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SYNTHESES AND SPECTROSCOPIC STUDIES OF MONO- AND DI-CYCLOPENTADIENYLZIRCONIUM(IV) DERIVATIVES WITH HETEROCYCLIC THIONES

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Summary

The reactions of dichlorodi-cyclopentadienylzirconium(IV) with two important series of heterocyclic thiones, viz. oxadiazolethione (OxtH) and thiohydantoin (ThtH) in anhydrous tetrahydrofuran (molar ratios 1/1 and 1/3) in the presence of base, led to the formation of derivatives of the types [$Cp_2Zr(Oxt)Cl$], [$CpZr(Oxt)_3$], [$Cp_2Zr(Tht)Cl$] and [$CpZr(Tht)_3$]. The complexes were characterized by elemental analysis, electrical conductance, magnetic measurements and spectral (electronic, infrared and ^{1}H NMR) studies. Possible structures are proposed for these derivatives.

Introduction

Since the discovery of the Ziegler–Natta catalyst in polymerization of olefins, considerable importance has recently been attached to the chemistry of organic derivatives of zirconium due to their increasing applications in the field of homogeneous catalysis and chemical fixation of molecular nitrogen [1,2]. In addition to the above, a marked tendency of zirconium to form complexes of higher coordination number has also stimulated interest in the study of its complexes with various ligands [2]. In the present communication, we report the synthesis and characterization of dicyclopentadienylzirconium(IV) and monocyclopentadienylzirconium(IV) derivatives containing heterocyclic thiones as chelating agents. These ligands containing a thioamide bond and capable of undergoing thione $\rightleftharpoons$ thiol (NH–C=S $\rightleftharpoons$ N=C–SH) tautomerism can coordinate to a metal atom through nitrogen or through sulphur or simultaneously through nitrogen and sulphur. The chemistry of transition metal complexes with heterocyclic thiones continues to be of unabated interest on account of the striking structural features presented by this class of compounds and also because of their biological importance [3–8].

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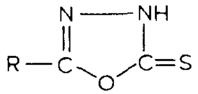
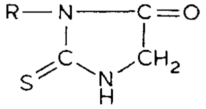
The structures of the ligands are given below.

(a) 5-Substituted 1,3,4-oxadiazole-2-thione



(R = C_6H_5 (BOxtH),
R = $C_6H_4NO_2$ - *m* (MOxtH),
R = $C_6H_4NO_2$ - *p* (POxtH),
R = C_6H_4Cl - *o* (COxtH))

(b) 1-Aryl-2-thiohydantoin



(R = C_6H_5 (PThtH),
R = $C_6H_4CH_3$ (TThtH),
R = $C_6H_5CH_2$ (BThtH),
R = $C_6H_4CH_3O$-*p* (MPThtH),
R = $C_6H_4CH_3O$-*o* (MOThtH),
R = $C_{10}H_7$ (NThtH))

Experimental

All of the reactions were carried out under strictly anhydrous conditions. Tetrahydrofuran (British Drug House) was dried by storage on sodium wire overnight and then refluxed until it gave a blue colour with benzophenone. Triethylamine and n-butylamine were purified by a known method [9]. Dichlorodicyclopentadienylzirconium(IV) was prepared by treatment of sodium cyclopentadienide with zirconium(IV) chloride in a nitrogen atmosphere [10]. The oxadiazole thione and thiohydantoin ligands were prepared by the methods of refs. 11 and 12.

Zirconium was estimated gravimetrically as ZrO_2, chlorine as AgCl, and nitrogen was estimated by Kjeldahl's method. The details of the physical measurements were the same as those described earlier [13].

Reactions of Cp_2ZrCl_2 with oxadiazole thione or thiohydantoin (molar ratio 1/1)

A mixture of Cp_2ZrCl_2, the appropriate oxadiazole thione or thiohydantoin, and triethylamine in 1/1/1 molar ratio was stirred in dry tetrahydrofuran (60 ml) for about 40–50 h at room temperature. The reaction mixture was filtered to remove triethylamine hydrochloride and the clear filtrate was evaporated to dryness under reduced pressure. The complex was recrystallised from a THF/petroleum ether mixture.

