



Ruthenium(II) Chiral Schiff Base Complexes

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Abstract — A series of chiral ruthenium(II) carbonyl salen complexes of general formula $[\text{Ru}(\text{CO})(\text{B})(\text{L})]$ (where E = P, B = PPh₃, ASPH₃, py, pip and L = dibasic tetradentate chiral Schiff base ligands) have been synthesized from the reaction of $[\text{RuHCl}(\text{CO})(\text{B})(\text{EPh}_3)_2]$ (where E = P, B = PPh₃py, pip; E = As, B = As) with appropriate chiral Schiff base ligand. The characterization of the complexes was accomplished by analytical and spectral (FT-IR, UV-Vis, ¹H-NMR) methods.

Keywords: Schiff Base, ruthenium(II) complexes, tetradentate ligands,

I. INTRODUCTION

Chiral ligands attract considerable attention commensurate their role in asymmetric catalysis promoted by complexes of transition metals. The use of catalytic asymmetry reaction for the synthesis of highly enantiomerically enriched chiral compound is of growing importance in organic chemistry and in the chemical industry at large [1]. Chiral metal complexes are the most effective enantioselective catalysts for much asymmetric reaction.

Further ruthenium forms many complexes with a number of novel ligands containing nitrogen donor atoms have been largely investigated in asymmetric oxidation catalysis [2]. Furthermore, ruthenium complexes containing chiral Schiff base ligand are successfully used in asymmetric epoxidation of unfunctionalised olefins, oxidation, aziridination, amidation, Michael reaction [3].

In addition tertiaryphosphine/arsine ligands co-ordinate to transition metal complexes throughout the catalytic cycle because of their high affinity especially with late transition metals and they can stabilize low-valent metal intermediate to keep the high activity of the catalyst. Complexes of transition metals with tertiaryphosphine /arsine have gained considerable interest during the last three decades [4]-[6]. Most of ruthenium (II) and ruthenium (III) complexes containing PPh₃/AsPh₃ have been used as catalyst in many reactions [7]-[9].

Examples such as hydrogenation, oxidation and carboxylation and some of the complexes have been used as starting materials [10]-[11] for the synthesis of novel ruthenium (II) and ruthenium (III) complexes.

Though there is a wealth of information available on transition metal complexes of chiral Schiff base [12]-[14] only very few reports are available on chiral Schiff base complexes of ruthenium containing carbonyl ligands, With this fact in mind, we set out to design new chiral tetradentate Schiff base ligands and the synthesis of their ruthenium(II) complexes containing carbonyl and triphenylphosphine/arsine. Further the characterization of the chiral ruthenium(II) carbonyl Schiff base complexes were accomplished by analytical and spectral methods.

II. EXPERIMENTAL METHODS

Commercially available RuCl₃·3H₂O was used as supplied from Loba Chemie Pvt. Ltd., Bombay, were chemically pure and annular grade. The solvents were purified and dried according to standard procedures [15]. The analysis of carbon, hydrogen and nitrogen were performed at Sophisticated Test and Instrumentation Centre (STIC) Cochin University, Kochi. Infra-red spectra of complexes were recorded in KBr pellets with a Perkin - Elmer 597 spectrophotometer in the range 4000-400cm⁻¹. Electronic spectra of the complexes were recorded in CHCl₃ solution with a Cary 300 Bio UV-Vis Varian spectrophotometer in the range 800-200nm. The ¹H-NMR spectra were recorded in CDCl₃ with Bruker 400MHz instrument using TMS as internal reference. Melting Point was recorded in the Boetius micro heating table and is uncorrected.

1. Preparation of Ru(II) precursor complexes

A. Carbonylchlorohydridotris(triphenylphosphine) ruthenium(II) $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ [16]

A solution of 0.26 g (1.0 mol) of hydrated ruthenium trichloride in 20 ml of 2-methoxyethanol and aqueous formaldehyde(20ml;40%) were added rapidly and successively to a vigorously stirred boiling solution of

1.58 g (6 moles) of triphenylphosphine in 60ml of 2-methoxyethanol. The mixture was heated under reflux for 10 minutes and allowed to cool. The precipitate that formed was separated and washed successively with ethanol (small quantity), water, n-hexane, dried in vacuum.

