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## Synthesis of bis(cyclopentadienyl) titanium(IV) and zirconium(IV) chlorides with 1,1'-diacetyl ruthenocetyl bis(hydrazones), Formation of trimetallic derivatives

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### ABSTRACT

Metal complexes of Schiff bases represent an important class of coordination compounds. Bis(cyclopentadienyl)titanium(IV) and zirconium(IV) chlorides react with bis(hydrazones) derived from 1,1'-diacetyl ruthenocetyl in anhydrous THF in the presence of base to give complexes of the type  $[(Cp_2MCl)_2L]$  [ $M=Ti$  or  $Zr$ ;  $LH_2 =$  ruthenocetyl bis(hydrazones)]. Tentative structures are proposed for these complexes based upon elemental analyses, electrical conductance, magnetic moment and spectroscopic data.

**Key words:** Spectral data, Schiff's base, Magnetic susceptibility.

### INTRODUCTION

Aroyl hydrazones and their metal derivatives are applied widely in the treatment of various diseases and are also used as pesticides and plant growth regulators. Edwards et al. have shown that replacement of the aromatic group by the ruthenocetyl moiety in penicillins and cephalosporins improves their antibiotic activity [1]. ruthenocetyl aroyl hydrazones are also used as analytical and metal extracting specific reagents. Although, recently papers have appeared on the coordination behaviour of ruthenocetyl aroyl hydrazones towards transition metal ions [2-14], practically no systematic study has been done on the coordination behaviour of bis(hydrazones) derived from 1,1'-diacetylferrocene. Zhang et al. [15] reported Zn, Cu, Co and Ni complexes of 1,1'-bis(N-furoyl hydrazonoethyl) ruthenocetyl. These ligands are capable of undergoing keto-enol tautomerism and can coordinate to a metal through nitrogen and/or oxygen. Their coordination behaviour depends upon the pH of the medium, the nature of the substituents and of the metal. In this paper, we describe the reactions of  $Cp_2MCl_2$  ( $M = Ti$  or  $Zr$ ) with bis(hydrazones) derived from 1,1'-diacetyl ruthenocetyl and aromatic acid hydrazides.

### MATERIALS AND METHODS

All reactions were carried out under strictly anhydrous conditions. Tetrahydrofuran (THF) was dried over Na wire and was then boiled under reflux until it became blue with benzophenone.  $Et_3N$  was purified by a published method [16].  $Cp_2TiCl_2$  and  $Cp_2ZrCl_2$  were prepared by treating NaCp with the relevant  $MCl_4$  under  $N_2$  [17].

The analyses and physical measurements were as described earlier [18].

*1,1'-Diacetyl ruthenocetyl bis(hydrazones):*

The hydrazones were prepared [15] by boiling under reflux a mixture of 1,1'-diacetyl ruthenocetyl (15 mmol) and appropriate acid hydrazide (25 mmol) in EtOH (ca. 35 cm<sup>3</sup>) for 26-32h. The resulting solution

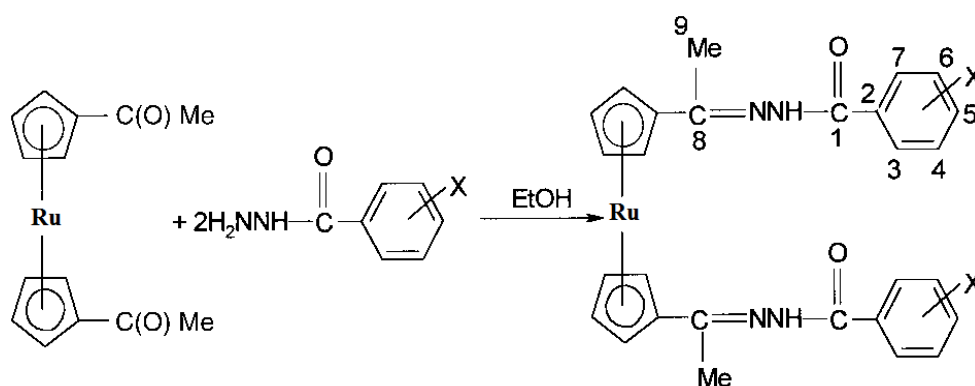
was concentrated to ca. 20cm<sup>3</sup>. The crystals which separated on adding petroleum ether (ca.20cm<sup>3</sup>) were filtered off and dried in vacuo.