Reactions of Cp_2ZrCl_2 with oxadiazole thione or thiohydantoin (molar ratio 1/3)

The appropriate oxadiazole thione or thiohydantoin (30 mmol) was added to a solution of Cp_2ZrCl_2 (10 mmol) in dry tetrahydrofuran (60 ml). To this, n-butylamine (20 mmol) was added and the mixture stirred for about 50–60 h. The precipitated complex was removed and thoroughly washed with tetrahydrofuran.

The reactions of Cp_2ZrCl_2 with oxadiazole thione or thiohydantoin in 1/2 molar ratio were also studied in dry tetrahydrofuran. However, these reactions gave a mixture of the compounds obtained in the reactions of Cp_2ZrCl_2 with oxadiazole thione or thiohydantoin in 1/1 and 1/3 molar ratios, respectively. The two types of compounds present in the mixture were separated with the help of thin-layer chromatography.

Details of the reactions and the analytical data of the complexes are given in Tables 1 and 2.

Results and discussion

The reactions of dichlorodicyclopentadienylzirconium(IV) with oxadiazole thione (OxtH) or thiohydantoin (ThtH) in 1/1 and 1/3 molar ratios in tetrahydrofuran in the presence of amine yielded complexes of the types [$Cp_2Zr(Oxt)Cl$], [$CpZr(Oxt)_3$], [$Cp_2Zr(Tht)Cl$] and [$CpZr(Tht)_3$] according to the following equations.

$$Cp_2ZrCl_2 + OxtH + Et_3N \xrightarrow{THF} [Cp_2Zr(Oxt)Cl] + Et_3N \cdot HCl$$

$$Cp_2ZrCl_2 + ThtH + Et_3N \xrightarrow{THF} [Cp_2Zr(Tht)Cl] + Et_3N \cdot HCl$$

$$Cp_2ZrCl_2 + 3 OxtH + 2\ Bu\text{-}NH_2 \xrightarrow{THF} [CpZr(Oxt)_3] + 2\ BuNH_2 \cdot HCl + C_5H_6$$

$$Cp_2ZrCl_2 + 3\ ThtH + 2\ BuNH_2 \xrightarrow{THF} [CpZr(Tht)_3] + 2\ BuNH_2 \cdot HCl + C_5H_6$$

All of these complexes are susceptible to hydrolysis and decompose on heating in the temperature range of 148–237°C. The magnetic susceptibilities measured at room temperature by Gouy's method using $CuSO_4$ as calibrator show that all the complexes are diamagnetic. Electrical conductances measured in nitrobenzene show them to be essentially non-electrolytes. The electronic spectra of all these complexes show a single band in the region of 22500–23200 cm^{-1} which can be assigned [10] to the charge transfer band. This is in accord with their $(n-1)d^0$, ns^0 electronic configuration.

Infrared spectra

(a) Oxadiazole thione derivatives. The 5-substituted 1,3,4-oxadiazole-2-thione ligands have one phenyl ring, one oxadiazole ring and a $>C{=}S$ group, resulting in the presence of four donor sites (two nitrogen atoms, one oxygen atom and one sulphur atom). The $\nu(NH)$ and $\delta(NH)$ vibration bands, which appear at ca. 3350 and 1630 cm^{-1} in the spectra of the ligands, disappear in the spectra of the complexes, indicating [14] the coordination of amino-nitrogen to the zirconium atom through deprotonation. This is confirmed by the appearance of new bands at ca. 480–460 cm^{-1}, assignable [15] to $\nu(Zr{-}N)$.

Organic compounds having a thioamide group (HNC=S) give rise [16–18] to four thioamide bands in the IR spectra. These are thioamide (I) at about 1500 cm^{-1}, band II at about 1300–1400 cm^{-1}, band III at about 1000 cm^{-1} and band IV at about 700–850 cm^{-1}. These bands have contributions from $\delta(C{-}H)+\delta(N{-}H)$, $\nu(C{=}S)+\nu(C{=}N)+\delta(C{-}H)$, $\nu(C{-}N)+\nu(C{=}S)$ and $\nu(C{=}S)$ modes of vibrations, respectively. In our ligand spectra, these bands appear at ca. 1560–1550, 1250, 1090–1080 and 790–780 cm^{-1}. These bands are expected [17,18] to be affected differently by different modes of coordination after complexation with the metal ions. The thioamide III and IV vibrations, which have the largest contribution from $\nu(C{=}S)$, undergo a red shift in the zirconium(IV) complexes, suggesting coordination of the sulphur atom to the zirconium atom in the thione form. The $\nu(Zr{-}S)$ vibration