Colour: Cream white, M.P: 210°C, Yield: 75%

B. Carbonylchlorohydridopyridinebis (triphenylphosphine) ruthenium(II), $[\text{RuHCl}(\text{CO})(\text{py})(\text{PPh}_3)_2]$ [17]

$[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ (0.24g; 0.24 mmol) was added to benzene (20ml) containing pyridine (0.5ml) and the mixture was stirred at room temperature for 24 hours under nitrogen atmosphere. The green solution was concentrated in vacuum and the solid that separated by adding Petroleum Ether was washed with hexane, ether to get a green microcrystalline solid Colour: Green, M.P: 175 °C, Yield: 70%

C. Carbonylchlorohydridopiperidinebis (triphenylphosphine) ruthenium(II), $[\text{RuHCl}(\text{CO})(\text{pip})(\text{PPh}_3)_2]$ [18]

$[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ (0.24g; 0.24 mmol) was added to benzene (20ml) containing piperidine (0.5ml) and the mixture was stirred at room temperature for 24 hrs. under nitrogen atmosphere. The green solution was concentrated in vacuum and the solid that separated by adding petroleum ether was washed with hexane, ether to get a green microcrystalline solid.

Colour: Pink, M.P: 117 °C, Yield: 60%

D. Carbonylchlorohydridotris(triphenylarsine) ruthenium(II), $[\text{RuHCl}(\text{CO})(\text{AsPh}_3)_3]$ [19]

A solution of 0.29 g of hydrated ruthenium trichloride in 2-methoxyethanol (5 ml) and aqueous formaldehyde (20 ml, 40%) were added rapidly and successively to a vigorously stirred boiling solution of 1.58g of triphenylarsine in 60 ml of 2-methoxyethanol. The mixture was heated under reflux for 1 hrs. and allowed to cool. The precipitate that formed was separated and washed with ethanol and n-hexane, dried in vacuum.

Colour: Yellow, M.P: 180°C, Yield: 70%

2. Preparation of Schiff base ligands

A. Resolution of 1,2-diamino cyclohexane

A 250 ml beaker was charged with L(+) – tartaric acid (250mmol, 375.5g) and distilled water (100ml). The mixture was stirred at room temperature. At this point a mixture of cis/trans-1,2-diamino cyclohexane (500 mmol, 60 ml) was added at the rate such that reaction temperature in below 700°C (keep ice bath). To the resulting solution glacial acetic acid (25 ml) was added at the rate such that the reaction temperature is below 90° C. A precipitate formed immediately upon the addition of glacial acetic acid and the slurry was vigorously stirred. It was cooled over a period of 2 hrs. The mixture was cooled to 5°C for 2 hrs. and the

precipitate suction filtration. The wet precipitate was washed with cold water (25ml) followed by cold methanol till the precipitate turned to white solid. The product was purified by vacuum distillation.

3. Preparation of chiral Schiff base ligands

The dibasic tetradentate chiral Schiff base ligands (1R,2R)-bis(salicylaldehyde)-trans-cyclohexylamine, (L_1), (1R,2R)-bis(3-methoxysalicylaldehyde)-trans-hexyldiamine, (L_2), were prepared by the following procedure. Salicylaldehyde (20mmol) dissolved in methanol (10ml) was added to a solution of the tartaric acid salt of trans cyclohexanediamine (10mmol) and anhydrous potassium carbonate 4.15 g (30mmol) dissolved in water 30 ml. The mixture was stirred at 60°C for 1 hrs. Diluted with water and extracted with ether. Extract was washed with brine solution and dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residues was dissolved in hexane and cooled to -10°C. Using similar procedure the new chiral Schiff bases such as (1R,2R)-bis(3-methoxysalicylaldehyde)-(1R,2R)-bis(2-hydroxy-1-Naphthaldehyde) were obtained by reacting 3-methoxysalicylaldehyde and with tartaric acid salt of trans cyclohexanediamine [20]-[21].

