



Synthesis and Characterization of Bis(cyclopentadienyl)Zirconium(IV)Bis(o,o-dialkyl and alkylenedithiophosphate) Complexes

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Abstract

$Cp_2Zr[S_2P(OR)_2]_2$ (where $R = C_2H_5$, $CH_3CH_2CH_2$, $(CH_3)_2CH$, $(CH_3)_3C$ and C_6H_5), $Cp_2Zr[S_2POGO]_2$ (where $G = -CH_2C(CH_3)_2CH_2-$, $-CH_2C(C_2H_5)_2CH_2-$ and $-C(CH_3)_2C(CH_3)_2-$) have been synthesized by the reaction of Bis(cyclopentadienyl) zirconium(IV)dichloride with O,O-dialkyl and alkylenedithiophosphoric acids in molar ratio 1:2 in refluxing benzene. All products were yellow solids, soluble in organic solvent, monomeric in nature and have been characterized by elemental analyses, molecular weight determinations, and have been further characterized by some spectroscopical data IR and NMR (1H , ^{13}C and ^{31}P).

Keywords: Zirconium, alkylene dithiophosphoric, cyclopentadienyl, complexes, ligand.

Introduction

Zirconocene complexes are amongst the most widely used transition metal complexes. Over last several decades, they have been utilized for a variety of applications, such as catalytic properties of zirconium metallocenes, and in the development of modern synthetic methodology of such complexes has been demonstrated¹. O,O-dialkyl and alkylenedithiophosphoric acids act as versatile bidentate dithio ligands and form a variety of stable complexes with transition^{2,3} and non transition^{4,7} elements. The preparation and structure of metal dithiophosphate has received considerable interest during one half decades due to their application in the area of antioxidants, anti wear^{8,9} and pesticides^{10,11}.

Material and Methods

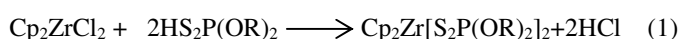
Moisture was carefully excluded throughout the experimental work, solvents were dried according to the standard methods prior to their use. Distilled Glycols were used, Bis(cyclopentadienyl) zirconium (IV) dichloride (Aldrich) was used as supplied, Dialkyl and alkylenedithiophosphoric were synthesized as describe in the literature¹²⁻¹³. Sulfur was estimated as $BaSO_4$ (Messenger's method). IR spectra were recorded in KBr mulls in the range 4000-400 cm^{-1} on a Perkin Elmer= 377 spectrophotometer. The 1H , ^{13}C and ^{31}P NMR spectra were recorded on a Bruker DRX 300 (120 MHz) spectrometer using TMS as the internal reference.

Reaction of Bis (Cyclo Pentadienyl Zirconium (IV) Dichloride with Dialkyl (OPr-n) and Alkylene Dithiophosphoric acids in 1:2 Molar Ratios: $HS_2P(OPr-n)_2$ (0.219 g) was dissolved in 10 ml benzene and was added drop wise with stirring to a solution of Cp_2ZrCl_2 (0.150 g) in 15 ml benzene. The reaction mixture was refluxed for 5 hour at 25°C.

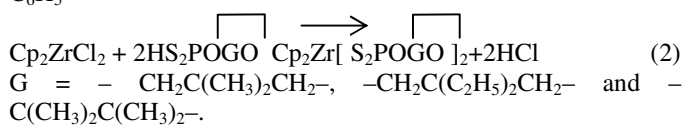
The colorless reaction mixture changed to yellow color. Vacuum was used to remove the excess solvent. Finally the yellow product was washed with n-hexane and dried in vacuo.

Results and Discussion

Bis(cyclopentadienyl) zirconium(IV) Bis(O-Odialkyl and alkylene dithiophosphate) derivatives have been synthesized by the reaction of dialkyl and alkylenedithiophosphoric acids with Bis(cyclopentadienyl) zirconium(IV) dichloride. All these reaction carried out under refluxing in benzene for 6 h, in 1:2 molar ratio as in equation 1 and 2.



