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Synthesis and Catalytic Properties of Ruthenium(III) Unsymmetrical Schiff Base Complexes

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Ruthenium(III) unsymmetrical Schiff base complexes, $[\text{Ru}(\text{CHBPH-TP})\text{Cl}_2]$ and $\text{K}[\text{Ru}(\text{CHBPH-HB})\text{Cl}_2]$ were synthesized, where CHBPH-TP and CHBPH-HB are 5-chloro-2-hydroxybenzophenonethiophenecarbaldehydephenylenediimine and 5-chloro-2-hydroxybenzophenonehydroxybenzophenonephenylenediimine. These Schiff bases were obtained from the reactions of 5-chloro-2-hydroxybenzophenone (CHB) and 2-Thiophenecarbaldehyde (TP) or hydroxybenzophenone (HB) and 1,2-diaminobenzene. Elemental analysis, conductivity and infrared studies of the complexes suggest an octahedral geometry around ruthenium. Magnetic moments of the complexes indicate a single unpaired electron in a low spin d^5 configuration. The complexes are capable of catalyzing the oxidation of styrene with sodium hypochlorite in the presence of phase transfer agent. Oxidative cleavage of C=C bond is the major reaction pathway to form benzaldehyde for styrene oxidation.

Introduction

Symmetric tetradentate Schiff base complexes have been used extensively as macrocycle models,¹ while unsymmetric

complexes are required to model the irregular binding of peptides. Unsymmetric complexes are very important in biological systems as well as in industrial catalysis and are interesting also from theoretical point of view.²

Kusta *et al.* obtained several metal complexes with unsymmetrical Schiff bases by reacting Cu(II), Ni(II), Pd(II) salt

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with a mixture of the condensation products of acetylacetone, ethylenediamine and salicylaldehyde or its derivatives.²

The oxidation of hydrocarbons by inexpensive oxidants is an area of intensive study. In particular, catalysis of alkene oxidation by transition metal complexes is of interest in both biomimetic and synthetic chemistry.

The oxidized products of ruthenium complexes of Schiff base ligands have been variously formulated as monomers.³ High oxidation state ruthenium complexes are of great importance in biological systems and in catalytic oxidative processes.⁴ The use of monomeric ruthenium complexes of porphyrine and Schiff base ligands as metal catalysts for the epoxidation (or oxidation) of alkenes has recently attracted considerable attention.⁵⁻⁹ The use of hypochlorite ion for the oxidation of alkenes was initially limited to the activated carbon-carbon double bonds of certain arenes¹⁰ or α,β -unsaturated ketones.¹¹

More recently, hypochlorite ion has been effectively used in the presence of metal porphyrin catalysts to epoxidize a variety of olefins.¹² Only a few non-porphyrin metal complexes have been studied.¹³ These reactions generally yield a large amount of C=C bond cleavage products when either hypochlorite or hyperiodate ion is employed as oxidant.

The present paper deals with the synthesis of the unsymmetrical Schiff bases complexes of ruthenium and the study of their catalytic activity towards oxygenation of olefins in the presence of sodium hypochlorite.

Experimental

Materials. Potassium pentachloroaquoruthenium, $K_2[RuCl_5(H_2O)]$ was purchased from Aldrich Chemical Co. CHB and CHBPH were prepared according to the literature method.¹⁴ All reagents and solvents for syntheses were AR grade from MERCK Co., and were used without further purification: Anhydrous Aluminum Chloride, Benzoyl Chloride, 4-Chlorophenol, 1,2-diaminobenzene, triethylorthoformate, piperidine, TP and HB.

Measurement. The elemental analyses were carried out by a Carlo Erba Analyzer (Model 1106). UV-visible spectra were recorded on a Shimadzu UV-265 spectrophotometer and infrared spectra were recorded on BOMEM FT-IR spectrophotometer. The melting points were measured on a Perkin Elmer II differential scanning calorimeter. Molar conductance was measured at room temperature on a conductivity bridge. Magnetic moments were determined on a Johnson Mattney magnetic susceptibility balance. Organic products were analyzed on a Varian 3300 gas chromatography equipped with a flame ionization detector.