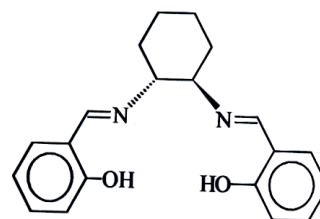


Fig. 1. $L_1 = (1R,2R)$ -bis(salicylaldehyde)-trans-cyclohexyldiamine

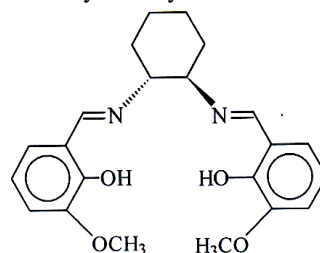


Fig. 2. $L_2 = (1R, 2R)$ bis(3methoxysalicylaldehyde)-trans-cyclohexyldiamine

4. Synthesis of new chiral Ru (II) Schiff base complexes

The appropriate chiral Schiff base ligand (0.026-0.034g; 0.08mmol) was added to a solution of $\{\text{RuHCl}(\text{CO})(\text{B})(\text{EPh}_3)_2\}$ (where E = P, B = PPh_3 , py, pip; E=As, B=As) (0.072-0.101g; 0.08 mmol) in ethanol (metal: ligand ratio 1:1) and the mixture was stirred for 24 hrs. After stirring the solution was concentrated to about 3 ml and the complex was separated by the addition of small amount of petroleum ether (60-

80°C). The resulting complex was recrystallized from CH_2Cl_2 /petroleum ether and dried under vacuum.

The above mentioned procedure is followed for the preparation of all the following complexes.

1. $[\text{Ru}(\text{CO})(\text{PPh}_3)(\text{L}_1)]$

This is prepared from $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ (75 mg) and (L_1) (25.38) mg in ethanol (20 ml).

Yield: 68%, Colour: Green, Melting point: 150°C

2. $[\text{Ru}(\text{CO})(\text{Py})(\text{L}_1)]$

This is prepared from $[\text{RuHCl}(\text{CO})(\text{py})(\text{PPh}_3)_2]$ (75 mg) and (L_1) (31.43) mg in ethanol (20 ml).

Yield: 68%, Colour: Green, Melting point: 150°C

3. $[\text{Ru}(\text{CO})(\text{Pip})(\text{L}_1)]$

This is prepared from $[\text{RuHCl}(\text{CO})(\text{pip})(\text{PPh}_3)_2]$ (75 mg) and (L_1) (31.18) mg in ethanol (20 ml).

Yield: 72%, Colour: Green, Melting point: 192°C

4. $[\text{Ru}(\text{CO})(\text{AsPh}_3)(\text{L}_1)]$

This is prepared from $[\text{RuHCl}(\text{CO})(\text{pip})(\text{AsPh}_3)_3]$ (75 mg) and (L_1) (22.30) mg in ethanol (20 ml).

Yield: 68%, Colour: Brown, Melting point: 160°C

5. $[\text{Ru}(\text{CO})(\text{PPh}_3)(\text{L}_2)]$

This is prepared from $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ (75 mg) and (L_2) (30.11) mg in ethanol (20 ml).

Yield: 75%, Colour: Green, Melting point: 175°C

6. $[\text{Ru}(\text{CO})(\text{Py})(\text{L}_2)]$

This is prepared from $[\text{RuHCl}(\text{CO})(\text{py})(\text{PPh}_3)_2]$ (75 mg) and (L_2) (37.28) mg in ethanol (20 ml).

Yield: 72%, Colour: Green, Melting point: 198°C

7. $[\text{Ru}(\text{CO})(\text{Pip})(\text{L}_2)]$

This is prepared from $[\text{RuHCl}(\text{CO})(\text{pip})(\text{PPh}_3)_2]$ (75 mg) and (L_2) (36.99) mg in ethanol (20 ml).

