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Bis(indenyl)zirconium(IV) Complexes of Monofunctional Bidentate Salicylidimines

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A series of $(C_9H_7)_2Zr(SB)Cl$ complexes where SB^- is the anion of bidentate *Schiff* base derived from salicylaldehyde and 4-substituted anilines, viz. salicylidene-4-ansidine, salicylidene-4-phenetidine, salicylidene-4-chloroaniline, salicylidene-4-bromoaniline, salicylidene-4-iodoaniline and salicylidene-4-nitroaniline, have been synthesized by the reaction of bis(indenyl)zirconium(IV) dichloride and *Schiff* base (*SB*H) in 1:1 molar ratio in refluxing *THF* in the presence of triethylamine. The new derivatives have been characterized on the basis of their elemental analyses, conductance measurements and spectral (IR, ^{1}H-NMR, UV-VIS) studies.

[Keywords: Bis(indenyl)zirconium(IV) complexes; Schiff base; Conductance; IR; ^{1}H NMR; UV-VIS]

Bis(indenyl)zirkonium(IV)-Komplexe monofunktioneller zweizähniger Salicylidimine

Es wurde eine Reihe von $(C_9H_7)_2Zr(SB)Cl$-Komplexen synthetisiert, wobei SB^- für das Anion einer zweizähnigen *Schiff*-Base steht. Die *Schiff*-Basen sind von Salicylaldehyd und 4-substituierten Anilinen hergeleitet: Salicyliden-4-anisidin, -4-phenetidin, -4-Cl-, -4-Br-, -4-I-anilin und -4-Nitroanilin. Die Synthese erfolgte über die Reaktion von Bis(indenyl)zirkonium(IV)-dichlorid mit der *Schiff*-Base (*SB*H) in einem molaren Verhältnis von 1:1 am Rückfluß in Gegenwart von Triethylamin und *THF* als Lösungsmittel. Zur Charakterisierung der neuen Derivate wurden Elementaranalysen, Leitfähigkeitsmessungen und spektroskopische Daten (IR, ^{1}H-NMR, UV-VIS) herangezogen.

Introduction

Schiff base complexes of transition metals have played a prominent rôle in the development of coordination chemistry[1–5]. Recently some *Schiff* base derivatives of bis(cyclopentadienyl)zirconium(IV) with bidentate, tridentate and quadridentate *Schiff* bases have

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been reported by *Kapoor* et al.[6–7]. However, reactions of bis(indenyl)zirconium(IV) dichloride with *Schiff* bases have not been studied so far. The present work describes the reactions of bis(indenyl)zirconium(IV) with bidentate *Schiff* bases derived from salicylaldehyde and 4-substituted anilines.

Results and Discussion

Dichlorobis(indenyl)zirconium(IV), $(C_9H_7)_2ZrCl_2$ reacts with bidentate *Schiff* bases in 1:1 molar ratio to yield complexes of the type, $(C_9H_7)_2Zr(SB)Cl$, according to the following equation:

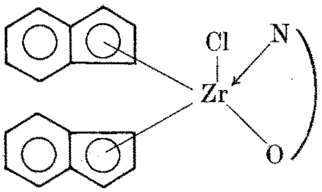
$$(C_9H_7)_2ZrCl_2 + SBH + Et_3N \xrightarrow[68\,^{\circ}C]{THF} (C_9H_7)_2Zr(SB)Cl + Et_3N \cdot HCl$$

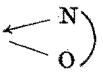
where $(SB)^-$ represents the anion of the corresponding bidentate *Schiff* base *SB*H.

The reactions were carried out in dry tetrahydrofuran at 68 °C and Et_3N was used as HCl-recovering agent. Electrical conductance measurements in nitrobenzene show them to be non-electrolytes and to be susceptible to hydrolysis.

All the *Schiff* base complexes crystallyze as yellowish brown crystals. They are highly soluble in common organic solvents, viz., benzene, *THF*, acetone, dichloromethane, nitrobenzene and chloroform. The analytical and physical data of the complexes are given in Table 1.

On the basis of elemental analyses and spectral studies, the following structure is assigned to the $(C_9H_7)_2Zr(SB)Cl$ complexes



where  represents the anion of bidentate *Schiff* base.

The structure shown is analogous to those already reported for *Schiff* base complexes of zirconium(IV)[6,7]. The presence of coordinated chlorine has been confirmed by the appearance of a band at ca. 355 cm^{-1} due to ν(Zr—Cl) vibrations. Zirconium evidently attains a coordination number of five in these complexes which is in accordance with Ref.[6,7].

