

Some New Derivatives of Organozirconium(IV) and Organotitanium(IV) with Thiophenecarboxylic Acids

SATISH C. DIXIT, RAM SHARAN and RAMESH N. KAPOOR*

Department of Chemistry, University of Delhi, Delhi-110007, India

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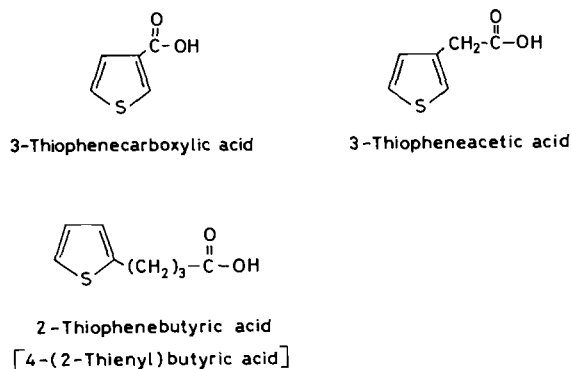
Abstract

The complexes of the type $Cp_2M(3-TC)Cl$, $Cp_2M(3-TC)_2$, $Cp_2M(3-TA)Cl$, $Cp_2M(3-TA)_2$, $Cp_2M(2-TB)Cl$, $Cp_2M(2-TB)_2$ [where Cp = cyclopentadienyl, M = Zr or Ti] were synthesized by the reactions of dichlorobis(cyclopentadienyl)zirconium(IV) and dichlorobis(cyclopentadienyl)titanium(IV) with 3-thiophenecarboxylic acid (3-TCH), 3-thiopheneacetic acid (3-TAH) and 2-thiophenebutyric acid (2-TBH) respectively in different stoichiometric ratios. The new complexes were characterized by their elemental analysis, 1H NMR, IR, and electronic spectral data.

Introduction

The rapid growth of interest in recent years in metallocene research may be attributed in part to the applications of metallocene derivatives as anti-tumor agents, radiopharmaceutical agents etc. [1-7]. Several thiophenecarboxylic acids and their esters have been investigated for their anticancer effects [8-10]. Recently, Kapoor and coworkers [11] reported the reactions of thiophenecarboxylic acids with pentaethoxides and pentachlorides of niobium and tantalum and obtained interesting results. A survey of the literature reveals that no work has been carried out on the reactions of 3-thiophenecarboxylic acid, 3-thiopheneacetic acid and 2-thiophenebutyric acid. It was, therefore, considered of interest to carry out the reactions of dichlorobis(cyclopentadienyl)zirconium(IV), Cp_2ZrCl_2 and dichlorobis(cyclopentadienyl)titanium(IV), Cp_2TiCl_2 with 3-thiophenecarboxylic acid (3-TCH), 3-thiopheneacetic acid (3-TAH) and 2-thiophenebutyric acid (2-TBH).

The structure of the ligands used is given in Scheme 1.



Scheme 1.

Experimental

Glass apparatus with interchangeable standard joints were used throughout this work; stringent precautions were taken to exclude moisture from the system. The reactions were carried out under nitrogen and the system was well protected from atmospheric moisture by means of calcium chloride guard tubes. THF (Merck) was dried by storage over sodium wire overnight and was then refluxed till it gave a blue colouration with benzophenone. It was finally dried by distilling over $LiAlH_4$. n-Hexane and triethylamine were dried by the reported method [12]. Sodium cyclopentadienide and dichlorobis(cyclopentadienyl)zirconium(IV) were prepared as reported in the literature [13, 14]. Dichlorobis(cyclopentadienyl)titanium(IV) was prepared by a known method [15]. 3-Thiophenecarboxylic acid (Aldrich), 3-thiopheneacetic acid (Aldrich) and 2-thiophenebutyric acid (Aldrich) were used as supplied.

