

Synthesis & Characterisation of Some Non-bridged & Bridged $\eta^1:\eta^5$ -Dicyclopentadienyl Zirconium Pyrazolone Complexes

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The complexes of the types $(C_5H_5)_2ZrClL$, $C_5H_5ZrClL_2$ and $[(C_5H_4)ZrL_2]_2$ have been synthesized by the reaction of zirconocene dichloride, $(C_5H_5)_2ZrCl_2$ and substituted pyrazolones of the type $RCOC:C(OH)N(C_6H_5)N:CCH_3$ (where $R = -CH_3$, $-C_2H_5$, $-C_6H_5$ and $p\text{-Cl}-C_6H_4$) in the presence of triethylamine in refluxing THF solution. The structures of these complexes have been elucidated on the basis of elemental analyses, molecular weight measurements and IR and PMR spectral evidences.

The reactions of zirconocene dichloride¹⁻⁵ $(C_5H_5)_2ZrCl_2$, with monofunctional bidentate ligands in 1:2 molar ratio yield products of the type $C_5H_5ZrClL_2$ or $(C_5H_5)_2ZrL_2$ depending upon the nature of the ligand employed. In view of the interesting results obtained in our previous communication⁶, we now report preparation and characterisation of some bridged $\eta^1:\eta^5$ -dicyclopentadienyl zirconium pyrazolone complexes.

Materials and Methods

The solvents were dried before use and all manipulations were carried out under strictly anhydrous conditions. The ligands were synthesized by the procedure reported by Jensen⁷. Zirconium was estimated as ZrO_2 and chlorine was estimated by Volhard's method⁸.

General procedure of synthesis of the complexes

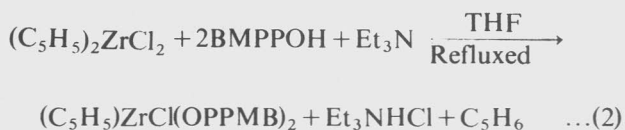
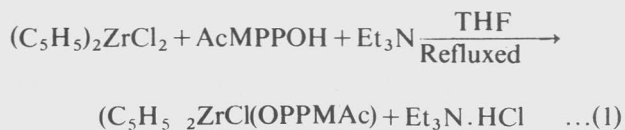
To a suspension of Cp_2ZrCl_2 (1.83 g, 6.26 mmol) in dry tetrahydrofuran containing triethylamine (0.63 g, 6.25 mmol) was added 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (BMPPOH) (1.74 g, 6.25 mmol) and the reaction mixture was refluxed for ~3 to 4 hr. The white precipitate, so formed, was filtered off. On stripping off the excess solvent under reduced pressure, a foamy light yellow coloured solid was obtained. The complexes with other ligands were prepared in a similar manner and the experimental details have been summed up in Table 1.

Molecular weights were determined in a semi-micro ebulliometer (Gallen Kamp) equipped with a thermister sensor. Infrared spectra were recorded in nujol on a Perkin Elmer 577 grating spectrophotometer using cesium iodide optics. The PMR spectra

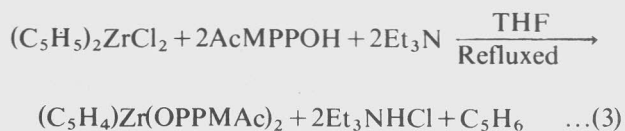
were recorded in $CDCl_3$ on a R12B spectrophotometer.

Results and Discussion

The reactions of the enolic form of 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-ones (AcMPPOH) (where Acyl = acetyl, propionyl, benzoyl and $p\text{-Cl}$ -benzoyl) with zirconocene dichloride, $(C_5H_5)_2ZrCl_2$, in 1:1 and 2:1 molar ratios in the presence of triethylamine in dry tetrahydrofuran yielded the complexes $(C_5H_5)_2ZrCl(PPMAc)$ and $(C_5H_5)ZrCl(PPMB)_2$ respectively.