Where $R = C_2H_5$, $CH_3CH_2CH_2$, $(CH_3)_2CH$, $(CH_3)_3C$ and C_6H_5 -



The colorless reaction mixture has been changed to yellow. These newly synthesized Bis (cyclopentadienyl) zirconium (IV) Bis (dialkyl and alkylene dithiophosphate) complexes are yellow colored crystalline solid, non-volatile in nature, freely soluble in common organic solvents, and extremely sensitive towards atmospheric moisture. The molecular weights of all derivatives were determined and tabulated in table 1, which indicated that all of them are in monomeric form.

IR Spectra: On the bases of recent reports¹⁴ IR spectra of the new derivatives was analyzed. The IR spectra recorded in the region 4000-400 cm^{-1} . The S-H stretching band at 2544 – 2400 cm^{-1} which has been observed for the parent acid¹⁵ disappeared

in the derivative spectra as a result of formation of Zr-S. A new band¹⁴ for Zr-S appeared in the region 402-440 cm⁻¹. Two bands corresponding to $\nu(P)-O-C$ and $\nu P-O-(C)$ vibration at the region 974.0-1099.0 cm⁻¹ and 810.0 – 889.1 cm⁻¹ respectively¹⁶. A band in the region 912.3 – 940.0 cm⁻¹ is the most probably due to dioxaphospholane and dioxaphosphorinane ring vibrations.¹⁷⁻¹⁸ A sharp band present in the region 630.7– 684.7 cm⁻¹ can be assigned to $\nu P=S$ vibrations¹⁶. Bands in medium intensities in the region 505.3– 580.0 cm⁻¹ attributed to $\nu P-S$ asymmetric and symmetric vibrations¹⁹. Detailed peak data is recorded in table 2.

¹H NMR Spectra: The ¹H NMR spectra of all derivative complexes recorded in CDL₃ table 3, show the characteristic resonance due to alkoxy and glycoxy (dithio moiety) protons. The singlet peak at (3.1- 3.5ppm)²⁰ of the SH proton is absent in the spectra of all derivative complexes which means disappearance of S-H bond and formation of Zr -S bond.

¹³C NMR Spectra: The ¹³C NMR spectra of all derivative complexes were recorded in deuterated chloroform at ambient temperature. Table 4 Shows small chemical shifts to those obtained spectra for the parent dithiophosphoric acids that indicates no substantial change in the structure.

Table-1
Analytical and Physicochemical Data for Some New Products

SI. No.	Compounds	Physical State	M. P. °C	Mol. Wt. Found / (Calc.)	% S Found / (Calc.)	%Zr Found / (Calc.)
I	Cp ₂ Zr[S ₂ P(OC ₂ H ₅) ₂] ₂	Yellow solid ⁰	578 / (591.78)	20.53/(21..67)	14.10 / (15.41)
II	Cp ₂ Zr[S ₂ P(OCH ₂ CH ₂ CH ₃) ₂] ₂	Yellow solid	155 ⁰ / (647.89)	18.78/ (19.80)	13.44/(14.08)
III	Cp ₂ Zr[S ₂ P(OCH(CH ₃) ₂) ₂] ₂	Yellow solid ⁰	634/ (647.89)	18.60 / (19.80)/(14.08)
IV	Cp ₂ Zr[S ₂ P(OC(CH ₃) ₃) ₂] ₂	Yellow solid ⁰	689 / (704.00) / (18.22)	12.10./ (12.96)
V	Cp ₂ Zr[S ₂ P(OC ₆ H ₅) ₂] ₂	Yellow solid ⁰ / (783.96)	15.50 / (16.36)/(11.64)
VI	Cp ₂ Zr[S ₂ POCH ₂ C(CH ₃) ₂ CH ₂ O] ₂	Yellow solid	143 ⁰	602/ (615.62)	20.11 / (20.83)	14.00../ (14.82)
VII	Cp ₂ Zr[S ₂ POCH ₂ C(C ₂ H ₅) ₂ CH ₂ O] ₂	Yellow solid	136	663 / (671.72)	18.21 / (19.09)	12.70/(13.58)
VIII	Cp ₂ Zr[S ₂ POC(CH ₃) ₂ C(CH ₃) ₂ O] ₂	Yellow solid	189	630 / (643.68)	18.30 / (19.99)	13.50/(14.17)