Yield: 64%, Colour: Green, Melting point: 165°C

8. $[\text{Ru}(\text{CO})(\text{AsPh}_3)(\text{L}_1)]$

This is prepared from $[\text{RuHCl}(\text{CO})(\text{pip})(\text{AsPh}_3)_3]$ (75 mg) and (L_2) (26.45) mg in ethanol (20 ml).

Yield: 78%, Colour: Green, Melting point: 145°C

III. RESULTS AND DISCUSSION

New hexa coordinated ruthenium(II) Schiff base complexes of the type $[\text{Ru}(\text{CO})(\text{B})(\text{L})]$ (Where $\text{B} = \text{PPh}_3, \text{AsPh}_3, \text{py}, \text{pip}$ and $\text{L} =$ dibasic tetradentate chiral Schiff base ligands) were synthesized from the reaction of $[\text{RuHCl}(\text{CO})(\text{B})(\text{EPh}_3)_2]$ [Where $\text{E} = \text{As}, \text{B} = \text{AsPh}_3; \text{E} = \text{P}, \text{B} = \text{PPh}_3, \text{py}, \text{pip}$] with various chiral tetradentate Schiff base ligands, viz., $\text{L}_1 = (1R,2R)$ -bis(salicylaldehyde)-trans-cyclohexyldiamine and $\text{L}_2 = (1R,2R)$ -bis(3-methoxy

salicylaldehyde)-trans-cyclohexyldiamine in ethanol in 1:1 molar ratio.

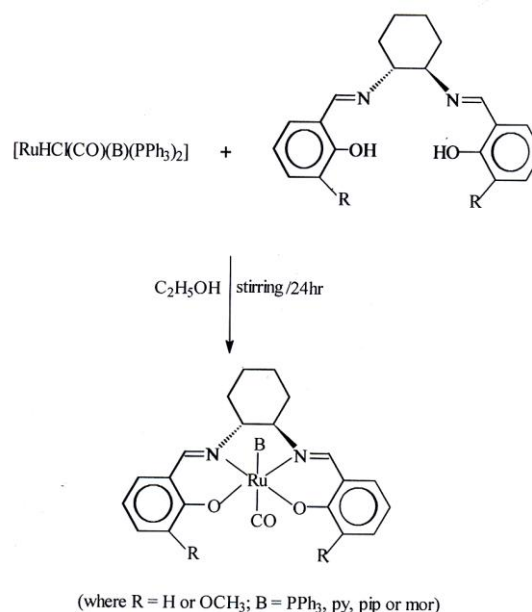


Fig 3. Synthesis of Chiral Ru(II) Schiff base Complexes

TABLE I. ANALYTICAL DATA FOR CHIRAL SCHIFF BASE LIGANDS

Ligand	Colour	Melting Point	Calculated (found)%		
			C	H	N
L_1	Yellow	64-66	74.49 (74.9)	6.88 (6.38)	8.65 (8.52)
L_2	Yellow	128-130	69.07 (69.53)	6.85 (6.35)	7.32 (7.17)

TABLE II. IR ABSORPTION FREQUENCIES OF CHIRAL SCHIFF BASE LIGANDS (cm^{-1})

Ligand	R	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	ν_{OH}
L_1	H	1278	1633	3412
L_2	OCH_3	1261	1626	3416

TABLE III. ^1H NMR SPECTRA (δ ppm) AND OPTICAL ROTATION OF CHIRAL SCHIFF BASE LIGANDS

Ligand	$-\text{CH}_2$	$-\text{CHN}$	Ar-H	$-\text{CH=N}$	$-\text{OH}$	$-\text{OCH}_3$	$[\alpha]_D$
L_1	1.6 (m)	3.5 (m)	7.5 (m)	8.3(s)	13.0 (s)	-	-15.6
L_2	1.6 (m)	3.3 (m)	6.8 (m)	8.2(s)	14.0 (s)	3.99(s)	-46.9

All the complexes are in green and brown colour, stable in air, non-hygroscopic in nature and highly soluble in common solvent such as dichloromethane, acetonitrile and chloroform producing intense green and brown solutions. The analytical data of the free Chiral Schiff base ligands (Table 1) and Ru(II) Chiral Schiff base complex are listed and are in good agreement with the general molecular formula proposed. Optical rotation for the chiral Schiff base ligands were measured using polarimeter and are given in Table III.