However, the reaction of zirconocene dichloride with these ligands in 1:2 molar ratio in presence of two moles of Et_3N gave the product $[(C_5H_4)Zr(PPMAc)_2]_2$.



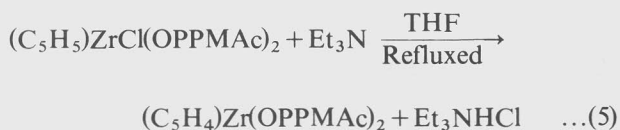
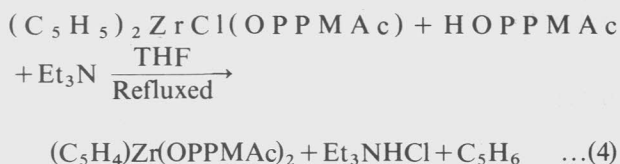
The above class of complexes has also been synthesized by the reaction of $(C_5H_5)_2ZrCl(PPMAc)$ with another mol of ligand in the presence of triethylamine

Table 1—Reactions of Zirconocene Dichloride with 4-Acyl-3-methyl-1-phenyl-2-pyrazolin-5-ones

Sl. No.	(C ₅ H ₅) ₂ ZrCl ₂ (g)	Pyrazolone (g)	Et ₃ N (g)	Product (%, Yield)	Found (Calc.), %			
					Et ₃ N.HCl	Zr	Cl	Mol. wt. Found (Calc.)
1	(C ₅ H ₅) ₂ ZrCl ₂	BMPPOH	0.63	(C ₅ H ₅) ₂ ZrCl(OPPMB)	0.80	17.41	6.54	524
	1.83	1.74		(55)	(0.86)	(17.09)	(6.64)	(534)
2	(C ₅ H ₅) ₂ ZrCl ₂	BMPPOH	1.08	[(C ₅ H ₄)Zr(OPPMB) ₂] ₂	1.40	12.88	—	1387
	1.56	2.97		(58)	(1.47)	(12.86)		(709)
3	(C ₅ H ₅) ₂ ZrCl ₂	PMPPOH	0.42	(C ₅ H ₅) ₂ ZrCl(OPPMP)	0.50	18.90	7.20	—
	1.20	0.95		(52)	(0.56)	(18.77)	(7.29)	—
4	(C ₅ H ₅) ₂ ZrCl ₂	PMPPOH	0.72	[(C ₅ H ₄)Zr(OPPMP) ₂] ₂	0.95	14.89	—	—
	1.04	1.64		(57)	(0.98)	(14.87)		
5	(C ₅ H ₅) ₂ ZrCl ₂	AMPPOH	0.63	(C ₅ H ₅) ₂ ZrCl(OPPMA)	0.84	19.42	7.40	457
	1.82	1.35		(54)	(0.85)	(19.33)	(7.51)	(472)
6	(C ₅ H ₅) ₂ ZrCl ₂	AMPPOH	0.94	[(C ₅ H ₄)Zr(OPPMA) ₂] ₂	1.25	15.81	—	1143
	1.35	2.00		(53)	(1.27)	(15.58)		(585)
7	(C ₅ H ₅) ₂ ZrCl ₂	CMPPOH	0.38	(C ₅ H ₅) ₂ ZrCl(OPPMC)	0.50	16.10	6.10	—
	1.11	1.19		(56)	(0.52)	(16.05)	(6.24)	
8	(C ₅ H ₅) ₂ ZrCl ₂	CMPPOH	0.56	[(C ₅ H ₄)Zr(OPPMC) ₂] ₂	0.54	11.80	—	—
	0.80	1.72		(51)	(0.55)	(11.72)		
9	(C ₅ H ₅) ₂ ZrCl ₂	BMPPOH		C ₅ H ₅ ZrCl(OPPMB) ₂	0.25	12.34	4.66	731
	0.59	1.14	0.21	(56)	(0.28)	(12.23)	(4.75)	(746)

Where BMPPOH = 4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one
 PMPPOH = 4-Propionyl-3-methyl-1-phenyl-2-pyrazolin-5-one
 AMPPOH = 4-Acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one
 CMPPOH = 4-Chlorobenzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one

or by the reaction of C₅H₅ZrCl(OPPMAc)₂ with another mol of triethylamine.