### Reactions of bis(cyclopentadienyl) titanium(IV)/zirconium(IV) with bis(hydrazones):

Cp<sub>2</sub>MCl<sub>2</sub>(70mmol) and the appropriate bis(hydrazone) (40 mmol) were dissolved in THF (ca.70cm<sup>3</sup>.Et<sub>3</sub>N(70 mmol) was added and the mixture was stirred for 35-45h at room temperature. Precipitated Et<sub>3</sub>NHCl was removed by filtration and the clear filtrate was evaporated to dryness under reduced pressure. The complex was recrystallised from THF/petroleumether. Details of the reactions and analytical data for the complexes are given in Table 1.

## RESULTS AND DISCUSSION

The condensations of 1,1'-diacetyl ruthenocene with aromatic acid hydrazides in absolute ethanol give bis(hydrazone) ligands as shown in Scheme 1. The bis(hydrazones) (LH<sub>2</sub>) were reacted with two equivalent of bis(cyclopentadienyl)titanium(IV)/zirconium(IV) dichloride in the presence of base, in THF, to give mixed metal complexes [(Cp<sub>2</sub>MCl)<sub>2</sub>L] (M=Ti or Zr). The elemental analyses (Table 1) are compatible with a 2:1 metal-to-ligand stoichiometry.



Scheme 1. X=H, DRPH<sub>2</sub>; X=2-cl, DRCH<sub>2</sub>; X=4-NO<sub>2</sub>, DRNH<sub>2</sub>; X=4-Me, DRMH<sub>2</sub>

The complexes are soluble in THF, DMF, DMSO and pNO<sub>2</sub>, and their electrical conductivities in DMF solution indicate that they are non-electrolytes. The room temperature magnetic susceptibilities measured by Gouy's method showed that all the complexes are diamagnetic. Their electronic spectra exhibited a single band in the 445-420 nm region, assigned [19] to a charge-transfer, in accord with a (n-1) d<sup>0</sup> ns<sup>0</sup> electronic configuration. In addition, the hydrazones and their titanium(IV) and zirconium(IV) complexes show bands at ca.460 and 310-300nm. The first band is assigned to the <sup>1</sup>A<sub>1g</sub>-<sup>1</sup>E<sub>g</sub> transition in the iron atom of the ruthenocetyl ring and the second to the intra-ligand [azomethine and aromatic ring (π→π\*)] transitions.

### I.R. Spectra:

Significant absorptions of the complexes are presented in Table 2. The ν(N-H) band at ca. 3350 cm<sup>-1</sup> in the free hydrazones is absent from the complexes. The hydrazones all show bands in the 1650-1665, 1540-1560 and 1350-1330 cm<sup>-1</sup> regions assignable [20] to amide-I [ν(C=O)], amide-II [ν(C-N) + δ(N-H)] and amide-III δ(N-H) vibrations, respectively. These bands disappear, suggesting enolization and deprotonation of the keto group upon complex formation. The presence of strong characteristic bands in the 1580, 1520-1540 and 1225cm<sup>-1</sup> regions, which can be attributed [20] to ν(C=N), ν(N-C-O-) and ν(C-O), respectively, further supports enolization of the keto group. The spectra of the free ligands show a weak band at ca.1620 - 1625 cm<sup>-1</sup> Assigned to ν(C=N) of the azomethine linkage. This band appears at ca.1600 cm<sup>-1</sup> in all of the complexes suggesting that the azomethine nitrogen atom is coordinated to the metal the ligands ν(N-N) band at 1010 cm<sup>-1</sup> is shifted to higher wave-number (by ca. 25 cm<sup>-1</sup>) in all of the complexes, further supporting coordination through the azomethine nitrogen. The non-ligand bands in the complexes in the 450-480, 425-440, 340-350 cm<sup>-1</sup> regions are assigned [19] to ν(M-N), ν(M-O) and ν(M-Cl), respectively. In addition bands at ca.3000 (C-H stretch), 1430 (C-C stretch) and 800 (C-H out-of-plane deformation) for all complexes indicate the presence of cyclopentadienyl rings, and correspond [21] to those of bis(cyclopentadienyl)titanium/zirconium dichloride.