Table 1. *Analytical and physical data for the complexes* **1-6**

No.	Compound	Yield (%)	Dec. temp. (°C)	Conductance $M \cdot 10^3 = 0.5$ $\mathrm{Ohm^{-1}\,cm^2\,mol^{-1}}$	% Found(Calc.) Zr	N	Halogen
1	$(C_9H_7)_2$Zr(*sal*-4-anisidine)Cl	72	116-118	0.25	15.60 (15.65)	2.29 (2.40)	6.01 (6.09)
2	$(C_9H_7)_2$Zr(*sal*-4-phenetidine)Cl	76	112-115	0.22	15.32 (15.29)	2.30 (2.35)	5.90 (5.95)
3	$(C_9H_7)_2$Zr(*sal*-4-claniline)Cl	68	110-112	0.30	15.47 (15.52)	2.32 (2.38)	11.52 (12.08)
4	$(C_9H_7)_2$Zr(*sal*-4-Br aniline)Cl	74	105-107	0.28	14.32 (14.44)	2.20 (2.22)	18.20 (18.28)
5	$(C_9H_7)_2$Zr(*sal*-4-I aniline)Cl	70	104-106	0.26	13.48 (13.44)	2.01 (2.06)	24.02 (23.94)
6	$(C_9H_7)_2$Zr(*sal*-4-NO_2 aniline)Cl	74	152-154	0.24	15.39 (15.22)	4.60 (4.68)	6.09 (5.94)

IR Spectra

The assignment of characteristic infrared frequencies for $(C_9H_7)_2Zr(SB)Cl$ complexes are listed in Table 2.

Table 2. *Characteristic infrared bands for the complexes* **1**-**6**

No.	ν(C—H)	ν(C—C)	δ i.p. (C—H)	δ o.p. (C—H)	ν(C=N)	ν(C—O)
1	3 100 (s)	1 440 (m)	1 025 (m)	815 (w)	1 600 (s)	1 300 (s)
2	3 100 (s)	1 440 (m)	1 020 (m)	820 (m)	1 600 (m)	1 300 (s)
3	3 100 (s)	1 430 (m)	1 020 (m)	805 (m)	1 610 (m)	1 305 (m)
4	3 080 (s)	1 440 (m)	1 025 (m)	810 (w)	1 610 (s)	1 295 (m)
5	3 100 (s)	1 445 (m)	1 025 (m)	810 (m)	1 605 (s)	1 295 (s)
6	3 100 (s)	1 430 (m)	1 020 (m)	820 (m)	1 600 (vs)	1 300 (s)

Absorption bands indicating the presence of the indenyl group are found at ca. 3 100 ν(C—H), 1 450 ν(C—C), 1 015 δ i.p. (C—H) and 810 cm^{-1} δ o.p. (C—H). Appearance of these indenyl bands in the *Schiff* base derivatives indicate that electrons in these groups remain delocalised and π-bonded (η^5) to the metal[8].

A strong band is observed at ca. 1 625 cm^{-1} in the spectra of the *Schiff* bases, which is characteristic for the azomethine (—HC=N—) group. Coordination of the nitrogen to the metal atom would, however, be expected to reduce the electron density in the azomethine link and thus lower the (C=N) frequency. In the *Schiff* base complexes this band is very slightly shifted to the lower side in our studies (ca. 1 600 cm^{-1}), showing the presence of coordination through the azomethine nitrogen. Similar observations have also been made by other workers[6,7,9,10]. A high intensity band at ca. 1 275 cm^{-1} in the *Schiff* bases can be assigned to the phenolic C—O stretching[10]. In the complexes, the C—O stretching vibrations appear at 1 320-1 310 cm^{-1}. This shift to higher frequency indicates bonding of ligand to the metal through oxygen. This is further supported by the disappearance of the broad ν(O—H) band in the 3 300-3 150 cm^{-1} region in the complexes.

Bands at 570-540 and 525-430 cm^{-1} can be tentatively assigned to Zr—O and Zr—N bonds, however, specific arrangements are difficult[9].