In these derivatives, one of the cyclopentadienyl rings is knocked-off in the form of cyclopentadiene alongwith the two chlorine atoms. The source of hydrogen for the formation of C₅H₆ appears to be the adjacent C₅H₅ ring^{9,10}.

These derivatives are found to be coloured solids and melt with decomposition. They are soluble in common organic solvents and have been purified by repeated crystallizations from benzene/pet. ether or THF/pet. ether mixtures. The molecular weights determined indicate the monomeric nature of the complexes, (C₅H₅)₂ZrCl(OPPMAc) and (C₅H₅)ZrCl(OPPMB)₂ whereas the derivatives (C₅H₄)Zr(OPPMAc)₂ are dimeric in nature.

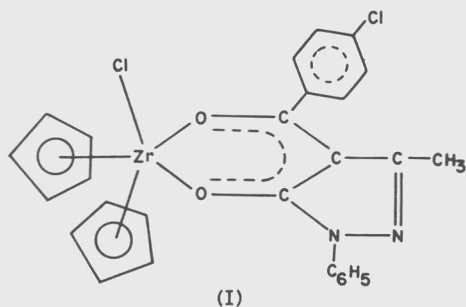
The infrared spectra of these compounds show two medium intensity bands in the region 610-550 cm⁻¹ which may be assigned to (Zr—O) stretching¹¹. A band observed at 1545 cm⁻¹ in the spectra of the ligands is due to ν(C=O) mode¹¹. This band is lowered to ~1515-1525 cm⁻¹ in the spectra of the complexes indicating coordination through carbonyl oxygen of the ligand¹². The absence of absorption bands in the region 1675-1655 cm⁻¹ rules out the possibility of the monodentate nature of the ligands¹³ in these complexes. The other less significant bands appearing at ~1590 and at ~1575 cm⁻¹ in the ligands as well as the complexes have been assigned to phenyl and νC=C/N modes.

The medium intensity bands observed at ~810 and at ~1020 cm⁻¹ may be assigned to C—H deformation (out of plane) and C—H deformation (in plane) vibrations¹⁴. A medium intensity band observed at 390 ± 10 cm⁻¹ in (C₅H₅)₂ZrCl(OPPMAc) and (C₅H₅)ZrCl(OPPMB)₂ derivatives may be assigned to (Zr—Cl) stretching whereas this band was found to be absent in the bis-derivatives [(C₅H₄)Zr(OPPMAc)₂]₂.

Another medium intensity band assignable to ν(Zr-ring) vibrations¹ was observed at 350 ± 10 cm⁻¹ in all the derivatives. However, in [(C₅H₄)Zr(OPPMAc)₂]₂ complexes, a very strong absorption band at ~460 cm⁻¹ due to νZr—C (σ) (ref. 15) has been observed in addition to ν(Zr-ring) band.

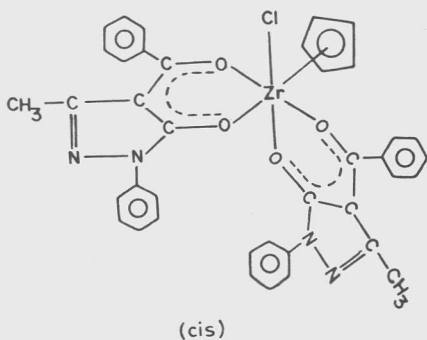
The PMR spectrum of the derivative, $(C_5H_5)_2ZrCl(PPMC)$, shows a singlet at δ 2.0 ppm due to the methyl protons. A multiplet centred at δ 6.8-7.9 ppm due to phenyl protons and a broad doublet at δ 6.4 ppm due to the C_5H_5 group have also been observed. The appearance of a broad doublet instead of a singlet for C_5H_5 protons is due to the presence of two C_5H_5 rings at axial and equatorial positions in a trigonal bipyramidal geometry as well as their restricted rotations¹⁶.

