

Synthesis and characterisation of some diphenylcyclopentadienyltin carboxylates

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Hitherto unknown diphenylcyclopentadienyltin carboxylates, $\text{SnPh}_2(\text{Cp})(\text{OOCR})$ [$\text{R} = \text{CH}_2\text{Cl}$, C_6H_5 , $p\text{-ClC}_6\text{H}_4$, $m\text{-NH}_2\text{C}_6\text{H}_4$, $p\text{-NH}_2\text{C}_6\text{H}_4$, $p\text{-NO}_2\text{C}_6\text{H}_4$, 3,5- $(\text{NO}_2)_2\text{C}_6\text{H}_3$, $o\text{-(HO)C}_6\text{H}_4$, $\text{C}_6\text{H}_5\text{CH}=\text{CH}$ and $\text{C}_6\text{H}_5\text{CH(OH)}$] have been synthesised and characterised on the basis of their elemental analysis, molecular weight, molar conductance, IR and ^1H NMR spectral data.

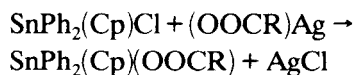
In continuation of our earlier work¹⁻⁴ on synthesis, reactivity and characterisation of phenyltin compounds, we report here the synthesis of diphenylcyclopentadienyltin carboxylates of the type $\text{SnPh}_2(\text{Cp})(\text{OOCR})$ [$\text{R} = \text{CH}_2\text{Cl}$, C_6H_5 , $p\text{-ClC}_6\text{H}_4$, $m\text{-NH}_2\text{C}_6\text{H}_4$, $p\text{-NH}_2\text{C}_6\text{H}_4$, $p\text{-NO}_2\text{C}_6\text{H}_4$, 3,5- $(\text{NO}_2)_2\text{C}_6\text{H}_3$, $o\text{-(HO)C}_6\text{H}_4$, $\text{C}_6\text{H}_5\text{CH}=\text{CH}$ and $\text{C}_6\text{H}_5\text{CH(OH)}$]. They have been characterised on the basis of their elemental analysis, molecular weight, molar conductance and IR data. ^1H NMR data of some representative compounds are also reported. Diphenylcyclopentadienyltin acetate is the only carboxylate reported so far with the SnPh_2Cp species¹.

Experimental

$\text{SnPh}_2(\text{Cp})\text{Cl}$ was prepared by the reaction of Ph_2SnCl_2 with CpTi in anhydrous chloroform¹. Ph_2SnCl_2 and CpTi ⁵ were prepared by the reported methods. Cyclopentadiene dimer (Fluka), thallous sulphate (BDH) and carboxylic acids (BDH) were commercial samples. The silver carboxylates were prepared by the interaction of sodium salts of carboxylic acid with AgNO_3 . They were dried thoroughly before use.

All the reactions and manipulations were carried out under nitrogen atmosphere and physicochemical measurements were carried out as reported earlier².

The SnPh_2Cp carboxylates were prepared by the reactions of $\text{SnPh}_2(\text{Cp})\text{Cl}$ with silver carboxylates:



[$\text{R} = \text{CH}_2\text{Cl}$, C_6H_5 , $p\text{-ClC}_6\text{H}_4$, $m\text{-NH}_2\text{C}_6\text{H}_4$, $p\text{-NH}_2\text{C}_6\text{H}_4$, $p\text{-NO}_2\text{C}_6\text{H}_4$, 3,5- $(\text{NO}_2)_2\text{C}_6\text{H}_3$, $o\text{-(HO)C}_6\text{H}_4$, $\text{C}_6\text{H}_5\text{CH}=\text{CH}$ and $\text{C}_6\text{H}_5\text{CH(OH)}$].

A typical preparation of $\text{SnPh}_2(\text{Cp})\text{OOCCH}_3$ is described below: To a suspension of freshly prepared dry silver benzoate (4.58 g, 0.02 mol) in anhydrous THF (20 ml) was added a solution of $\text{SnPh}_2(\text{Cp})\text{Cl}$ (3.73 g, 0.01 mol) in THF (25 ml) dropwise at 0°C with constant stirring. The reaction mixture was further stirred for ~ 3 hr and the precipitated AgCl and excess of silver benzoate were filtered off. The filtrate was concentrated (~ 4 ml) and to the concentrate was added petroleum ether ($60\text{--}80^\circ$) to get a pale yellow solid, $\text{SnPh}_2(\text{Cp})\text{OOCCH}_3$, which was washed with petroleum ether ($60\text{--}80^\circ$) and dried at $20^\circ/10$ mm Hg.

Results and discussion

The compounds with their characterisation and IR spectral data are listed in Table 1. They are pale yellow and brown, thermally-stable solids and are sensitive to light, oxygen and moisture. The molar conductances of their 10^{-3} M solutions in nitrobenzene at 25°C are in the range $0.45\text{--}3.46 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ indicating them to be non-electrolytes⁶. The molecular weights of the compounds determined in the same solvent (Table 1) indicate them to be monomeric in nature.

In the above compounds observed IR absorption bands associated with cyclopentadienyl group due to CH stretch ($3105\text{--}3046 \text{ cm}^{-1}$), CC stretch ($1450\text{--}1424 \text{ cm}^{-1}$ & $1180\text{--}1150 \text{ cm}^{-1}$) and CH deformation ($995\text{--}900 \text{ cm}^{-1}$ & $860\text{--}820 \text{ cm}^{-1}$) are in conformity with the earlier reports^{1,8,9}.