(Continued on p. 400)

TABLE 1

REACTIONS OF Cp_2ZrCl_2 WITH OXADIAZOLE THIONES IN TETRAHYDROFURAN

Reactants (molar ratio)	Stirring time (h)	Product, yield (%)	Colour, decomp. temp. (°C)	(Found (Calcd.) (%))				
				C	H	N	Zr	Cl
Cp_2ZrCl_2 + BOxtH + Et_3N (1/1/1)	40	$Cp_2Zr(BOxt)Cl$, 60	Grey, 195	49.6 (49.8)	3.4 (3.4)	6.2 (6.4)	21.0 (21.0)	7.9 (8.1)
Cp_2ZrCl_2 + BOxtH + $BuNH_2$ (1/3/2)	50	$CpZr(BOxt)_3$, 54	brown, 205	50.4 (50.6)	2.9 (2.9)	12.1 (12.2)	13.1 (13.2)	–
Cp_2ZrCl_2 + MOxtH + Et_3N (1/1/1)	40	$Cp_2Zr(MOxt)Cl$, 62	cream, 165	45.1 (45.1)	2.7 (2.9)	8.7 (8.7)	18.9 (19.0)	7.4 (7.4)
Cp_2ZrCl_2 + MOxtH + $BuNH_2$ (1/3/2)	60	$CpZr(MOxt)_3$, 58	brown, 190	42.0 (42.3)	2.0 (2.0)	15.3 (15.3)	10.8 (11.0)	–
Cp_2ZrCl_2 + POxtH + Et_3N (1/1/1)	50	$Cp_2Zr(POxt)Cl$, 68	brown, 162	45.0 (45.1)	2.8 (2.9)	8.5 (8.7)	18.7 (19.0)	7.4 (7.4)
Cp_2ZrCl_2 + POxtH + $BuNH_2$ (1/3/2)	60	$CpZr(POxt)_3$ 60	yellowish brown, 237	42.2 (42.3)	2.0 (2.0)	15.0 (15.3)	11.0 (11.0)	–
Cp_2ZrCl_2 + COxtH + Et_3N (1/1/1)	45	$Cp_2Zr(COxt)Cl$, 65	brown, 194	46.0 (46.1)	2.7 (2.9)	5.9 (5.9)	19.4 (19.4)	15.0 (15.1)
Cp_2ZrCl_2 + COxtH + $BuNH_2$ (1/3/2)	55	$CpZr(COxt)_3$, 60	brown, 168	44.0 (44.0)	2.0 (2.1)	10.4 (10.6)	11.5 (11.5)	13.2 (13.4)