On the basis of the above spectral data, the following structure for the complex $(C_5H_5)_2ZrCl(PPMC)$ may be proposed (structure I).

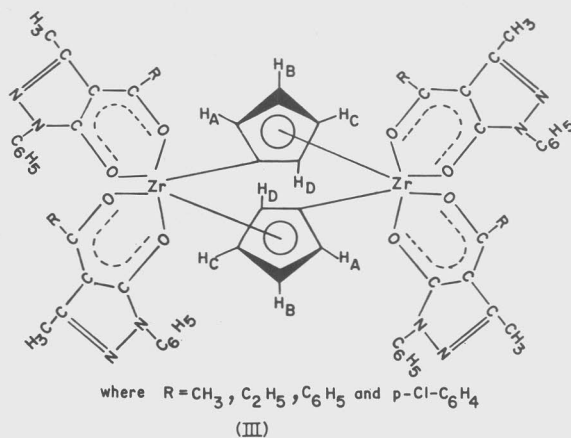


The 1H NMR spectrum of the complex, $C_5H_5ZrCl(PPMB)_2$, shows a doublet at δ 1.7 ppm which may be assigned to CH_3 protons of the pyrazolone ring. The splitting of the methyl protons clearly indicates that the two methyl groups are in different environments. A singlet at δ 6.5 ppm and a multiplet centred at δ 6.8-8.0 ppm may be attributed to the C_5H_5 and phenyl protons, respectively. This monomeric complex may exist in two *trans* and several *cis*-configurations and only one of the former configurations would have equivalent methyl groups. However, only one *cis* and one *trans* form are shown here (structure II).

Although steric factors favour the *trans* geometry, the electronic factors tend to stabilize the *cis*-configuration which is preferred for this octahedral complex. The spectral evidences are not conclusive about the existence of either of the two configurations.



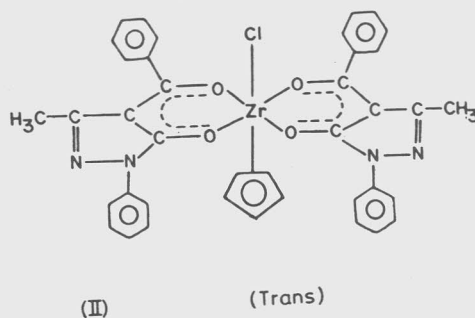
The derivatives, $[(C_5H_4)Zr(PPMAc)_2]_2$, are found to be dimeric in nature and the following structure has been proposed for these (structure III).



The above structure is supported by 1H NMR spectra. In the spectrum of complex $[(C_5H_4)Zr(p-Cl-C_6H_4COC:CON(C_6H_5N:CCH_3)_2)_2]$, two singlets observed at δ 1.6 and δ 1.8 ppm may be assigned to the methyl protons. The two methyl signals may be due to the existence of the complex in the *trans*-geometry. These methyl signals are shifted upfield as compared to their position in the ligand. The shift may be due to the differential shielding.

A double-doublet centred at δ 6.3 ppm may be due to the presence of C_5H_4 moiety in the dimeric complex. The double-doublet may be due to the coupling of H_B protons with the neighbouring protons (chemically equivalent but magnetically non-equivalent)¹⁷ of the C_5H_4 moiety in the complex. Similar type of splitting has been reported earlier in other $\eta^1:\eta^5$ -cyclopentadienyl bridged complexes^{18,19}. A multiplet centred at δ 6.6-8.0 ppm may be due to the phenyl protons.

The possibility of bridging of two zirconium atoms through ligand is completely ruled out on the basis of 1H NMR spectral evidence. In case, the bridging is through ligand and the C_5H_5 ring occupies the terminal position, a singlet for C_5H_5 protons is expected instead of splitting of the C_5H_5 protons into a double-doublet. A similar type of mechanism seems to



be operative in the formation of $[(C_5H_4)ZrL_2]_2$ derivatives as suggested by us earlier⁶.

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