Table-2
IR Spectral Data (cm⁻¹) for Some New Products

SI. No.	Compounds	$\nu P-O-(C)$	$\nu (P)-O-C$	Ring Vibration	$\nu (Zr-S)$	$\nu P=S$	$\nu P-S$
I	Cp ₂ Zr[S ₂ P(OC ₂ H ₅) ₂] ₂	810.0 s	1016.4 s	--	405.0 m	655.8 m	540.0 m
II	Cp ₂ Zr[S ₂ P(OCH ₂ CH ₂ CH ₃) ₂] ₂	850.5m	993.0 s	--	440.0 w	630.7 m	543.9 m
III	Cp ₂ Zr[S ₂ P(OCH(CH ₃) ₂) ₂] ₂	889.1 m	974.0m	--	402.0 m	651.9 m	542.0 m
IV	Cp ₂ Zr[S ₂ P(OC(CH ₃) ₃) ₂] ₂	820.0 s	990.0s	--	413.0 w	650.0 m	532.0 m
V	Cp ₂ Zr[S ₂ P(O C ₆ H ₅) ₂] ₂	820.8 s	1099.0 m	--	422.0w	670.5 s	513.0w
VI	Cp ₂ Zr[S ₂ POCH ₂ C(CH ₃) ₂ CH ₂ O] ₂	815.8 m	1056.9 s	912.3 m	410.0 w	684.7 m	505.3 m
VII	Cp ₂ Zr[S ₂ POCH ₂ C(C ₂ H ₅) ₂ CH ₂ O] ₂	830.0 m	1020.2 s	940.0 m	407 0 m	660.0 m	530.0 m
VIII	Cp ₂ Zr[S ₂ POC(CH ₃) ₂ C(CH ₃) ₂ O] ₂	858.3 s	1010.6 s	923.8 m	409.0 m	661.5 m	580.0 m

b = broad, s = strong, w = weak and m = medium absorption bands

Table-3
¹H and ³¹P NMR Data for Some New Products

SI. No.	Compounds	¹ H chemical shift in δ ppm in CDCl ₃ (parent acid)	³¹ P chemical shift in δ ppm
I	Cp ₂ Zr[S ₂ P(OC ₂ H ₅) ₂] ₂	1.188 – 1.288, m, 12H(CH ₃) 4.062– 4.12, m, 8H(OCH ₂) 6.42 –6.56, m, 10H(C ₅ H ₅)	86.13 (85.700)
II	Cp ₂ Zr[S ₂ P(OCH ₂ CH ₂ CH ₃) ₂] ₂	0.764 – 0.857, m, 12H(CH ₃) 1.341 – 1.364, d, 8H(CH ₂) 3.375– 3. 561 m, 8H(OCH ₂) 6.193 – 6.483, m, 10H(C ₅ H ₅) (86.100)
III	Cp ₂ Zr[S ₂ P(OCH(CH ₃) ₂) ₂] ₂	1.219– 1.270, m, 24H(CH ₃) 4.402 – 4.423, m, 4H(OCH) 6.326 – 6.521, m, 10H(C ₅ H ₅)	83.56 (82.300)
IV	Cp ₂ Zr[S ₂ P(OC(CH ₃) ₃) ₂] ₂	0.788– 0.887, m, 24H(CH ₃) 1.728, s, 4H(CH) 3.460 – 3.709, m, 8H(OCH ₂) 6.309 –6.475, m, 10H(C ₅ H ₅) (85.700)
V	Cp ₂ Zr[S ₂ P(OC ₆ H ₅) ₂] ₂	6. 236 –6.881, m 10H(C ₅ H ₅) 7.004-7.440, m, 20H(OC ₆ H ₅) (79.900)
VI	Cp ₂ Zr[S ₂ POCH ₂ C(CH ₃) ₂ CH ₂ O] ₂	0.828-1.126, m, 12H(CH ₃) 3.705 – 3.756, m, 8H(OCH ₂). 6.354- 6.533, m, 10H(C ₅ H ₅)	77.93 (77.300)
VII	Cp ₂ Zr[S ₂ POCH ₂ C(C ₂ H ₅) ₂ CH ₂ O] ₂	0.615, m, 0.804, 12H(CH ₃) 1.117 – 1.539, m, 8H(CH ₂) 4. 022 – 4.203, m, 8H(OCH ₂), 6.280– 6.412, m, 10H(C ₅ H ₅) (78.500)
VIII	Cp ₂ Zr[S ₂ POC(CH ₃) ₂ C(CH ₃) ₂ O] ₂	1.065-1.438, m, 24H(CH ₃) 6.451 – 6.576 m, 10H(C ₅ H ₅)	93.72 (93.100)

