

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

Muthiah Senthil Kumar, Shailesh Upreti, Hanuman P. Gupta, Anil J. Elias \*

*Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110 016, India*

Received 31 May 2006; received in revised form 11 July 2006; accepted 13 July 2006

Available online 27 July 2006

## Abstract

Reactions of [ $\eta^5$ -carboxycyclopentadienyl][ $\eta^4$ -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.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** [ $\eta^5$ -Carboxycyclopentadiene][ $\eta^4$ -tetraphenylcyclobutadiene]cobalt; Alkyl; Aryl; Stannoxanes; Monomer; Dimer

## 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

\* Corresponding author. Tel.: + 91 11 26591504.  
E-mail address: [eliasanil@gmail.com](mailto:eliasanil@gmail.com) (A.J. Elias).

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.

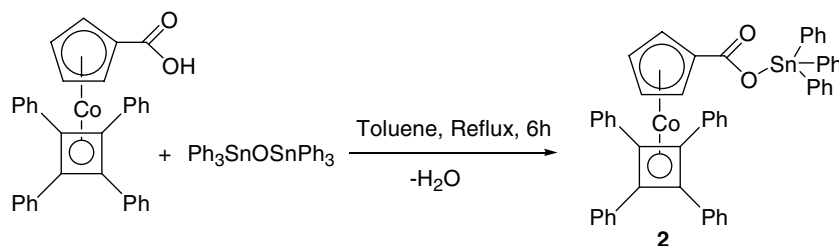
The reaction of bis(triphenyltin) oxide with **1** in 1:2 molar ratio afforded the compound  $[\text{Ph}_3\text{SnOC(O)C}_5\text{H}_4\text{-CoC}_4\text{Ph}_4]$  (**2**) (Scheme 1) in 70% yield. Compound **2** is very stable and was recrystallized from a chloroform/hexane mixture. Under analogous reaction conditions, ferrocene carboxylic acid yielded a similar monomeric compound [7,12]. The  $^{119}\text{Sn}$  NMR spectrum of compound **2** in  $\text{CDCl}_3$  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

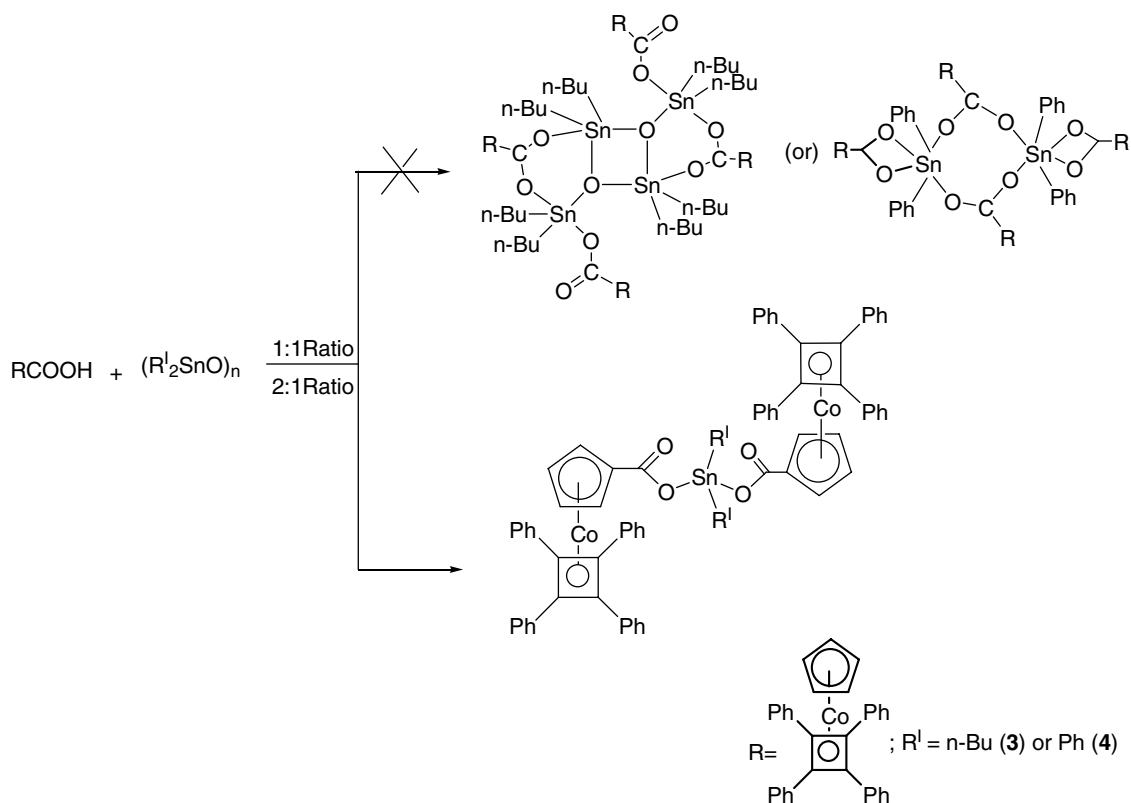
ratio of di-*n*-butyltin oxide and ferrocene carboxylic acid gave exclusively the mononuclear dicarboxylate  $n\text{-Bu}_2\text{Sn}[\text{OC(O)Fc}]_2$  which had both *cis* and *trans* forms in the same unit cell [7]. A reaction in 1:1 molar ratio of ferrocene carboxylic acid with di-*n*-butyltin oxide 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  $^{119}\text{Sn}$  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  $^{119}\text{Sn}$  NMR peak at  $-280.80$  ppm. This chemical shift value is consistent with the hexacoordinate environment around tin (2C, 4O) [7].



