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Mono- and Bisphenoxy Derivatives of Bis(indenyl) Titanium(IV)

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A series of $(C_9H_7)_2Ti(OAr)Cl$ and $(C_9H_7)_2Ti(OAr)_2$ complexes where $Ar = C_6H_5$, p-ClC_6H_4, α-$C_{10}H_7$ or β-$C_{10}H_7$, have been synthesised by the reaction of bis(indenyl) titanium(IV) dichloride with an appropriate phenol in a 1:1 and 1:2 molar ratio in refluxing benzene in the presence of triethylamine. The new derivatives have been characterized on the basis of their elemental analyses, conductance measurements and spectral (IR, ^{1}H-NMR and electronic) studies.

[Keywords: Bis(indenyl) titanium(IV); Conductance; Phenoxy derivatives]

Mono- und Biskomplexe des Bis(indenyl)titan(IV)

Die Reaktion von Bis(indenyl)titan(IV)dichlorid mit verschiedenen Phenolen im molaren Verhältnis 1:1 oder 1:2 ergab in Anwesenheit von Triethylamin in Benzol am Rückfluß Komplexe vom Typ $(C_9H_7)_2Ti(OAr)Cl$ und $(C_9H_7)_2Ti(OAr)$; $Ar = C_6H_5$, p-ClC_6H_4, α-$C_{10}H_7$, β-$C_{10}H_7$. Die neuen Derivate wurden mittels Elementaranalyse, Leitfähigkeitsmessungen und ihrer spektroskopischen Eigenschaften (IR, UV-VIS, ^{1}H-NMR) charakterisiert.

Introduction

The study of organotitanium compounds has been a subject of keen interest over the last few years because they act as catalysts for polymerisation[1,2] and hydrogenation[3,4] of olefins and dienes. On the other hand, transition metal phenoxides have been used as olefin polymerisation catalysts in many organic reactions[5]. Some phenoxo and diphenoxo derivatives of bis(cyclopentadienyl)/(methylcyclopentadienyl)titanium(IV) and zirconium(IV) have been reported[6–11].

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However, reactions of bis(indenyl)-titanium(IV) dichloride with phenols have not been studied so far. The present work describes the preparation and characterization of such compounds.

Results and Discussion

Dichlorobis(indenyl)titanium(IV), $(C_9H_7)_2TiCl_2$,reacts with phenols in a 1:1 and 1:2 molar ratio to yield complexes of the type I and II according to the following equations:

$$(C_9H_7)_2TiCl_2 + ArOH + Et_3N \xrightarrow[80\,°C]{\text{Benzene}} (C_9H_7)_2Ti(OAr)Cl + Et_3N \cdot HCl \qquad (1)$$

I

$$(C_9H_7)_2TiCl_2 + 2\,ArOH + 2\,Et_3N \xrightarrow[80\,°C]{\text{Benzene}} (C_9H_7)_2Ti(OAr)_2 + 2\,Et_3N \cdot HCl \qquad (2)$$

II

where $Ar = C_6H_5$, p-ClC_6H_4, α-$C_{10}H_7$ or β-$C_{10}H_7$. The reactions were carried out in benzene at 80 °C and Et_3N was used as HCl-recovering agent.

All the complexes crystallyze as yellow to yellowish brown crystals. The compounds so obtained decompose slightly in air to brown amorphous solids over a period of several days. These are soluble in common organic solvents, viz., benzene, nitrobenzene, dichloromethane, chloroform, carbon disulphide, ethanol and acetone. It is evident from conductance in nitrobenzene that the compounds are non-electrolytes. The analytical and physical data of the complexes are given in Table 1.

The assignment of characteristic infrared frequencies for the complexes are listed in Table 2. The C—H stretching frequencies at $\sim 3\,100\,\mathrm{cm}^{-1}$ in the complexes are indicative of the indenyl group. The perpendicular hydrogen wagging vibration around $840\,\mathrm{cm}^{-1}$, the parallel hydrogen wagging mode at $\sim 1\,015\,\mathrm{cm}^{-1}$, the band owing to C—C stretching and ring breathing mode of π-bond at ~ 1450 and $\sim 1\,160\,\mathrm{cm}^{-1}$, respectively further confirm the presence of the indenyl group[12]. The bands occurring at $\sim 630\,\mathrm{cm}^{-1}$ may be assigned to the Ti—O—C group[13]. Besides these, the $(C_9H_7)_2Ti(OAr)Cl$ complexes also absorb at $\sim 380^{-1}$ due to the Ti—Cl band.