Preparations. CHBPH-TP. CHBPH (0.1 g, 0.3 mmol), TP (0.03 mL, 0.3 mmol), and piperidine (0.026 g, 0.3 mmol) were refluxed in methanol (1.5 mL) until all the reactants dissolved. The solution was allowed to evaporate until the solid residue precipitated from solution. A 0.01 g (10% yield) of yellow crystals of CHBPH-TP was obtained. Anal. Calcd. for $C_{22}H_{17}N_2SOCl$: C, 67.26; H, 4.33; N, 7.13; O, 4.08. Found: C, 68.57; H, 4.72; N, 7.03; O, 4.14. IR (cm^{-1}): $\nu(C=N)$ 1620, $\nu(C-O)$ 1255, ν (thiophene ring) 720, 1H -NMR($CDCl_3$): δ 6.9-7.5 (m, aromatic), δ 6.2-6.8 (m, thienyl=CH), δ 8.3 (s, CH=N), δ 10.6 (s, OH).

CHBPH-HB. CHBPH (0.1 g, 0.3 mmol) and HB (0.06

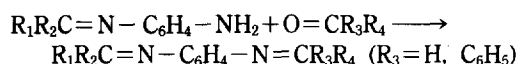
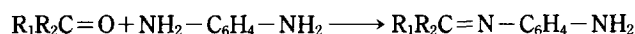
g, 0.3 mmol) were refluxed, without solvent, for 30 min. The resulting melt was allowed to cool to room temperature and was dissolved in hot 1-butanol (1 mL). The resulting solid residue was filtered off. A 0.012 g of crystals of CHBPH-HB was obtained. Anal. Calcd. for $C_{30}H_{23}N_2O_2Cl$: C, 77.84; H, 4.97; N, 7.13; O, 6.92. Found: C, 78.01; H, 4.86; N, 7.26; O, 7.10. IR (cm^{-1}): $\nu(C=N)$ 1630, $\nu(C-O)$ 1235. 1H -NMR($CDCl_3$): δ 6.4-7.4 (m, aromatic), δ 10.8 (s, OH).

Metal Complexes. To hot ethanolic solutions of the above Schiff bases (0.5 mmol) were added $K_2[RuCl_5(H_2O)]$ (0.5 mmol). The reaction mixture was refluxed up to 24 h under nitrogen atmosphere. The solution was filtered under nitrogen atmosphere and the filtrate was concentrated to one tenth. To the solution was added an excess of ether and the precipitated complex was filtered, washed first with ethanol and finally with ether, and dried under vacuum.: Yield 40% $[Ru(CHBPH-TP)Cl_2]$, IR (cm^{-1}): $\nu(C=N)$ 1599, $\nu(C-O)$ 1218.; UV-Vis(CH_2Cl_2): 685, 546, 454, 342, 264 (nm). $K[Ru(CHBPH-HB)Cl_2]$, IR (cm^{-1}): $\nu(C=N)$ 1590, $\nu(C-O)$ 1183.; UV-Vis(CH_2Cl_2): 538, 672, 425, 338, 272 (nm).

Catalytic Oxidation of Styrene. 4.0 mmol Styrene, 0.1 mmol ruthenium complexes, and 0.15 mmol benzyldimethyltetradecylammonium chloride (phase transfer agent, PTA) in 10 mL of methylene chloride were stirred vigorously with 20 mL of sodium hypochlorite (pH=13) at 25°C for 5 h. Aliquots (1 μ L) of the dichloromethane layer were analyzed by gas chromatography and compared to an internal standard.

Results and Discussion

The unsymmetric ligands were prepared by two step process⁴ may be considered according to the following scheme:



In the first step, one mole of 1,2-diaminobenzene is reacted with one mole of CHB to afford a 1:1 condensation product (half-unit reaction), which is then reacted with one mole of either TP or HB to yield unsymmetrical diimines. If half-unit reaction is carried out in the absence of solvent, condensation does occur at both amine groups.

The compounds CHBPH-TP and CHBPH-HB are yellow solids, very stable at room temperature.

