Review Article

Catalytic studies on Complexes of Organic Compounds: Part-5. Review on use of Chiral Schiff base Complexes as Catalyst

C. J Patil[*], Sanjiv B. Salve
Organic Research Laboratory, Department of Chemistry, Smt. G. G. Khadse College, Muktainagar-425 306, Dist. Jalgaon, M.S., India.
*Corresponding author's E-mail: drcjpatil@yahoo.com

ABSTRACT

Schiff base and its complexes with catalytic activity have rich diversity and the reactions catalysed by these catalyst were reviewed. These complexes are of salen type and some are of other (Salophen and Salcyclo etc.). Here we have the salen and salcyclo types of the complexes. The varied synthetic ligands are available for asymmetric catalysis. They have been highly enantioselective and of synthetic utility for transformation by catalytic behavior. Their catalysis involves many types of organic reactions such as Diels Alder, Aldol, Epoxidation, Polymerization and many more. In addition, they have exciting therapeutic activity. Literature shows very few oxidation reactions of benzyl alcohol and alkanol types of the compound.

Keywords: Chiral Schiff bases, Complexes, Salophen and Salcyclo, Catalysis, Oxidation, organic reactions.

QUICK RESPONSE CODE →

INTRODUCTION

We know that the catalyst (or biochemical enzymes) plays an important role in the catalysis of many kind of reactions. Schiff base - complex have catalyzed many Name reactions and other reactions too. Schiff base complex plays a key role in various homogeneous catalytic reactions and the activity of these complexes changes with the type of ligands, coordination sites and metal ions.

Survey of the Literature have shown that the coordination compounds have been used in human life as analgesic[1], antibiotic[2], antioxidative[3], antifungal[4-5], antibacterial[6-8], antiviral[9], antifertility[10], antitoxic against insects[11], antiulcer[12], anti-HIV[13] and antitumor[14-15], coating materials[16], as catalysts in polymerization, oxidation, decomposition, hydrolysis and electro-reduction[17-18], heat resistant adhesives[19], electric insulating materials[20], corrosion inhibitors[21], dye and pigment industries[22], pigments[23], photographic developers[24], plant growth regulators[25-26], as models for molecules to absorb and release molecular oxygen reversibly similar to natural oxygen carriers like hemoglobin, hemocyanin and non-heme proteins[27].

Chiral Schiff bases transition metal complexes, so-called salen-type ligands, are one of the most studied chiral catalysts in asymmetric synthesis because of their ability to act as chiral catalysts or as co-catalysts[28-32]. Schiff-base ligands derived from salicylaldehyde and chiral amines have been widely applied in enantioselective cyclopropanation of styrenes[33], asymmetric aziridination of olefins[34], enantioselective epoxidation[35-36], enantioselective ring opening of epoxides[37], borohydride reduction of aromatic ketones, asymmetric oxidation of methyl phenyl sulfide[38], enantioselective oxidation of silyl enol and trimethylsilylcyanation of benzaldehydes[39]. The E. Merck, in particular, has successfully developed a process for the industrial manufacture of antibacterial drug Cilastatin using chiral copper (II) Schiff-base complexes derived from salicylaldehyde and chiral amine[40].

Literature reports revealed that the large number of Schiff base metal complexes exhibit catalytic activities. Now-a-days it is well known that chiral Schiff base complexes are more selective in various reactions such as epoxidation, oxidation, aldol condensation and hydroxylation etc.[41] Progress on the catalytic activity of Schiff base - complexes in various reactions are outlined in this review. Some types of reaction catalysed by Salen[42], salophen, salcyclo and different types of Schiff base catalysts are as follows:

1) Diels–Alder reaction
2) Epoxidation reaction
3) Oxidation reaction
4) Heck reaction
5) Michael addition
6) Aldol condensation reaction
7) Polymerization reaction
8) Hydrogenation reaction
9) Hydrogenation of imine
10) Hydrogenation of ketone
11) Hydrogenation of alkene and alkyne
12) Ring opening reaction of epoxide
13) Cyclopropanation reaction
14) Decomposition of hydrogen peroxide
15) C-C, C-H and C-Metal bond formation

16) Epoxide decomposition

17) Hydroxylation of styrene

Some of these reactions are explained below as an illustration. The present review mainly considered Cr and Cd complexes, and if suitable examples of these complexes were not available, other complexes were also included to illustrate the use of Schiff base metal complexes for different reactions.

Diels–Alder reaction

The first target-oriented synthesis of pyranoquinolines as potential antibacterial agents by electron demand Diels–Alder reaction (ED-DA) was accomplished using high diastereoselective chiral salen–AlCl complex as catalyst[43]. Addition of molecular sieves in the reaction increases the yield and enantiomeric excess (ee). Use of the salen–AlCl complex catalyzed EDDA reaction in the presence of different mol% of molecular sieves in reaction mixture of 2,3-dihydrofuran and 2-azadiene reported, which showed marginalized increase in the diastereomeric excess (**Scheme 1**).

Scheme 1: Diels-Alder reaction using chiral salen-AlCl[43].

Schiff base complex catalyzed acylation of 4-furyl-4-*N*-benzylaminobut-1-enes with maleic anhydride produced 4-oxo-3-aza-10-oxatricyclo[5.2.1.0]dec-8-ene-6-carboxylic acid via amide formation through intramolecular Diels–Alder reaction of furan (IMDAF) [44-45]. The new family of enantiomerically enriched 1,1'-binapthyl 2,2'-diamine (BINAM)-derived Schiff base chromium(III) complexes (Figure 1 compound **4**) were used as catalysts in Diels–Alder reactions[46]. Chiral Schiff base lanthanum(III) complexes displayed catalytic activity in the asymmetric Diels–Alder reaction of 3-(2-propenoyl)-2-oxazolidinone with cyclopentadiene[47].

Chromium(III) complexes of binaphthyl chiral Schiff base were efficient catalysts in Diels–Alder reaction of protected 1,2-dihydropyridines. The reaction of 1-phenoxycarbonyl-1,2-dihydropyridine with *N*-acryloyloxazolidinone **5** in the presence of binaphthyl

catalysts afforded endo-cycloadduct in 23-85 % ee and 61-99 % ee (**Scheme 2** reactions 1 and 2).
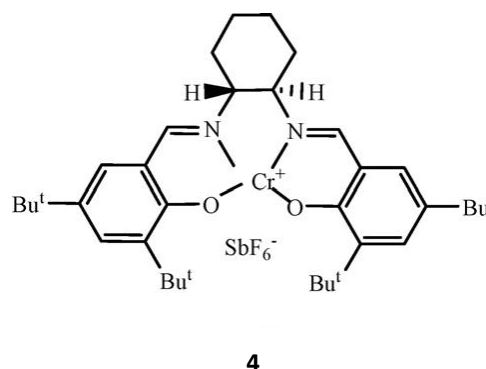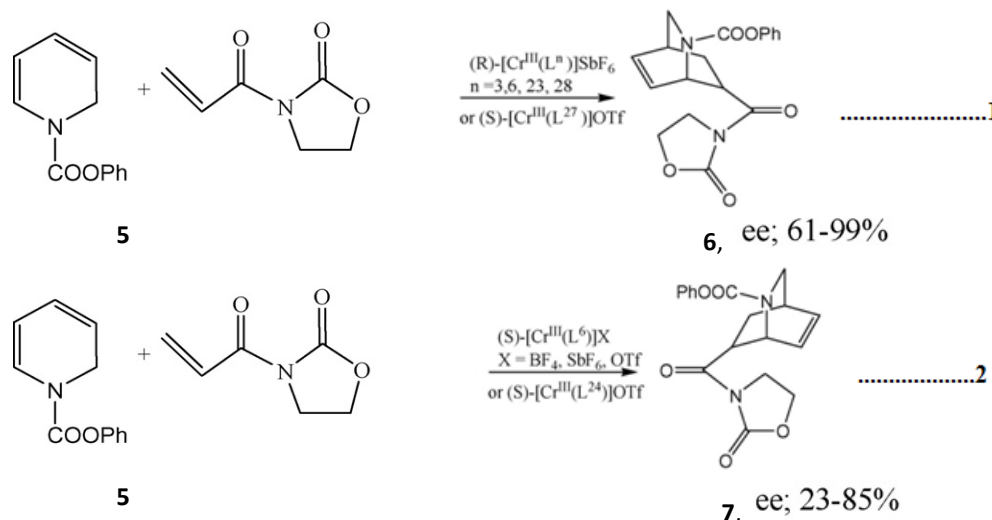

Figure 1: BINAM-derived Schiff bases chromium(III) complexes. BINAM = 1,1'-binapthyl 2,2'-diamine.

Scheme 2: (reaction 1 and 2)

10

When acetone was used as a solvent, the endo-cycloadduct showed 86 – 99 % yield and 70–85% ee except for (*S*)-[Cr(III)(L[1])]OTf catalyst. The reaction of 1-phenoxycarbonyl-1,2-dihydropyridine **8** with metha-acrolein **9** in the presence of (*S*)-[Cr(III)(L[6])]SbF$_6$ catalyst produced endo-cycloadduct with 89% yield and 67 % ee (**Scheme 3**).
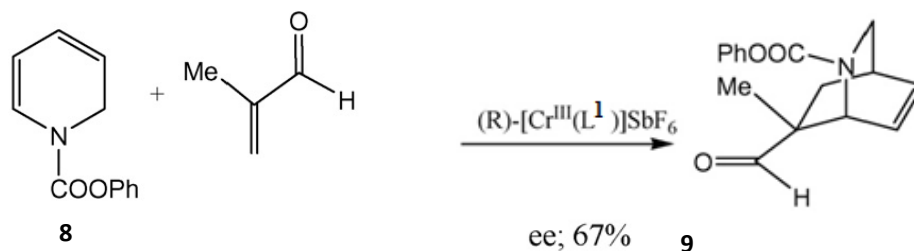

Scheme 3: The reaction of 1-phenoxycarbonyl-1,2-dihydropyridine **8** with metha-acrolein.

Enantioselectivity marked was 10% higher than observed with 1,2-cyclohexyl analogue of (*S*)-[Cr(III)(L[1])]SbF$_6$ [42,46]. Asymmetric hetero-Diels–Alder reaction between [(2-chlorobenzoyl)oxy]-acetaldehyde and [(trimethylsilyl)oxy]buta-1,3-diene was carried out using chromium(III) salen complexes using 4°A molecular sieves (at −30°C) in non-coordinating ethereal solvent[48]. The nature of the catalyst showed a significant effect on both enantioselectivity and yield of reaction. The chiral Schiff base complexes of aluminium and titanium were also used as catalyst in Diels–Alder reactions[48].

