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Preparation and Characterization of Complexes of Dichlorobis(cyclopentadienyl)zirconium(IV) with Bidentate, Terdentate, and Quadridentate Schiff Bases

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Bis(cyclopentadienyl)zirconium(IV) Schiff base derivatives have been synthesized by treating dichlorobis(cyclopentadienyl)zirconium(IV) (Cp_2ZrCl_2) with bidentate Schiff bases (SBH) *viz.*, *N*-salicylidenaniline, *N*-salicylidene-*o*-toluidine, *N*-salicylidene-*m*-toluidine, *N*-salicylidene-*p*-toluidine, and *N*-(2-hydroxyl-1-naphthyliden)aniline, terdentate Schiff bases ($SB'H_2$) *viz.*, *N*-(3-oxo-1-methylbutyliden)-*o*-aminophenol and *N*-(3-oxo-1-phenylbutyliden)-*o*-aminophenol; quadridentate Schiff base ($SB''H_2$) *N,N'*-disalicylidene-*o*-phenylenediamine, in THF, in the presence of triethylamine at room temperature. The resulting derivatives of the type $Cp_2Zr(SB)Cl$, $Cp_2Zr(SB)_2$, $Cp_2Zr(SB')$, $Cp_2Zr(SB'')$, and $(Cp_2ZrCl)SB''$ [where $[SB]^-$, $[SB']^{2-}$, and $[SB'']^{2-}$ represent the anion of corresponding Schiff bases SBH, $SB'H_2$, and $SB''H_2$] have been characterised by their elemental analysis and by IR, electronic spectra, electrical conductance and molecular weight determinations.

A number of transition metal complexes of Schiff bases have been synthesized and characterized during recent years.[1,2] In view of the interesting synthetic and structural aspects of these complexes, interest in the study of Schiff base complexes continues to increase. However, few Schiff base complexes of organometallic derivatives such as dichlorobis(cyclopentadieyl)zirconium(IV) and dichlorobis(cyclopentadieyl)titanium(IV) have been studied.[3,4] Recently, a series of complexes of dichlorobis(cyclopentadienyl)titanium(IV) with Schiff bases has been reported.[5] Now these studies have been extended to the complexes of dichlorobis(cyclopentadienyl)zirconium(IV) with bidentate, terdentate and quadridentate Schiff bases. Such a study appears to be useful in view of the fact that organometallic compounds of titanium[6] and zirconium[7] are found to be capable of activating molecular nitrogen. In one instance, alkoxy derivatives of zirconium(IV) have been investigated as potential agent in the nitrogen fixation processes.[8]

Experimental

Dichlorobis(cyclopentadienyl)zirconium(IV) was prepared by CpNa method.[9,10] Schiff bases were synthesised by the usual methods[11-13] and recrystallized from absolute ethanol.

THF (Baker AR) was dried by storage on sodium wire overnight and then refluxed until it gave a blue colouration with benzophenone. It was finally dried by distilling over $LiAlH_4$. Hexane was dried by distilling over sodium wire. Triethylamine was purified by the given method.[14] All the reactions were carried out in anhydrous conditions.

Zirconium was estimated gravimetrically as ZrO_2, chlorine as AgCl, and nitrogen was estimated by Kjeldahl's method. Analytical data of these complexes are given in Tables 1—3. The IR spectra were recorded on Perkin-Elmer IR-621 and IR-137 instruments in KBr phase in the ranges of 4000—200 cm^{-1} and 4000—700 cm^{-1}. The electronic spectra of the complexes were run on Perkin-Elmer 4000A in the range of 400—750 $cm.^{-1}$ Molecular weight of the complexes were determined by Gallen-Kamp Ebulliometer, W. G. Pye & Co. Electrical conductance measurements were carried out in nitrobenzene on a Beckmann conductivity Bridge Model RC-18A.

Reactions of Dichlorobis(cyclopentadienyl)zirconium(IV) (1 mol) with N-*Salicylidene*-p-*toluidine (1 mol).* Schiff base (0.64 g) was added to a solution of dichlorobis(cyclopentadienyl)ziroconium(IV) (0.89 g) in dry THF (80 g). To this triethylamine (0.50 g) was added, the mixture was stirred for 24 h. Precipitated $Et_3N\cdot HCl$ was removed by filtration and the complex was crystallised by a hexane/THF mixture (yield 85%).