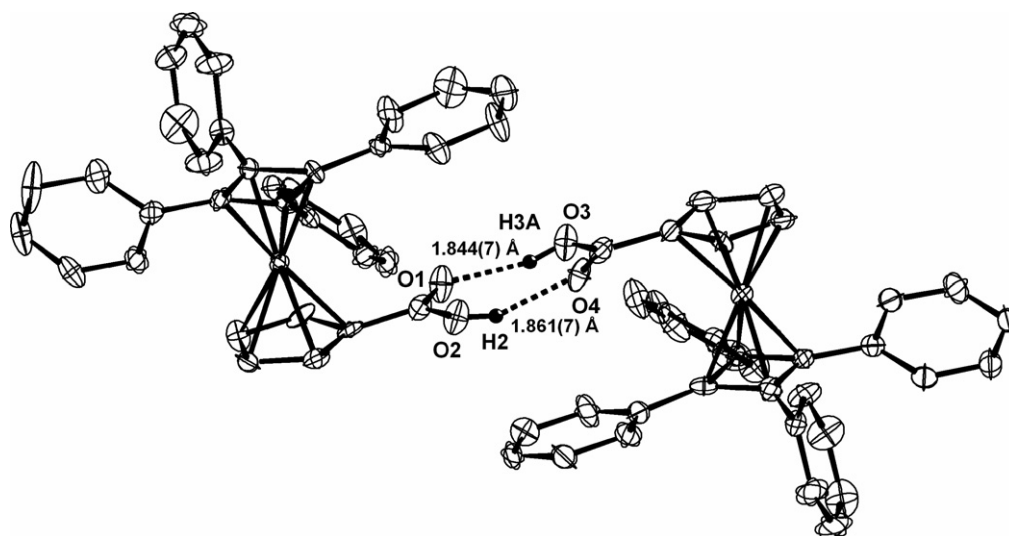
Scheme 1. Reaction of **1** with bis(triphenyltin) oxide forming monomeric organostannoxane **2**.

Scheme 2. Reactions of **1** with di-*n*-butyltin oxide and diphenyltin oxide.

### 2.1. Molecular structures of **1**, **2**, **3** and **4**

Since the crystal structure of the parent carboxylic acid has not been reported so far, we have carried out its crystal structure to compare its structural features to that of its organostannoxane complexes. Red colored crystals of **1**, suitable for X-ray crystallography were obtained by slow evaporation of its chloroform solution. The crystal structure of **1** shows that it exists as a dimer and the car-

boxylic acid group is hydrogen bonded [ $\text{O} \cdots \text{H}$  1.844(7) Å and 1.861(7) Å, Fig. 1], similar to ferrocene carboxylic acid. Further, one of the phenyl groups present on the cyclobutadiene ring makes weak  $\text{C-H} \cdots \pi$  interaction with the centroid of the cyclopentadienyl ring of the neighbouring molecule [2.983(1) Å]. The combination of comparatively stronger H-bonding and weak  $\text{C-H} \cdots \pi$  interaction in **1** leads to a three-dimensional supramolecular architecture.

Fig. 1. Thermal ellipsoid view of **1** showing  $\text{O-H} \cdots \text{O}$  hydrogen bonding (with 30% probability factor).

The molecular structure of **2** shows that the triorganotin carboxylate adopts a discrete monomeric structure which resembled structures of few other triphenyltin aryl carboxylates [1,7]. The two oxygen atoms present in the carboxylate group attached to the tin were in an anisobidentate chelating [Sn1–O1 2.750(3) Å and Sn1–O2 2.057(3) Å] coordination mode (Fig. 2). Similar anisobidentate bonding distances for the analogous ferrocenecarboxylate were Sn1–O1 2.080(2) Å and Sn1–O2 2.598(2) Å, respectively [7]. The presence of seven phenyl groups and cyclopentadienyl group lead to an unusual supramolecular assembly.

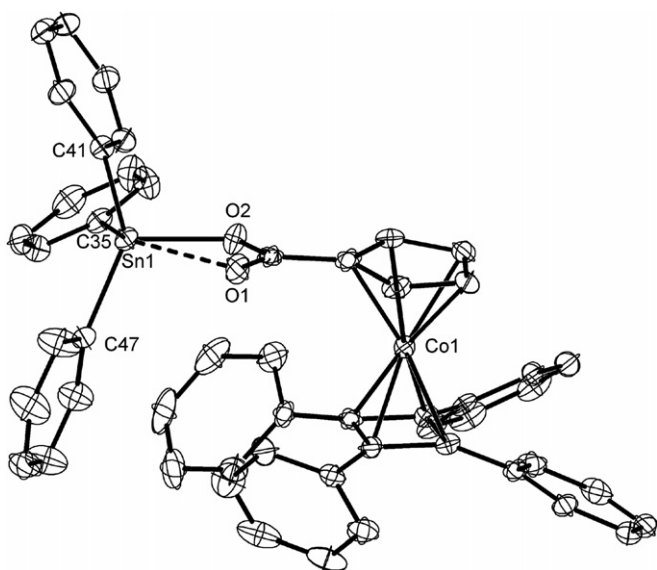


Fig. 2. Thermal ellipsoid view of compound **2** (with 30% probability factor).

Three different C–H··· $\pi$  interactions were observed in between the phenyl groups (2.658(6) Å and 3.201(1) Å, Fig. 3) and between the cyclopentadienyl and phenyl groups. It is of interest to note that the novel CO<sub>2</sub>– $\pi$  weak interaction reported in the ferrocene analogue was absent in this molecule [7].