Epoxidation reaction

Chiral manganese(II) complexes of 1,2-bis(salicylideneamino) cyclohexane entrapped in zeolite showed catalytic activity in the enantioselective epoxidation of alkenes[49]. The manganese(II) complexes of bis(2-pyridinaldehyde) ethylenediamine, bis(2-pyridinaldehyde) propylenediamine ligands were used in epoxidation of olefins but reasonable epoxide selectivity was possible only in the presence of iodosylbensene (PhIO) oxidant[49]. Compounds 12-15 obtained from 10 and 11 constituted a new class of salen based Schiff base ligands to form complexes with transition and heavy metal ions[50]. The manganese(III) complexes (Scheme 4) 23–26 corresponding to Schiff base ligands 12-15 were chiral catalysts and used in asymmetric epoxidation of indene (Scheme 5)[50]. The manganese(III) salen complexes catalyzed the asymmetric epoxidation of conjugated olefins 23 and 25 (Scheme 6). The addition of bulky Lewis acids such as zinc tetraphenyl (ZnTPP) 27a or zinc octaethylporphyrin (ZnOEP) 27b (Scheme 7) formed stable supramolecular complexes, which showed enhanced catalytic activity of manganese(III) salen complexes[51].
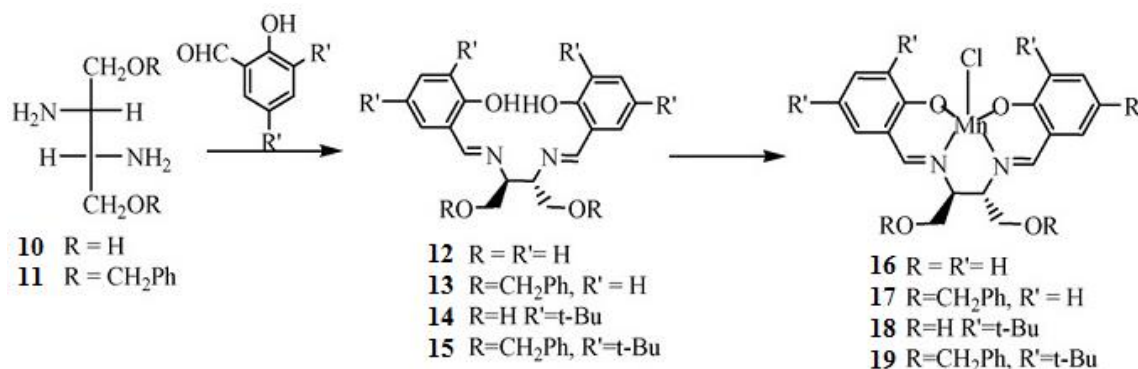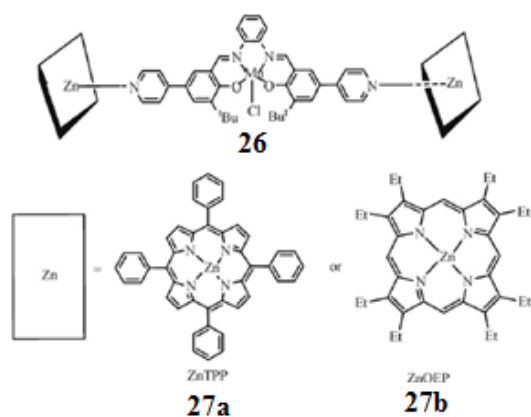

Scheme 4: The synthesis of 2,3-bis(arylideneamino)-1,4-butanediol derivatives[50] (**19, 21**) and of their manganese(III) complexes(**24, 26**).
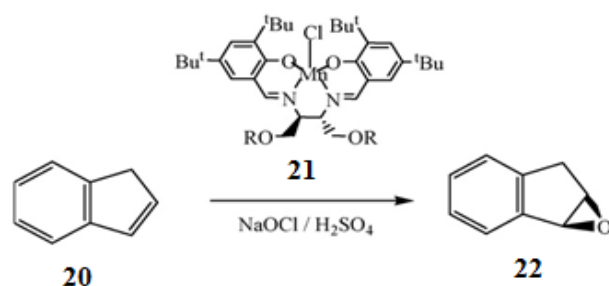
Scheme 5: The epoxidation of indene[50] using the manganese(III) complexes of d-2,3-bis(di-*t*-butyl-salicylideneamino)-1,4-butanediol and-dibenzyl ether.
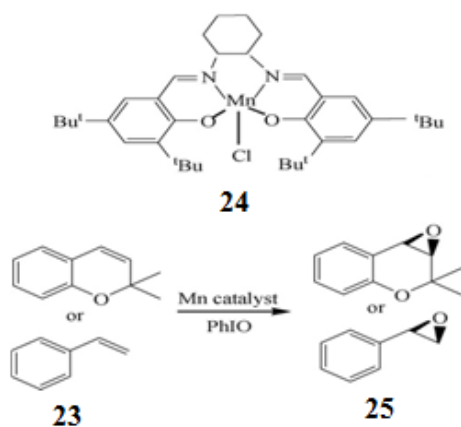
Scheme 6: Epoxidation of conjugated olefins by manganese(III) complex[51].

Scheme 7. Structures of ZnTPP and ZnOEP supramolecular complexes

McGarrigle and Gilheany[52] have given a detailed discussion on the achiral and asymmetric epoxidations of alkenes catalysed by chromium and manganese-salen complexes. They mainly focused on the mechanism, catalytic cycle, intermediates, and mode of selectivity. Among these Mn-(salen)-type complexes Jacobsen's complex (Figure 2 compound **28**), has been demonstrated to be very effective for the enantioselective epoxidation of unfunctionalised olefins[53-54].
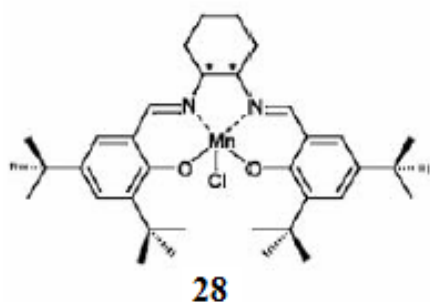

Figure 2: Jacobsen's complex.

Katsuki and co-workers[55-56] first reported the synthesis and catalytic application of ruthenium(II)-complex, (Figure 3 compound **29)**, containing chiral tetradentate (N₂O₂) Schiff base ligand in the asymmetric epoxidation of conjugated olefins in the presence of various terminal oxidants.
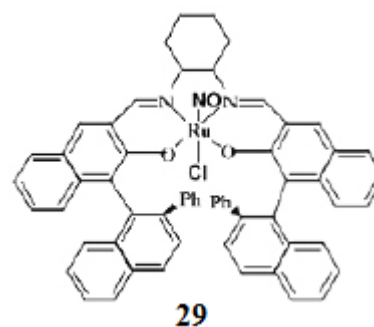

Figure 3: Ruthenium(II)-complex, containing chiral tetradentate (N_2O_2) Schiff base ligand.

Mezzetti and co-workers[57-58] have carried out the asymmetric epoxidation using ruthenium(II) complexes containing tetradentate chiral Schiff base ligands with N2P2 donors, (Figure 4, compounds **30, 31**), with hydrogen peroxide as terminal oxidant.
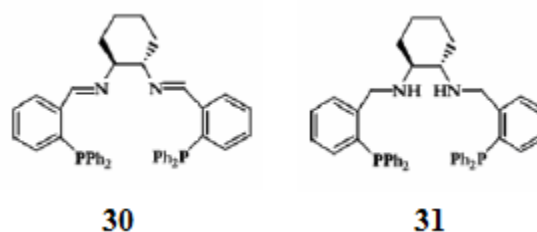

Figure 4: Ruthenium(II) complexes containing tetradentate chiral Schiff base ligands with N2P2 donors.

Oxidation reaction

Chiral Schiff base ligands of ONO type with transition metal ions, i. e., titanium(IV), vanadium(IV), copper(II) or zinc(II), were used in various asymmetric chemical transformations. The addition of trimethylsilylcyanide to benzaldehyde, 32 in the presence of titanium(IV) ions resulted in trimethylsilyl cyanohydrins 34 in 40–85 % enantioselectivity (Scheme 8a)[59].
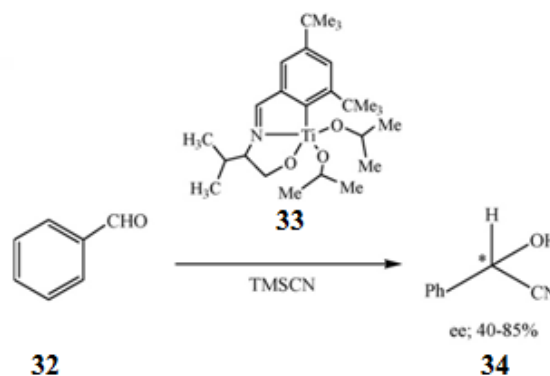
Scheme 8a: Chiral Schiff base catalyzed synthesis of trimethylsilyl cyanohydrins[59]

Chiral Schiff base ligands of ON type with transition metal ion, i. e., Chromium(III) was used in the chemical transformation. The oxidation of benzylalcohol, **34a** to benzaldehyde, **34c** using 30 % H_2O_2 in the presence Cr

complex of chiral schiff base catalyst, **34b** resulted in benzaldehyde, **34c** in 75.0 % and some benzoic acid (**Scheme 8b**)[60a]. The oxidation of benzyl alcohol was used
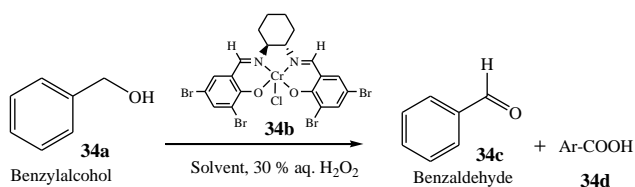
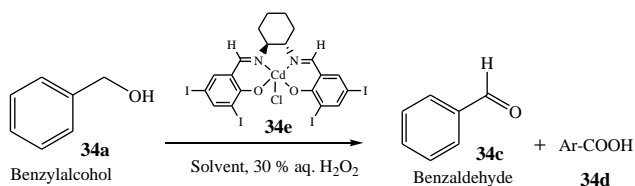**Scheme 8b:** Chiral Schiff base, **34b** catalyzed synthesis of benzaldehyde[60]

Chiral Schiff base ligands of ON type with transition metal ion, i. e., cadmium(II) was used in the chemical transformation. The oxidation of benzylalcohol, **34a** to benzaldehyde, **34c** using 30 % H_2O_2 in the presence Cd complex of chiral schiff base catalyst, **34e** resulted in benzaldehyde, **34c** in 51.33 % and some benzoic acid (**Scheme 8c**)[60b]. The oxidation of benzyl alcohol was used as model reaction using acetonitrile as solvent. The present reaction system was heterogeneous system of catalysis.