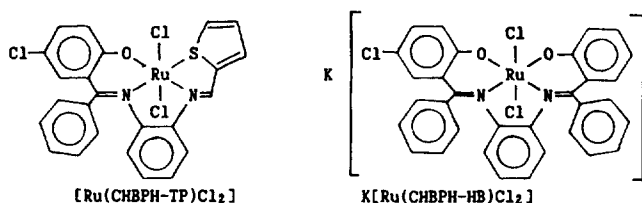
The metal complexes were characterized by elemental (C, H, O, N) analysis, spectra (IR and UV-Vis), and conductivity and magnetic moment measurements. The analytical data of the solid ruthenium(III) unsymmetrical Schiff base complexes along with conductivity results in dichloromethane are given in Table 1.

The data are consistent with the formation of octahedral ruthenium(III) complexes with the general composition $[RuLX_2]$, where L=Schiff base, X=Cl (Figure 1). The complexes are high melting solids. Both of the ruthenium complexes are air stable dark brown solids.

Conductivities of a millimolar solution of $[Ru(CHBPH-TP)Cl_2]$ and $K[Ru(CHBPH-HB)Cl_2]$ complex are 12 and 85 $\Omega^{-1}cm^2mol^{-1}$, indicating that the former complex is non-electrolyte while the latter complex is a 1:1 electrolyte. Both of

Table 1. Elemental Analysis, Melting Points and Magnetic Moment of Ruthenium(III) Schiff Base Complexes

Complex	MP. (°C)	C (%) Found (Calc.)	H (%) Found (Calc.)	O (%) Found (Calc.)	N (%) Found (calc.)	Λ_M^*	Magnetic moment (B.M.)
[Ru(CHBPH-TP)Cl ₂]	247.4	47.05 (46.93)	2.74 (2.67)	2.92 (2.84)	5.04 (4.98)	12	1.98
K[Ru(CHBPH-HB)Cl ₂]	278.7	52.57 (52.44)	3.01 (2.91)	4.73 (4.66)	4.12 (4.08)	85	1.97

*Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)**Figure 1.** The structure of the ruthenium(III) complexes**Table 2.** Catalytic Oxidation by NaOCl with Ruthenium Schiff Base Complexes*

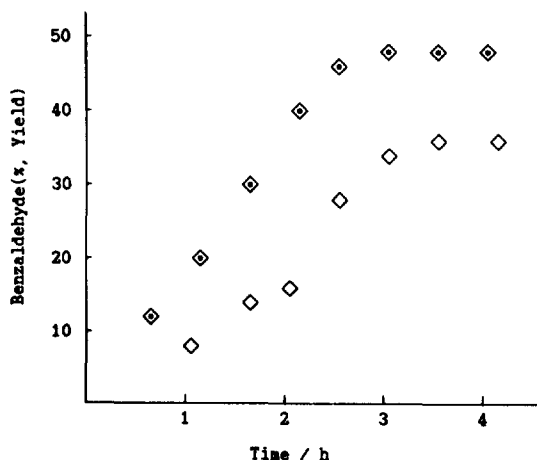
Complex	Substrate	Product (% yield)	
		benzaldehyde	styrene oxide
[Ru(CHBPH-TP)Cl ₂]	Styrene	34	3.5
K[Ru(CHBPH-HB)Cl ₂]		49	4.5

*Reaction conditions: Ru complex (0.002 mmol); solvent, dichloromethane (10 mL); styrene (0.01 mmol); NaOCl (20 mL); phase transfer agent, Benzyltetramethyldecylammonium chloride (0.015 mmol); stirred at room temperature for 5 h.

the complexes are paramagnetic with magnetic moment in the range 1.97-2.06 B.M. indicating that the complexes are low spin Ru(III) species with a $(t_{2g})^5$ ground state configuration.

The broad ligational $\nu(\text{O}-\text{H})$ band of the Schiff bases near 3300 cm^{-1} disappeared on complexation of the $\text{O}-\text{H}$ to the metal ion. The $\nu(\text{C}-\text{O})$ band at 1280 cm^{-1} in the free Schiff base ligands was shifted slightly to lower wave number upon coordination. The azomethine $\nu(\text{C}=\text{N})$ band in the Schiff base ligands in the range $1625\text{--}1635\text{ cm}^{-1}$ is shifted towards lower energy on coordination indicating the coordination of the imine group to the metal ion. The complex involving thiophene ring was observed near 700 cm^{-1} . Both of the ruthenium complexes are soluble in dichloromethane. In the UV region bands around 260 nm may be due to transitions of the double band of the azomethine group while a band near 340 nm is due to the transition of nonbonding electrons present on the nitrogen of the azomethine group. A moderately intense band near 440 nm can be attributed to the charge transfer transition of the chloride ion.