The mononuclear tin dicarboxylate **3** crystallizes as a chloroform solvate. Unlike the ferrocene analogue, which crystallizes in *cis* and *trans* forms in the same unit cell, **3** crystallizes only in *trans* form, which can be attributed to the steric bulkiness of the tetraphenyl cyclobutadiene moiety [7]. The tin atom is hexacoordinate and the geometry around the tin can be described as a skewed trapezoidal bipyramid [16]. The two carboxylate ligands are coordinated to the tin atom in an anisobidentate mode [Sn1–O1 2.650(6) Å, Sn1–O2 2.096(5) Å, Sn1–O3 2.115(5) Å and Sn1–O4 2.439(7) Å (Fig. 4)]. The angle subtended by the butyl carbon atoms on the tin atom (C69–Sn1–C73) is 132.52(34)°, whereas in the *trans* ferrocene analogue it was 145.0(3)° and 146.6(2)° in the case of the *cis* isomer [7]. Similar to compound **1**, compound **2** is rich in weak interactions. For example, the cyclopentadienyl ring of one molecule makes weak C–H··· $\pi$  parallel displaced stacking (3.812(1) Å) interaction with the cyclopentadienyl ring of the neighbouring molecule.

The mononuclear tin dicarboxylate **4** crystallizes as a dichloromethane solvate. The unit cell contains two independent molecules in the asymmetric unit. Similar to compound **3**, here also the tin atom is six-coordinate with a C2O4 coordination environment with skewed trapezoidal bipyramidal geometry. The two cobalt sandwich moieties are *trans* to each other. The two carboxylate ligands are coordinated to the tin atom in an anisobidentate coordination

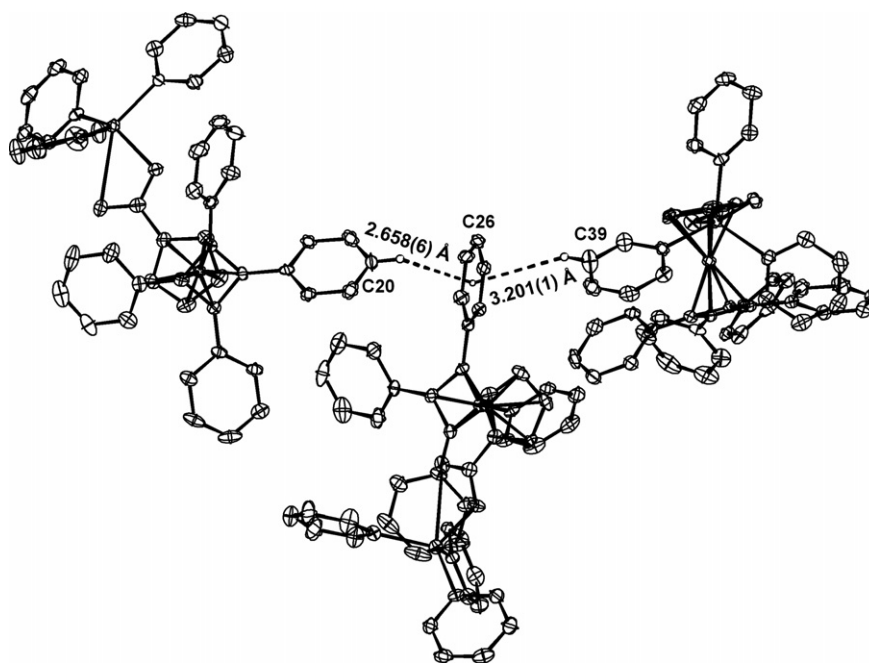


Fig. 3. Thermal ellipsoid view of compound **2** showing weak intermolecular C–H··· $\pi$  interaction (with 30% probability factor).

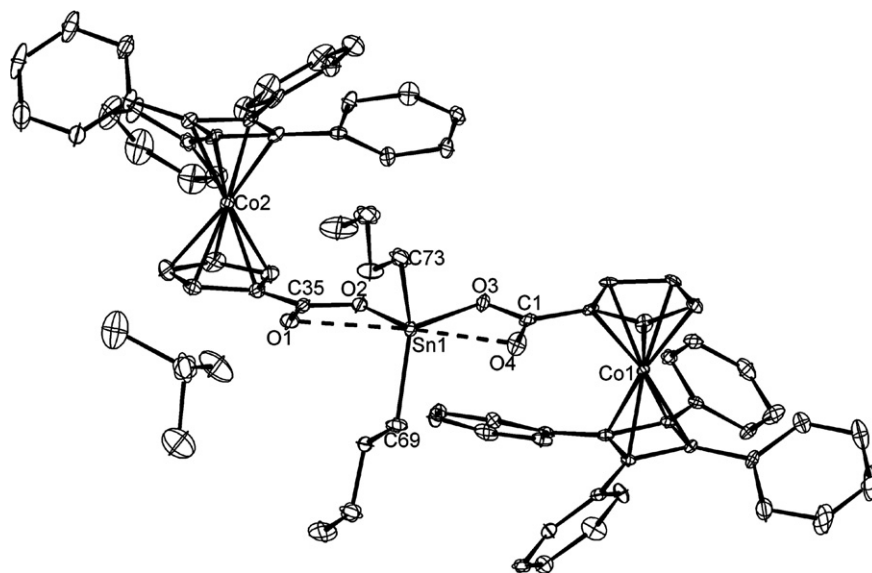


Fig. 4. Thermal ellipsoid view of compound **3** with chloroform as a solvate (with 30% probability factor).

mode. However, unlike compound **3**, which has four different Sn–O bond distances for two carboxylate ligands, compound **4** has only two different values of Sn–O bond distances for two carboxylate ligands [Sn1–O1 2.521(5) Å and Sn1–O2 2.087(5) Å]. The two independent asymmetric units differ from each other from the angles between the mean planes containing O–Sn–O atoms [O1'–Sn1–O1 21.04° and O3'–Sn1–O3 14.67°] (Fig. 5). The tin atom is flanked by the two phenyl groups (C75–Sn1–C75') by an angle of 122.56(37)° (see Tables 1 and 2).