Scheme 8c: Chiral Schiff base, **34e** catalyzed synthesis of benzaldehyde[60b]

Schiff base complexes of chromium(III), manganese(II), iron(II), cobalt(II), nickel(II) and copper(II) were encapsulated in zeolites and tested for their activity in the formation of cyclohexanol and cyclohexanone by oxidation of cyclohexane[61]. Reaction was catalyzed more successfully with manganese(II) ions than other ions complexed with Schiff bases. The conversion of cyclohexane was enhanced from 2.4 % to 60 % with immobilized metal complexes, which indicated that zeolites-Y acted as cytochrome P-450 oxidation system[61]. The manganese(III) complexes of *N,N*-ethylene bis-(salicylidene aminato)salen; *N,N*-ethylenebis-(5-chlorosalicylidene aminato)Cl salen; *N,N*-ethylene bis-(5-bromosalicylidene aminato) Br-salen and *N,N*-ethylene bis-(5-nitrosalicyli-2,2-diene aminato) NO salen were encapsulated in zeolites-Y for aerobic oxidation of styrene to benzaldehyde, styrene oxide and phenyl acetaldehyde[62]. The cobalt(II) complexes were effective in the oxidation of reactive substrates, such as aldehydes and phenols. The phenoxy radicals were assumed to be responsible for the oxidation of phenols in the presence of cobalt(II) complexes[63]. These complexes showed high catalytic activity in the oxidation of phenols in super critical CO_2, which suggested that this high activity of cobalt(II) salen complex in super critical CO_2 would expand the range of substrates for oxidation. The oxidation resistant substrates such as hydrocarbons and lignins could be

as model reaction using acetonitrile as solvent. The present reaction system was heterogeneous system of catalysis.

oxidized using these catalysts in super critical CO_2[64-65]. The iron, manganese and chromium ions complexes of *meso*-tetrakis(2,6-dichloro-3-sulfophenyl)-porphyrin chloride Schiff base were used as catalyst in the presence of hypochlorite as terminal oxidant[65]. Cobalt(II) salen complexes were also used as catalyst in oxidation of 2,6-di-tert-butylphenol (2,6-DTBP) and 3,5-di-tert-butylphenol (3,5-DTBP) in super critical CO_2[66]. The conversion and catalyst selectivity were studied as a function of temperature, pressure, and concentration of catalyst and terminal oxidant. Selectivity in favour of oxygen transfer product 2,6-di-tert-butyl-1,4-benzoquinone (DTBQ) **36** over self-coupling phenoxy radicals (**Scheme 9**) was observed[66] on varying the concentration of oxygen and total pressure.
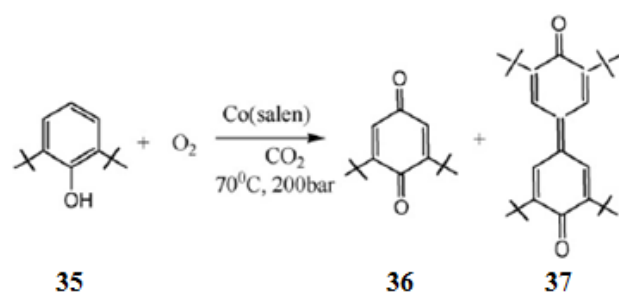
Scheme 9: Cobalt(II) salen catalyzed aerobic oxidation of DTBP[66], DTBP = 2,6-di-tert-butylphenol.

The selectivity in oxidation remained unaffected over a wide range of temperature and concentration of catalyst. The dioxygen complex as effective oxidant in both initial radical formation step and in oxygenation of phenoxy radical was studied but no direct reaction was found between phenoxy radicals and O_2. The observed behaviour of radicals has provided support for the mechanism proposed for these reactions (**Scheme 10**)[66-67].
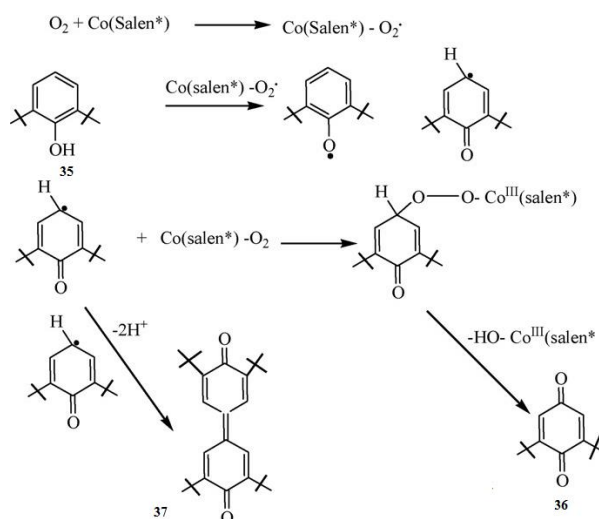

Scheme 10: Proposed reaction mechanism for the oxidation of DTBP by cobalt(II) salen[66-67]. DTBP = 2,6-di-tert-butylphenol.

Waldemar et al. showed that4 also catalyses the asymmetric oxidation of silyl ketene acetals in high enantioselectivity[39].

In 1986 Nakajima et al. studied the application of chiral Schiff base complexes in enantioselective sulfide oxidations[68]. Using tetradentate Schiff base-oxovanadium(IV) complex, (Figure 5, compound **38**), as catalyst, they could achieve an enantioselectivity of 42% ee in the oxidation of methylphenyl sulfide to the corresponding sulfoxide.
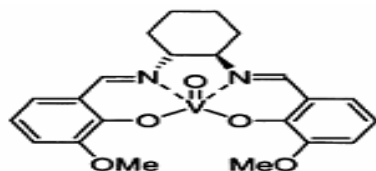
38

Figure 5: Schiff base-oxovanadium(IV) complex.

Titanium(IV), vanadium(IV), copper(II) or zinc(II) complexes of chiral Schiff base ligands of –O-N-O- type were used in various asymmetric chemical transformations[60,69] The binuclear palladium Schiff base complex, (Figure 6, compound **39**), was found to be effective catalysts in direct oxygenation of unfunctionalized hydrocarbons and phenols[70-74].
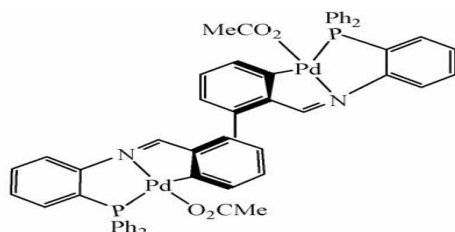

39

Figure 6: The binuclear palladium Schiff base complex.

Co(salen) and its analogues, (Figure 7, compound **40**), have been used for catalyzing the oxidation of phenols and alcohols with dioxygen as oxidant[75]. To efficiently bind dioxygen and to be catalytically active, Co(salen) needs an axial ligand. The dioxygen is coordinated orthogonally to the square planar coordination sphere of Co(salen). The axial ligand is needed to fill the sixth coordination site, opposite to dioxygen. Pyridine is the most common axial ligand used in the Co(salen) catalysed oxidation reactions[76].
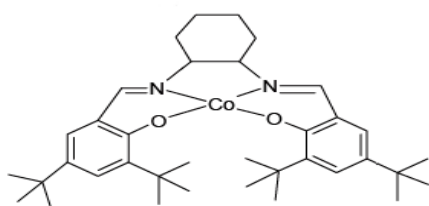
40

Figure 7: Co(salen) complex.

Heck reaction

Palladium(II) complexes of nitrogen Schiff base ligands showed higher catalytic activity in Heck reaction compared to commercially used phosphene Schiff base complexes[77]. High yields of the E-cinnamates and E-stilbenes were obtained by the Mizoroki–Heck reaction with Pd(II) complexes of 8- hydroxyquinoline(**a**), **41**, dimethyl glyoxime(**b**), and picolinic acid (**c**),ligands.
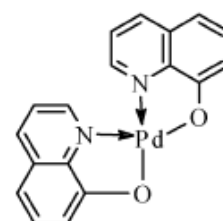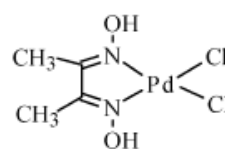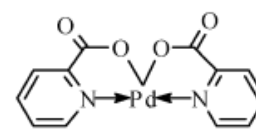
41

Metal complexes of the Schiff bases derived from quinoxaline-2-carboxaldehyde and 3-hydroxyquionxaline-2-carboxaldehyde are rare[78-82]. However there are many reports on the synthesis, biological and other applications of the compounds having quinoxaline rings. So a brief discussion on these types of compounds is included in this review.

Michael Addition

Belokon[82] et al., have elaborated of a new type of a substrate based on the Ni(II) complex of a Schiff base of dehydroalanine, **42**, and Michael addition of nucleophiles to it, leading to the synthesis of racemic α-amino acids **(Scheme 11)**.
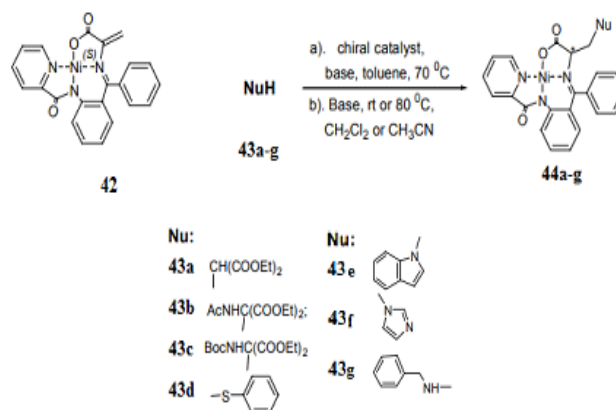

Scheme 11: Michael addition of various nucleophiles 43a-g to substrate **42.**

Aldol condensation reaction

Aldol condensation between ketones and aldehydes is an easy way for carbon-carbon bond. Metal oxides have been used as catalysts in difficult Aldol condensation reactions with acetaldehydes or formaldehydes[83-84]. Pyridoxal-catalysed aldol reaction of amino acid with aldehydes or ketones is a biologically important process to add new carbon-carbon bonds. The Aldol condensation of glycine and acetaldehyde was catalyzed using pyridoxal as catalyst, which produced a significant amount of threonine and aldothreonine as reaction products[84-85].

Titanium(IV) binaphthyl(Di-t-butylsalicylicacid, DTBSA), Schiff base complexes showed activity in enantioselective aldol condensation of dienolate with a variety of aldehydes **46 – 49, 50 - 53** (Reactions 1 and 2 in **Scheme 12**), which produced about 88–97 % ee[86-87].
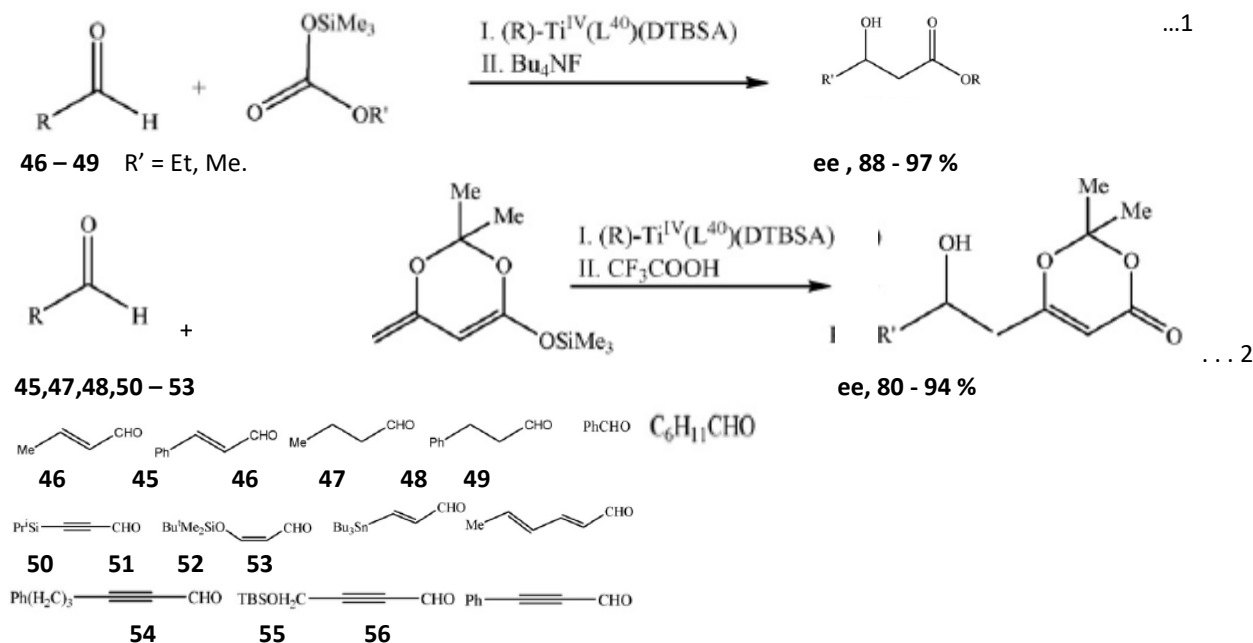
Scheme 12 : Reactions 1 and 2 and various aldehydes **46 - 49, 50 – 53** used.