<sup>1</sup>H-NMR Spectra:

The <sup>1</sup>H-n.m.r. spectra of the complexes were recorded in DMF-d<sub>7</sub> (Table 3). A single, sharp signal at 6.5-6.8 ppm is assigned to the protons of the rapidly rotating cyclopentadienyl ring attached to titanium or zirconium. The free ligands exhibit a broad peak due to the NAH proton at ca.11.3 ppm. In the complexes, neither this signal nor an enol OH signal is visible. However, the complexes do show the CH<sub>3</sub> proton signal at ca. 2.5ppm and the aromatic ring signal at ca.7.5 ppm, plus two resonances assigned to the ruthenocenyl group.

Table1. Characterization data for the titanium(IV)/zirconium(IV) complexes

Reaction time (h)	Product	Yield (%)	Found (Calcd.) (%)			
			C	H	N	Cl
40	[(Cp <sub>2</sub> TiCl) <sub>2</sub> DRP]	80	66.7 (66.9)	5.6 (5.8)	7.0 (7.0)	8.5 (7.6)
40	[(Cp <sub>2</sub> ZrCl) <sub>2</sub> DRP]	76	61.4 (61.6)	5.2 (5.3)	6.3 (6.5)	7.9 (8.0)
50	[(Cp <sub>2</sub> TiCl) <sub>2</sub> DRC]	70	62.5 (62.6)	5.1 (5.2)	6.4 (6.6)	15.1 (15.2)
50	[(Cp <sub>2</sub> ZrCl) <sub>2</sub> DRC]	65	57.9 (58.0)	4.8 (4.9)	6.1 (6.1)	14.0 (14.0)
50	[(Cp <sub>2</sub> TiCl) <sub>2</sub> DRN]	74	61.2 (61.4)	9.1 (9.2)	5.0 (5.1)	7.9 (7.9)
50	[(Cp <sub>2</sub> ZrCl) <sub>2</sub> DRN]	70	57.0 (57.0)	4.6 (4.8)	8.5 (8.6)	7.3 (7.4)
40	[(Cp <sub>2</sub> TiCl) <sub>2</sub> DRM]	75	67.4 (67.6)	6.0 (6.0)	6.6 (6.8)	8.3 (8.4)
40	[(Cp <sub>2</sub> ZrCl) <sub>2</sub> DRM]	75	62.2 (57.4)	5.4 (5.6)	6.2 (6.3)	7.7 (7.7)

Table 2. Characteristic i.r. bands (cm<sup>-1</sup>) for the complexes

Complex	ν(C-N)	ν(C-O)	ν(N-N)	ν(M-N)	ν(M-O)	ν(M-Cl)	C <sub>5</sub> H <sub>5</sub> ring
[(Cp <sub>2</sub> TiCl) <sub>2</sub> DRP]	1600w, 1580s	1225s	1035m	480m	430m	350m	3000w, 1430m,800m
[(Cp <sub>2</sub> ZrCl) <sub>2</sub> DRP]	1605w, 1575s	1220s	1030m	460m	425m	340m	3010w, 1420m,780m
[(Cp <sub>2</sub> TiCl) <sub>2</sub> DRC]	1600w, 1570s	1230s	1040m	470m	440m	355m	3000w, 1425m,810m
[(Cp <sub>2</sub> ZrCl) <sub>2</sub> DRC]	1600w, 1585s	1215s	1030m	455m	435m	340m	3020w, 1420m,800m
[(Cp <sub>2</sub> TiCl) <sub>2</sub> DRN]	1610w, 1580s	1220s	1030m	475m	430m	348m	3025w, 1430m,810m
[(Cp <sub>2</sub> ZrCl) <sub>2</sub> DRN]	1605w, 1580s	1225s	1035m	450m	428m	345m	3010w, 1410m,800m
[(Cp <sub>2</sub> TiCl) <sub>2</sub> DRM]	1600w, 1585s	1228s	1040m	470m	440m	350m	3025w, 1425m,810m
[(Cp <sub>2</sub> ZrCl) <sub>2</sub> DRM]	1600w, 1585s	1225s	1028m	460m	430m	345m	3010w, 1420m,815m