Reaction of Dichlorobis(cyclopentadienyl)zirconium(IV) (1 mol) with N-*Salicylidene*-p-*toludidine (2 mol).* To dichlorobis(cyclopentadienyl)zirconium(IV) (0.72 g) and Schiff base (1.05 g) dissolved in THF (80 g) was added triethylamine (0.51 g) and the mixture was stirred for 18 h. $Et_3N\cdot HCl$ which precipitated was removed by filtration. After distilling the solvent under reduced pressure, the product was recrystallised from a hexane/THF mixture (yield=82%).

Reaction of Dichlorobis(cyclopentadienyl)zirconium(IV) (1 mol) with N-*(3-Oxo-1-methylbutylidene)*-o-*aminophenol (1 mol).* A mixture of dichlorobis(cyclopentadienyl)zirconium(IV) (1.20 g) and Schiff base (0.72 g) was dissolved in THF (80 g) and triethylamine (0.84 g) was added. The mixture was stirred for 24 h. Precipitated $Et_3N\cdot HCl$ was removed by filtration and complex was crystallised from a hexane/THF mixture (yield 80%).

Reaction of Dichlorobis(cyclopentadienyl)zirconium(IV) (2 mol) with N,N'-*Disalicylidene*-o-*phenylenediamine (1 mol).* Schiff base (0.68 g) was added to a solution of Cp_2ZrCl_2 (1.27 g) in dry THF(75 g). To this triethylamine (0.88 g) was added, and the mixture was stirred for 30 h. $Et_3N\cdot HCl$ which precipitated out was removed and solvent was removed under reduced pressure. The complex was crystallized from a hexane/THF mixture (yield 83%).

Results and Discussion

Dichlorobis(cyclopentadienyl)zirconium(IV) reacts with bidentate Schiff bases (1:1 and 1:2 molar ratios) in anhydrous THF, in the presence of triethylamine.

$$Cp_2ZrCl_2 + SBH + Et_3N \xrightarrow[\text{room temp}]{\text{THF}} Cp_2Zr(SB)Cl + Et_3N\cdot HCl,$$

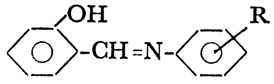
$$Cp_2ZrCl_2 + 2SBH + 2Et_3N \xrightarrow[\text{room temp}]{\text{THF}} Cp_2Zr(SB)_2 + 2Et_3N\cdot HCl,$$

where SB^- represents the anion of corresponding bidentate Schiff bases SBH.

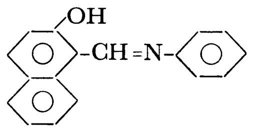
Table 1. Reactions of Cp_2ZrCl_2 with bidentate Schiff bases

Reactants (Molar ratio)	Stirring time (h)	Product, colour and dec temp	Mol wt Found (Calcd)	Found (Calcd) %		
				Zr	N	Cl
Cp_2ZrCl_2 + SBH + Et_3N (1:1:1)	26	$Cp_2Zr(SB)Cl$ Reddish brown, 138	491 (453)	19.8 (20.1)	2.95 (3.1)	7.5 (7.8)
Cp_2ZrCl_2 + SBH + Et_3N (1:2:2)	24	$Cp_2Zr(SBH_2)$ Dark brown, 112	668 (613)	14.8 (14.9)	4.4 (4.6)	— —
Cp_2ZrCl_2 + SB′H + Et_3N (1:1:1)	18	$Cp_2Zr(SB')Cl$ Brownish red, 152	— —	19.2 (19.5)	2.8 (3.0)	7.3 (7.6)
Cp_2ZrCl_2 + SB′H + Et_3N (1:2:2)	24	$CpZr(SB')_2$ Light brown, 95	— —	13.9 (14.2)	4.2 (4.4)	— —
Cp_2ZrCl_2 + S′BH + Et_3N (1:1:1)	24	$Cp_2Zr(S'B)Cl$ Brown, 165	— —	19.1 (19.5)	2.8 (3.0)	7.3 (7.6)
Cp_2ZrCl_2 + S′BH + Et_3N (1:2:2)	30	$Cp_2Zr(S'B)_2$ Yellowish brown 130	676 (641.4)	14.0 (14.2)	4.3 (4.4)	— —
Cp_2ZrCl_2 + S′B′H + Et_3N (1:1:1)	24	$Cp_2Zr(S'B')Cl$ Yellow orange, 115	483 (466.9)	19.3 (19.5)	2.9 (3.0)	7.4 (7.6)
Cp_2ZrCl_2 + S′B′H + Et_3N (1:2:2)	18	$Cp_2Zr(S'B')_2$ Yellowish brown 103	—	13.9 (14.2)	4.24 (4.4)	— —
Cp_2ZrCl_2 + S″B″H + Et_3N (1:1:1)	24	$Cp_2Zr(S''B'')Cl$ Light brown, 228	—	17.8 (18.1)	2.7 (2.8)	6.7 (7.05)
Cp_2ZrCl_2 + S″B″H + Et_3N (1:2:2)	30	$Cp_2Zr(S''B'')_2$ Dark yellow, 203	759 (713.5)	12.6 (12.8)	3.85 (3.9)	— —