Carbon and hydrogen were analysed at the Central Micro-Analytical Laboratory of the Indian Institute of Technology, Kanpur. Chlorine was estimated as $AgCl$. Zirconium and titanium were estimated gravimetrically as ZrO_2 and TiO_2 . The 1H NMR spectra were recorded on a JEOL JNM-FX200 Fourier Transform Spectrometer, using $CDCl_3$ as solvent. The IR

* Author to whom correspondence should be addressed.

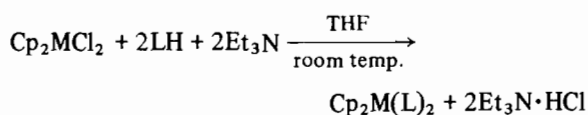
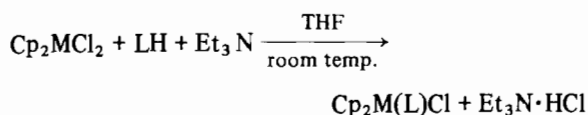
spectra were recorded in KBr pellets on a Perkin-Elmer 1710 Infrared Fourier Transform Spectrometer in the range 400–4000 cm^{-1} . The electronic spectra of the complexes were recorded in chloroform solution on a Shimadzu UV-260 spectrophotometer.

Preparation of Complexes

A general procedure was followed to synthesize the complexes of dichlorobis(cyclopentadienyl)zirconium(IV) and dichlorobis(cyclopentadienyl)titanium(IV) with 3-thiophenecarboxylic acid, 3-thiopheneacetic acid, 2-thiophenebutyric acid which involved the mixing of the reactants in anhydrous THF in the presence of triethylamine at room temperature. The reaction mixture was stirred for 35–40 h. The precipitated $\text{Et}_3\text{N}\cdot\text{HCl}$ was filtered off and the solvent was removed under reduced pressure. The product so obtained was recrystallized from n-Hexane/THF mixture. The synthesis of other derivatives was carried out by the same procedure and the details are given in Table I. The analytical data of the complexes obtained are mentioned in Table II.

Results and Discussion

Dichlorobis(cyclopentadienyl)zirconium(IV) and dichlorobis(cyclopentadienyl)titanium(IV) reacts with thiophenecarboxylic acids (1:1 and 1:2 molar ratio) in anhydrous THF, in the presence of triethylamine.



(where Cp = cyclopentadienyl; M = Zr, Ti, LH = 3-TCH, 3-TAH, 2-TBH)

These complexes are crystalline solids and susceptible to hydrolysis. These are soluble in tetrahydrofuran, acetone and chloroform but insoluble in n-Hexane and petroleum ether.