TABLE 2

REACTIONS OF Cp_2ZrCl_2 WITH THIOHYDANTOINS IN TETRAHYDROFURAN

Reactants (molar ratio)	Stirring time (h)	Product, yield (%)	Colour decomp. temp. (°C)	(Found (Calcd.) (%))				
				C	H	N	Zr	Cl
Cp_2ZrCl_2 + PThtH + Et_3N (1/1/1)	40	$Cp_2Zr(PTht)Cl$, 58	brown, 148	50.6 (50.9)	3.5 (3.8)	6.1 (6.2)	20.2 (20.4)	7.8 (7.9)
Cp_2ZrCl_2 + PThtH + $BuNH_2$ (1/3/2)	55	$CpZr(PTht)_3$, 52	cream, 167	52.6 (52.7)	3.6 (3.6)	11.3 (11.5)	12.5 (12.5)	–
Cp_2ZrCl_2 + TThtH + Et_3N (1/1/1)	45	$Cp_2Zr(TTht)Cl$, 62	cream, 168	51.7 (51.9)	4.0 (4.1)	6.0 (6.06)	7.6 (7.7)	19.5 (19.7)
Cp_2ZrCl_2 + TThtH + $BuNH_2$ (1/3/2)	60	$CpZr(TTht)_3$ 58	light brown, 160	54.3 (54.5)	4.0 (4.2)	10.6 (10.9)	11.8 (11.8)	–
Cp_2ZrCl_2 + BThtH + Et_3N (1/1/1)	50	$Cp_2Zr(BTht)Cl$, 65	brown, 163	51.8 (51.9)	4.1 (4.1)	6.0 (6.0)	19.6 (19.7)	7.7 (7.7)
Cp_2ZrCl_2 + BThtH + $BuNH_2$ (1/3/2)	60	$CpZr(BTht)_3$, 52	light brown, 179	54.3 (54.5)	4.1 (4.2)	10.8 (10.9)	11.8 (11.8)	–
Cp_2ZrCl_2 + MPThtH + Et_3H (1/1/1)	45	$Cp_2Zr(MPTht)Cl$, 68	dark brown, 182	50.1 (50.2)	3.8 (3.9)	5.8 (5.9)	19.0 (19.0)	7.4 (7.4)
Cp_2ZrCl_2 + MPThtH + $BuNH_2$ (1/3/2)	55	$CpZr(MPTht)_3$, 60	brown, 210	51.2 (51.3)	3.9 (3.9)	10.2 (10.3)	11.1 (11.2)	–
Cp_2ZrCl_2 + MOThtH + Et_3N (1/1/1)	40	$Cp_2Zr(MOTht)Cl$, 65	brown, 145	50.2 (50.2)	3.8 (3.9)	5.8 (5.9)	19.0 (19.0)	7.3 (7.4)
Cp_2ZrCl_2 + MOThtH + $BuNH_2$ (1/3/2)	50	$CpZr(MOTht)_3$, 62	brown, 165	51.1 (51.3)	3.9 (3.9)	10.1 (10.3)	11.2 (11.2)	–
Cp_2ZrCl_2 + NThtH + Et_3N (1/1/1)	45	$Cp_2Zr(NTht)Cl$, 63	dark brown, 172	55.2 (55.4)	3.7 (3.8)	5.4 (5.6)	18.3 (18.3)	7.1 (7.1)
Cp_2ZrCl_2 + NThtH + $BuNH_2$ (1/3/2)	60	$CpZr(NTht)_3$, 60	cream, 193	60.0 (60.0)	4.1 (4.3)	9.4 (9.6)	10.4 (10.4)	–

[19] appears at 400–360 cm^{-1}. The positions [8,14] of IR bands due to the phenyl and oxadiazole group (C–O–C) do not change in the spectra of the complexes, indicating the non-coordination of the oxygen atom. The above observations indicate that possibly the bonding in zirconium complexes is through the amino nitrogen and thiocarbonyl sulphur.

(b) Thiohydantoin derivatives. The infrared spectra of the 1-aryl-2-thiohydantoin ligands show sharp bands at ca. 3300 and 1050 cm^{-1} which may be assigned [14] to ν(N–H) and δ(N–H), respectively. However, in the spectra of zirconium complexes, these bands disappear, indicating the displacement of N–H hydrogen by zirconium ion. This is further confirmed by the appearance of new bands around 480–450 cm^{-1}, assignable [15] to ν(Zr–N). A sharp band appearing at 1720–1700 cm^{-1} (due to ν(C=O)) in the spectra of the ligands appears at the same place in the spectra of the complexes, ruling out the possibility of coordination through the carbonyl group. The ligand thiohydantoin contains a thioamide group. The four thioamide bands, thioamide I, II, III and IV, typical of molecules containing a HNC=S skeleton, are found at ca. 1500, 1400–1300, 1000 and 850–700 cm^{-1}, respectively. The appearance of four thioamide bands and the absence of any band near 2500 cm^{-1} (due to ν(S–H)) indicate the existence of ligands in the thione form [17]. The thioamide III and IV bands, having main contribution from ν(C=S), are shifted towards lower energies in the complexes, indicating [20,21] the coordination of thioketo sulphur to the zirconium atom. The ν(Zr–S) vibrations appear at 390–370 cm^{-1}. Thus, it becomes evident that the thiohydantoin ligands act as bidentate chelating agents, coordinating through thione sulphur and amino nitrogen.