Proton magnetic resonance spectra of the complexes were taken in

Table 1. *Analytical and physical data*

Compound	No.	Yield (%)	Dec. temp.[a] (°C)	Conductance[b] M × 10^3 = 0.5	% Found (Calc.)	
					Ti	Cl
$(C_9H_7)_2Ti(OC_6H_5)Cl$	**1**	70	78-80	0.22	11.89(11.81)	8.78 (8.73)
$(C_9H_7)_2Ti(OC_6H_4Cl)Cl$	**2**	70	72-74	0.28	10.76(10.88)	16.21(16.10)
$(C_9H_7)_2Ti(\alpha\text{-}OC_{10}H_7)Cl$	**3**	74	70-71	0.26	10.42(10.51)	7.71 (7.78)
$(C_9H_7)_2Ti(\beta\text{-}OC_{10}H_7)Cl$	**4**	62	55-57	0.28	10.46(10.51)	7.64 (7.78)
$(C_9H_7)_2Ti(OC_6H_5)_2$	**5**	72	98-100	0.28	10.27(10.34)	—
$(C_9H_7)_2Ti(OC_6H_4Cl)_2$	**6**	60	63-65	0.32	8.92 (9.01)	13.20(13.32)
$(C_9H_7)_2Ti(\alpha\text{-}OC_{10}H_7)_2$	**7**	65	54-56	0.24	8.38 (8.51)	—
$(C_9H_7)_2Ti(\beta\text{-}OC_{10}H_7)_2$	**8**	68	44-45	0.30	8.42 (8.51)	—

[a] Uncorrected values; [b] in ohm^{-1} cm^2 mol^{-1}.

Table 2. *Characteristic infrared bands*

Compound No.	ν (Ti—Cl)	ν (Ti—O—C)	ν (C—H) stretching band	ν (C—C) asymmetric ring breating	ν (C—H) in plane bending	ν (C—H) bending out of plane deformation
1	385 (m)	625 (m)	3 100 (s)	1 440 (m)	1 025 (m)	835 (m)
2	385 (m)	630 (m)	3 080 (s)	1 445 (m)	1 015 (m)	835 (m)
3	390 (m)	625 (m)	3 100 (s)	1 450 (m)	1 015 (m)	830 (w)
4	380 (m)	625 (m)	3 100 (s)	1 435 (m)	1 020 (m)	835 (m)
5	—	625 (m)	3 100 (s)	1 440 (m)	1 030 (m)	840 (w)
6	—	620 (m)	3 110 (s)	1 450 (m)	1 025 (m)	830 (m)
7	—	630 (m)	3 100 (s)	1 440 (m)	1 020 (m)	835 (m)
8	—	625 (m)	3 080 (s)	1 440 (m)	1 015 (m)	840 (m)

deuterated chloroform. The reasonance signals due to indenyl protons overlap with that of phenoxy ring protons. Thus, a complex multiplet appeared in the region δ 6.70–7.80 ppm and these groups could not be identified separately.

The electronic spectra of the complexes in chloroform show a single band in the region 24775–24225 cm^{-1}. Absence of a d—d transition rules out the presence of an unpaired electron in the titanium ion and corresponds to the electronic configuration $(n-1)\,d^{\circ}$, ns°[14, 15].

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Experimental

Materials and Methods

All the reagents used were of analytical grade. Bis(indenyl)titanium(IV) dichloride, $(C_9H_7)_2TiCl_2$, was prepared by the reaction of indenyl thallium(I) and titanium tetrachloride in 2 : 1 molar ratio in tetrahydrofuran. *THF* (Baker AR) was dried over sodium metal and then boiled under reflux until it gave a blue colouration with Ph_2CO. It was finally dried by distillation from $LiAlH_4$. Benzene and triethylamine were dried as reported in Ref.[16]. Nitrobenzene for conductance measurements was purified by the method described by *Fay* and *Lowry*[17]. Titanium was determined gravimetrically as its oxide whereas chlorine was estimated as silver chloride.

Conductance measurements were made in nitrobenzene at 20 ± 0.05 °C using a Systronic Digital Direct Reading Conductivity Meter Type 304. IR spectra were recorded in "KBr pellets" in the 4000–200 cm^{-1} region on a Perkin-Elmer 621 grating spectrophotometer. The proton NMR spectra were recorded at ambient temperature (20 °C) at a sweep width of 900 Hz with a Perkin-Elmer R-32 spectrometer. Chemical shifts (δ, ppm) are expressed relative to an internal reference of *TMS* (1% by volume). Electronic spectra of the complexes in chloroform were recorded on Perkin-Elmer UV-visible spectrophotometer, Model 554.

Preparation of the Complexes

I. $(C_9H_7)_2Ti(OAr)Cl$. An appropriate phenol (5 mmol) in 50 ml benzene was added to a solution containing bis(indenyl)-titanium(IV) dichloride, $(C_9H_7)_2TiCl_2$ (5 mmol) and Et_3N (8 mmol) in 50 ml benzene. The reaction mixture was refluxed for 4 h and then allowed to cool at room temperature. The precipitate of $Et_3N \cdot HCl$ was filtered and the filtrate so obtained was concentrated under reduced pressure. An excess of petroleum ether (40–60 °C) was added to the concentrated filtrate and the mixture was allowed to stand for 1 h when crystals of the product separated out. These were filtered, washed with ether and dried under vacuum.

II. $(C_9H_7)Ti(OAr)_2$. A solution of $(C_9H_7)_2TiCl_2$ and an appropriate phenol in 1 : 2 molar ratio in benzene containing Et_3N was refluxed for 4 h and the product was isolated by a similar method as described for $(C_9H_7)_2Ti(OAr)Cl$.

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