TABLE I. Reactions of Cp_2ZrCl_2 and Cp_2TiCl_2 with Thiophenecarboxylic Acids

Reactants ^a (g)			Molar ratio	Stirring time (h)	Product	Colour	Melting point (°C)
Cp_2MCl_2	Thiophene carboxylic acid	Et_3N					
Cp_2ZrCl_2 0.57	3-TAH 0.28	0.20	1:1:1	30	$(\text{C}_5\text{H}_5)_2\text{Zr(3-TA)Cl}$	brown	113
Cp_2ZrCl_2 0.39	3-TAH 0.38	0.27	1:2:2	31	$(\text{C}_5\text{H}_5)_2\text{Zr(3-TA)}_2$	brown	104
Cp_2ZrCl_2 0.62	3-TCH 0.27	0.22	1:1:1	60	$(\text{C}_5\text{H}_5)_2\text{Zr(3-TC)Cl}$	light brown	130 (dec.)
Cp_2ZrCl_2 0.82	3-TCH 0.72	0.57	1:2:2	40	$(\text{C}_5\text{H}_5)_2\text{Zr(3-TC)}_2$	dark brown	95
Cp_2ZrCl_2 0.69	2-TBH 0.40	0.24	1:1:1	41	$(\text{C}_5\text{H}_5)_2\text{Zr(2-TB)Cl}$	light brown	100
Cp_2ZrCl_2 0.27	2-TBH 0.31	0.19	1:2:2	40	$(\text{C}_5\text{H}_5)_2\text{Zr(2-TB)}_2$	brown	103
Cp_2TiCl_2 1.12	3-TAH 0.64	0.45	1:1:1	31	$(\text{C}_5\text{H}_5)_2\text{Ti(3-TA)Cl}$	reddish brown	110
Cp_2TiCl_2 0.63	3-TAH 0.72	0.51	1:2:2	30	$(\text{C}_5\text{H}_5)_2\text{Ti(3-TA)}_2$	reddish brown	114
Cp_2TiCl_2 0.72	3-TCH 0.37	0.29	1:1:1	42	$(\text{C}_5\text{H}_5)_2\text{Ti(3-TC)Cl}$	brick red	105
Cp_2TiCl_2 0.51	3-TCH 0.52	0.41	1:2:2	40	$(\text{C}_5\text{H}_5)_2\text{Ti(3-TC)}_2$	reddish brown	106
Cp_2TiCl_2 0.69	2-TBH 0.47	0.28	1:1:1	40	$(\text{C}_5\text{H}_5)_2\text{Ti(2-TB)Cl}$	brick red	135
Cp_2TiCl_2 0.38	2-TBH 0.52	0.31	1:2:2	43	$(\text{C}_5\text{H}_5)_2\text{Ti(2-TB)}_2$	reddish brown	102

^a3-TAH = 3-thiopheneacetic acid; 3-TCH = 3-thiophenecarboxylic acid; 2-TBH = 2-thiophenebutyric acid.

TABLE II. Characterization Data

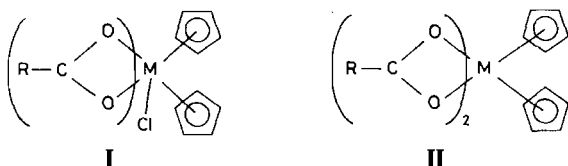
Complex	Analysis, found(calc.) (%)				λ_{max} (nm) (in CHCl_3)	C_5H_5 $^1\text{H NMR}$ δ (ppm)
	M	C	H	Cl		
$(\text{C}_5\text{H}_5)_2\text{Zr}(3\text{-TA})\text{Cl}$	22.85 (22.93)		3.13 (3.77)	8.87 (8.92)	242.8	6.52
$(\text{C}_5\text{H}_5)_2\text{Zr}(3\text{-TA})_2$	18.09 (18.12)	51.36 (52.46)	3.77 (3.97)		249.2	6.56
$(\text{C}_5\text{H}_5)_2\text{Zr}(3\text{-TC})\text{Cl}$	23.61 (23.79)	44.95 (46.9)	4.13 (3.38)	9.14 (9.25)	252.4	6.36
$(\text{C}_5\text{H}_5)_2\text{Zr}(3\text{-TC})_2$	19.04 (19.2)	50.09 (50.5)	3.33 (3.37)		247.8	6.56
$(\text{C}_5\text{H}_5)_2\text{Zr}(2\text{-TB})\text{Cl}$	21.28 (21.43)		4.32 (4.46)	8.27 (8.34)	246.2	6.52
$(\text{C}_5\text{H}_5)_2\text{Zr}(2\text{-TB})_2$	16.17 (16.30)				250.0	6.6
$(\text{C}_5\text{H}_5)_2\text{Ti}(3\text{-TA})\text{Cl}$	13.47 (13.54)	54.82 (54.16)	3.62 (4.3)	9.96 (10.01)	252.6	6.64
$(\text{C}_5\text{H}_5)_2\text{Ti}(3\text{-TA})_2$	10.32 (10.43)	55.92 (57.39)	4.18 (4.34)		243.6	6.44
$(\text{C}_5\text{H}_5)_2\text{Ti}(3\text{-TC})\text{Cl}$	13.94 (14.09)	50.87 (52.86)	3.84 (3.82)	10.35 (10.42)	251.0	6.64
$(\text{C}_5\text{H}_5)_2\text{Ti}(3\text{-TC})_2$	10.95 (11.1)	55.22 (55.51)	3.65 (3.7)		245.0	6.64
$(\text{C}_5\text{H}_5)_2\text{Ti}(2\text{-TB})\text{Cl}$	12.41 (12.55)	56.23 (56.47)	4.32 (4.97)	9.12 (9.28)	252.4	6.64
$(\text{C}_5\text{H}_5)_2\text{Ti}(2\text{-TB})_2$	9.2 (9.3)				242.0	6.8