SBH = *N*-salicylidenaniline, SB′H = *N*-salicylidene-*o*-toludine, S′BH = *N*-salicylidene-*m*-toludine, S′B′H = *N*-salicylidene-*p*-toluidine and S″B″H = *N*-(2-hydroxy-1-naphthyliden)aniline.



[R = H, *o*-Me, *m*-Me, and *p*-Me]

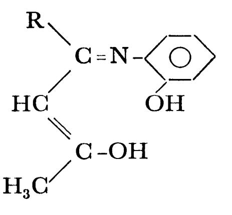


These Schiff base complexes are yellow to dark brown in colour and are soluble in benzene, tetrahydrofuran, chloroform and acetone. Analytical data and physical measurements are given in Table 1.

Reactions of Cp_2ZrCl_2 with terdentate Schiff bases (1:1 molar ratio) in THF, in the presence of triethylamine yielded complexes of the type $Cp_2Zr(SB')$.

$$Cp_2ZrCl_2 + SB'H_2 + 2Et_3N \xrightarrow[\text{room temp}]{\text{THF}} Cp_2Zr(SB') + 2Et_3N\cdot HCl$$

$[SB']^{2-}$ represents the anion of terdentate Schiff base $SB'H_2$



[R = Me, Ph]

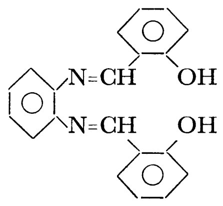
These complexes are yellowish green and orange in colour and are soluble in organic solvents. Analytical data and physical properties are given in Table 2.

Quadridentate Schiff base reacts with Cp_2ZrCl_2 (1:1 and 1:2 molar ratios) in anhydrous THF, in the presence of triethylamine giving soluble products.

$$Cp_2ZrCl_2 + SB''H_2 + 2Et_3N \xrightarrow[\text{room temp}]{\text{THF}} Cp_2Zr(SB'') + 2Et_3N\cdot HCl$$

$$2Cp_2ZrCl_2 + SB''H_2 + 2Et_3N \xrightarrow[\text{room temp}]{\text{THF}} (Cp_2ZrCl)_2SB'' + 2Et_2N\cdot HCl$$

$[SB'']^{2-}$ represents the anion of quadridentate Schiff base $SB''H_2$



These complexes are brown or dark brown in colour and are soluble in organic solvents. The analytical data of these complexes is given in Table 3.

All the above reactions are quite facile and the resulting compounds could be isolated in almost quantitative yields. The complexes are involatile, very senstive to oxygen but relatively stable in an inert atmosphere and decomposes on heating between 95—325 °C. All complexes are monomeric except binuclear complex(E) with a dimeric structure (Tables 1—3). Electrical conductance measured in nitrobenzene showed them to be essentially nonelectrolytes.

On the basis of elemental analysis, IR and electronic spectra, molecular weight determination and electrical conductance, following structures are tentatively assigned for the complexes of the type (A) $Cp_2Zr(SB)Cl$; (B) $Cp_2Zr(SB)_2$; (C) $Cp_2Zr(SB')$; (D) $Cp_2Zr(SB'')$ and (E) $(Cp_2ZrCl)_2SB$.

