NOTE

MONO- AND BISPHENOXY DERIVATIVES OF BIS(INDENYL)ZIRCONIUM(IV)

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Abstract—A series of $(C_9H_7)_2Zr(OAr)Cl$ and $(C_9H_7)_2Zr(OAr)_2$ complexes, where $Ar = C_6H_5$, p-ClC₆H₄, α -C₁₀H₇, or β -C₁₀H₇, have been synthesised by the reaction of bis(indenyl)zirconium(IV)-dichloride with an appropriate phenol in a 1:1 and 1:2 molar ratio in refluxing benzene in the presence of triethylamine. These complexes have been characterised by elemental analyses, conductance measurements and spectral (IR, ¹H NMR and electronic) studies.

The organometallic chemistry of titanium has been extensively developed over the past three decades, while that of zirconium is only now beginning to be developed. Organo-titanium compounds are known as catalysts for the polymerisation^{1,2} and hydrogenation^{3,4} of olefins and dienes. Transition metal phenoxides on the other hand have been used as olefin polymerisation catalysts in many organic reactions.⁵ Some phenoxo and diphenoxo derivatives of bis(cyclopentadienyl)/(methyl cyclopentadienyl)titanium(IV) and zirconium(IV) have been reported.⁶⁻¹¹ However, reactions of bis-(indenyl)zirconium(IV)dichloride with phenols have not been reported previously. The present work describes the preparation and characterisation of such compounds.

EXPERIMENTAL

Reagents and general techniques

All the reagents used were of analytical grade. Bis(indenyl)zirconium(IV) dichloride, $(C_9H_7)_2ZrCl_2$ was prepared by the reaction of indenyl thallium(I)¹² and zirconium tetrachloride in anhydrous tetrahydrofuran in a 2:1 molar ratio. THF (Baker, AR) was dried over sodium metal and then boiled under reflux until it gave a blue colouration with Ph₂CO. It was finally dried by distillation from LiAlH₄. Benzene and triethylamine were dried as reported in the literature.¹³ Nitrobenzene for conductance measurements was purified by the method described by

*Author to whom correspondence should be addressed. POLY Vol. 3, No. 5-G Fay *et al.*¹⁴ Zirconium was determined gravimetrically as its oxide whereas chlorine was estimated as silver chloride.

Conductance measurements were made in nitrobenzene at $30 \pm 0.05^{\circ}$ C using a Systronic Digital Direct Reading Conductivity Meter Type 304. IR spectra in the region 4000–200 cm⁻¹ were recorded as KBr discs using a Perkin–Elmer 621 spectrophotometer. The proton NMR spectra were determined using Perkin–Elmer R-32 spectrometer (with TMS as internal standard). Electronic spectra of the complexes in chloroform were recorded on a Perkin–Elmer UV-visible spectrophotometer, Model 554.

Preparation of the complexes

(1) $(C_9H_7)_2Zr(OAr)Cl$. All operations were carried out under strictly anhydrous conditions. An appropriate phenol (5 mmol) in 20 cm³ benzene was added to a solution containing bis(indenyl)zirconium(IV)dichloride, (C₉H₇)₂ZrCl₂ (5 mmol) and Et₃N (8 mmol) in 40 cm³ benzene. The reaction mixture was refluxed for 4 hr and then allowed to cool at room temperature. The precipitate of $Et_3N \cdot HCl$ was filtered and the filtrate so obtained was concentrated to about 1/3of the initial volume 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 some time when crystals of the product separated out. These were filtered, washed with ether and dried under vacuum.

(2) $(C_9H_7)_2Zr(OAr)_2$. A solution of $(C_9H_7)_2ZrCl_2$ and an appropriate phenol in a 1:2 molar ratio in benzene containing Et₃N was refluxed for 4 hr and the product was isolated by a similar method as described for $(C_9H_7)_2Zr(OAr)Cl$.

RESULTS AND DISCUSSION

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

$$(C_{9}H_{7})_{2}ZrCl_{2} + ArOH + Et_{3}N \xrightarrow{\text{benzene}} \\ (C_{9}H_{7})_{2}Zr(OAr)Cl + Et_{3}N \cdot HCl \qquad I \quad (1)$$

$$(C_{9}H_{7})_{2}ZrCl_{2} + 2ArOH + 2Et_{3}N \xrightarrow{\text{benzene}}_{80^{\circ}C}$$
$$(C_{9}H_{7})_{2}Zr(OAr)_{2} + 2Et_{3}N \cdot HCl \qquad II \quad (2)$$

where $Ar = C_6H_5$, *p*-ClC₆H₄, α -Cl₁₀H₇ or β -C₁₀H₇.