TABLE IV. ANALYTICAL DATA FOR Ru(II) SCHIFF BASE COMPLEXES

S. No	Complexes	Colour	Mp (oC)	Calculated (Found %)		
				C	H	N
1	[Ru(CO) (PPh ₃) (L ₁)]	Green	150	76.70 (76.35)	5.77 (5.35)	4.58 (4.18)
2	[Ru(CO) (py) (L ₁)]	Green	185	73.05 (72.85)	5.89 (5.63)	9.80 (9.50)
3	[Ru(CO) (pip) (L ₁)]	Green	192	72.19 (71.78)	6.99 (6.55)	9.70 (9.35)
4	[Ru(CO) (AsPh ₃) (L ₁)]	Brown	160	71.55 (71.04)	5.38 (4.98)	4.27 (3.89)
5	[Ru(CO) (PPh ₃) (L ₂)]	Green	175	74.98 (74.45)	5.82 (5.45)	4.30 (3.95)
6	[Ru(CO) (py) (L ₂)]	Green	198	70.88 (70.56)	5.94 (5.56)	9.10 (3.78)
7	[Ru(CO) (pip) (L ₂)]	Green	165	70.10 (69.75)	6.70 (6.25)	9.07 (8.68)
8	[Ru(CO) (AsPh ₃) (L ₂)]	Green	145	70.17 (69.86)	5.40 (4.98)	4.08 (3.75)

TABLE V. IR SPECTRA DATA

Complexes	IR absorption frequencies(cm ⁻¹)		
	$\nu_{C=O}$	ν_{C-O}	ν_{C-N}
[Ru(CO) (PPh ₃) (L ₁)]	1947	1315	1600
[Ru(CO) (py) (L ₁)]	1946	1315	16.3
[Ru(CO) (pip) (L ₁)]	1939	1316	1631
[Ru(CO) (AsPh ₃) (L ₁)]	1950	1318	1598
[Ru(CO)(PPh ₃)(L ₂)]	1949	1317	1599
[Ru(CO)(py)(L ₂)]	1946	1315	1600
[Ru(CO)(pip)(L ₂)]	1947	1314	1598
[Ru(CO)(AsPh ₃)(L ₂)]	1956	1315	1601

In order to study the binding mode of chiral Schiff base ligand to ruthenium metal in the new complex, IR spectra of free Schiff base have been compared with that of the complexes. This is normally indicated by slight changes in the IR frequencies, shown by the complexes as compared to that of the free ligands and the IR data of the free ligands Table II and their complexes are given Table V.

A strong band has been observed around 1625-1635 cm⁻¹ is characteristic of azomethine[22]-[24] group of the free chiral Schiff base ligands. Co-ordination of chiral Schiff ligand to the ruthenium through azomethine nitrogen atom is expected to reduce the electron density in the azomethine link. Hence this band undergoes a shift to lower frequency in the region 1598-1631cm⁻¹ after complexation indicates that azomethine nitrogen is the coordinating atom. In the IR spectra of the for chiral Schiff baseligands, a band of medium intensity appeared around 3400-3450 cm⁻¹ due to ν_{O-H} . On complexation this band was disappeared indicating deprotonation prior to coordination through oxygen atom.. A high intensity band at 1225-1280cm⁻¹ in the chiral Schiff base ligands may be assigned to the phenolic ν_{C-O} stretching[25]-[27]. In all the complexes ($\nu_{C=O}$) the terminal carbonyl appeared in the region of 1939-1356 cm⁻¹. In addition to the above absorption other characteristic band due to PPh₃/AsPh₃ were present around 14320 to 1436cm⁻¹ in the spectra of all complexes.

