

Reactions of dichloro-bis(cyclopentadienyl)titanium(IV) with bidentate Schiff bases

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Abstract. A series of $\text{Cp}_2\text{Ti}(\text{SB})\text{Cl}$ complexes, where *SB* is the anion of bidentate Schiff bases derived from salicylaldehyde and different primary amines *viz* *o*-anisidine, *m*-anisidine, *o*-phenetidine, *o*-chloroaniline, *m*-chloroaniline, *m*-nitroaniline, α -naphthylamine and benzylamine, have been synthesised by the reaction of dichloro-bis(cyclopentadienyl) titanium(IV), Cp_2TiCl_2 , and bidentate Schiff base (*SBH*) in a 1 : 1 molar ratio in refluxing THF in the presence of triethylamine. The new derivatives have been characterised on the basis of their elemental analyses, conductance measurements and spectral (IR, $^1\text{H NMR}$ and electronic) studies.

Keywords. Cyclopentadienyl; titanium(IV); Schiff bases.

1. Introduction

Schiff bases derived from the reaction of salicylaldehyde with primary amines represent a versatile series of ligands, the metal complexes of which have been widely studied (Sacconi 1966; Yamada 1966; Holm *et al* 1966). Some organometallic complexes of titanium(IV) with bidentate, terdentate and quadridentate Schiff bases are known (Sharan *et al* 1978; Sharma *et al* 1980). Recently, we have reported (Sharma *et al* 1984) some reactions of dichloro-bis(cyclopentadienyl) zirconium(IV) with *N*-aryl salicylidimines. The present work describes the reactions of dichloro-bis(cyclopentadienyl) titanium(IV) with bidentate Schiff bases derived from salicylaldehyde and different primary amines.

2. Experimental

2.1 Materials and methods

All the reagents used were of analytical grade. Dichloro-bis(cyclopentadienyl) titanium(IV), Cp_2TiCl_2 , was obtained from Fluka AG, Switzerland and was used without further purification. Schiff bases were prepared by the condensation of salicylaldehyde and an appropriate amine in ethanol as reported earlier (Sharma *et al* 1983). 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. Nitrobenzene for conductance measurements was purified as given in the literature (Fay and Lowry 1967).

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Titanium was determined gravimetrically as its oxide whereas chlorine was estimated as silver chloride. Nitrogen was estimated by Kjeldahl's method.

Conductance was measured in nitrobenzene at $20 \pm 0.05^\circ\text{C}$ using a Systronic digital direct reading conductivity meter type 304. Infrared spectra were recorded in KBr pellets in the $4000\text{--}200\text{ cm}^{-1}$ region on a Perkin-Elmer 621 grating spectrophotometer. The proton NMR spectra were recorded with a Perkin-Elmer R-32 spectrometer. Chemical shifts (δ) are expressed relative to an internal reference of TMS (1% by volume). Electronic spectra of the complexes in acetone were recorded on a Perkin-Elmer UV-visible spectrophotometer, model 554.

2.2 Preparation of the complexes

All operations were carried out under strictly anhydrous conditions. Special precautions were taken to exclude moisture from apparatus and chemicals. Quickfit apparatus of standard interchangeable glass joints lubricated with silicon grease was employed throughout the experimental work. The Schiff base (5 mmol) was added to a solution of dichloro-*bis*(cyclopentadienyl)titanium(IV), Cp_2TiCl_2 , (5 mmol) in 40 ml of dry tetrahydrofuran. Triethylamine, Et_3N , (6 mmol) was added to the mixture and it was refluxed for 10–12 hr. Precipitated $\text{Et}_3\text{N} \cdot \text{HCl}$ was removed by filtration and the volume of the filtrate was reduced to *ca* 25 ml by evaporating the solvent under reduced pressure at room temperature. The crystals of the product were obtained by adding about 50 ml of dry *n*-hexane. All the complexes were prepared by a similar method.