## 2.2. Electrochemical studies

Electrochemical studies on compounds **1–4** were carried out using cyclic voltammetry. The cyclic voltammogram of **1** (Fig. 6) shows only one reversible peak with  $E_{1/2}$  at

862.5 mV. Compound **2** shows one irreversible process with anodic potential  $E_p^A$  value at 1287 mV, indicating that for compound **2**, oxidation process is more facile than the reduction process. This observation is not unusual as we have observed that although the tetraphenylcyclobutadienyl carboxylic acid **1** gives a reversible voltammogram, related carboxylic acids having other substituents on the cyclopentadienyl ring gives quasi-reversible cyclic voltammograms under identical conditions of measurement with a dominant oxidation peak [17]. Cyclic voltammogram of compound **3** shows no electron transfer processes indicating its electrochemical stability under the given conditions. In contrast, compound **4** shows one reversible redox couple at an  $E_{1/2}$  value of 806 mV (Fig. 7). The occurrence of a single reversible peak indicates that, the electrochemical behaviour of two metallocenyl units in **4** are same and this

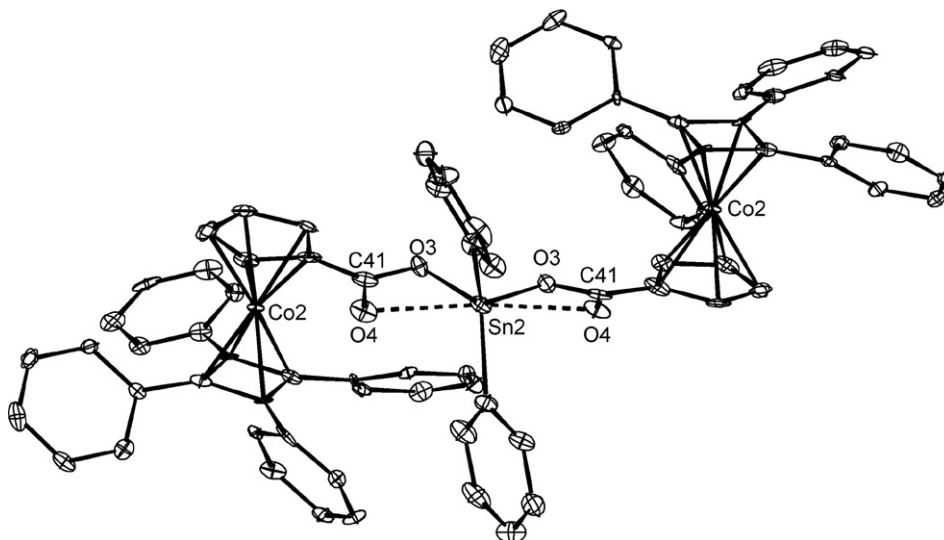


Fig. 5. Thermal ellipsoid view of compound **4** (with 50% probability factor).

Table 1  
Crystallographic data of compounds **1–4**

Compound	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Empirical formula	C <sub>35</sub> H <sub>27</sub> CoO <sub>2</sub> ·CHCl <sub>3</sub>	C <sub>52</sub> H <sub>39</sub> CoO <sub>2</sub> Sn	C <sub>76</sub> H <sub>66</sub> Co <sub>2</sub> O <sub>4</sub> Sn · 2CHCl <sub>3</sub> C <sub>80</sub> H <sub>54</sub>	Co <sub>2</sub> O <sub>4</sub> Sn <sub>3</sub> ·3CH <sub>2</sub> Cl <sub>2</sub>
Formula weight	655.00	873.47	1518.60	1570.58
Temperature (K)	298(2)	150(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	11.4656(16)	14.310(3)	27.880(3)	24.3056(16)
<i>b</i> (Å)	17.134(2)	15.527(4)	9.3487(9)	26.1679(17)
<i>c</i> (Å)	15.774(2)	18.308(4)	28.443(3)	22.0854(14)
$\alpha$ (°)	90	90	90	90
$\beta$ (°)	103.489(3)	90	112.213(2)	91.158(2)
$\gamma$ (°)	90	90	90	90
<i>V</i> (Å <sup>3</sup> )	3013.3(7)	4067.8(16)	6863.4(12)	14044.0(16)
<i>D</i> <sub>calc</sub> (Mg/m <sup>3</sup> )	1.418	1.426	1.470	1.486
Minimum and maximum transmission	0.901 and 0.933	0.733 and 0.875	0.759 and 0.887	0.839 and 0.889
Absorption coefficient (mm <sup>-1</sup> )	0.867	1.063	1.123	1.101
<i>F</i> (000)	1318	1776	2978	6368
Crystal habit, color	Rod, Red	Block, Red	Block, Red	Block, Red
Crystal size (mm)	0.219 × 0.098 × 0.082	0.371 × 0.247 × 0.129	0.327 × 0.203 × 0.109	0.218 × 0.130 × 0.110
$\theta$ Range for data collection (°)	1.33–25.08	2.22–25.00	1.30–25.50	1.46–25.23
Index ranges	–13 ≤ <i>h</i> ≤ 13, –20 ≤ <i>k</i> ≤ 20, –18 ≤ <i>l</i> ≤ 18	–17 ≤ <i>h</i> ≤ 17, –18 ≤ <i>k</i> ≤ 18, –21 ≤ <i>l</i> ≤ 21	–33 ≤ <i>h</i> ≤ 33, –11 ≤ <i>k</i> ≤ 11, –34 ≤ <i>l</i> ≤ 34	–29 ≤ <i>h</i> ≤ 29, –31 ≤ <i>k</i> ≤ 31, –26 ≤ <i>l</i> ≤ 26
Number of reflections collected	28 946	37 981	66 204	66 517
Number of independent reflections ( <i>R</i> <sub>int</sub> )	5553 (0.0661)	4029 (0.0477)	12 726 (0.5783)	12 698 (0.0845)
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.0943	0.0288	0.0966	0.0993
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>b</sup>	0.2045	0.0760	0.2039	0.2076
<i>S</i> (all data) <sup>c</sup>	1.166	1.236	1.385	1.128
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.721 and –0.865	0.854 and –0.517	2.005 and –1.518	0.973 and –1.843