TABLE VI. ELECTRONIC SPECTRA DATA

S. N	Complexes	$\lambda_{max}(nm)(dm^3 mol^{-1}cm^{-1})$
1	[Ru(CO)(PPh ₃)(L ₁)]	752(170),329(9436),281(14,616),274(14,816)
2	[Ru(CO)(py)(L ₁)]	668(354),406(2148),317(2948),247(9308)
3	[Ru(CO)(pip)(L ₁)]	-----
4	[Ru(CO)(AsPh ₃)(L ₁)]	637(507),400(1916),305(7004),284(13,120),271(14,968)
5	[Ru(CO)(PPh ₃)(L ₂)]	643(350),380(2176),258(10,636).
6	[Ru(CO)(py)(L ₂)]	672(317),400(2480),245(10,876)
7	[Ru(CO)(pip)(L ₂)]	-----
8	[Ru(CO)(AsPh ₃)(L ₂)]	698(151),394(4268),310(7928),272(14,968),264(15,980)

All the Schiff base ruthenium complexes are diamagnetic, indicating the presence of ruthenium in +2 oxidation state. The electronic absorption spectra of all the complexes in CHCl₃ showed three to four bands in the region 206-610 nm. The ground state of Ru(II) in octahedral environment is ¹A_{1g}, arising from the t_{2g}⁶ configuration, and the excited state corresponding to the t_{2g}⁵ e_g¹ configurations are ³T_{1g}, ³T_{2g}, ¹T_{1g} and ¹T_{2g}. Hence, four bands corresponding to the transitions ¹A_{1g} → ³T_{1g}, ¹A_{1g} → ³T_{2g}, ¹A_{1g} → ¹T_{1g} and ¹A_{1g} → ¹T_{2g} are possible in the order of the increasing energy. The other high intensity band around 442-464 nm has been assigned to the charge transfer transitions arising from the excitation of an electron from metal t_{2g}⁵ level to unfilled molecular orbitals derived from the π* level of the ligands. The slightly lower MLCT transition energy is probably due to the chelate ring of the complexes. The other high intensity bands lower than 350 nm region were intensity band around 442-464 nm has been assigned to the charge transfer transitions arising from the excitation of an electron from metal t_{2g}⁵ level to unfilled molecular orbitals derived from the π* level of the ligands. The slightly lower MLCT transition energy is probably due to the chelate ring of the complexes [28]. The other high intensity bands lower than 350 nm region were characterized by the ligand-centered (LC) band have been designated as π-π and n-π* transitions for the electrons localized on the azomethine of the Schiff bases Table VI.

TABLE VII. ¹H NMR SPECTRAL (δppm)

S. NO	Complexes	-CH ₂	-CHN	Ar-H	-CH=N	-OCH ₃
1	[Ru(CO) (PPh ₃) (L ₁)]	1.4 (m)	3.3 (m)	7.0-7.8 (m)	8.0 (m)	-
2	[Ru(CO) (py) (L ₁)]	1.4(m)	3.4 (m)	6.8-7.6 (m)	8.0(m)	-
3	[Ru(CO) (AsPh ₃) (L ₁)]	1.5(m)	3.5 (m)	7.07.6 (m)	7.9(m)	-
4	[Ru(CO) (PPh ₃) (L ₂)]	1.5(m)	6.4 (m)	7.0-7.6 (m)	8.0(m)	3.9 (m)

	(L ₂)					
5	[Ru(CO) (AsPh ₃)L 2]	1.4(m)	3.6 (m)	6.97.8 (m)	8.0(m)	3.9 (m)

The bonding arrangement is further confirmed by ¹H-NMR spectra Table VII. In the spectra of the complexes the multiples observed around δ 6.8 – 7.8 ppm have been assigned to aromatic protons of the phenyl group of triphenylphosphine/arsine and the Schiff base ligands. The azomethine proton appeared as a singlet in the region δ 7.9-8.0 ppm. The methylene proton appeared as a singlet in the region δ 1.4-1.5 ppm in the complexes. One sharp singlet observed at δ 3.9 ppm is assigned to the methoxy proton in the complexes. The multiplets observed in the region 3.3-3.6 ppm are due to methane proton in the ligands. The absence of resonance for OH protons in the complex indicated deprotonation of the phenolic group of the Schiff bases on complexation and coordination to ruthenium through phenolic oxygen.