The IR spectra of the complexes exhibit the usual absorptions due to cyclopentadienyl groups at ~ 3100 [$\nu(\text{C-H})$], ~ 1435 [$\nu(\text{C-C})$], ~ 1020 [$\delta_{\text{i.p.}}(-\text{CH})$] and ~ 810 cm^{-1} [$\delta_{\text{o.p.}}(-\text{CH})$] [16]. The persistence of the bands of cyclopentadienyl rings in the complexes indicates that these groups remain delocalized and π -bonded to the metal and retain their aromatic character. In the IR spectra of the free acids, 3-thiophenecarboxylic acid, 3-thiopheneacetic acid and 2-thiophenebutyric acid, the bands due to $\nu(\text{OH})$ and $\nu(\text{C=O})$ appear in the regions 3100 and 1700, 1680, 1700 cm^{-1} respectively. The disappearance of the band due to $\nu(\text{OH})$ indicates the complete removal of the hydroxyl proton of the acids. The bands at 1700, 1680 and 1700 cm^{-1} due to $\nu(\text{C=O})$ show a downward shift of (~ 120 cm^{-1}) and appear in the region 1620–1580 cm^{-1} indicating that carbonyl oxygen is coordinated to the metal. This suggests that bonding of the carboxylate group to the metal is bidentate in these complexes. The 2-thiophenebutyric acid derivatives showed the usual 2-substituted thiophene [17] IR vibrations with the ring breathing mode in the region 850–848 cm^{-1} . The 3-thiophenecarboxylic acid and 3-thiopheneacetic acid derivatives showed the usual 3-substituted thiophene IR vibra-

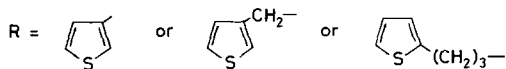
tions. The band in the region 860–855 cm^{-1} may be assigned to the ring breathing mode. The ring breathing vibrations of thiophene do not show any appreciable positive shift in these derivatives and occur almost at the same positions as in free acids indicating that the heterosulphur is not involved in the coordination. Bands occurring in the region 580–444 cm^{-1} are assigned to the metal–oxygen stretching vibration [18–20].

The $^1\text{H NMR}$ spectra of these complexes showed no signal in the region δ 11.52–11.2 indicating the complete removal of the hydroxyl proton of the carboxylic groups. The spectra of these complexes showed a sharp resonance due to cyclopentadienyl groups in the region δ 6.36–6.8 ppm (the different PMR signals are given in Table II). The electronic spectra of the complexes showed a single band in the region 253–242 nm which can be assigned to the charge transfer band [21, 22] (The positions of the absorption bands in the UV and visible regions of the electronic spectra of the complexes are tabulated in Table II.)

On the basis of the above spectral features and elemental analyses, the following structures (I and II) may be proposed for the $(\text{C}_5\text{H}_5)_2\text{M}(\text{L})\text{Cl}$ and $(\text{C}_5\text{H}_5)_2\text{M}(\text{L})_2$ complexes respectively.



where M = Zr or Ti, L = 3-TCH or 3-TAH or 2-TBH



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