$$^a R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|.$$

$$^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)] \}^{1/2}.$$

Table 2  
Selected bond lengths (Å) and bond angles (°) of compounds **1–4**

Compounds	Bond lengths (Å)		Bond angles (°)	
Ph <sub>4</sub> C <sub>4</sub> CoC <sub>5</sub> H <sub>4</sub> COOH ( <b>1</b> )	Co1–C2	2.068(8)	O1–C1–O2	124.33(90)
	Co1–C7	1.994(7)		
[Ph <sub>3</sub> SnOC(O)CpCoCbPh <sub>4</sub> ] ( <b>2</b> )	Sn1–O2	2.057(3)	C41–Sn1–C35	112.37(15)
	Sn1–O1	2.750(3)	C35–Sn1–O2	92.44(12)
			C35–Sn1–C47	112.37(15)
			C41–Sn1–C47	114.92(13)
[ <i>n</i> -Bu <sub>2</sub> Sn{OC(O)C <sub>5</sub> H <sub>4</sub> CoPh <sub>4</sub> } <sub>2</sub> ] ( <b>3</b> )	Sn1–O1	2.650(6)	C69–Sn1–C73	132.52(34)
	Sn1–O2	2.096(5)	O2–Sn1–O3	81.35(19)
	Sn1–O3	2.115(5)	O1–Sn1–O4	167.97(18)
	Sn1–O4	2.439(7)		
[Ph <sub>2</sub> Sn{OC(O)C <sub>5</sub> H <sub>4</sub> CoC <sub>4</sub> Ph <sub>4</sub> } <sub>2</sub> ] ( <b>4</b> )	Sn1–O1	2.521(5)	C75–Sn2–C75'	122.56(37)
	Sn1–O2	2.087(5)	O3–C41–O1	118.89(71)
	Sn2–O4	2.493(7)	O3–Sn2–O4	56.40(19)
	Sn2–O3	2.077(5)	O1–Sn1–O2	55.60(17)

is in accordance with the results obtained from the molecular structure of **4**. The *E*<sub>1/2</sub> values obtained for **1**, **2** and **4** are within the range of values reported by Gleiter et al. for similar cobalt metallocenyl systems [18]. It is very interesting to note that, while compound **1** shows slow electrochemical decomposition after second cycle, compounds **2**

and **4** are very stable even after five electrochemical cycles. The difference observed between the cyclic voltammograms of **2**, **3** and **4** compared to the free acid **1**, suggests that the stannoxane framework affects the electrochemical behaviour of compounds **2**, **3** and **4**. These results are in contrast with the results obtained from the ferrocene carboxylic acid

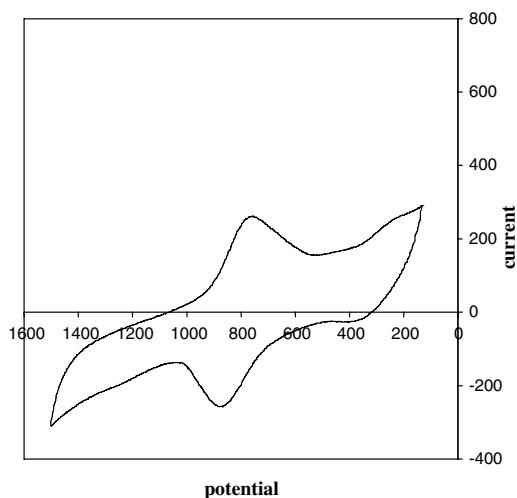


Fig. 6. Cyclic voltammogram of **1** in  $\text{CH}_2\text{Cl}_2$  with 0.1 M  $\text{Bu}_4\text{NClO}_4$  as supporting electrolyte at  $0.1 \text{ V s}^{-1}$  at  $25^\circ\text{C}$  using  $\text{Ag}/\text{AgCl}$  electrode as a reference.