These complexes were also used as catalysts in the aldol addition reaction between $CH_2C(OMe)$ Me and aldehydes **47 – 49, 54 – 56**, which showed 95–99% ee (**Scheme 13**).
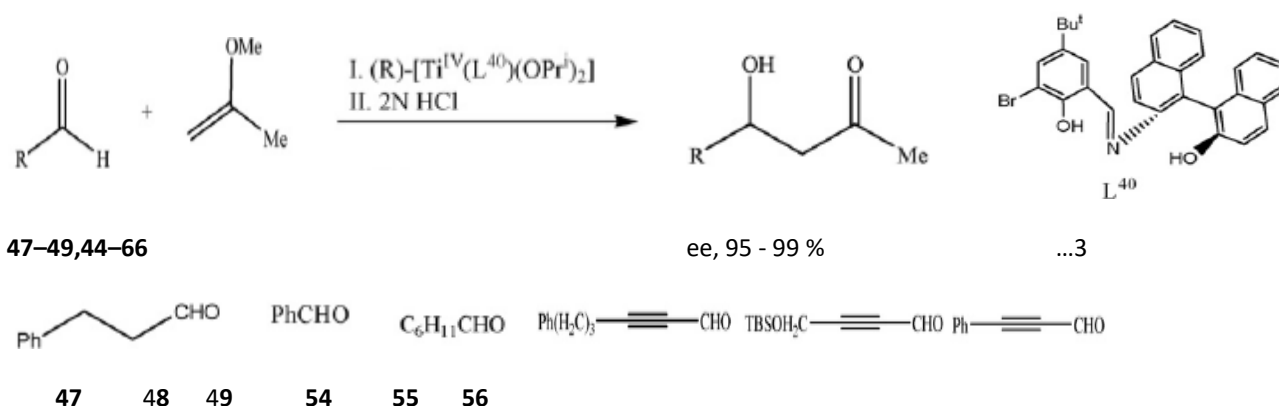
Scheme 13: Reaction and various aldehydes **7 – 9, 14 – 16** used.

To facilitate the separation of catalyst in aldol addition reactions between silyl ketene, acetals and aldehydes, polymer supported chiral binaphthal Schiff base titanium(IV) complexes were used, which showed 26 % ee[88]. Recently aluminum(III) chiral complexes of binaphthal Schiff base ligand were also used to catalyze the aldol addition/acyl transfer reactions between 5-methoxyoxazoles and aldehydes[89], which afforded corresponding (4*S*, 5*S*)-oxazoline products with 98 % ee and 60 % turnover number. Schiff base complexes of aluminum(III) were active in the reaction between 5-methoxyoxazoles and benzaldehydes to produce optically active *cis*-oxazoline adducts with > 99% ee[89].

Polymerization reaction

Drozdzak et al. reported a detailed discussion on catalytic activity in the atom transfer radical polymerization and ring opening metathesis polymerization of various substrates using Ru-catalysts having salicylaldiminato-type Schiff bases as one of the ligands,(Figure 8 compound **57**)[90].

Polymethylmethacrylate was prepared in presence of Cr(III) and Ni(II)salen complexes as catalysts for the controlled radical polymerization of the methylmethacrylate monomer[91].
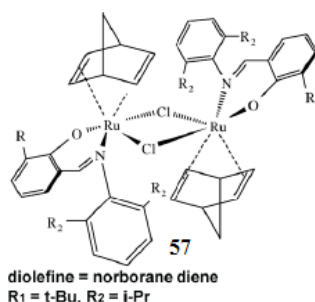

Figure 8: Ru-catalyst with salicylaldiminato-type Schiff base as aligand.

Hydrogenation reaction

A series of chiral N4-Schiff bases, containing amine or sulfonamide functionalities has been synthesized by Karame et al.[92]. Coupled with ruthenium catalysts, these Schiff bases induce interesting results in the hydrogenation of acetophenone. The asymmetric hydrogenation reaction was carried out under hydrogen pressure (p = 30 bar) at room temperature in the presence of the chiral catalyst prepared in situ.

Hydrogenation of imines

Venkatachalam and Ramesh also reported the transfer hydrogenation of imines to amines mediated by ruthenium(III) bis-bidentate Schiff base complexes[93].

Hydrogenation of ketones

Schiff base complexes of transition metals are efficient catalysts in carrying out asymmetric reduction of dialkyl ketones[94-97]. The catalytic activity in the transfer hydrogenation of aliphatic and aromatic ketones in the presence of isopropanol and KOH has been investigated with ruthenium(III) Schiff base complexes of general formula [RuX(EPh3)(LL')] where X = Cl or Br, E = P or As and LL' = [ONNO] donor of the heterocyclic Schiff base ligands, (Figure 9 compounds **58-60**)[98].
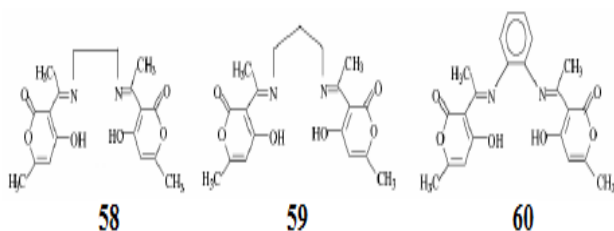

Figure 9: Ruthenium(III) Schiff base complexes of general formula [RuX(EPh3)(LL')] where X = Cl or Br, E = P or As and LL' = [ONNO] donor of the heterocyclic Schiff base ligands.

Hydrogenation of alkene and alkynes

A series of palladium(II) complexes of Schiff bases with the nitrogen ligands have been synthesised and their catalytic activity in the hydrogenation of alkenes and alkynes in mild conditions (with 1 atm dihydrogen pressure at 40 °C) has

been studied by Costa et al.[99]. Two representative examples of these Schiff base complexes are given below (Figure 10 compounds **61** and **62**).
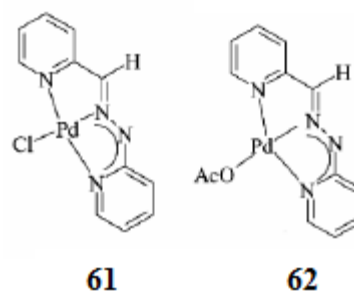

Figure 10: Palladium(II) complexes of Schiff bases with the nitrogen ligands.

Ring opening reaction of epoxides

The ring-opening of cyclohexa-1,4-diene monoepoxide was carried out by Jacobsen's group[100] under solvent free conditions in presence of 7.5 mol% of (Figure 11 compound **63**) and azidotrimethylsilanolate to produce the azido silyl ether in 92% enantiomeric excess(**Scheme-14**).
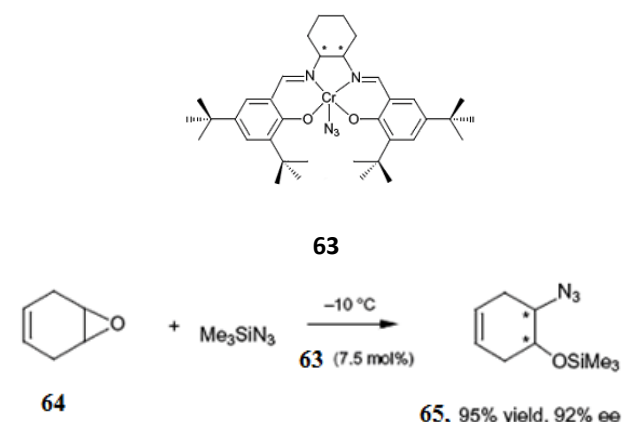
Scheme-14: Ring-opening reaction of epoxide

Jacobsen also discovered[101] that the Co(salen) complex **66** was active in the hydrolytic kinetic resolution of racemic epoxides which enables access to terminal epoxides and diols in high enantiomeric purity (**Scheme 15**).
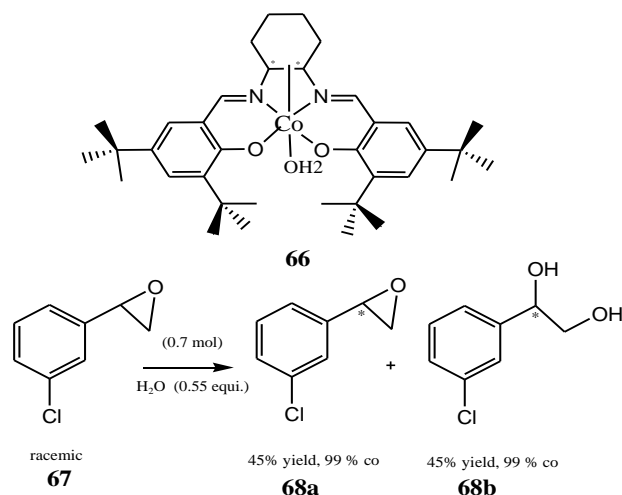
Scheme 15: Resolution of racemic epoxides.

Cyclopropanation reaction The catalytic cyclopropanation of olefins using diazo compounds has been one of the highlights since Nozaki and co-workers introduced the use of transition metal catalysts for this purpose about 55 years ago[102,103].

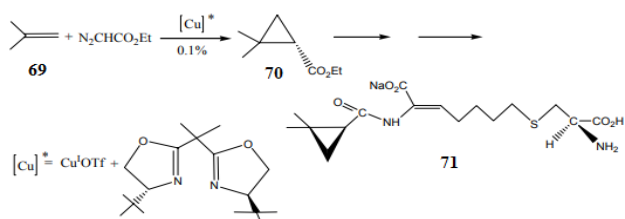**Application:** Practical application include the synthesis of 2,2-dimethylcyclopropane carboxylate from isobutene[104], a key step in the commercial production of cilastatin (**Scheme 16**) and of the esters of chrysanthemic acid[105,106].

