

## Synthesis and characterisation of organozirconium(IV) and organotitanium(IV) – acid complexes

Pushpamma Lukose & A K Narula\*

Department of Chemistry, Kurukshetra University,  
Kurukshetra 132 119

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Reactions of dichlorodicyclopentadienylzirconium(IV) and dichlorodicyclopentadienyltitanium(IV) with monobasic bidentate carboxylic acids such as *trans*-cinnamic acid (HCA) and dihydrocinnamic acid (HDCA) and with dibasic tridentate carboxylic acid such as benzoic acid (H<sub>2</sub>BA) have been studied. Complexes of the type Cp<sub>2</sub>M(CA)Cl, Cp<sub>2</sub>M(CA)<sub>2</sub>, Cp<sub>2</sub>M(DCA)Cl, Cp<sub>2</sub>M(DCA)<sub>2</sub> and Cp<sub>2</sub>M(BA) (where M = zirconium or titanium) have been isolated and characterised on the basis of elemental analyses and spectral studies.

Cinnamic acid and dihydrocinnamic acid are interesting ligands because carboxylate group can coordinate in a monodentate or bidentate manner with different metal ions. Apart from this, there is a possibility that olefinic (C=C) double bond may also take part in bonding. On the other hand, benzoic acid can act as a bidentate or tridentate ligand. Because of the ambidentate nature of the above three acids, it was considered of interest to study the reaction of dichlorodicyclopentadienylzirconium(IV) and titanium(IV) with *trans*-cinnamic acid (HCA), dihydrocinnamic acid (HDCA) and benzoic acid (H<sub>2</sub>BA). A literature survey revealed that no work was reported on cinnamates and benzoates of organozirconium(IV) and organotitanium(IV).

### Experimental

All reactions were carried out under nitrogen using the Schlenk tube technique. Common organic solvents were dried under nitrogen by standard methods<sup>1</sup>. Cyclopentadiene, sodium cyclopentadienide, dichlorodicyclopentadienyl-zirconium(IV) and -titanium(IV) were prepared by standard methods<sup>2-5</sup>. Infrared spectra were recorded in KBr on a Perkin-Elmer 1710 FT-IR spectrophotometer over the range 4000-400 cm<sup>-1</sup>. <sup>1</sup>H NMR spectra were recorded on a R-32 Perkin-Elmer spectrometer using CDCl<sub>3</sub> as solvent. Zirconium and titanium were estimated as ZrO<sub>2</sub> and TiO<sub>2</sub><sup>6</sup>. Analyses for carbon and hydrogen were carried out at the Micro-analytical Laboratory of Kurukshetra University, Kuruk-

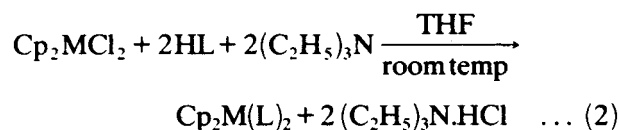
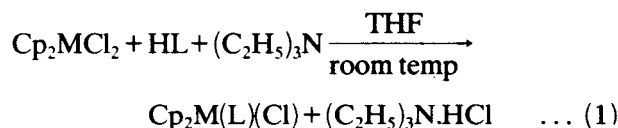
shetra. Chlorine was estimated as AgCl. The electronic spectra were recorded on a Shimadzu UV-260 spectrophotometer.

### Preparation of 1:1 (metal:ligand) complexes

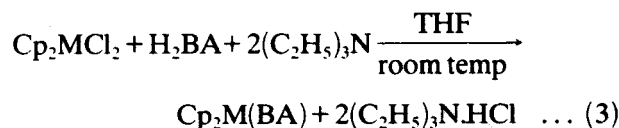
To a solution of Cp<sub>2</sub>ZrCl<sub>2</sub> (0.54 g, 1.86 mmol) in dry tetrahydrofuran (~80 ml) was added cinnamic acid (0.27 g, 1.86 mmol) and triethylamine (0.19 g, 1.86 mmol). The mixture was stirred for ~24 h at room temperature, the precipitated (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N.HCl was filtered off, and the solvent was removed *in vacuo*. The solid obtained was washed with heptane and recrystallized from *n*-hexane/THF mixture. Similarly, other complexes listed in Table 1 were prepared by using 1:1 or 1:2 (metal:ligand) molar ratios of the reactants.

### Results and discussion

The reaction of dichlorodicyclopentadienylzirconium(IV) and dichlorodicyclopentadienyltitanium(IV) with *trans*-cinnamic acid, dihydrocinnamic acid and benzoic acid in different molar ratios in anhydrous THF in the presence of triethylamine may be represented by the following equations:



where, HL = cinnamic acid/dihydrocinnamic acid, and M = zirconium(IV) or titanium(IV).



where H<sub>2</sub>BA = benzoic acid, and M = zirconium(IV) or titanium(IV).

All the complexes were crystalline and extremely sensitive to hydrolysis. These were soluble in tetrahydrofuran and chloroform but insoluble in *n*-hexane and petroleum ether. Other details regarding physical properties of complexes are given in Table 1.