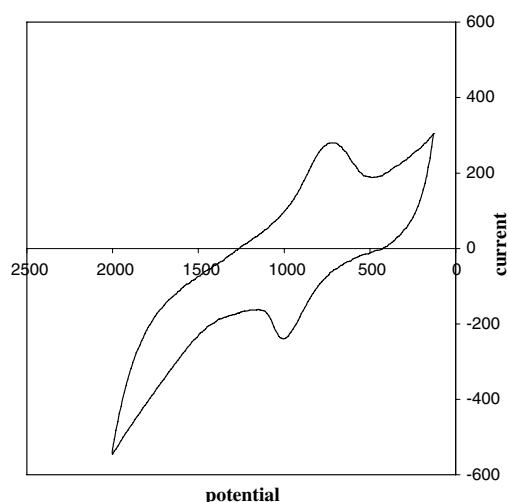


Fig. 7. Cyclic voltammogram of **4** in  $\text{CH}_2\text{Cl}_2$  with 0.1 M  $\text{Bu}_4\text{NClO}_4$  as supporting electrolyte at  $0.15 \text{ V s}^{-1}$  at  $25^\circ\text{C}$  using  $\text{Ag}/\text{AgCl}$  electrode as a reference.

based stannoxanes, which showed an almost complete redox-inactivity of stannoxane cores [8]. However, a detailed electrochemical study on more examples of similar type of compounds is required to ascertain these observations.

### 3. Conclusions

We have carried out the first reactions of  $[\eta^5\text{-carboxycyclopentadienyl}][\eta^4\text{-tetraphenylcyclobutadiene}]$ cobalt,  $\text{Ph}_4\text{C}_4\text{CoC}_5\text{H}_4\text{COOH}$  with alkyl and aryl tin oxides. New organometallic cobalt based stannoxanes **2**, **3** and **4** have been prepared and structurally characterized. 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 seems to suggest that the formation of stannoxane assemblies having more than two carboxylate units are not favored in these reactions indicating that **1** is a highly sterically hindered metallocene carboxylic acid. Also we wish to report that our preliminary attempts of the reaction of **1** with *n*-butylstannonic acid in both solution phase and solvent-free methods, which is expected to give hexameric drum cluster failed to give any isolable product, further conforming the above findings. Electrochemical studies on compounds **1** to **4** show that unlike ferrocene derived stannoxanes which in almost all cases showed redox inactivity [10] the stannoxane cores seems to influence the electrochemical behaviour of the metallocenyl units in these compounds.

## 4. Experimental

### 4.1. General procedure

All manipulations of the complexes were carried out using standard Schlenk techniques under nitrogen atmosphere. All reactions were carried out by two different methods namely using toluene as solvent with azeotropic removal of water and by the solvent free method involving mechanical grinding. Toluene was freshly distilled from sodium benzophenone ketyl under nitrogen atmosphere and used.  $[(n\text{-Bu})_2\text{SnO}]_n$ ,  $(\text{Ph}_3\text{Sn})_2\text{O}$  and  $(\text{Ph}_2\text{SnO})_n$  were procured from Aldrich and used as such.  $\text{Ph}_4\text{C}_4\text{CoC}_5\text{H}_4\text{COOH}$  (**1**) was prepared following the reported procedure [11].  $^1\text{H}$ ,  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR and spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13 and 75.47 MHz, respectively.  $^{119}\text{Sn}$  NMR was recorded on a JEOL GSX 400 NB FT-NMR spectrometer. IR spectra in the range  $4000\text{--}250 \text{ cm}^{-1}$  were recorded on a Nicolet Protège 460 FT-IR spectrometer as KBr pellets. Elemental analyses were carried out on a Carlo Erba CHNSO 1108 elemental analyzer.

### 4.2. Crystal structure studies

Single-crystal diffraction studies were carried out on a Bruker Smart Apex CCD diffractometer with a  $\text{Mo K}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) sealed tube. All crystal structures were solved by direct methods and refined using the SHELXTL package [19]. All hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters.

### 4.3. Electrochemical studies

All electrochemical measurements were taken in basic electrochemistry system ECDA-001, using a three-electrode configuration of a Pt working electrode (0.1 mm diameter), commercially available  $\text{Ag}/\text{AgCl}$  electrode as the reference electrode and a Pt mesh electrode as a counter

electrode. Half-way potentials were measured as the average of the cathodic and anodic peak potentials. The voltammograms were recorded in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte, and the potential was scanned from 0 to +2 V at various scan rates. Ferrocene gave a reversible single redox couple with  $E_{1/2}$  at 664 mV under the same experimental condition.

#### 4.4. General synthetic procedure for the preparation of **2**, **3** and **4**

A stoichiometric mixture of the organotin oxide and **1** in toluene (100 mL) was heated under reflux for 6 h. The water formed in the reaction was removed by using a Dean-Stark apparatus. Solvent was evaporated from the mixture and dried in vacuo for 2 h. The resulting solid material was dissolved in dichloromethane, filtered using a G3 frit and recrystallized from corresponding solvents. Crystals of **1**, **2**, **3** and **4** suitable for X-ray analysis were obtained by slow evaporation of their saturated solutions in chloroform/hexane mixture for compounds **1**, **2** and **3** and in dichloromethane/hexane mixture for compound **4**. All the above compounds are stable at room temperature and to air.

Compounds **2**, **3**, and **4** were also prepared by a solvent-free method. In this method, similar to the procedure reported by Chandrasekhar and co-workers [8], a stoichiometric mixture of the organotin precursor and **1** were ground to a fine powder for 45 min using a mortar and pestle. At the completion of the grinding period, the product was extracted in dichloromethane, filtered and recrystallized.