Table 3. <sup>1</sup>H chemical shifts (δ, ppm)

Ligand/Complex	η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub>	ruthenocenyl group	Aromatic ring	-CH <sub>3</sub>
DRPH <sub>2</sub>	-	3.35(t, 4H), 3.70(t, 4H)	7.36(s)	2.42(s, 6H)
DRCH <sub>2</sub>	-	3.38(t, 4H), 3.68(t, 4H)	7.60-7.82(m, 8H)	2.50(s, 6H)
DRNH <sub>2</sub>	-	3.32(t, 4H), 3.72(t, 4H)	8.10(b, 8H)	2.45(s, 6H)
DRMH <sub>2</sub>	-	3.36(t, 4H), 3.70(t, 4H)	7.55-7.88(m, 4H)	2.10(s, 6H), 2.55(s, 6H)
[(Cp <sub>2</sub> TiCl) <sub>2</sub> DRP]	6.70(s, 20H)	3.40(t, 4H), 3.75(t, 4H)	7.40(s, 10H)	2.52(s, 6H)
[(Cp <sub>2</sub> ZrCl) <sub>2</sub> DRP]	6.62(s, 20H)	3.35(t, 4H), 3.70(t, 4H)	7.35(s, 10H)	2.50(s, 6H)
[(Cp <sub>2</sub> TiCl) <sub>2</sub> DRC]	6.80(s, 20H)	3.45(t, 4H), 3.80(t, 4H)	7.65-7.85(m, 8H)	2.58(s, 6H)
[(Cp <sub>2</sub> ZrCl) <sub>2</sub> DRC]	6.68(s, 20H)	3.40(t, 4H), 3.70(t, 4H)	7.70-7.90(m, 8H)	2.55(s, 6H)
[(Cp <sub>2</sub> TiCl) <sub>2</sub> DRN]	6.65(s, 20H)	3.40(t, 4H), 3.78(t, 4H)	8.15(b, 8H)	2.55(s, 6H)
[(Cp <sub>2</sub> ZrCl) <sub>2</sub> DRN]	6.50(s, 20H)	3.35(t, 4H), 3.75(t, 4H)	8.10(b, 8H)	2.50(s, 6H)
[(Cp <sub>2</sub> TiCl) <sub>2</sub> DRM]	6.75(s, 20H)	3.45(t, 4H), 3.80(t, 4H)	7.60-7.90(m, 8H)	2.20(s, 6H), 2.60(s, 6H)
[(Cp <sub>2</sub> ZrCl) <sub>2</sub> DRM]	6.65(s, 20H)	3.40(t, 4H), 3.75(t, 4H)	7.58-7.90(m, 8H)	2.15(s, 6H), 2.58(s, 6H)

**Table 4.**  $^{13}\text{C}$  chemical shifts ( $\delta$ , ppm) for the complexes

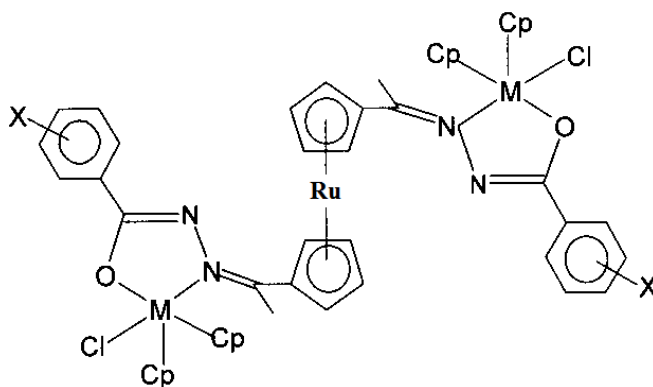
Complex	$g^5\text{-C}_5\text{H}_5$	ruthenocenylyl	groupC-1(C-1)	Aromatic ring	C-8(C-8 <sup>b</sup> )C-9(C-9)
[(Cp <sub>2</sub> TiCl) <sub>2</sub> DRP]	117.2	65.50, 66.50, 67.60	163.30	130.00, 128.5, 112.62	154.70 14.25
[(Cp <sub>2</sub> ZrCl) <sub>2</sub> DRP]	116.5	65.60, 66.28, 67.52	162.28	130.00, 126.25, 110.60	154.28 14.20
[(Cp <sub>2</sub> TiCl) <sub>2</sub> DRC]	117.0	65.40, 66.45, 67.55	164.50	132.25, 128.60, 120.58, 112.80	156.80 14.72
[(Cp <sub>2</sub> ZrCl) <sub>2</sub> DRC]	116.8	65.30, 66.20, 67.50	163.30	132.20, 126.55, 118.50, 112.25	155.72 14.70
[(Cp <sub>2</sub> TiCl) <sub>2</sub> DRN]	117.4	65.50, 66.55, 67.50	165.80	140.62, 130.80, 122.62, 114.85	158.85 14.80
[(Cp <sub>2</sub> ZrCl) <sub>2</sub> DRN]	116.8	65.45, 66.42, 67.48	165.20	138.60, 130.60, 121.52, 114.42	158.25 14.78
[(Cp <sub>2</sub> TiCl) <sub>2</sub> DRM]	117.5	65.40, 66.50, 67.55	164.85	130.25, 125.28, 119.25, 113.20, 35.80	156.40 14.80
[(Cp <sub>2</sub> ZrCl) <sub>2</sub> DRM]	116.5	65.38, 66.38, 67.52	163.80	128.28, 125.0, 118.85, 113.0, 35.72	156.0 14.65