IV. CONCLUSION

A series of chiral ruthenium(II) carbonyl salen complexes of general formula [Ru(CO)(B)(L)] (where E = P, B = PPh₃, ASPH₃, py, pip and L = dibasic tetradentate chiral Schiff base ligands) have been synthesized from the reaction of [RuHCl(CO)(B)(EPh₃)₂] (where E = P, B = PPh₃py, pip; E = As, B = As) with appropriate chiral Schiff base ligand. The characterization of the complexes was accomplished by analytical and spectral (FT-IR, UV-Vis, ¹H-NMR) methods. An octahedral geometry has been tentatively proposed for all the complexes.

V. REFERENCES

- [1] (a) I. Ojima, Ed.: VCH: Catalytic Asymmetric synthesis New york 1913
(b) W. A Nugent, T. V RajanBabu, M. Burk, "Beyond Nature's Chiral Pool Enantioselective Catalysis in Industry", J.Science, vol 259, pp 479-483, 1993.
- [2] (a) E. N. Jacobsen, W. Zhang, A. R. Muci, J. R. Ecker, and L. Deng, "Highly enantioselective epoxidation catalysts derived from 1,2-diaminocyclohexane", J. Am. Chem. Soc., vol. 13, pp. 7063-7064, 1991.
(b) N. H. Lee, A. R. Muciand and E. N. Jacobsen "Catalytic asymmetric synthesis of epoxides mediated by chiral iminiumsalts", TetrahedronLet., vol. 32, pp. 5055, 1991.
- [3] R. M. Stoop. S. Bachmann, M. Valentini, A. Mezzetti "Ruthenium(II) Complexes with Chiral Tetradentate P₂N₂ ligands Catalyze the Asymmetric Epoxidation of Olefins with H₂O₂ Organometallics, vol. 19, pp 4117, 2000.
- [4] G.Booth, "Advances in Inorg. Chem. and Radiochemistry", Academic press, Newyork, vol. 6, 1, 1964.
- [5] S. D. Robinson, "M. T. P. International Review of science", Inorg.Chem.Seriesone, Trans metal part -2, vol. 6, pp 121, 1972.
- [6] C. A. McAuliffe, "Transition metal complexes of phosphorus, Arsenic, and Antimony ligands" Macmillan, 1973
- [7] M. M. Taquikhan, A. E. Martel, "Homogeneous catalysis by metal complexes", Academicpress, Newyork, 1974.
- [8] R. A. Sanchez, J. S. Delgado, G. Bradely, J. Wilkinson, Chem.Soc.Paton, pp 390, 1976.
- [9] K. Mikami, T. Kovenga, M. Tereda, J. Ukhuma, T. pham, R. Noyori, "Chiral reagents for Asymmetric synthesis" Angew.Chem.Int.Ed.Engl, vol. 38, pp 95, 1999.
- [10] J. P. Collamn, W. P. Roper, "Bridged Polycyclic Compounds. XXXI. Stereochemical Aspects of the Solvolysis of Cyclopropyl Chlorides", J.Am.Chem.Soc., vol. 87, pp 4008, 1965.
- [11] T. A. Stephenson, G. Wilkinson, "New complexes of ruthenium (II) and (III) with triphenylphosphine, triphenylarsine, trichlorostannate, pyridine and other ligands" J.Inorg.Nucl.Chem., vol. 28, pp 945-946, 1966.
- [12] J. F. Larrow, E. N. Jacobsen, "A Practical Method for the Large-Scale Preparation of [N,N'-Bis(3,5-di-tertbutylsalicylidene)-1,2-cyclohexanediaminato(2)] manganese(III) chloride, a Highly Enantioselective Epoxidation Catalyst" J.Org.Chem, vol. 59, pp 1939-1942, 1994.
- [13] S. C. Jha, N. M. Joshi, "Asymmetry Aluminium-SALEN complex: a new catalyst for the enantioselective Michael reaction", tetrahedron, vol. 12, pp 2463- 2466, 2001
- [14] Jiang-Linliang, Xxiao-Qi Yu, chi-Mingche, "Amidation of silylenol ethers and cholesteryl acetates with chiral ruthenium(II) Schiff-base catalysts catalytic and enantioselective studies", Chem.Commun. pp 124-125, 2002
- [15] A. I. Vogel, TextBook of Practical Organic Chemistry, 5th ed., Longmon, London, 1989.
- [16] R. K. Poddar, U. Agarwalla, Ind.J.Chem., vol. 9, pp 477, 1971
- [17] N. Ahmed, J. J. Levison, S. D. Robinson, M. F. Uttley, "Complexes of Ruthenium, Osmium, Rhodium, and Iridium Containing Hydride Carbonyl, or Nitrosyl Ligands", Inorg.Synth., vol. 15, pp 48, 1974