##### 4.4.1. $\text{Ph}_3\text{SnOC}(\text{O})\text{C}_5\text{H}_4\text{CoC}_4\text{Ph}_4$ (**2**)

Bis(triphenyltin)oxide (0.17 g, 0.20 mmol), **1** (0.25 g, 0.48 mmol), 0.14 g (70% yield); solvent-free method, grinding time is 45 min (70% yield); m.p.: 175 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  4.69 (d, 2H, Cp-H), 5.28 (d, 2H, Cp-H), 7.00–7.05 (m, 9H, SnAr-H), 7.08–7.13 (m, 6H, SnAr-H), 7.34–7.40 (m, 12H, CbAr-H), 7.57–7.60 (m, 8H, CbAr-H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  76.40 (Cb C), 84.44 (Cp C), 86.09 (Cp C), 87.64 (Cp C), 126.53 (CbAr C), 127.91 (CbAr C), 128.60 (CbAr C), 128.70 (SnAr C), 129.01 (SnAr C), 135.03 (CbAr C), 136.91 (SnAr C), 138.78 (SnAr C);  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  -117.82; IR (KBr disk,  $\text{v}/\text{cm}^{-1}$ ): 3427m, 3057 m, 2924vw, 1616vs ( $\nu_{\text{asymOCO}}$ ), 1461s, 1498s, 1430m, 1369s ( $\nu_{\text{symOCO}}$ ), 1319m, 1172s, 1073m, 1024m, 996vw, 917vw, 814m, 736vs, 698vs, 614vw, 587s, 564m, 491s ( $\nu_{\text{SnO}}$ ), 446m; Anal. Calc. for  $\text{C}_{54}\text{H}_{45}\text{CoO}_2\text{Sn}$ : C, 71.78; H, 5.02. Found: C, 71.93; H, 5.19%.

##### 4.4.2. $\{n\text{-Bu}_2\text{Sn}[\text{OC}(\text{O})\text{C}_5\text{H}_4\text{CoC}_4\text{Ph}_4]_2\}$ (**3**)

Di-*n*-butyltin oxide (0.07 g, 0.2 mmol), **1** (0.07 g, 0.1 mmol), **3** (65% yield); solvent-free method, grinding time is 45 min (45% yield).

M.p.: 168 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  0.87 (t, 12H, butyl methyl); 1.16–1.26 (m, 4H, butyl- $\text{CH}_2$ ); 1.42 (m, 4H, butyl- $\text{CH}_2$ ), 1.56 (t, 4H, butyl- $\text{CH}_2$ ), 4.76 (d, 4H, Cp-H), 5.31 (d, 4H, Cp-H), 7.20–7.22 (m, 24H, Ar-H); 7.43–7.46 (m, 16H, Ar-H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  13.62 ( $-\text{CH}_3$  C), 24.78 ( $-\text{CH}_2\text{C}$ ), 26.46 ( $-\text{CH}_2$  C), 26.80 ( $-\text{CH}_2$  C), 84.26 (Cb C), 87.88 (Cp C), 126.69 (Ar C), 128.06 (Ar C), 128.90 (Ar C), 135.03 (Ar C);  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  -140.34; IR (KBr disk,  $\text{v}/\text{cm}^{-1}$ ): 3428m, 3054m, 3026m, 2954s, 2923s, 2854m, 2361w, 1599vs ( $\nu_{\text{asymOCO}}$ ), 1577vs ( $\nu_{\text{asymOCO}}$ ), 1498vs, 1463vs, 1400w, 1371s ( $\nu_{\text{symOCO}}$ ), 1352s ( $\nu_{\text{symOCO}}$ ), 1175s, 1070m, 1024s, 918w, 816s, 780s, 619w, 698vs, 586s, 562vs, 490s ( $\nu_{\text{SnO}}$ ). Anal. Calc. for  $\text{C}_{76}\text{H}_{66}\text{Co}_2\text{O}_4\text{Sn} \cdot 2\text{CHCl}_3$ : C, 61.64; H, 4.48. Found: C, 61.10; H, 4.41%.

##### 4.4.3. $\{\text{Ph}_2\text{Sn}[\text{OC}(\text{O})\text{C}_5\text{H}_4\text{CoC}_4\text{Ph}_4]_2\}$ (**4**)

Diphenyltin oxide (0.05 g, 0.17 mmol), **1** (0.18 g, 0.34 mmol) (0.17 g), **4** (77% yield); solvent-free method, grinding time is 45 min (70% yield);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  4.80 (4H, CpH); 5.37 (4H, CpH); 6.83 (4H, ArH); 7.09–7.12 (12H, ArH); 7.23–7.25 (6H, ArH), 7.39–7.41 (8H, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  84.68 (Cb C), 87.98 (Cp C), 125.15(Ar C), 126.70 (Ar C), 128.01 (Ar C), 128.77 (Ar C), 129.77 (Ar C), 131.39(Ar C), 134.83 (Ar C), 135.99 (Ar C), 136.94 (Ar C);  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  -280.80; IR (KBr disk,  $\text{v}/\text{cm}^{-1}$ ): 2923w, 2800w, 1950w, 1597vs ( $\nu_{\text{asymOCO}}$ ), 1566vs ( $\nu_{\text{asymOCO}}$ ), 1464s, 1372s ( $\nu_{\text{symOCO}}$ ), 1324s ( $\nu_{\text{symOCO}}$ ), 1175s, 1069m, 916w, 785m, 822s, 736vs, 696vs, 588w, 563s, 493s ( $\nu_{\text{SnO}}$ ), 446m. Anal. Calc. for  $\text{C}_{83}\text{H}_{60}\text{Co}_2\text{O}_4\text{Sn} \cdot 3\text{CH}_2\text{Cl}_2$ : C, 63.42; H, 3.82. Found: C, 63.38; H 3.79%.