 **$^{13}\text{C}$ -NMR Spectra:**

The  $^{13}\text{C}$ -n.m.r. spectra of the complexes were recorded in DMSO- $d_6$  (Table 4). They show the cyclopentadienyl peak at ca.  $\delta$  117 (relative to TMS); a considerable shift in the positions of carbon (1) (ca. 160.0 ppm, ligands) and carbon (8) (ca. 150.0 ppm, ligands), indicating coordination through the azomethine nitrogen and the enol group. The Cp ring in the ruthenocenylyl entity shows three peaks, virtually unshifted compared to the corresponding ligands.

On the basis of above discussion, we conclude that these ligands act as dibasic, tetradentate chelating agents, coordinating to two metal atoms. The proposed structural formula is shown in Figure 1.

Attempts are being made to obtain single crystals of the complexes suitable for X-ray structure determination.

**Fig. 1.** Cp = cyclopentadienyl; M = Ti or Zr**Anti-microbial Activity:**

The compounds are found to show low bactericidal behavior against most of the bacterial culture and resistance towards the other. In general the results reveal that the activity of the ligand was found to enhance on complexation with metal. The inhibition effect of the ligand and its metal complexes on the growth of various bacteria is summarized.

In an urge to develop new antimicrobial compound, a number of hydrazones were tested for their antimicrobial activities because of the evolution of drug-resistant microbial pathogens. Some derivatives of flavanol hydrazones were synthesized and screened for their in vitro anti-bacterial activity against 25 strains of Gram -ve and Gram +ve pathogenic bacteria. The synthesized compound demonstrates inhibitory effect (MIC < 392  $\mu\text{g}$ ) resistant Staphylococcus aureus strain may be due to the presence of carbonyl region and nitro group[23]

A series of quinoxaline derivatives was synthesized and evaluated for their antimicrobial activity. The compounds which were bearing highly electronegative chloro and nitro substituents at the para position of phenyl ring exhibited good activity as compared to those compounds having these atoms at either ortho or meta position or the containing other compounds the less electronegative/ electropositive substituent at these positions[24]

Thirty new hydrazones of 1,1'-diacetyl ruthenocenylyl bis(hydrosone) were tested for antibacterial activities against E.coli, Staphylococcus aureas, B. subtilis an albicans and Saccharomyces cerevisiae. Among thirty hydrazones, 1,1'-diacetyl ruthenocenylyl bis(hydrosone) showed a broad spectrum of activity.[25]

## CONCLUSION

Metal complexes of schiffs bases represents an in important class of coordination compounds. we can determined from above data Bis(cyclopentadienyl)titanium(IV)zirconium(IV)chlorides react with bis(hydrazones) derived from 1,1'-diacetyl ruthenocene. It is characterisaton with elemental analysis, NMR and IR spectroscopy. the biological behavior revealed the above compound active as a antibacterial activity. The compound have electron withdrawing group which will increase the activity of antibacterial.

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