Complexes with bidentate Schiff bases:

TABLE 2. REACTIONS OF Cp_2ZrCl_2 WITH TERDENTATE SCHIFF BASES

Reactants (Molar ratio)	Stirring time (h)	Product, colour and dec temp	Mol wt Found (Calcd)	Found (Calcd) %	
				Zr	N
Cp_2ZrCl_2 + SBH_2 + Et_3N (1:1:2)	24	$Cp_2Zr(SB)$ Dark yellow, 225 °C	435 (410.4)	22.0 (22.2)	3.2 (3.4)
Cp_2ZrCl_2 + $SB'H_2$ + Et_3N (1:1:2)	24	$Cp_2Zr(SB')$ Orange, 245 °C	— —	19.0 (19.3)	2.7 (3.0)

SBH_2 = *N*-(3-oxo-1-methylbutyliden)-*o*-aminophenol and $SB'H$ = *N*-(3-oxo-1-phenylbutyliden)-*o*-aminophenol.

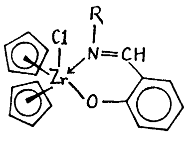
TABLE 3. REACTIONS OF Cp_2ZrCl_2 WITH QUADRIDENTATE SCHIFF BASE

Reactants (Molar ratio)	Stirring time (h)	Product, colour and dec temp	Mol wt Found (Calcd)	Found (Calcd) %		
				Zr	N	Cl
Cp_2ZrCl_2 + $SB''H_2$ + Et_3N (1:1:2)	36	$Cp_2Zr(SB'')$ Yellowish green, 290	—	16.9 (17.0)	5.1 (5.2)	— —
Cp_2ZrCl_2 + $SB''H_2$ + Et_3N (2:1:2)	30	$(Cp_2ZrCl)_2SB''$ Dark brown, 325	885 (827.4)	22.4 (22.05)	3.3 (3.4)	8.3 (8.6)

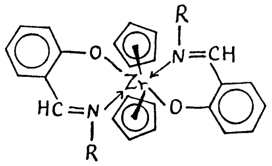
$SB''H_2$ = *N,N'*-disalicylidene-*o*-phenylenediamine.

TABLE 4. IR FREQUENCIES (cm^{-1}) FOR BIS(π-CYCLOPENTADIENYL)ZIRCONIUM(IV) SCHIFF BASE COMPLEXES

Complex	ν(C-H)	ν(C-C)	$\delta^{i.p.}$(-CH)	$\delta^{o.p.}$(-CH)	ν(C=N)	ν(C=O)
Cp_2ZrCl_2	3100 s	1435 s	1020m	820 mb	—	—
$Cp_2Zr(SB)Cl$	3000 s	1442 s	1010 b	800 b	1590 s	1315m
$Cp_2Zr(SB)_2$	2995 w	1445 s	1005 b	810 b	1590 s	1305 b
$Cp_2Zr(SB')Cl$	3000 w	1440 s	1015m	800 s	1600 s	1305 s
$Cp_2Zr(SB')_2$	2995 s	1435 s	1015m	800 b	1600 s	1305 s
$Cp_2Zr(S'B)Cl$	2995m	1440 s	1020 w	805 w	1600 s	1310 w
$Cp_2Zr(S'B)_2$	3000 s	1440 s	1018 b	800 b	1595 s	1305 w
$Cp_2Zr(S'B')Cl$	2990 s	1440 s	1016 s	800 b	1590 s	1220 s
$Cp_2Ze(S'B')_2$	3000 w	1445 s	1016 s	810 b	1595 s	1340 w
$Cp_2Zr(S''B'')Cl$	2990 s	1430 s	1018m	820 b	1613 w	1335 s
$Cp_2Zr(S''B'')_2$	3000 w	1425 s	1018m	820 b	1613 w	1345 s
$Cp_2Zr(SB)$	2910 w	1430m	1018 s	805m	1580 s	1305 w
$Cp_2Zr(SB')$	2930 w	1430 s	1020 s	800 s	1588 s	1310m
$Cp_2Zr(SB'')$	2960 w	1445 s	1018 s	815 b	1610 s	1315 s
$(Cp_2ZrCl)_2SB''$	2970 b	1445 s	1018 s	810 s	1605 s	1310 s