3. Results and discussion

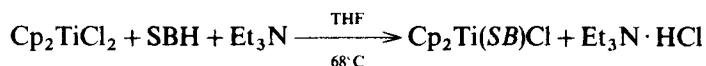
Dichloro-*bis*(cyclopentadienyl)titanium(IV), Cp_2TiCl_2 , reacts with bidentate Schiff

Table 1. Analytical data and physical characteristics of the complexes.

Compound	Yield (%)	Dec. temp. ^a (°C)	Conductance $M \times 10^3 = 0.5$ ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	% Found (Calc.)		
				Ti	N	Cl
$\text{Cp}_2\text{Ti}(\text{sal-}o\text{-anisidine})\text{Cl}$	62	130–132	0.26	10.80 (10.89)	3.10 (3.18)	7.97 (8.07)
$\text{Cp}_2\text{Ti}(\text{sal-}m\text{-anisidine})\text{Cl}$	65	135–136	0.22	10.76 (10.89)	3.06 (3.18)	8.01 (8.07)
$\text{Cp}_2\text{Ti}(\text{sal-}o\text{-phenetidine})\text{Cl}$	70	166–168	0.22	10.42 (10.56)	3.01 (3.09)	7.72 (7.82)
$\text{Cp}_2\text{Ti}(\text{sal-}o\text{-Claniline})\text{Cl}$	68	176–179	0.24	10.73 (10.79)	3.23 (3.15)	16.12 (15.99)
$\text{Cp}_2\text{Ti}(\text{sal-}m\text{-Claniline})\text{Cl}$	60	143–146	0.28	10.86 (10.79)	3.08 (3.15)	15.92 (15.99)
$\text{Cp}_2\text{Ti}(\text{sal-}m\text{-NO}_2 \text{ aniline})\text{Cl}$	62	147–149	0.24	10.60 (10.54)	6.24 (6.16)	7.96 (7.81)
$\text{Cp}_2\text{Ti}(\text{sal-}\alpha\text{-naphthylamine})\text{Cl}$	63	188–191	0.30	10.31 (10.43)	3.13 (3.04)	7.64 (7.72)
$\text{Cp}_2\text{Ti}(\text{sal-benzylamine})\text{Cl}$	65	195–197	0.24	11.40 (11.32)	3.18 (3.30)	8.26 (8.37)

^a Uncorrected values.

bases in a 1 : 1 molar ratio to yield complexes of the type $\text{Cp}_2\text{Ti}(\text{SB})\text{Cl}$ according to the following equation:



where $(\text{SB})^-$ represents the anion of the corresponding bidentate Schiff base SBH.

All the Schiff base complexes crystallise as yellow to yellowish brown crystals. They are highly soluble in common organic solvents, *viz* benzene, nitrobenzene, THF, acetone, dichloromethane and chloroform. Electrical conductance measurements in nitrobenzene show these complexes to be nonelectrolytes and susceptible to hydrolysis. The analytical and physical data of the complexes are given in table 1.

3.1 IR spectra

The assignment of characteristic infrared frequencies for $\text{Cp}_2\text{Ti}(\text{SB})\text{Cl}$ complexes is listed in table 2.

A strong band is observed at *ca* 1630 cm^{-1} in the spectra of the Schiff bases, which may be assigned to the azomethine ($-\text{HC}=\text{N}-$) group. In the Schiff base complexes, this band is very slightly shifted to the lower wave number in our studies (*ca* 1600 cm^{-1}), suggesting coordination through the azomethine nitrogen (Sharan *et al* 1978; Sharma *et al* 1980; Uttamchandani and Kapoor 1978). A high intensity band at *ca* 1275 cm^{-1} in the Schiff bases can be assigned to the phenolic C–O stretching (Sharan *et al* 1978). In the complexes, the C–O stretching vibrations appear at $\sim 1320\text{ cm}^{-1}$. This shift to higher frequency indicates bonding of the ligand to the metal through oxygen.