In addition, all of these complexes show bands at ~ 3000 (ν(C–H)), ~ 1430 (ν(C–C)), and ~ 1020, 800 cm^{-1} (δ(C–H), in-plane and out-of-plane, respectively) characteristic of the cyclopentadienyl ring. The persistence of bands due to the cyclopentadienyl rings in the spectra of the complexes indicate that these groups remain delocalized and π-bonded (η^5) to the metal and retain their aromatic character [22].

^{1}H NMR spectra

The ^{1}H NMR spectra (90 MHz) of these complexes were recorded in deuterated chloroform and dimethylformamide. The intensities of all the resonance lines were determined by planimetric integration. In general, a low-field shift of the resonance signals of various protons (R) in these complexes, in comparison with the respective proton signals in the free ligands, may be attributed to deshielding upon coordination. The resonance line for the protons on the C_5H_5 rings always falls near δ 6.65–6.80 ppm (Table 3). The appearance of a single sharp signal for the protons of the cyclopentadienyl ring indicates rapid rotation of the ring about the metal-ring axis. The two kinetic possibilities, viz. metal-centred rearrangement is slow or fast, can be distinguished by analysis of the NMR spectra. In the spectra of the 1/3 derivatives $(C_5H_5)Zr(L)_3$, two distinct resonance lines for the protons of the ligands are observed which must result from the non-equivalent environments for the different ligands. The spectra of oxadiazole thiones and thiohydantoins show one sharp signal at δ 4.8–4.9 ppm due to the NH proton which disappears in the corresponding complexes. The integrated proton ratios correspond to the proposed formula.

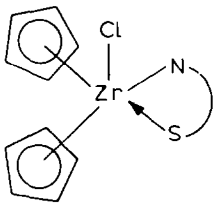
On the basis of the spectral features mentioned above, the structures **1** and **2**, are

TABLE 3

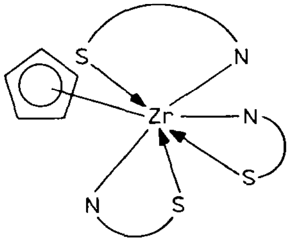
PROTON CHEMICAL SHIFTS (δ ppm) AT 25°C

Complex	π-C_5H_5	Aromatic ring	CH_2	CH_3
$Cp_2Zr(BOxt)Cl$	6.65(s)	7.30(s)	–	–
$CpZr(BOxt)_3$	6.70(s)	7.25(s),7.40(s)	–	–
$Cp_2Zr(MOxt)Cl$	6.72(s)	7.40(s)	–	–
$CpZr(MOxt)_3$	6.70(s)	7.70(s),7.40(s)	–	–
$Cp_2Zr(POxt)Cl$	6.80(s)	7.20(s)	–	–
$CpZr(POxt)_3$	6.70(s)	7.25(s),7.45(s)	–	–
$Cp_2Zr(COxt)Cl$	6.75(s)	7.20(s)	–	–
$CpZr(COxt)_3$	6.80(s)	7.20(s),7.30(s)	–	–
$Cp_2Zr(PTht)Cl$	6.70(s)	7.50(s)	–	–
$CpZr(PTht)_3$	6.75(s)	7.40(s),(7.50(s)	–	–
$Cp_2Zr(TTht)Cl$	6.80(s)	7.40(q)	–	3.00(m)
$CpZr(TTht)_3$	6.80(s)	7.30(q),7.50(q)	–	3.10(d) each split into m
$Cp_2Zr(BTht)Cl$	6.70(s)	7.20(t)	3.22(m)	–
$CpZr(BTht)_3$	6.60(s)	7.00(q),7.20(q)	3.20(d) each split into m	
$Cp_2Zr(MPTht)Cl$	6.60(s)	7.30(s)	–	2.90(s)
$CpZr(MPTht)_3$	6.70(s)	7.10(s),7.25(s)	–	2.85(d)
$Cp_2Zr(MOTht)Cl$	6.68(s)	7.40(s)	–	2.95(s)
$CpZr(MOTht)_3$	6.70(s)	7.10(s),7.30(s)	–	2.90(d)
$CpZr(NTht)Cl$	6.65(s)	8.0(s)	–	–
$CpZr(NTht)_3$	6.80(s)	7.80(s),8.0(s)	–	–

proposed for $[Cp_2Zr(L)Cl]$ and $[Cp_2Zr(L)_3]$ complexes, respectively:



(1)



(2)

Acknowledgements

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