Catalytic Oxidation of Styrene by Sodium Hypochlorite. Ruthenium unsymmetrical Schiff base complexes are able to catalyze oxidation of styrene of sodium hypochlorite. Blank reactions has also been carried out using sodium

**Figure 2.** Plot of amount of benzaldehyde vs. time in the catalytic oxidation of styrene: [Ru(CHBPH-TP)Cl₂] (\diamond) and K[Ru(CHBPH-HB)Cl₂] (\blacklozenge).

hypochlorite whether styrene could be oxidized in the absence of the catalyst. This reaction takes place to give an extremely low quantity of benzaldehyde in the absence of catalyst (less than 5% yield).

A fine black precipitate has been formed slowly in the reaction mixture upon addition of sodium hypochlorite but sometimes disappeared after all of the styrene has been consumed. Then the catalytic reactions usually complete within 5 h. Table 2 shows the results of the catalytic oxidation of styrene by sodium hypochlorite under the phase transfer agent.

Significantly amount of benzaldehyde, which is due to oxidation cleavage of $\text{C}=\text{C}$ bond, is produced in the oxidation of styrene. A typical plot of time dependence of amount of benzaldehyde in the oxidation of styrene is shown in Figure 2.

The yield of benzaldehyde levels off after 3 h. The complexes are able to react efficiently with hypochlorite to yield a high valent ruthenium-oxo species¹⁵ capable of oxygen atom transfer to styrene. The intermediate by hypochlorite provides an explanation for the appearance of benzaldehyde in the reactions of styrene.

In summary, oxidative cleavage of the $\text{C}=\text{C}$ bond in the styrene takes place to yield the major product of benzaldehyde. This suggested that if the intermediate is an oxoruthenium species, it reacts with styrene *via* a nonconcerted pathway.

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Syntheses, X-ray Structures and Second Harmonic Generation Efficiencies of MAP (Methyl (2,4-dinitrophenyl)-aminopropanoate) Analogues

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An attempt to improve the second harmonic generation (SHG) efficiency of MAP (methyl (2,4-dinitrophenyl)aminopropanoate) by modifying the substituents on the amino group of MAP is described. Several MAP analogues have been prepared using optically active amino acids alanine, phenylalanine and serine, and their SHG efficiencies measured. None of the MAP analogues exhibited SHG efficiencies as high as that of MAP. X-ray crystal structures of three MAP analogues have been determined. In the crystal structures of two of them, which were the derivatives of phenylalanine, two crystallographically-independent molecules existing in the asymmetric unit are aligned almost antiparallel. These structures are consistent with the very low SHG efficiencies of these compounds. On the other hand, the crystal structure of a serine derivative reveals substantial alignment of the dinitroaniline chromophore along the polar axis. However, the angle of 86.2° between the molecular charge transfer axis and the polar axis of the crystal is still far away from the optimum value of 54.74° for the phase-matchable SHG. The structure is consistent with the SHG efficiency of this compound which is much higher than those of the phenylalanine derivatives but still lower than that of MAP. This study demonstrates the importance of the orientation of molecules in the crystal lattice in determining second-order nonlinear optical properties of crystalline materials.

Introduction

There has been much interest in organic compounds with large second-order nonlinear optical (NLO) properties.¹⁻⁶ These materials can be used in second harmonic generation (SHG; i.e. doubling the frequency of laser light) or in electro-optic phase modulation. Effective SHG materials have both

high second-order molecular hyperpolarizability, β , and high second-order bulk susceptibility, $\chi^{(2)}$. Conjugated organic molecules with electron donating and electron accepting groups can exhibit large β .² However, if the molecular hyperpolarizability is to result in a nonzero macroscopic nonlinearity ($\chi^{(2)}$), the molecule must crystallize in a noncentrosymmetric space group. Unfortunately, many compounds with