Bands in the region $570\text{--}540$ and $525\text{--}425\text{ cm}^{-1}$ are attributed to the $\nu(\text{Ti-O})$ and $\nu(\text{Ti-N})$ vibrations, respectively (Sharan *et al* 1978). Besides, the band at *ca* 355 cm^{-1} may be assigned to $\nu(\text{Ti-Cl})$ (Sharma and Kaushik 1981) vibration.

3.2 $^1\text{H NMR}$ spectra

Proton magnetic resonance spectra of the complexes were taken in deuterated chloroform. Chemical shifts for protons (δ scale) have been indicated in table 2. The azomethine and aromatic protons in the Schiff base complexes show a considerable downfield shift as compared to the corresponding Schiff base ligands ($\sim \delta 8.45$ ppm and $\sim \delta 6.6\text{--}7.3$ ppm respectively) indicating the coordination of the azomethine nitrogen of the Schiff base to the metal.

3.3 Electronic spectra

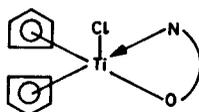
The electronic spectra of the complexes were observed in chloroform. The bands appearing at *ca* 250, 325 and 385 nm are due to the $\pi \rightarrow \pi^*$ (benzoid), $\pi \rightarrow \pi^*$ (azomethine) and $n \rightarrow \pi^*$ (azomethine) electronic transitions, respectively. In the ligands (Schiff bases) the first two bands were observed at the same positions, whereas the third band was observed at *ca* 425 nm. A single band in the 402–412 nm region may be assigned to a charge transfer band in accordance with the electronic configuration $(n-1)d^0, ns^0$ (Kaushik *et al* 1980, 1981).

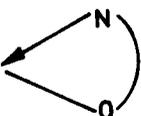
On the basis of elemental analyses and spectral studies, the following structure may be assigned to the $\text{Cp}_2\text{Ti}(\text{SB})\text{Cl}$ complexes.

Table 2. Characteristic IR bands and ^1H NMR data.

Compound	IR (cm^{-1})		^1H NMR (δ , ppm)			
	ν (C=N)	ν (C-O)	C_3H_5	-CH=N-	Aromatic ring protons	-OCH ₃ /OC ₂ H ₅
$\text{Cp}_2\text{Ti}(\text{sal-}o\text{-anisidine})\text{Cl}$	1600	1310	6.42 (s)	8.60 (s)	6.78-7.60 (m)	3.62 (s)
$\text{Cp}_2\text{Ti}(\text{sal-}m\text{-anisidine})\text{Cl}$	1610	1300	6.40 (s)	8.62 (s)	6.70-7.62 (m)	3.65 (s)
$\text{Cp}_2\text{Ti}(\text{sal-}o\text{-phenetidine})\text{Cl}$	1600	1320	6.38 (s)	8.62 (s)	6.76-7.68 (m)	3.70 (q) 1.32 (t)
$\text{Cp}_2\text{Ti}(\text{sal-}o\text{-claniline})\text{Cl}$	1600	1310	6.32 (s)	8.62 (s)	6.80-7.60 (m)	—
$\text{Cp}_2\text{Ti}(\text{sal-}m\text{-claniline})\text{Cl}$	1605	1320	6.32 (s)	8.58 (s)	6.72-7.70 (m)	—
$\text{Cp}_2\text{Ti}(\text{sal-}m\text{-NO}_2\text{ aniline})\text{Cl}$	1610	1305	6.40 (s)	8.60 (s)	6.70-7.68 (m)	—
$\text{Cp}_2\text{Ti}(\text{sal-}\alpha\text{-naphthylamine})\text{Cl}$	1600	1310	6.38 (s)	8.62 (s)	6.74-7.60 (m)	—
$\text{Cp}_2\text{Ti}(\text{sal-benzylamine})\text{Cl}$	1605	1310	6.40 (s)	8.60 (s)	6.76-7.70 (m)	—

s = singlet, t = triplet, q = quartet, m = multiplet.



where,  represents the anion of a bidentate Schiff base.

The structure shown is analogous to those already reported for Schiff base complexes of titanium (Sharan *et al* 1978; Sharma *et al* 1980).

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