**Scheme 16:** Synthesis of Cilastatin

Cilastatin is a dehydropeptidase and acts as an in-vivo stabilizer of the carbapenem antibiotic imipenem with achiral diazoeasters. Similarly, the chiral ruthenium complexes discovered for cyclopropanation include many ruthenium chiral Schiff base complexes[107,108].

In 2002, another type of highly enantioselective and diastereoselective cyclopropanation catalyst was reported by J A. Miller and co-worker. Schiff base ligands containing chiral centers were prepared, and implemented on runthenium resulting in chiral Ru(II) complexes. These complexes have two pyridine ligands at axial positions. By using EDA, trans-isomers in a highly enantioselective way were (obtained in all case at least 10.6:1). These compounds are also very efficient catalysts for the asymmetric cyclopropanation of both electron rich and electron deficient olefins. It was observed that side reactions barely occurred(dimerization products).
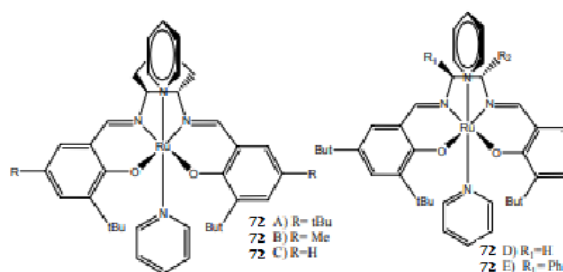
Scheme 17: Chiral Schiff base ruthenium complexes (compound 72)

A Ru (II) catalyst with a chiral PNNP-type ligand was reported to highly increase cis enantioselectivity in cyclopropanation when styrene or its derivatives were used as substrates; especially, when they carry an electron donating group at the para-position. From this result, the electronic tuning of the ligands could optimize the results for asymmetric cyclopropanation. Also the detection of and intermediate by ^{1}H and ^{31}P NMR was successful.
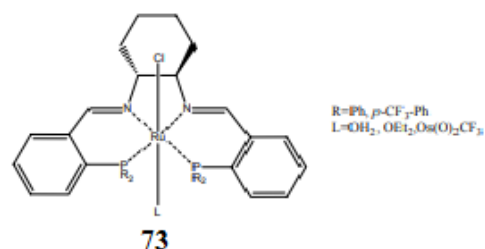
Scheme 18: Ru (II) catalyst with a chiral PNNP-type ligand (compound 72) reported by Mezzetti.

Decomposition of Hydrogenperoxide

Using the aqueous hydrogen peroxide in the (salen)Mn(III) catalyzed epoxidations is related to the hydrogen peroxide decomposition (homolitic cleavage of O–O bond) catalyzed by the salen itself[109]. The tetradentate Schiff bases N,N'-bis(salicylidene) ethylenediamine(salen), N,N-bis-(salicylidene) hexylenediamine(salhex), and N,N'-bis(salicylidene)-o-phenylenediamine(sal-o-phen) are very strongly adsorbed by cation exchange resins (Dowex-50W) with manganese(II) as a counter ion, forming stable complexes. The kinetics of the catalytic decomposition of H_2O_2 in presence of these complexes has been studied in aqueous medium. The decomposition reaction is first order with respect to H_2O_2 in the case of salen and sal-o-phen and third order in the case of salhex. The greater the ligand methylene chain length or the greater the steric effect of the ligand, the greater will be the rate of reaction. The reaction is governed by the entropy of activation. A reaction mechanism is proposed[109].

Carbon-carbon, carbon-hydrogen and carbon-heteroatom bond formation

The Schiff base approach afforded quite active and stable ruthenium catalysts successfully initiating a variety of organic transformations spanning carbon-carbon, carbon hydrogen and carbon-heteroatom bond formation[110].

Epoxide decomposition

The hydrolysis of styrene oxide seems to be the main pathway to the diol. This was confirmed by an experiment employing the usual conditions and using styrene oxide as the substrate. When styrene oxide is treated with H_2O_2 in acetone, no epoxide is degraded. In the presence of 1 mol% of ligand and 1 mol % of $Mn(ClO_4)_2.6H_2O$, after 1 h, 18 % of the initial amount of epoxide is degraded.

Addition of base increased the decomposition of H_2O_2 and yields dropped dramatically (< 5%). Hydrolysis of epoxides is a common problem in epoxidations using H_2O_2[111,112]. Therefore pyridine is used as additional base and ligand in rhenium catalyzed epoxidations[113]. Instead, addition of base ($NaHCO_3$ or triethylamine) did not lead to improved catalytic activity or suppression of epoxide hydrolysis.
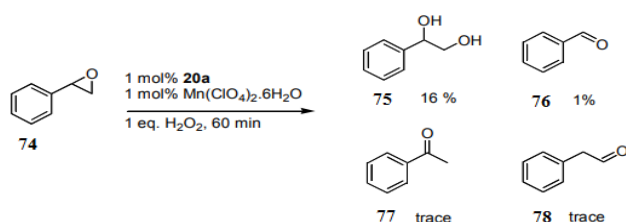
Scheme 19: Decomposition of styrene oxide under conditions employed in catalytic Epoxidation reaction.
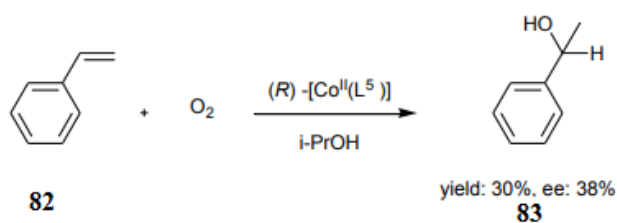
Hydroxylation of styrene

The metal complexes of chiral Schiff base ligands showed stereoselectivity in organic transformation like the hydroxylation of styrene: the enantioselective hydroxylation of styrene was the first organic reaction to involve a metal complex of a binaphthyl Schiff-base ligand as catalyst[114]. In 1988, Nishinaga and co-workers reported that (R)-[$Co^{II}(L^n)$] (n = 1, 6) (**Scheme 20**) can catalyze hydroxylation of styrene with dioxygen[115].
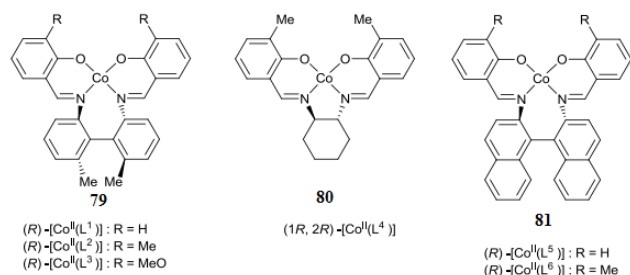
Scheme 20: Cobalt schiff base complexes used as catalysts in oxygenation of styrene

The reactions were conducted in the presence of alcohol, affording optically active 1- phenylethanol in 30 % yield and 38 % ee for catalyst (R)-[$Co^{II}(L^5)$] as more efficient one (**Scheme 21**).

Scheme 21: Hydroxylation of styrene with(R)-[$Co^{II}(L^5)$].

CONCLUSION

The present review paper gives an overview of catalysis properties of chiral schiff base metal complexes synthesized and used in various reactions. The compounds synthesized from the Chiral amines and their metal complexes are useful for many applications such as Diels–Alder reaction, Epoxidation reaction, Oxidation reaction, Heck reaction, Michael addition, Aldol condensation reaction, Polymerization reaction, Hydrogenation reaction, Hydrogenation of imine, Hydrogenation of Ketone, Hydrogenation of alkene and alkyne, Ring opening reaction of epoxide, Cyclopropanation reaction , Decomposition of hydrogen peroxide, C-C, C-H and C-Metal Bond formation, Epoxide Decomposition and

Hydroxylation of styrene etc. In some cases these chiral schiff base serves to build a chemical skeleton for many intermediates. Thus, this review may be useful to many researchers for further developments of catalysis properties of chiral schiff base metal complexes and useful to study their varied reactions in near future.

REFERENCES

1. Hunoor RS, Patil BR, Badiger DS, Vadavi RS, Gudasi KB, Magannavar CV and Muchandi IS. A Study of Anti-inflammatory and Analgesic Activity of New 2,3-Disubstituted-1,2-dihydroquinazolin-4(3H)-one Derivative and Its Transition Metal Complexes. Chem Pharm Bull (Tokyo), 2010; 58(5): 712-16. Doi:10.1248/cpb.58.712; De B, Ramasarma GVS. Indian Drugs. 1999; 36: 583.

2. Schwietert CW and McCue JP. Coordination compounds in medicinal chemistry. Coord Chem Rev. 1999; 184(1): 67-89. Doi:10.1016/S0010-8545(98)00205-7.

3. Yang ZY. Synthesis, Characterization, and Biological Activity of Rare Earth Complexes of 1-Phenyl-3-Methyl-4-Benzoyl-5-Pyrazolone Benzoylhydrazone. Synth React Inorg Met-org Chem. 2002; 32(5): 903-12. Doi:10.1081/Sim-120005610.

4. Chohan ZH, Prevez H, Khan KM, Rauf A, Maharvi GM and Supuran CT. Antifungal Cobalt(II), Copper(II), Nickel(II) and Zinc(II) Complexes of Furanyl-, Thiophenyl-, Pyrrolyl-, Salicylyl- and Pyridyl-derived Cephalexins. J Enzy Inhib Med Chem. 2004; 19(1): 85-90. Doi:10.1080/14756360310001650183.

5. Zhang H, Norman DW, Wentzell TM, Irving AM, Edwards JP, Wheaton SL, Vogels CM, Westcotts SA, Baerlocher FJ, Decken A. Palladium salicylaldimine complexes containing boronate esters. Trans. Met. Chem. 2005; 30(1): 63-8. Doi:10.1007/s11243-004-2851-3.

6. Hossain ME, Alam MA, Ali MA, Nazimuddin M, Smith FE, Hynes R. The synthesis, characterization and bioactivities of some copper(II) complexes of the 2-acetylpyridine schiff bases of s-methyl- and s-benzyldithiocarbazate, and the x-ray crystal structure of the nitrato(s-benzyl-β-n-(2-acetylpyridyl) methylenedithiocarbazato)copper(II) complex. Polyhedron, 1996; 15(5-6): 973, doi: 10.1016/0277-5387(95)00310-X.

7. Zhang S, Jiang Y, Chen M, Shifan G, Xuebao D. Ziran Kexueban. 2004; 22: 59; Chem Abstr., 2005; 142, 347400.

8. Stanila A, Braicu C, Stanila S, Pop RM. Antibacterial Activity of Copper and Cobalt Amino Acids Complexes. Not Bot Horti Agrobo. 2011; 39(2): 124-9. Doi:10.15835/nbha3926847.

9. a) Das A, Trousdale MD, Ren S, Lien EJ. Inhibition of herpes simplex virus type 1 and adenovirus type 5 by heterocyclic Schiff bases of aminohydroxyguanidine tosylate. Antiviral Res. 1999; 44(3): 201-8. Doi:10.1016/S0166-3542(99)00070-4; b) Meng F, Zhao Q, Li M, Xin Y, Yingyong Huaxue., 2002; 19: 1183; c) Brandi-Blanco MP, Choquesillo-Lazarte D, Dominguez-Martin A, Gonzalez-Perez JM, Castineiras A, Niclos-Gutierrez J. Metal ion binding patterns of

acyclovir: Molecular recognition between this antiviral agent and copper(II) chelates with iminodiacetate or glycylglycinate. J Inorg Biochem. 2011; 105: 616-23. Doi:10.1016/j.jinorgbio.2011.02.001.