The infrared spectra of complexes showed the usual absorption due to cyclopentadienyl groups at

Table 1—Characterization data of the complexes

Complex	Colour (m.p., °C)	Found (Calc.), %			
		Metal	C	H	Cl
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Zr(CA)Cl	Pale yellow (109)	22.01 (22.58)	56.07 (56.48)	4.03 (4.24)	8.62 (8.78)
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Zr(CA) <sub>2</sub>	Pale yellow (102)	17.23 (17.69)	64.89 (65.21)	4.12 (4.69)	—
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti(CA)Cl	Orange (78)	13.27 (13.28)	63.00 (63.27)	4.01 (4.75)	9.24 (9.82)
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti(CA) <sub>2</sub>	Brown (122)	10.08 (10.13)	70.67 (71.19)	5.0 (5.12)	—
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Zr(DCA)Cl	Pale yellow (119)	22.27 (22.46)	55.93 (56.20)	4.22 (4.72)	8.72 (8.73)
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Zr(DCA) <sub>2</sub>	Pale yellow (68)	17.23 (17.54)	64.08 (64.68)	5.40 (5.43)	—
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti(DCA)Cl	Red (102)	13.20 (13.21)	62.07 (62.92)	5.00 (5.28)	9.46 (9.77)
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti(DCA) <sub>2</sub>	Brown (112)	10.70 (10.05)	70.05 (70.59)	5.23 (5.92)	—
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Zr(BA)	Pale yellow (115)	20.21 (20.37)	63.97 (64.39)	3.87 (4.50)	—
(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti(BA)	Orange (129)	11.88 (11.84)	— (71.29)	— (4.98)	—

~ 3100 cm<sup>-1</sup> (νC-H), ~ 1435 cm<sup>-1</sup> (νC-C), ~ 1020 cm<sup>-1</sup> (δ<sub>i.p.</sub> CH) and ~ 820 cm<sup>-1</sup> (δ<sub>o.p.</sub> CH)<sup>7</sup>. The persistence of the bands of the cyclopentadienyl rings in the complexes indicated that these groups are π-bonded to metal and retain their aromatic character.

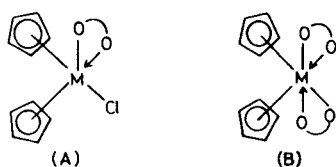
The IR spectra of the complexes of *trans*-cinnamic acid (HCA) and dihydrocinnamic acid (HDCA) showed no absorption in the region 2700-2500 cm<sup>-1</sup> indicating deprotonation of the carboxylic group on complex formation. Apart from this, ν<sub>as</sub> (COO) mode which appears in *trans*-cinnamic acid and dihydrocinnamic acid at 1675 and 1705 cm<sup>-1</sup> respectively shifted to 1525-1500 cm<sup>-1</sup> (~ 110 cm<sup>-1</sup>) in the corresponding complexes, indicating coordination through the carbonyl moiety. The IR spectra of the complexes formed with benzoic acid showed no absorption around 3420 and 3400 cm<sup>-1</sup>; indicating the absence of hydroxy group. The disappearance of the band in the region 2700-2500 cm<sup>-1</sup> indicated the deprotonation of the carboxylic group also. The asymmetric carbonyl stretching which appears at 1740 cm<sup>-1</sup> in benzoic acid shifted to a lower frequency of 1600 cm<sup>-1</sup> (~ 140 cm<sup>-1</sup>) indicating the coordination of oxygen of C=O group of carboxylic to zirconium and titanium in the complexes<sup>8</sup>.

In the present case of acid derivatives, low shifts of νC=O (80-150 cm<sup>-1</sup>) may, therefore, be attrib-

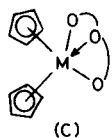
uted to the presence of chelate type coordination. Infrared spectra of *trans*-cinnamic acid derivatives showed no noticeable shift in (νC=C), which suggests that olefinic bond is not involved in coordination. The absorption bands in the region 590-460 cm<sup>-1</sup> are assigned to (νM-O) vibration<sup>9-11</sup>.

<sup>1</sup>H NMR spectra of all the complexes showed a signal due to cyclopentadienyl groups at δ 6.4 ppm<sup>12,13</sup>. The <sup>1</sup>H NMR spectra of *trans*-cinnamic acid and dihydrocinnamic acid recorded in deuterated chloroform showed a signal at δ 11.4 and δ 10.8 ppm, respectively due to the carboxylic proton, but the signal was absent from the spectra of corresponding zirconium and titanium complexes. The -CH proton in case of cinnamic acid was observed at δ 6.5-7.8 having coupling constant of the order of 16 Hz. The CH<sub>2</sub> protons of dihydrocinnamic acid were observed as two triplets at δ 2.5-3.1. Little change was observed in the resonances of C<sub>6</sub>H<sub>5</sub>-, CH=CH, CH<sub>2</sub>-CH<sub>2</sub> protons on going from free acids to complexes. The <sup>1</sup>H NMR spectra of benzoates of zirconium(IV) and titanium(IV) showed a multiplet in the region δ 6.9-7.2 ppm for the phenyl protons; the absence of OH peak at δ 8.23 confirmed deprotonation of the ligand. The integrated proton ratios were in accordance with the formulae assigned to the complexes.

The electronic spectra of all the complexes recorded in chloroform showed fairly intense bands



M = Zirconium or titanium  
 $\widehat{O\ O}$  = Anion of cinnamic acid or dihydrocinnamic acid



M = Zirconium or titanium  
 $\widehat{O\ O\ O}$  = Anion of benzoic acid.

between 242 and 294 nm which could be assigned to the charge transfer<sup>14</sup> in accordance with the  $(n-1)d^0, ns^0$  electronic configurations of complexes.

From the elemental analyses and spectral data, it appears that *trans*-cinnamic acid and dihydrocinnamic acid behave as monofunctional bidentate ( $\widehat{O, O}$ ) chelating ligands and benzoic acid behaves as bifunctional tridentate ( $\widehat{O, O, O}$ ) chelating ligand. The penta- and hexa-coordinated structures A, B

and C are tentatively proposed for complexes of the type  $Cp_2M(L)Cl$  (A) and  $Cp_2M(L)_2$  (B) and  $Cp_2ML$  (C) (where N = zirconium or titanium).

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