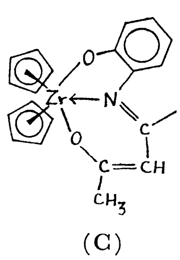
(A)



(B)

[R = C_6H_5, *o*-$CH_3C_6H_5$, *m*-$CH_3C_6H_5$, and *p*-$CH_3C_6H_5$]

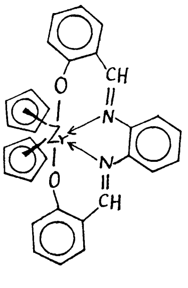
Complexes with terdentate Schiff bases:



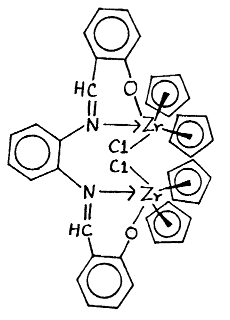
(C)

[R' = CH_3 and C_6H_5]

Complexes with quadridentate Schiff base:



(D)



(E)

Similar structures have been reported for oximate complexes of dichlorobis(cyclopentadienyl)ziroconium.[15] In all complexes having structures (A), (C), and (E), the coordination number of zirconium appears to be five. This coordination number is well known for zirconium complexes.[15,16] For complexes with structures (A) and (E), the appearance of band at ≈350 cm^{-1} due to ν(Zr–Cl) confirms the presence of coordinated chlorine. In complexes having structures (B) and (D) zirconium attains the well known coordination number six.[15,17] In the structure (B) the Schiff base acts as a bidentate ligand while in the case of (D) the denticity of the ligand is four *i.e.* it behaves as quadridentate ligand. Both these complexes are examples of twenty-electron system which has been reported for several other titanium[18,19] and zirconium[15] complexes. A twenty-electron system is also well documented for nickelocene.[20]

In all the complexes the cyclopentadienyl rings are *cis*, as their IR frequencies in the complexes coincide with those of dichlorobis(cyclopentadienyl)zirconium(IV), supporting "angular" sandwich structure as reported by Giddings *et al.*[21]

Infrared Spectra. The important IR frequencies are given in Table 4. Absorption bands occurring at $\approx 3000\ \mathrm{cm}^{-1}$ ν(C–H), $\approx 1435\ \mathrm{cm}^{-1}$ ν(C–C), $\approx 1020\ \mathrm{cm}^{-1}$ $\delta^{\mathrm{i.p.}}$(–CH), and at $\approx 810\ \mathrm{cm}^{-1}$ $\delta^{\mathrm{o.p.}}$(–CH) indicated the presence of the cyclopentadienyl groups. All these bands are similar to these of dichlorobis(cyclopentadienyl)zirconium(IV).[22]

In the spectra of Schiff bases, a strong band is observed in the 1617—1613 cm^{-1} region, which can be assigned to the absorption basd of the azomethine group ($>$C=N–). In these complexes, this band is slightly shifted to the lower side as given in Table 4. Similar observations have also been made by a number of workers.[23,24] But in case of complexes with Schiff base, *N*-(2-hydroxy-1-naphtyliden)aniline, there is no appreciable shift in ν(C=N) band compared to Schiff base as reported by Bailar.[25]

The strong band in the region of 1300—1282 cm^{-1} in the Schiff bases is attributed to the phenolic ν(C–O) in view of previous assignments. This ν(C–O) band shifts by $\approx 30\ \mathrm{cm}^{-1}$ towards higher frequency upon complexation, suggesting bonding between zirconium and oxygen as observed by Poddar *et al.*[26]

The disappearance of the weak and broad bands in the region 3300—3100 cm^{-1} (–OH) in the complexes suggests that the (–OH) group of the Schiff base has taken part in the bond formation, and confirms the complex formation. Bands in the region 570—530 cm^{-1} and 520—420 cm^{-1} are attributed to ν(Zr–N) and ν(Zr–O), respectively as reported.[27,28]

Electronic Spectra. The electronic spectra of all the Schiff base complexes of dichlorobis(cyclopentadienyl)zirconium(IV) complexes were recorded in chloroform and acetone. All complexes show a single band in the region 25250—24280 cm^{-1} which can be assigned to the charge transfer band,[29] and is in accordance with their $(n-1)\mathrm{d}^0\mathrm{ns}^0$ electronic configuration.

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