10. a) Singh R, Gupta N, Fahmi N. Stereochemical, thermal and biochemical aspects of dioxomolybdenum(VI) and manganese(II) complexes. Ind J Chem. 1999; 38A: 1150-58. http://hdl.handle.net/123456789/16102; b) Kumar D, Sharma J. Manganese coordination compounds: synthesis, chemistry and applications. Integr Res Adv. 2016; 3(2): 40-4. b) Singh R, Mitharwal P, Singh R, Mital SP. Synthesis, Characterization, Spectral (FT-IR, 1H, 13C NMR, Mass and UV) and Biological Aspects of the Coordination Complexes of Sulfur Donor Ligands with Some Rare Earth Elements. Am Chem Sci J. 2014; 4: 117.

11. a) Siddiqi KS, Kureshy RI, Khan NH, Tabassum S, Zaidi S. Characterization and toxicity of lanthanide complexes with nitrogen- and sulphur-containing Schiff bases. Inorg Chim Acta. 1988; 151(2): 95-100. Doi: 10.1016/S0020-1693(00)91888-7; b) Pataskar M, Rao JT. Synthesis and Characterization of Biologically Significant Bis-[2-(aryl/furyl)-5-H-4-thiazolidinone]dapsone Derivatives. Asian J Chem. 2005; 17: 319-22.

12. Parashar RK, Sharma RC, Mohan G. Biological activity of some schiff bases and their metal complexes. Biol Trace Elem Res. 1989; 23(1): 145-50. Doi:10.1007/BF02917185.

13. a) Pendya SN, Sriram D, Nath G, De CE. Synthesis and antimicrobial activity of Schiff and Mannich bases of isatin and its derivatives with pyrimidine. Farmaco, 1999; 54(9): 624-28. Doi:10.1016/S0014-827X(99)00075-0; b) Kar DM, Sahu SK, Pradhan D, Dash GK, Mishra PK, J Tech Res Chem. 2003; 10: 20.

14. Gaowen Y, Xiaping X, Huan T, Chenxue Z. Synthesis anti tumor activity of Schiff base Coordination compounds. Yingyoung Huaxue. 1995; 12: 13-15. Che, Abstr, 123; 101: 089.

15. Marzano C, Pellei M, Tisato F, Santini C. Copper Complexes as Anticancer Agents. Antican Agen Med Chem. 2009; 9(2): 185-211. Doi:10.2174/187152009787313837.

16. Trojer MA, Movahedi A, Blanck H, Nyden M. Imidazole and Triazole Coordination Chemistry for Antifouling Coatings. J Chem. 2013; ID 946739. Doi:10.1155/2013/946739.

17. Charleton KDM, Prokopchuk EM. Coordination Complexes as Catalysts: The Oxidation of Anthracene by Hydrogen Peroxide in the Presence of VO(acac)₂. J Chem Educ. 2011; 88: 1155-57. Doi:10.1021/ed100843a.

18. Chakraborty H, Paul N, Rahman ML. Catalytic activities of Schiff base aquocomplexes of copper(II) towards hydrolysis of amino acid esters. Trans Met Chem. 1994; 19(5): 524-26. Doi:10.1007/BF00136366.

19. Hitahi Ltd. Jpn Kokai Tokkyo Koho. JP. 8110492.

20. Dainichi Nippon Cables Ltd. Jpn. Kokai Tokkyo. JP. 81133348.

21. Desai MN, Pya MM, Shah GB. Ind J Technol. 1981; 19: 292.

22. Kumar S, Dhar DN, Saxena PN. Applications of metal complexes of Schiff bases-A review. J Sci Ind Res. 2009; 68: 181-87.

23. a) Zabin SA, Jejurkar CR. Fluorescence, Antibacterial and Pigmentation Studies of Some binuclear Schiff base Complexes. Asian J Chem. 1995; 7(3): 542-50. b) Jauma A, Farrera JA, Ribo JM. Reactivity of pyrrole pigments, XX. On the structure of Cu(II) and Zn(II) tripyrrin-1-one chelates in solution. Monatshefte fur Chemie, 1996; 127: 935-46. Doi:10.1007/BF00807033.

24. Brown DJ. The Chemistry of Heterocyclic Compounds, Pyridine Metal Complexes. Wiley. 14. 2008; p. 408.

25. Wang Y, Lu B, Yu X, Ye W, Wang S. Studies of Synthesis and Plant harmone on Schiff bases of Tetrazole. Chem J Internet. 2001; 3: Chem. Abstr. 2002; 137: 109238.

26. Song X, Wang Z, Wang Y, Zhang Z, Chen C. Yingyong Huaxue. 2-amino-5-(4-pyridyl)-1,2,4-thiadiazole schiff base Synthesis and its biological activity. 2005; 22: 334.

27. Jones RD, Summerville DA, Basolo F. Synthetic oxygen carriers related to biological systems. Chem Rev. 1979; 79(2): 139-79. Doi:10.1021/cr60318a002.

28. Bryliakov KP, Talsi EP. Cr^III(salen)Cl Catalyzed Asymmetric Epoxidations: Insight into the Catalytic Cycle. Inorg Chem. 2003; 42: 7258-65. Doi:10.1021/ic034578w.

29. Adao P, Pessoa JC, Henriques RT, Kuznetsov ML, Avecilla F, Maurya MR, Kumar U, Correia I. Synthesis, Characterization, and Application of Vanadium–Salan Complexes in Oxygen Transfer Reactions. Inorg Chem. 2009; 48: 3542-61. Doi:10.1021/ic8017985.

30. Oxford GAE, Snurr RQ, Broadbelt LJ. Hybrid Quantum Mechanics/Molecular Mechanics Investigation of (salen)Mn for use in Metal–Organic Frameworks. Ind Eng Chem Res. 2010; 49(21): 10965-73. Doi:10.1021/ie100165j.

31. a) Zhao ZP, Li MS, Zhang JY, Li HN, Zhu PP, Liu WF. New Chiral Catalytic Membranes Created by Coupling UV-Photografting with Covalent Immobilization of Salen–Co(III) for Hydrolytic Kinetic Resolution of Racemic Epichlorohydrin. Ind Eng Chem Res. 2012; 51(28): 9531-39. Doi:10.1021/ie3011935; b) Kurahashi T, Hada M, Fujii H. Critical Role of External Axial Ligands in Chirality Amplification of trans-Cyclohexane-1,2-diamine in Salen Complexes. J Am Chem Soc. 2009; 131: 12394-405. Doi:10.1021/ja904635n.

32. Nielsen LPC, Zuend SJ, Ford DD, Jacobsen EN. Mechanistic Basis for High Reactivity of (salen)Co-OTs in the Hydrolytic Kinetic Resolution of Terminal Epoxides. J Org Chem. 2012; 77(5): 2486-95. Doi:10.1021/jo300181f.

33. Zhang JX, Zhou Y, Cai G. Synthesis of Copper Complex and Its Application in Asymmetric Synthesis of Polyacids. J Mol Catal. 1997; 1: 42-5.

34. Kenneth JO, Shiow JW, Cynthia JB. Alkene aziridination and epoxidation catalyzed by chiral metal salen complexes. Tetra Lett. 1992; 33(8): 1001-1004. Doi:10.1016/S0040-4039(00)91844-6.

35. Jacobsen EJ, Zhang W, Guler ML. Electronic tuning of asymmetric catalysts. J Am Chem Soc. 1991; 113: 6703-04. Doi:10.1021/ja00017a069; (b) Jacobsen EJ, Zhang W, Muci AR. Highly enantioselective epoxidation catalysts derived from 1,2-diaminocyclohexane. J Am Chem Soc. 1991; 113: 7063-64. Doi:10.1021/ja00018a068.

36. Kim GJ, Shin JH. Application of new unsymmetrical chiral Mn(III), Co(II,III) and Ti(IV) salen complexes in enantioselective catalytic reactions. Cat Lett. 1999; 63(1-2): 83-9. Doi:10.1023/A:1019040215323.

37. Sasaki C, Nakajima K, Kojima M, Fujita J. Preparation and Characterization of Optically Active Quadridentate Schiff Base-Titanium(IV) Complexes and the Catalytic Properties of These Complexes on Asymmetric Oxidation of Methyl Phenyl Sulfide with Organic Hydroperoxides. Bull Chem Soc Jpn. 1991; 64(4): 1318-24. Doi:10.1246/bcsj.64.1318.

38. Waldemar A, Rainer T, Veit RS. Synthesis of Optically Active α-Hydroxy Carbonyl Compounds by the Catalytic, Enantioselective Oxidation of Silyl Enol Ethers and Ketene Acetals with (Salen)manganese(III) Complexes. J Am Chem Soc. 1998; 120: 708-14. Doi:10.1021/ja9726668.

39. Hayashi M, Inoue T, Miyamoto Y. Asymmetric carbon-carbon bond forming reactions catalyzed by chiral Schiff base—titanium alkoxide complexes. Tetrahedron. 1994; 50(15): 4385-98. Doi:10.1016/S0040-4020(01)89374-1.

40. Aratani T, Yoneyoshi Y, Nagase T. Asymmetric synthesis of chrysanthemic acid. An application of copper carbenoid reaction.

Tetra Lett. 1975; 16(21): 1707-10. Doi:10.1016/S0040-4039(00)72239-8.

41. Schaus SE, Brandes BD, Larrow JF, Tokunaga M, Hansen KB, Gould AE, Furrow ME, Jacobsen EJ. Highly Selective Hydrolytic Kinetic Resolution of Terminal Epoxides Catalyzed by Chiral (salen)Co^{III} Complexes. Practical Synthesis of Enantioenriched Terminal Epoxides and 1,2-Diols. J Am Chem Soc. 2002; 124(4): 1307. Doi:10.1021/ja016737l.

42. Gupta KC, Sutar AK. Catalytic activities of Schiff base transition metal complexes. Coordin Chem Rev. 2008; 252: 1420. Doi:10.1016/j.ccr.2007.09.005.

43. Magesh CJ, Makesh SV, Perumal PT. Highly diastereoselective inverse electron demand (IED) Diels–Alder reaction mediated by chiral salen–AlCl complex: the first, target-oriented synthesis of pyranoquinolines as potential antibacterial agents. Bioorg Med Chem Lett. 2004; 14: 2035-40. Doi:10.1016/j.bmcl.2004.02.057.

44. Zubkov FI, Boltukhina EV, Turchin KF, Varlamov AV. An efficient approach to isoindolo[2,1-b][2]benzazepines via intramolecular [4+2] cycloaddition of maleic anhydride to 4-α-furyl-4-N-benzylaminobut-1-enes. Tetrahedron. 2004; 60(38): 8455-63. Doi:10.1016/j.tet.2004.07.008.

