

Reactions of [η^5 -carboxycyclopentadiene][η^4 -tetraphenylcyclobutadiene] cobalt with alkyl and aryl tin oxides: Synthesis, structural studies and electrochemistry of novel monomeric and dimeric [η^5 -carboxycyclopentadiene][η^4 -tetraphenylcyclobutadiene]cobalt based stannoxanes

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Abstract

Reactions of [η^5 -carboxycyclopentadienyl][η^4 -tetraphenylcyclobutadiene] cobalt, $\text{Ph}_4\text{C}_4\text{CoC}_5\text{H}_4\text{COOH}$ (**1**), with $(\text{Ph}_3\text{Sn})_2\text{O}$, $[(n\text{-Bu})_2\text{SnO}]_n$, and $(\text{Ph}_2\text{SnO})_n$ in refluxing toluene resulted in the formation of the monomeric compound $\text{Ph}_3\text{SnOC}(\text{O})\text{C}_5\text{H}_4\text{CoC}_4\text{Ph}_4$ (**2**) and dimeric compounds $n\text{-Bu}_2\text{Sn}[\text{OC}(\text{O})\text{C}_5\text{H}_4\text{CoC}_4\text{Ph}_4]_2$ (**3**) and $\text{Ph}_2\text{Sn}[\text{OC}(\text{O})\text{C}_5\text{H}_4\text{CoC}_4\text{Ph}_4]_2$ (**4**), respectively. Reactions carried out in the solid state by mechanical grinding also yielded same results. Crystal structure determination and cyclic voltammetric studies of compounds **1**, **2**, **3** and **4** have been carried out and compared with similar ferrocene carboxylic acid derivatives. The structures and electrochemistry of these compounds are compared with analogous organotin ferrocene carboxylates. The results obtained from the reaction of **1** with alkyl and aryl tin oxides suggest that the formation of stannoxanes assemblies having more than two carboxylate units are not favored indicating that **1** is a highly sterically hindered metallocene carboxylic acid.

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1. Introduction

In recent years there has been considerable interest in organotin cages and clusters due to their stability and structural diversity as well as for their importance in catalysis and other applications [1,2]. Among several such organostannoxane compounds, the most versatile are compounds prepared by the reaction of organotin oxides and stannonic acids with a variety of carboxylic acids [3,4]. The structural diversity of these stannoxanes ranges from drums, ladders, tetramers and dimers to monomers [1,3–5]. The preference of a particular organostannoxane to

adopt these structures stems from a combination of steric and electronic factors. Stannoxanes having multiferrocenyl assemblies mimicking dendrimers have resulted when ferrocene based carboxylic acids are used in these reactions [6]. The robustness and redox inactivity of the stannoxane framework coupled with the control on the number and orientation of ferrocenyl groups and potential use as electroactive materials were reasons for introducing ferrocene units on organostannoxanes [6,7]. It is of interest to note that although a host of carboxylic acids have been reacted with tin oxides and other organotin compounds, the only carboxylic acid containing an organometallic unit among them is still that which contains a ferrocene moiety [6–8]. Unlike ferrocene based carboxylic acids, which has revealed a wide-ranging chemistry [9], very little has been

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explored on the synthesis and reactions of other metallocenyl carboxylic acids. In this regard, the chemistry of $[\eta^5\text{-carboxycyclopentadienyl}][\eta^4\text{-tetraphenylcyclobutadiene}]$ cobalt, $\text{Ph}_4\text{C}_4\text{CoC}_5\text{H}_4\text{COOH}$, a highly stable and neutral cobalt(I) carboxylic acid becomes significant. First prepared in 1996 by Mabrouk and Rausch [10], this compound has recently been used in making novel oxazolidine based chiral metallocenyl ligands and in asymmetric catalysis [11]. In this paper we report the reactions of this sterically hindered organometallic carboxylic acid with alkyl and aryl tin oxides and compare the products obtained and their electrochemistry with products from similar reactions of ferrocene carboxylic acid.

2. Results and discussion

Recent reports on the preparation of organostannoxane clusters using carboxylic acids indicate two different synthetic approaches. The traditional method involves reactions carried out in a solvent such as benzene or toluene with the azeotropic removal of water, while a more recent approach involves mechanical grinding of the two reactants at room temperature, followed by solvent extraction [8]. As our interest was to explore the reactions of **1** with organotin oxides and compare the chemistry to ferrocene carboxylic acid, we have carried out reactions under both these conditions. We have observed that for compounds **2**, **3** and **4**, the results obtained under both these reaction conditions are the same with slight variations in the yield of products.