The infrared spectra of various diphenylcyclopentadienyltin carboxylates in the solid state show $\Delta\nu_{\text{COO}} (= \nu_{\text{as}}\text{COO} - \nu_{\text{s}}\text{COO}) \approx 196\text{--}128 \text{ cm}^{-1}$. In chloroform solution of some representative compounds observed $\Delta\nu_{\text{COO}}$ value is $328\text{--}365 \text{ cm}^{-1}$. This information coupled with molecular weight data (Table 1) shows that these diphenylcyclopentadienyltin carboxylates are polymeric in solid state and are ester like monomers in dilute solution, like the trialkyltin carboxylates⁷. The IR band in the range $340\text{--}320 \text{ cm}^{-1}$ (Table 1) is assigned to $\nu_{\text{Sn}-\text{O}}$ mode^{10,11}. No band appears in this range in the IR spectrum of $\text{SnPh}_2(\text{Cp})\text{Cl}$. $\nu_{\text{as}}\text{Sn}-\text{C}(\text{phenyl})$ appear in the regions $285\text{--}260$ and $226\text{--}220 \text{ cm}^{-1}$ respectively¹².

In 90 MHz ^1H NMR spectra, the low field multiplets corresponding to o -protons and m - and p -protons

Table 1—Experimental data for $\text{SnPh}_2(\text{Cp})\text{OOCR}$ diphenylcyclopentadienyltin carboxylates

Compound $\text{SnPh}_2(\text{Cp})\text{OOCR}$ R	Yield % (m.p., °C)	Mol. wt obs. (calc.)	Found (calc.) %				IR frequencies (cm^{-1})			$\nu_{\text{Sn-O}}$
			Sn	C	H	N	$\nu_{\text{as}}\text{COO}$	$\nu_{\text{s}}\text{COO}$	$\Delta\nu_{\text{COO}}$	
ClCH_2	48 (246d)	368.1 (431.5)	27.45 (27.58)	52.62 (52.84)	3.86 (3.94)	—	1590 (1655)*	1410 (1310)*	180 (345)*	335
C_6H_5	57 (130-133d)	414.2 (459)	25.80 (25.93)	62.56 (62.75)	4.24 (4.36)	—	1545	1404	141	334
<i>p</i> - ClC_6H_4	55 (210d)	460.2 (493.2)	24.10 (24.11)	58.30 (58.36)	3.82 (3.85)	—	1550	1410	140	332
<i>m</i> - $\text{NH}_2\text{C}_6\text{H}_4$	53 (240d)	436 (474)	25.06 (25.11)	60.66 (60.76)	4.33 (4.43)	2.90 (2.95)	1580 (1670)*	1398 (1305)*	182 (365)*	—
<i>p</i> - $\text{NH}_2\text{C}_6\text{H}_4$	53 (160d)	452 (474)	25.00 (25.11)	60.70 (60.76)	4.38 (4.43)	2.86 (2.95)	1525	1390	135	329
<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4$	56 (300-305d)	510 (504)	23.50 (23.61)	57.12 (57.14)	3.73 (3.77)	2.72 (2.78)	1565	1409	156	332
3,5-(NO_2) $_2\text{C}_6\text{H}_3$	62 (278d)	487.3 (549)	21.62 (21.68)	52.42 (52.46)	3.22 (3.28)	5.04 (5.10)	1540	1344	196	340
<i>o</i> -(HO) C_6H_4	60 (180d)	422 (475)	24.98 (25.05)	60.59 (60.63)	4.20 (4.21)	—	1590	1462	128	339
$\text{C}_6\text{H}_5\text{CH}=\text{CH}$	55 (295-300d)	456 (485)	24.48 (24.54)	64.26 (64.33)	4.51 (4.54)	—	1550	1398	152	330
$\text{C}_6\text{H}_5\text{CH}(\text{OH})$	64 (118d)	495 (489.2)	24.29 (24.34)	61.32 (61.35)	4.48 (4.50)	—	1565 (1668)*	1433 (1340)*	132 (328)*	320

*Recorded in CHCl_3 solution.

of phenyl groups attached to Sn appear at δ 7.70, 7.25; 7.55, 7.37; and 7.50, 7.25 ppm for $\text{SnPh}_2(\text{Cp})\text{OOC-}o\text{-(HO)C}_6\text{H}_4$, $\text{SnPh}_2(\text{Cp})\text{OOC-}p\text{-NO}_2\text{C}_6\text{H}_4$ and $\text{SnPh}_2(\text{Cp})\text{OOC-}3, 5\text{-(NO}_2)_2\text{C}_6\text{H}_3$ respectively in acetone- d_6 + CDCl_3 and acetone- d_6 using TMS as internal standard^{3,4,13}. The other peaks attributable to aromatic protons of the carboxylate groups appear as multiplets centred at δ 8.10, 7.80; 8.52, 7.90 for $\text{SnPh}_2(\text{Cp})\text{OOC-}o\text{-(HO)C}_6\text{H}_4$, $\text{SnPh}_2(\text{Cp})\text{OOC-}3, 5\text{-(NO}_2)_2\text{C}_6\text{H}_3$ and doublets centered at δ 8.16, 7.79 for $\text{SnPh}_2(\text{Cp})\text{OOC-}p\text{-NO}_2\text{C}_6\text{H}_4$ respectively.

The presence of singlets at δ 6.74, 6.77 and 6.88 ppm in $\text{SnPh}_2(\text{Cp})\text{OOC-}o\text{-(HO)C}_6\text{H}_4$, $\text{SnPh}_2(\text{Cp})\text{OOC-}p\text{-NO}_2\text{C}_6\text{H}_4$ and $\text{SnPh}_2(\text{Cp})\text{OOC-}3, 5\text{-(NO}_2)_2\text{C}_6\text{H}_3$ respectively indicates occurrence of a fast degenerate metallotropic rearrangement over the cyclopentadienyl ring by 1, 2 shift mechanism¹⁴.

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