45. Varlamov AV, Zubkov FI, Boltukhina EV, Sidorenko NV, Borisov RS. A general strategy for the synthesis of oxoisoindolo[2,1-a]quinoline derivatives: the first efficient synthesis of 5,6,6a,11-tetrahydro-11-oxoisoindolo[2,1-a]-quinoline-10-carboxylic acids. Tetra Lett. 2003; 44: 3641-43. Doi:10.1016/S0040-4039(03)00705-6.

46. Takenaka N, Huang Y, Rawal VH, The first catalytic enantioselective Diels–Alder reactions of 1,2-dihydropyridine: Efficient syntheses of optically active 2-azabicyclo[2.2.2]octanes with chiral BINAM derived Cr(III) salen complexes. Tetrahedron. 2002; 58(41): 8299.

47. Kano S, Nakano H, Kojima M, Baba N, Nakajima K. An effect of the ionic radii of lanthanide(III) ions on the structure and catalytic properties of chiral Schiff base-lanthanide(III) complexes. Inorg Chim Acta. 2003; 349: 6. Doi: 10.1016/S0020-1693(03)00052-5.

48. Brunel D, Bellocq N, Sutra P, Cauvel A, Lasperas M, Moreau P, Di Renzo F, Galarneau A, Fajula F. Transition-metal ligands bound onto the micelle-templated silica surface. Coord Chem Rev. 1998; 178-180(2): 1085.

49. De Vos DE, Knops-Gerrits PP, Vanoppen DL, Jacobs PA. Catalytic and physico-chemical properties of new schiff base complexes in zeolites. Supramol Chem. 1995; 6(1/2): 49.

50. Star A, Goldberg I, Fuchs B. Diazadioxadecalin and salen podands and macrocycles within dynamic combinatorial virtual libraries: structure, prototropy, complexation and enantioselective catalysis. J Orgmet Chem. 2001; 630(1): 67. Doi:10.1016/S0022-328X(01)00882-8.

51. Morris GA, Nguyen ST, Hupp JT. Enhanced activity of enantioselective (salen)Mn(III) epoxidation catalysts through supramolecular complexation. J Mol Catal A. 2001; 174: 15-20. Doi:10.1016/S1381-1169(01)00165-0.

52. McGarrigle EM, Gilheany DG. Chromium– and Manganese–salen Promoted Epoxidation of Alkenes. Chem Rev. 2005; 105(5): 1563-602. Doi:10.1021/cr0306945.

53. Finnley N, Pospil PJ, Chang S, Palucki M, Konsler R, Hansen K, Jacobsen E. On the Viability of Oxametallacyclic Intermediates in the (salen)Mn-Catalyzed Asymmetric Epoxidation. Angew Chemie Int Ed (in English). 1997; 36(16): 1720-23. Doi:10.1002/anie.199717201.

54. Jacobsen EN. In: Comprehensive Organometallic Chemistry II, Abel EW, Stone FGA, Willinson E (Eds.). Pergamon: New York. 12. 1995; p. 1097.

55. Takeda T, Irie R, Shinoda Y, Katsuki T. Ru-Salen Catalyzed Asymmetric Epoxidation: Photoactivation of Catalytic Activity. Synlett. 1999; 7: 1157-59. Doi:10.1055/s-1999-2780.

56. Nakata K, Takeda T, Mihara J, Hamada T, Irie R, Katsuki T. Asymmetric epoxidation with a photoactivated [Ru(salen)] complex. Chem: A Eur J. 2001; 7: 3776-82. Doi:10.1002/1521-3765(20010903)7:17<3776::AID-CHEM3776>3.0.co;2-M.

57. Stoop RM, Bachmann S, Valentini M, Mezzetti A. Ruthenium(II) Complexes with Chiral Tetradentate P_2N_2 Ligands Catalyze the Asymmetric Epoxidation of Olefins with H_2O_2. Organomet. 2000; 19(20): 4117-26. Doi:10.1021/om000481v.

58. Bonaccorsi C, Mezzetti A. Ruthenium Complexes with Chiral Tetradentate PNNP Ligands in Asymmetric Catalytic Atom-Transfer Reactions. Curr Org Chem. 2006; 10(2): 225-40. Doi:10.2174/138527206775192951.

59. a) Flores-Lopez Z, Parra-Hake M, Somanathan R, Walsh PJ. Structure enantioselectivity study of the Asymmetric addition of trimethylsilylcyanide to Benzaldehyde catalysed by Ti(IV)-Schiff base complexes. Organomet. 2000; 19(11): 2153-60. Doi:10.1021/om000127x; b) Gama A, Flores-Lopez LZ, Aguirre G, Parra-Hake M, Somanathan R, Walsh PJ. Steric effects in the design of chiral Schiff base–titanium complexes: new catalysts for asymmetric trimethylsilylcyanation of aldehydes. Tetra Asym. 2002; 13(2): 149-54. Doi:10.1016/S0957-4166(02)00073-3.

60. a) Salve SB, Patil CJ. Catalytic Studies of Complexes of Organic Compounds. Part-3: Synthesis of Chiral Schiff base, Cr(III) Complex and its Characterization. Int J Res Anal Rev. 2019; 6(2): 331-43; b) Patil CJ, Salve SB. Catalytic Studies of Complexes of Organic Compounds. Part-4: Synthesis, Characterization, Catalytic activity of Cd(II) Complex of Chiral Schiff base. Orient J Chem. 2021; 37(1): 84-94.

61. Hueso-Urena F, Illan-Cabeza NA, Moreno-Carretero MN. Martinez-Martos JM, Ramirez-Exposito MJ. Synthesis and Spectroscopic studies on the new Schiff bases derived from the 1:2 condensation of 2,6-diformyl-4-methylphenol with 5-Amino uracil(BDF5AU) and its transition metal complexes: Influence on biologically active peptides-regulating aminopeptides. J Inorg Biochem. 2003; 94(4): 326-34. Doi:10.1016/S0162-0134(03)00025-4.

62. Farzaneh YF, Majidian M, Ghandi M. The oxyfunctionalization of cyclohexane catalyzed by Mn(II) complexes included in zeolite Y. J Mol Catal A. 1999; 148: 227-33. Doi:10.1016/S1381-1169(99)00151-X.

63. Musie GT, Wei M, Subramaniam B, Busch DH. Autoxidation of Substituted Phenols Catalyzed by Cobalt Schiff Base Complexes in Supercritical Carbon Dioxide. Inorg Chem. 2001; 40(14): 3336-41. Doi:10.1021/ic001288w.

64. Bottcher A, Birnbaum ER, Day MW, Gray HB, Grinstaff MW, Labinger JA. How do electronegative substituents make metal complexes better catalysts for the oxidation of hydrocarbons by dioxygen?. J Mol Catal A. 1997; 117(1-3): 229-42. 10.1016/S1381-1169(96)00299-3.

65. Dolphin D, Traylor TG, Xie LY. Polyhalophyrins: unusual ligand for Metals and Metals catalysed oxidations. Acc Chem Res. 1997; 30(6): 251-59. Doi:10.1021/ar960126u.

66. Musie G, Wei M, Subramaniam B, Busch DH. Catalytic oxidations in carbon dioxide-based reaction media, including novel CO_2-expanded phases. Coord Chem Rev. 2001; 219-221: 789-820. Doi:10.1016/S0010-8545(01)00367-8.

67. Varkey SP, Ratnasamy C, Ratnasamy P. Zeolite-encapsulated manganese(III)salen complexes. J Mol Catal A. 1998; 135: 295-306. Doi:10.1016/S1381-1169(97)00307-5.

68. Nakajima K, Aoyama KT, Fujita J. Asymmetric Oxidation of Sulfides to Sulfoxides by Organic Hydroperoxides with Optically active Schiff Base-Oxovanadium(IV) Catalysts. Chem Lett. 1986; 15(9): 1483-86.

69. Flores-Lopez Z, Parra-Hake M, Somanathan R, Walsh PJ. Structure/ Enantioselectivity Study of the Asymmetric Addition of Trimethylsilylcyanide to Benzaldehyde Catalyzed by Ti(IV)–Schiff Base Complexes. Organomet. 2000; 19(11): 2153-60. Doi:10.1021/om000127x.

70. Cabezon B, Sastre A, Torres T, Schafer W. Borras-Almenar JJ, Coronado EJ. Synthesis, Magnetic and Mass Spectrometric Studies on Dinuclear Complexes based on Schiff -base Triazolic Ligands. J Chem Soc Dalt Tr. 1995; 2305-10.

71. Matthews RC, Howell DK, Peng WJ, Train SG, Treleaven WD, Stanley GG. [Rh(7-SPh-8-Me-7,8-C2B9H10)(PPh3)2]: A new Rhodacarborane with Enhances Activity in the Hydrogenation of 1-Alkenes. Angew Chem Int Ed Eng. 1996; 35(19): 2253-56. Doi:10.1002/anie.199622511.

72. Komatsuzaki NO, Katoh R, Himeda Y, Sugihara H, Arakawa H, Kasuga K. Synthesis and Photochemical Properties of Novel Ruthenium(b)-Nickel(b) and Ruthenium(b)-Copper(b) Dinuclear Complexes. Bull Chem Soc Japn. 2003; 76(5): 977-84.

73. Beuken EK, Leeuwen PWNM, Budzelaar PHM, Veldman N, Spek AL, Feringa BL. Synthesis and crystal structure of a dinuclear rhodium complex. Catalytic activity of mono-and di-nuclear rhodium phosphite complexes in hydroformylation. J Chem Soc Dalt Tr. 1996; 3561-69.

74. Lubben M, Hage R, Meetsma A, Bijma K, Feringa BL. Modeling Dinuclear Copper Sites of Biological Relevance: Synthesis, Molecular Structure, Magnetic Properties, and 1H NMR Spectroscopy of a Nonsymmetric Dinuclear Copper(II) Complex. Microcalorimetric Determination of Stepwise Complexation of Copper(II) by a Nonsymmetric Dinucleating Ligand. Inorg Chem. 1995; 34: 2217-24. Doi:10.1021/ic00112a039.

75. Bozell J, Hames B, Dimmel D. Cobalt-Schiff Base Complex Catalyzed Oxidation of Para-Substituted Phenolics. Preparation of Benzoquinones. J Org Chem. 1995; 60: 2398-404. Doi:10.1021/jo00113a020.

76. Iyer S, Kulkarni GM, Ramesh C. Mizoroki–Heck reaction, catalysis by nitrogen ligand Pd complexes and activation of aryl bromides. Tetrahedron. 2004; 60(9): 2163-72. Doi:10.1016/j.tet.2003.12.012.

77. Chittilappilly PS, Sridevi N, Yusuff KKM. Ruthenium complexes of Schiff base ligands as efficient catalysts for catechol–hydrogen peroxide reaction. J Mol Catal A. 2008; 286: 92-7. Doi:doi:10.1016/j.molcata.2008.02.002.

78. Chittilappilly PS, Yusuff KKM. Synthesis characterization and biological properties of ruthenium (III) schiff base complexes derived from 3-hydroxyquinoxaline-2-carboxyaldehyde and salicylaldehyde. Ind J Chem. 2008; 47A: 848-53.