## 5. Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 609310, 609311, 609312 and 609313 for compounds **1**, **2**, **3** and **4**, respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (fax (int code): +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

## Acknowledgments

The authors thank Department of Science and Technology, India for financial assistance in the form of a research grant and IIT Delhi for an equipment grant. We acknowledge DST-FIST and IITD for funding of the single crystal X-ray diffraction facility at IIT Delhi. We thank Prof. P.S. Verma, Department of Chemistry, University of Rajasthan, Dr. J.K. Bera, and S.K. Patra, Department of Chemistry, IIT Kanpur, Mr. N.K. Nautiyal and Mr. J.P. Singh of Department of Chemistry, IIT, Delhi, for their assistance in electrochemical and spectral measurements. We thank Dr. M.S. Moni, and the NMR



facility at SAIF, IIT Madras for recording  $^{119}\text{Sn}$  NMR spectra.

## References

- [1] (a) V. Chandrasekhar, S. Nagendran, V. Baskar, *Coord. Chem. Rev.* 235 (2002) 1–52;  
(b) E.R.T. Tiekink, *Appl. Organomet. Chem.* 5 (1991) 1–23.
- [2] (a) Y. Arakawa, in: P.J. Smith (Ed.), *Chemistry of Tin*, Blackie Academic and Professional, London, 1998, p. 388;  
(b) M. Gielen, *Coord. Chem. Rev.* 151 (1996) 41–51;  
(c) J. Otera, *Chem. Rev.* 93 (1993) 1449–1470.
- [3] R.R. Holmes, *Acc. Chem. Res.* 22 (1989) 190–197.
- [4] E.R.T. Tiekink, *Trends Organomet. Chem.* 1 (1994) 7.
- [5] (a) G. Prabhushankar, R. Murugavel, *Organometallics* 23 (2004) 5644–5647;  
(b) K.C. Kumara Swamy, M.A. Said, S. Nagabrahmanandachari, D.M. Poojary, A. Clearfield, *J. Chem. Soc., Dalton Trans.* 10 (1997) 1645–1651;  
(c) K.C. Kumara Swamy, K. Raghuraman, S. Nagabrahmanandachari, *J. Organomet. Chem.* 587 (1999) 132–135.
- [6] V. Chandrasekhar, S. Nagendran, S. Bansal, M.A. Kozee, D.R. Powell, *Angew. Chem., Int. Ed. Engl.* 39 (2000) 1833–1835.
- [7] V. Chandrasekhar, K. Gopal, S. Nagendran, P. Singh, A. Steiner, S. Zacchini, J.F. Bickley, *Chem. Eur. J.* 11 (2005) 5437–5448.
- [8] V. Chandrasekhar, V. Baskar, R. Boomishankar, K. Gopal, S. Zacchini, J.F. Bickley, A. Steiner, *Organometallics* 22 (2003) 3710–3716.
- [9] (a) K. Sangit, S.K. Tripathi, H.B. Singh, G.J. Wolmershaeuser, *J. Organomet. Chem.* 689 (2004) 3046–3055;  
(b) J. Tomonori, J. Munehiro, S. Kato, M. Mizuta, *J. Organomet. Chem.* 129 (1977) 189–196;  
(c) T.H. Galow, J. Rodrigo, K. Cleary, G. Cooke, V.M. Rotello, *J. Org. Chem.* 64 (1999) 3745–3746;  
(d) C.J. Richards, A.W. Mulvaney, *Tetrahedron: Asymmetry* 7 (1996) 1419–1430.
- [10] S.T. Mabrouk, M.D. Rausch, *J. Organomet. Chem.* 523 (1996) 111–117.
- [11] (a) A.M. Stevens, C.J. Richards, *Organometallics* 18 (1999) 1346–1348;  
(b) R.S. Prasad, C.E. Anderson, C.J. Richards, L.E. Overman, *Organometallics* 24 (2005) 77–81;  
(c) G. Jones, C.J. Richards, *Tetrahedron: Asymmetry* 15 (2004) 653–664.
- [12] L. Jun, B. Yinjuan, J. Jianhui, Y. Bingqin, M. Huairang, Yingyong Huaxue 16 (1999) 82–84.
- [13] (a) J. Holeček, M. Nádvořník, K. Handlíř, A. Lyčka, *J. Organomet. Chem.* 241 (1983) 177–184;  
(b) J. Holeček, M. Nádvořník, K. Handlíř, A. Lyčka, *J. Organomet. Chem.* 315 (1986) 299–308.
- [14] M.G. Muralidhara, V. Chandrasekhar, *Indian J. Chem. A* 30 (1991) 487–492.
- [15] V. Chandrasekhar, S. Nagendran, K. Gopal, A. Steiner, S. Zacchini, *Chem. Commun.* (2003) 862–863.
- [16] S.-G. Teoh, S.-H. Ang, E.-S. Looi, S.-B. Keok, J.-P. Teo, J.-P. Declercq, *J. Organomet. Chem.* 523 (1996) 75–78.
- [17] H.P. Gupta, M.S. Kumar, A.J. Elias, unpublished results.
- [18] D.B. Werz, H.J. Schulte, R. Gleiter, *J. Organomet. Chem.* 689 (2004) 3132–3142.
- [19] (a) G.M. Sheldrick, *Acta Crystallogr., Sect. A* 46 (1990) 467–473;  
(b) G.M. Sheldrick, *SHELXTL-NT 2000*, Version 6.12, Reference Manual, University of Göttingen, Göttingen, Germany, 2000.