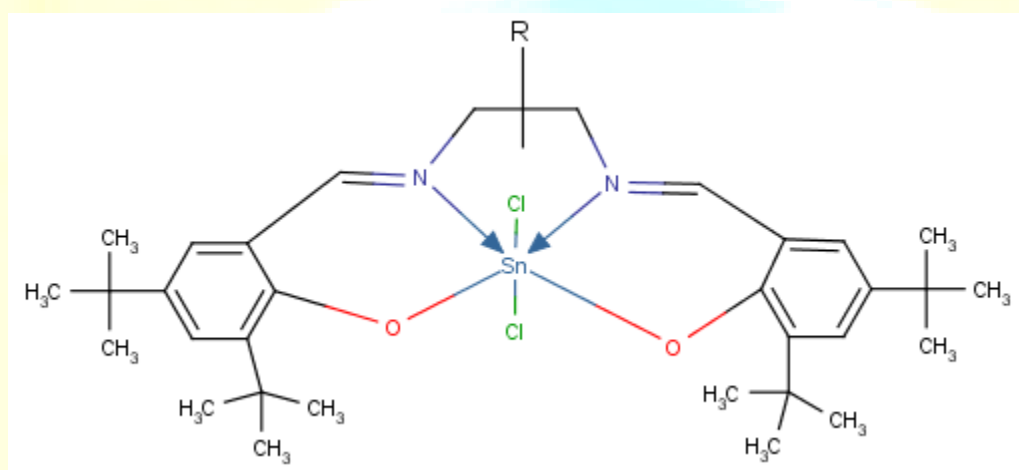


Figure 1. General structure of Butyltin trichloride Salhexen(tBu) [R = $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$] and Butyltin trichloride Salhepten(tBu) [R = $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$]

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