79. Sreekala R, Yusuff KKM. Thermal Decomposition Kinetics of Iron(III), Cobalt(II), Nickel(II) and Copper(II) Complexes of A Schiff Base Derived from Quinoxaline-2-Carboxaldehyde and Glycine. Rea Kinet Catal Lett. 1992; 48: 575-81.

80. Mayadevi S, Yusuff KKM. Synthesis and Characterization of some New transition Metal complexes of the Schiff bases derived from Quinoxaline-2-carboxaldehyde and 2-Aminophenol. Synth React Inorg Met-Org Chem. 1997; 27(2): 319-30. Doi:10.1080/00945719708000155.

81. Mayadevi S, Prasad PG, Yusuff KKM. Studies on some transition Metal complexes of Schiff bases derived from Quinoxaline-2-carboxaldehyde. Synth React Inorg Met-Org Chem. 2003; 33: 481-96. Doi:10.1051/SIM-12002000.

82. Belokon YN, Harutyunyan SR, Vorontsov EV, Peregudov AS, Chrustalev VN, Kochetkov K, Pripadchev DA, Sagyan AS, Beck AK, Seebach D. Nucleophilic addition to an achiral dehydroalanine Schiff base Ni(II) complex as a route to amino acids. A case of stereodetermining asymmetric protonation in the presence of TADDOL. ARKIVOC. 2004; (iii): 132-50.

83. Chapuis C, Jacoby D. Catalysis in the preparation of fragrances and flavours. Appl Catal A. 2001; 221(1-2): 93-117. Doi:10.1016/S0926-860X(01)00798-0.

84. Liu L, Rozenman M, Breslow R. Stereoselectivity in reactions of amino acids catalyzed by pyridoxal derivatives carrying rigidly-Attached chirally-Mounted basic groups—transamination, racemization, decarboxylation, retro-Aldol reaction, and aldol condensation. Bioorg Med Chem. 2002; 10(12): 3973-79. Doi:10.1016/S0968-0896(02)00334-6.

85. Hayashi H. Pyridoxal Enzymes: Mechanistic Diversity and Uniformity. J Biochem. 1995; 118(3): 463-73. Doi:10.1093/oxfordjournals.jbchem.a124931.

86. Singer RA, Carreira EM. Catalytic, Enantioselective Dienolate Additions to Aldehydes: Preparation of Optically Active Acetoacetate Aldol Adducts. J Am Chem Soc. 1995; 117(49): 12360-61. Doi:10.1021/ja00154a049.

87. Kim Y, Singer RA, Carreira EM. Total Synthesis of Macrolactin A with Versatile Catalytic, Enantioselective Dienolate Aldol Addition Reactions. Angew Chem Int Ed. 1998; 37(9): 1261-63. Doi:10.1002/(SICI)1521-3773(19980518)37:9<1261::AID-ANIE1261>3.0.CO;2-2.

88. Mandoli A, Pini D, Orlandi S, Mazzini F, Salvadori P. A first example of macromolecular Ti(IV) Lewis acid in the catalytic enantioselective Mukaiyama reaction. Tetra Asym. 1998; 9(9): 1479-82. Doi:10.1016/S0957-4166(98)00127-X.

89. Evans DA, Janey JM, Magomedov N, Tedrow JS. Chiral Salen–Aluminum Complexes as Catalysts for Enantioselective Aldol Reactions of Aldehydes and 5-Alkoxyoxazoles: An Efficient Approach to the Asymmetric Synthesis of syn and anti β-Hydroxy-α-amino Acid Derivatives. Angew Chem Int Ed. 2001; 40(10): 1884. Doi:10.1002/1521-3773(20010518)40:10<1884:AID-ANIE1884>3.0.CO;2-9.

90. Drozdzak R, Allaert B, Ledoux N, Dragutan I, Dragutan V, Verpoort F. Ruthenium complexes bearing bidentate Schiff base ligands as efficient catalysts for organic and polymer syntheses. Coordin Chem Rev. 2005; 249(24): 3055–74. Doi:10.1016/j.ccr.2005.05.003.

91. Mekewi MA. Salen Transition Metal Complexes as Catalysts for the Synthesis of Photostable Poly(methylmethacrylate). Int J Polym Mat Poly Biomat. 2006; 55(4): 219-34. Doi:10.1080/009140390927286.

92. Karame I, M Jahjah, Messaoudi A, Tommasino ML, Lemaire M. New ruthenium catalysts containing chiral Schiff bases for the asymmetric hydrogenation of acetophenone. Tetra Asymm. 2004; 15: 1569-81. Doi:10.1016/j.tetasy.2004.03.023.

93. Venkatachalam G, Ramesh R. Ruthenium(III) bis-bidentate Schiff base complexes mediated transfer hydrogenation of imines. Inorg Chem Commun. 2006; 9: 703-7. Doi:10.1016/j.inoche.2006.04.012.

94. Nishibayashi Y, Takei I, Vemara S, Hidai M. Extremely High Enantioselective Redox Reaction of Ketones and Alcohols Catalyzed by RuCl2(PPh3)(oxazolinylferrocenylphosphine). Organomet. 1999; 18(12): 2291-93. Doi:10.1021/om990210o.

95. Langer T, Helmchen G. Highly efficient new catalysts for enantioselective transfer hydrogenation of ketones. Tetra Lett. 1996; 37: 1381-84. Doi:10.1016/0040-4039(96)00011-1.

96. Faller JW, Lavoie AR. Catalysts for the Asymmetric Transfer Hydrogenation of Ketones Derived from L-Prolinamide and (p-CymeneRuCl2)2 or (Cp*RhCl2)2. Organomet. 2001; 20(24): 5245-47. Doi:10.1021/om010644v.

97. Cross DJ, Kenny JA, Houson I, Campbell L, Walsgrove T, Wills M. Rhodium versus ruthenium: contrasting behaviour in the asymmetric transfer hydrogenation of α-substituted acetophenones. Tetra Asymm. 2001; 12(12): 1801-06. Doi:10.1016/S0957-4166(01)00313-5.

98. Venkatachalam G, Ramesh R. Ruthenium(III) Schiff base complexes of [ONNO]-type mediated transfer hydrogenation of ketones. Inorg Chem Commun. 2005; 8(11): 1009–13. Doi:10.1016/j.inoche.2005.08.004.

99. Costa M, Pelagatti P, Pelizzi C, Rogolino D. Catalytic activity of Palladium(II) complexes with tridentate nitrogen ligands in the hydrogenation of alkenes and alkyenes. J Mol Catal A. 2002; 178(1-2): 21-6. Doi:10.1016/S1381-1169(01)00286-2.

100. Wu MH, Jacobsen EN. An Efficient Formal Synthesis of Balanol via the Asymmetric Epoxide Ring Opening Reaction. Tetra Lett. 1997; 38(10): 1693-96. Doi:10.1016/S0040-4039(97)00192-5.

101. Brandes BD, Jacobsen EN. Synthesis of enantiopure 3-chlorostyrene oxide via an asymmetric epoxidation-hydrolytic kinetic resolution sequence. Tetra. Asymm. 1997; 8(23): 3927-33. Doi:10.1016/S0957-4166(97)00568-5.

102. Nozaki H, Takaya H, Noyori R. The Reaction of Ethyl Diazoacetate with Styrene Oxide. Tetra Lett. 1965; 6(30): 2563-67. Doi:10.1016/S0040-4039(00)90208-9.

103. Nozaki H, Moriuti S, Takaya H, Noyori R. Asymmetric Induction in Carbenoid Reaction By means of A Dissymmepric Copper Chelate. Tetra Lett. 1966; 7(43): 5239-44. Doi:10.1016/S0040-4039(01)89263-7.

104. Evans DA, Keith AW, Mira MH, Margaret MF. Bis(oxazolines) as Chiral Ligands in Metal-Catalyzed Asymmetric Reactions. Catalytic, Asymmetric Cyclopropanation of Olefins. J Am Chem Soc. 1991; 113(2): 726-28. Doi: 10.1021/ja00002a080.

105. Noyori R. Asymmetric Catalysis in Organic Synthesis, ISBN: 978-0-471-57267-1. John Wiley and Sons: New York; 1994. p. 141 and references therein.

106. Noyori R. Enantiomeric isomerization of olefins. In: Asymmetric Catalysis in Organic Synthesis. ISBN: 978-0-471-57267-1. John Wiley and Sons: New York; 1994. p. 102.

107. Tang WJ, Hu XQ, Zhang XM. A new chiral ruthenium complex for catalytic asymmetric cyclopropanation. Tetra Lett. 2002; 43(16): 3075-78. Doi:10.1016/S0040-4039(02)00317-9.

108. Munslow IJ, Gillespie KM, Deeth RJ, Scott P. Bidentate carbenoid ester coordination in ruthenium(II) Schiff base complexes leading to excellent levels of diastereo- and enantioselectivity in catalytic alkene cyclopropanation. Chem Commu. 2001; 1638-39. Doi:10.1039/B104964J.

109. Salem IA, El-Sheikh MY, Zaki AB. Kinetics and mechanism of the decomposition of hydrogen peroxide catalyzed by Mn(II)-bis-salicylaldimine complexes. Monatsh Chem. 1995; 126: 393-9. Doi:10.1007/BF00813201.

110. Drozdzak R, Allaert B, Ledoux N, Dragutan I, Dragutan V, Verpoort F. Synthesis of Schiff base-Ruthenium complexes and their applications in catalytic processes. Adv Synth Catal. 2005; 347(14): 1721-43. Doi:10.1002/adsc.2004389.

111. Sato K, Aoki M, Ogawa M, Hashimoto T, Noyori R. A Practical Method for Epoxidation of Terminal Olefins with 30% Hydrogen Peroxide under Halide-Free Conditions. J Org Chem. 1996; 61: 8310–11. Doi:10.1021/jo961287e.

112. Sato K, Aoki M, Ogawa M, Hashimoto T, Panyella D, Noyori R. A Halide free method for olefin Epoxidation with 30 % Hydrogen peroxide. Bull Chem Soc Jpn. 1997; 70(4): 905–15. Doi:10.1246/bcsj.70.905.

113. Rudolph J, Reddy KL, Chiang JP, Sharpless KB. Highly efficient epoxidation of olefins using aq. H_2O_2 and catalytic methyltrioxorhenium/ Pyridine: Pyridine-Mediated ligand Acceleration. J Am Chem Soc. 1997; 119(26): 6189-90. Doi:10.1021/ja9706231.

114. Che CM, Huang JS. Metal complexes of chiral binaphthyl Schiff-base ligands and their application in stereoselective organic transformations. Coord Chem Rev. 2003; 242(1-2): 97-119. Doi:10.1016/S0010-8545(03)00065-1.

115. Nishinaga A, Yamato H, Abe T, Maruyama K, Matsuura T. Asymmetric induction in oxygenation of styrene catalyzed by cobalt schiff base complex. Tetra Lett. 1988; 29: 6309-12. Doi:10.1016/S0040-4039(00)82333-3.

For any question relates to this article, please reach us at: globalresearchonline@rediffmail.com

New manuscripts for publication can be submitted at: submit@globalresearchonline.net and submit_ijpsrr@rediffmail.com