- [18] S. Gopinath, I. R. Unny, S. S. Deshpande, C. Gopinath *Ind. J. Chem.*, vol. 25A, pp 1015, 1986.
- [19] R. A. Sanchez-Delgado, W. Y. Lee, S. R. Choi, Y. Cho, M. J. Jun, "Synthesis of new compounds containing arsine ligands and catalytic activity in the homogeneous hydrogenation of aldehydes" *Trans.Met.Chem.*, vol. 16, pp 241-244, 1991.
- [20] S. C. Jha, N. N. Joshi, "Epoxy ketones as versatile building blocks in organic synthesis", *Tetrahedron Asymmetry*, vol. 12, pp 2359-2495, 2001.
- [21] S. Muralidharan, R. Ramesh, C. Glidewell, "6,6'-Dimethoxy-2,2'-[1R,2R]-cyclohexane-1,2-diylbis(nitrimethyl-idyne)]diphenol: three C-H...O hydrogen bonds generate a three-dimensional framework", *Acta.Cryst.Sec.C*, vol. 59, pp 367-369, 2003
- [22] G.Muthusamy,K.Natarajan, "Chloro Bridged Binuclear Ruthenium(II) Beta-Diketonato Complexes Containing Triphenylphosphine And Triphenylarsine", *Ind.J.Chem.*, vol. 34A, pp 490-509, 1995.
- [23] M. M. Taqui Khan, Z. A. Shaikh, R. I. Kureshy, A. B. Boricha, "Synthesis, characterization and reversible binding of dioxygen and carbon monoxide in ruthenium(III) schiff-base complexes. Effect of equatorial substitution on the O₂ and Co affinities *Polyhedron*", vol. 11 pp. 91-100, 1992
- [24] M. M. Taqui Khan, S. A. Mizra, Z. A. Shaikh, Ch. Sreelatha, p. Paul, R. S. Shukla, D. Srinivas, A. PrakashRao, S. H. Abdi, S. D. Bhatt, G. Ramachandraiah, "Dioxygen affinities of some ruthenium(III) schiff base complexes *Polyhedron*", vol. 11, pp. 1821-1827, 1992
- [25] T. DanielThangadurai,K. Natarajan, "Ruthenium(III) Complexes containing α,β -unsaturated- β -ketoaminate and their biological activities" *Ind.J.Chem.*, vol. 40, 573-576, 2001.
- [26] R. Ramesh, K. Natarajan, *Indian.J.Chem.*, vol. 34A, 535, 1995.
- [27] K. Natarajan, U. Agarwala, "Some New β -Diketone Complexes of Ruthenium(III) with Triphenylphosphine and Triphenylarsine" *Bull.chem.soc.jp.*, vol. 49, 2877-2878, 1976
- [28] G. Harris, "Low spin ferric hemoglobin complexes" *Theoret. chim. Acta (Berl.)*, vol. 5, 379-397, 1966.