^{1}H-*NMR Spectra*

Proton magnetic resonance spectra of the complexes were taken in $CDCl_3$. The chemical shifts are listed in Table 3. The resonance signal due to the azomethine proton appears at ca. δ 8.60 ppm, showing downfield shift as compared to the corresponding *Schiff* base ligand (8.45) indicating its deshielding as a result of coordination through

Table 3. *^{1}H NMR and UV data for the complexes* **1-6**

No.	$C_9H_7^-$	Aromatic ring protons	(—CH=N)	π-π* (Benzoid)	π-π* (—CH=N)	n-π* (—CH=N)
1	6.58	7.72 (m)	8.65	255	320	378
2	6.60	7.52 (m)	8.70	254	322	372
3	6.52	7.58 (m)	8.60	250	325	380
4	6.48	7.62 (m)	8.68	252	326	375
5	6.44	7.60 (m)	8.65	252	322	378
6	6.48	7.50 (m)	8.62	255	324	374

nitrogen of the azomethine group to zirconium. The resonance signals due to indenyl protons overlap with that of aromatic protons signals of the *Schiff* base and result in a complex multiplet in the range of 6.70-7.70 ppm.

The disappearance of the phenolic-OH proton signal in the *Schiff* base complex indicates its deprotonation and having taken part in the bond formation to metal through oxygen.

UV Spectra

The UV spectra of the complexes were recorded in chloroform. The bands appearing at ca. 250, 320 and 385 nm are due to the π-π* (benzoid), π-π* (azomethine) and n-π* (azomethine) electronic transitions respectively. In the ligands (*Schiff* bases), the first two bands were observed at the same positions, whereas the third band was observed at ca. 425 nm. This hypsochromic shift in the *Schiff* base complexes may be due to the donation of a lone pair of electrons by the nitrogen of the azomethine group to the central metal atom[10].

The visible spectra of the complexes in chloroform show a single band in the 24800-24300 cm^{-1} region. Absence of a d—d transition rules out the presence of any unpaired electron in the zirconium ion and corresponds to the electronic configuration $(n\text{-}1)d^\circ$, ns°[11].

Experimental

Materials and Methods

All the reagents used for the preparation of these compounds were of analytical grade. Bis(indenyl)zirconium(IV) dichloride, $(C_9H_7)_2ZrCl_2$ was prepared by the reaction of indenylthallium(I) and zirconium tetrachloride in 2 : 1

molar ratio in tetrahydrofuran. *THF* (Baker AR) was dried over sodium metal and then boiled under reflux until it gave a blue colouration with Ph_2CO. It was finally dried by distillation from $LiAlH_4$. *n*-Hexane (BDH) was dried by refluxing over sodium metal followed by distillation. Benzene and triethylamine were dried as reported in Ref.[12]. Nitrobenzene for conductance measurements was purified by the method described by *Fay* et al.[13].

Zirconium was determined gravimetrically as its oxide whereas halogens were estimated as silver halides. Nitrogen was estimated by a standard method as described by *Vogel*[14].

Conductance measurements were made in nitrobenzene at 30 ± 0.05 °C using an Elico Conductivity Bridge Model CM-82. Infrared spectra were recorded in KBr pellets in the 4000–200 cm^{-1} region on a Perkin-Elmer 621 grating spectrometer. The proton NMR spectra were recorded at ambient temperature (30 °C) at a sweep width of 900 Hz with a Perkin-Elmer R-32 spectrophotometer. Chemical shifts (δ, ppm) are expressed relative to an internal reference of *TMS* (1% by volume). Electronic spectra of the complexes in acetone were recorded on Perkin Elmer UV-visible spectrophotometer Model 554.

Preparation of Schiff Bases

To an appropriate amine (6 mmol) in 60 ml of freshly distilled ethanol, salicylaldehyde (5 mmol) in 60 ml of freshly distilled ethanol was added dropwise with vigorous stirring. There was immediate precipitation of products on addition of reactants. The mixture was refluxed for 0.5 h, then cooled in an ice bath and filtered. The product was recrystallyzed by addition of 40 ml of hot ethanol. The mixture was cooled in an ice bath, filtered, and washed with sodium dried diethylether. The *Schiff* bases were dried *in vacuo* and stored in glass jars fitted with a screw cap. The yield was approximately 90%.

Preparation of the Complexes

All operations were carried out under strictly anhydrous conditions. The *Schiff* base (4 mmol) was added to a solution of bis(indenyl)zirconium(IV) dichloride, $(C_9H_7)_2ZrCl_2$ (4 mmol) in 40 ml of dry tetrahydrofuran. To this, triethylamine (6 mmol) was added and the mixture was refluxed for about 12–14 h. Precipitated $Et_3N \cdot HCl$ was removed by filtration and the volume of the filtrate was reduced to ca. 30 ml by evaporating the solvent under pressure at room temperature. The crystals of the product were obtained by adding 75 ml of dry *n*-hexane.

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