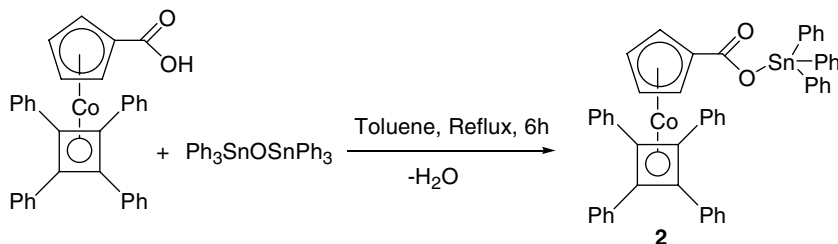
The reaction of bis(triphenyltin) oxide with **1** in 1:2 molar ratio afforded the compound $[\text{Ph}_3\text{SnOC(O)C}_5\text{H}_4\text{-CoC}_4\text{Ph}_4]$ (**2**) (Scheme 1) in 70% yield. Compound **2** is very stable and was recrystallized from a chloroform/hexane mixture. Under analogous reaction conditions, ferrocene carboxylic acid yielded a similar monomeric compound [7,12]. The ^{119}Sn NMR spectrum of compound **2** in CDCl_3 solution exhibit a single resonance peak at -117.82 ppm, which is observed in the range for four coordination of triphenyltin compounds in solution (-40 to -120 ppm) [13].

The reaction of di-*n*-butyltin oxide with **1** in 1:2 molar ratio gave exclusively the mononuclear dicarboxylate **3** (Scheme 2). In compound **3**, the two metallocenyl moieties are *trans* to each other. In contrast, a reaction of 1:2 molar

ratio of di-*n*-butyltin oxide and ferrocene carboxylic acid gave exclusively the mononuclear dicarboxylate $n\text{-Bu}_2\text{Sn}[\text{OC(O)Fc}]_2$ which had both *cis* and *trans* forms in the same unit cell [7]. A reaction in 1:1 molar ratio of ferrocene carboxylic acid with di-*n*-butyltin oxide had resulted in a tetranuclear tin derivative $\{[n\text{-Bu}_2\text{SnOC(O)Fc}]_2\text{O}\}_2$ [8,12]. However, under identical reaction conditions in 1:1 molar ratio, reaction of **1** with di-*n*-butyltin oxide gave exclusively the mononuclear dicarboxylate **3**. An attempt to make the tetrameric compound by carrying out the reaction in refluxing xylene also was not successful.

It is of interest to note that reactions of even moderately sterically bulky carboxylic acids such as 2,4,6-tris(trifluoromethyl)benzoic acid and 2,6-dimethylbenzoic acid with di-*n*-butyltin oxide in 1:1 molar ratio gave the tetranuclear tetracarboxylate $\{[n\text{-Bu}_2\text{SnOC(O)-2,4,6-(CF}_3)_3\text{C}_6\text{H}_2\text{O}]\}_2$ and $\{[n\text{-Bu}_2\text{SnOC(O)CH(CH}_3)_2\text{O}]\}_2$ [14], respectively. In addition, the reaction of 3,5-diisopropylsalicylic acid with di-*n*-butyltin oxide in 1:1 ratio resulted in a hexameric compound $[n\text{-Bu}_2\text{Sn-3,5-}i\text{-Pr}_2\text{C}_6\text{H}_2(\text{O})(\text{COO})_6]$ [5a].

The reaction of **1** when carried out with diphenyltin oxide in both 1:1 and 2:1 molar ratios afforded exclusively the *trans* mononuclear dicarboxylate compound **4** in almost quantitative yields similar to the reaction of **1** with di-*n*-butyltin oxide. Under similar reaction conditions, the reaction of ferrocene carboxylic acid with diphenyltin oxide in 1:1 and 2:1 molar ratios did not yield the mononuclear dicarboxylate, but resulted only in the dinuclear tetracarboxylate compound $\{\text{Ph}_2\text{Sn}[\text{OC(O)Fc}]_2\}_2$ (Scheme 2). The formation of both **3** and **4** only in the *trans* forms and also only as dicarboxylates from 1:1 and 1:2 molar ratio reactions indicates that the steric effect of the four phenyl groups present in the cyclobutadiene ring significantly influence the nature of the products formed, suggesting **1** as a highly sterically hindered carboxylic acid. The results also clearly indicate that reactivity of **1** with alkyl and aryl tin oxides differ considerably with that of ferrocene carboxylic acid and other moderately sterically bulky carboxylic acids [15]. The ^{119}Sn NMR spectra of compounds **3** exhibit a single resonance peak at -140.34 ppm, which confirms a five coordinate geometry of the tin atom in solution (-90 to -190 ppm) [13]. Compound **4** gave a single ^{119}Sn NMR peak at -280.80 ppm. This chemical shift value is consistent with the hexacoordinate environment around tin (2C, 4O) [7].



Scheme 1. Reaction of **1** with bis(triphenyltin) oxide forming monomeric organostannoxane **2**.

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