s = singlet, d = doublet, t = triplet, q = quartet m = multiplet .

Table-4
¹³C NMR Data for Some New Products

SI No.	Compound	¹³ C Chemical shift, in ppm					
		C	CH	CH ₂	CH ₃	CO	C ₅ H ₅
I	Cp ₂ Zr[S ₂ P(O C ₂ H ₅) ₂] ₂	15.913s	63.338 s	128.162s
II	Cp ₂ Zr[S ₂ P(OCH(CH ₃) ₂) ₂] ₂	23.192s	72..472s	117.344- 118.023 d
III	Cp ₂ Zr[S ₂ POCH ₂ C(CH ₃) ₂ CH ₂ O] ₂	32.981 s	19.953- 21.311,t	77.066- 77.169 d	117.489 s

t = triplet d = doublet and s = singlet

³¹P NMR Spectra: The proton decoupled ³¹P NMR spectra Bis(cyclopentadienyl) zirconium(iv) Bis(dialkyl and alkylene dithiophosphate) derivatives table 3 shows that each derivative have only one signal peak between 93.72 – 77.93 ppm. Similar peak indicating that all the derivative molecules contain only one type of phosphorous nucleus. However, no notable difference was observed in comparison to the parent acids²¹. It appears that small shift in ³¹P this shifting according the

Glidewell observations indicates bidentate behavior of the ligand²².

Structural Elucidation: IR spectra, (¹H, ¹³C) NMR, molecular weight determination and elemental analysis indicate that the ligand is a bidentate ligand. Monomeric nature of the complexes was also approved. From the above data the suggested structure for the produced is shown in figure 1.

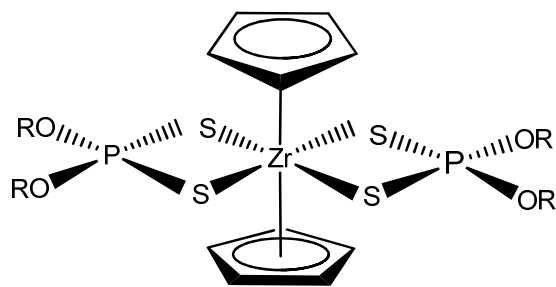


Figure-1

Suggested structure of Bis(cyclopentadienyl)zirconium(IV)-Bis(O-Dialkyl and alkylene dithiophosphate) complexes

Conclusion

The derivatives of the complex Bis (cyclopentadienyl) zirconium(IV) Bis(dialkyl and alkylenedithiophosphate) were synthesized. They were all yellow colored solid, non-volatile, freely soluble in common organic solvents and sensitive towards atmospheric moisture. IR spectra, (¹H, ¹³C) NMR, molecular weight determination and elemental analysis indicated that the ligand is a bidentate ligand, and the derivatives are in monomeric nature.

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