All the complexes form yellow to yellowishbrown 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

Complex	¥ 1eld (%)	Dec. temp. ^{a)} (^o C)	Conductance ^{b)} M x 10 ³ = 0.5	Elemental analyses \$ Found(Cale.)	
				Zr	Cl
(c ₉ H ₇) ₂ Zr(0c ₆ H ₅)c1	60	159-162	0,32	20,19(20,28)	7.80(7.89)
(c ₉ H ₇) ₂ Zr(0c ₆ H ₄ c1)c1	64	117119	0.24	18.72(18.84)	14.75(14.66)
$(c_{9}H_{7})_{2}Zr(< -0c_{10}H_{7})c_{1}$	70	9 79 9	0.28	18.20(18.25)	7.16(7.10)
(c9H7)2 ^{7r(, & -0c10H7)c1}	68	103-105	0.22	18,12(18,25)	7.06(7.10)
(°9 ^H 7)2 ^{%r(0°6^H5)2}	65	170-172	0,30	17.84(17.98)	-
(c9H7)2 ^{Zr(0C6H4C1)} 2	62	130-132	0,24	15,73(15,83)	12.37(12.32)
^{(c} 9 ^H 7)2 ^{Zr(~~-0C} 10 ^H 7)2	66	85-87	0,30	15.06(15.02)	-
^{(c} 9 ^H 7 ⁾ 2 ^{Zr(β} - ^{OC} 10 ^H 7 ⁾ 2	70	135-137	0,26	14.95(15.02)	-

Table 1. Analytical and physical data

a) Uncorrected values; b) in ohm⁻¹ cm² mole⁻¹

Table 2.	Characteristic	IR	bands
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Complex	√(Z r-C1)	ר) (ZF-0-C)	√(C-H) stretc- hing band	V(C-C) asymne- tric ring breathing	√(C-H) in plane bending	√(C-H) bending out of plane deformation
(c9H7)22r(0C6H5)C1	380(m)	620 (m)	3090(s)	1450(m)	1020(m)	820(w)
(c ₉ H ₇) ₂ Zr(0c ₆ H ₄ C1)C1	390(m)	6 25(m)	3 <u>11</u> 0(s)	1440(m)	1010(m)	835(m)
(C ₉ H ₇) ₂ Zr(∝ -0C ₁₀ H ₇)c1	385(m)	630(m)	3100(s)	1450(m)	1025(m)	830(w)
$(c_{9}H_{7})_{2}Zr(\beta - 3c_{10}H_{7})c1$	380(m)	630(m)	3080(s)	1445(m)	10 15(m)	840(m)
(C9H7)2 ^{Zr(0C6H5)} 2	-	635(m)	3085(s)	1450(m)	1020(m)	840(m)
(C9H7)2 ^{Zr(OC6H4C1)} 2	-	620(m)	3080(s)	1460(m)	1010(m)	820 (w)
(c ₉ H ₇) ₂ Zr(~ -)c ₁₀ H ₇) ₂	-	6 25(m)	3100(s)	1 44 0(m)	1015(m)	830(m)
(c ₉ H ₇) ₂ Zr(β -0c ₁₀ H ₇) ₂	-	630 (m)	3085(s)	1455(m)	1010(m)	825(m)

conductance measurements 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 IR frequencies for the complexes are listed in Table 2. The C–H stretching frequency at ~3080 cm⁻¹ in the complexes is indicative of the indenyl group.¹⁵ The perpendicular hydrogen wagging vibration around 840 cm^{-1} , the parallel hydrogen wagging mode at ~1015 cm⁻¹, the band due to C–C stretching and ring breathing mode of π -bond at ~1450 and ~1160 cm⁻¹, respectively, further confirm the presence of the indenyl group.¹⁵ The bands occurring at ~630 cm⁻¹ may be assigned to the Zr–O–C group.¹⁶ Besides these, the (C₉H₇)₂Zr(OAr)Cl complexes also absorb at ~380 cm⁻¹ due to Zr-Cl band.

Proton magnetic resonance spectra of the complexes were taken in deutero-chloroform. The resonance signals due to indenyl protons overlap with that of phenoxy ring protons. Thus, a complex multiplet appeared in the region $\delta 6.70-7.80$ ppm and these groups could not be identified separately.

The electronic spectra of all the complexes recorded in chloroform exhibit a single band in the region 24775-24225 cm⁻¹. Absence of a *d*-*d* transition rules out the presence of any unpaired electron in the zirconium ion confirming the quadrivalent state of zirconium.^{17,18}

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