

A REVIEW (PART B) – USE OF SCHIFF BASE TRANSITION METAL COMPLEXES AS A CATALYST

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Email: hocprc@yahoo.com. Dedicated to Dr. Zahra Noreen on the occasion of her birthday.

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ABSTRACT

Most of the metal complexes of Schiff bases illustrate soaring catalytic activity. This review goes over the main applications of Schiff bases and their complexes in chemical reactions as catalyst.

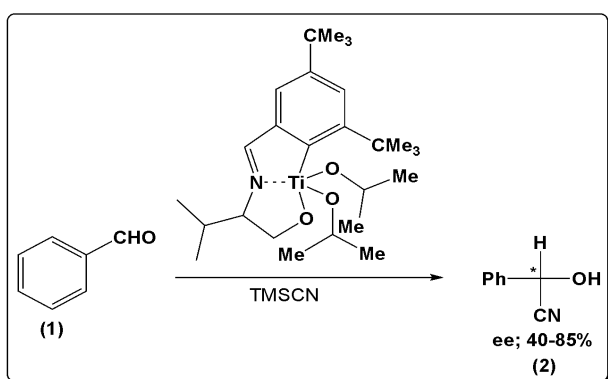
Keywords: Schiff base transition metal complexes; Hydroxylation; Oxidation; Epoxidation; Aldol condensation.

INTRODUCTION

A number of homogenous catalytic reactions involve Schiff base complexes which have a major role in such reactions and variation in the activity of such complexes is observed by alteration of metal ion, coordination site and the type of ligands. Catalytic activities of Schiff base metal complexes are abundantly found in literature. In this regard, more selective behavior of Schiff base complexes has been observed for a number of reactions like hydroxylation, oxidation, epoxidation and aldol condensation. A number of examples regarding catalytic activity of Schiff base complexes are discussed as under:

Oxidation reactions

A number of asymmetric chemical transformations employed ONO type chiral Schiff base ligands possessing ions of transition metals like zinc (II), titanium (IV), copper (II), vanadium (IV). Trimethylsilyl cyanohydrin (**1**) was achieved in 40-85 % enantioselectivity by the addition of benzaldehyde (**2**) to trimethylsilyl cyanide (Scheme 1)[1-2].



Scheme 1: Schiff base of trimethylsilyl cyanohydrins.

Baeyer-Villiger oxidation of 3-phenyl cyclobutanone was reported by Uchida and Katsuki with H₂O₂ or urea hydrogen peroxide adduct by employing cationic cobalt (III) salen complexes as catalyst[3]. Similarly cyclobutanone derivatives were converted to lactones with 69-78 % ee and 75-99 % yields by employing [Zr(salen)] catalysts in the presence of H₂O₂ as an oxidant by using Baeyer-Villiger oxidation. The oxidation of a range of ketone silyl enol ethers was reported by Reddy and Thoron by employing complexes (**3-4**) as catalysts in acetonitrile at room temperature which lead to the formation of α -hydroxyketones while an oxidant like iodosylbenzene was also employed[4]. The asymmetric oxidation of silyl ketene acetals was also catalyzed by complexes (**3**) with high enantioselectivity as described by Waldemar *et al.*[5].

The application of chiral Schiff base complexes was studied in enantioselective sulfide oxidations in 1986 by Nakajima *et al.*[6]. The enantioselectivity of about 42 % ee was achieved in the oxidation of methylphenyl sulfide to the corresponding sulfoxide by using oxovanadium (IV) complex (**5**) of tetradentate Schiff base. The asymmetric oxidation of sulphoxide was catalyzed by the oxovanadium (V) complex (**6**) which has tridentate amino acid derived ONO type Schiff base as ligand. The remarkable catalytic behavior for the oxidation of sulphides was observed for the complexes of salicylaldehyde and aminophenol derived Schiff base ligands (**7**) and significant oxidation of sulphides is also conducted in the presence of vanadyl acetylacetonate. Schiff base ligands (**8-10**) lead to the formation of vanadium catalysts and enantioselectivities associated with sulfoxidation were reported by Vetter and Berkessel[7]. This study was further expanded by Katsuki and coworkers[8] by employing vanadium as a metal and compound (**11**) as ligand (Scheme 2).

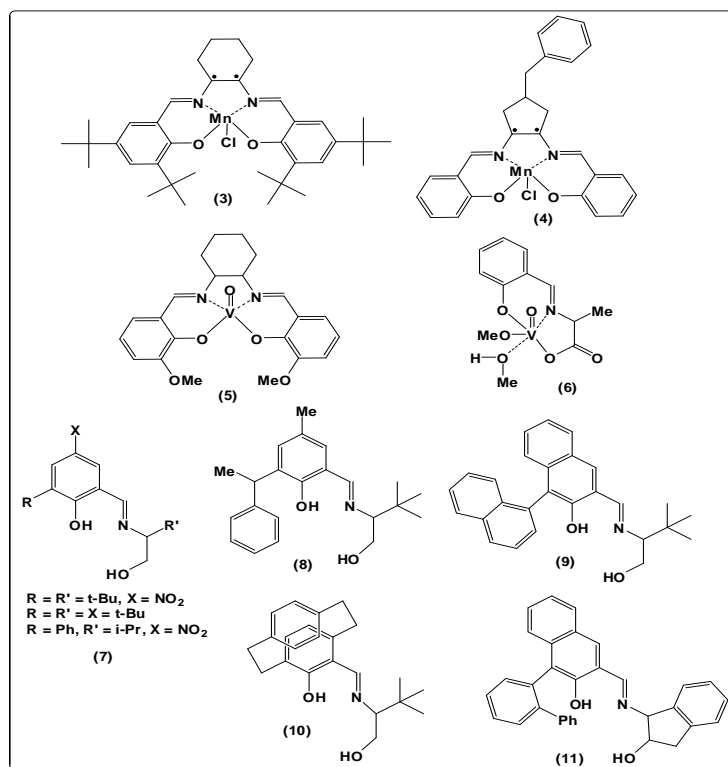
Baeyer-Villiger oxidation of 3-phenyl cyclobutanone (**12**) with urea hydrogen peroxide (UHP) adduct or H₂O₂ involves the active catalysts like complexes of binaphthyl chiral Schiff base and cobalt (III) (*R*)-[Co^{III}(L²)]SbF₆ (*n* = 1, 2, 4) and (*R*)-[Co^{III}(L²)I] (*n* = 2, 3) (Reaction 1 in Scheme 3). (*S*)-3-phenylbutano-4-lactone was produced by these reactions in dichloromethane with 69 % ee. The efficiency of catalysts was improved by the application of polar solvents like ethers and alcohols to give high enantioselectivity (60-79 %) except with catalysts of the type [Zr(salen)]. Baeyer-Villiger oxidation of cyclobutanone derivatives (**13-15**) also involves the activity of such catalysts to produce lactones in the presence of H₂O₂ as an oxidant in 69-78 % ee and 75-99 % yields (Reaction 2 in Scheme 3). Moreover, the enantioselectivity in Baeyer-Villiger oxidation reaction was enhanced significantly on replacing catalyst (*R*)-[Co^{III}(L²)I] with (*R*)-[Co^{III}(L²)I] (*n* = 3-5), and substituting UHP as oxidant instead of H₂O₂ (Reaction 3 in Scheme 3).

The unfunctionalized phenols and hydrocarbons were directly oxygenated in the presence of binuclear palladium Schiff base complex (**17**) which was found as effective catalysts[9-11]. Similarly, the hydroxylation of phenol was successfully carried out by dinuclear Schiff base complexes of copper (II) ions (**18**) (Scheme 4)[12].

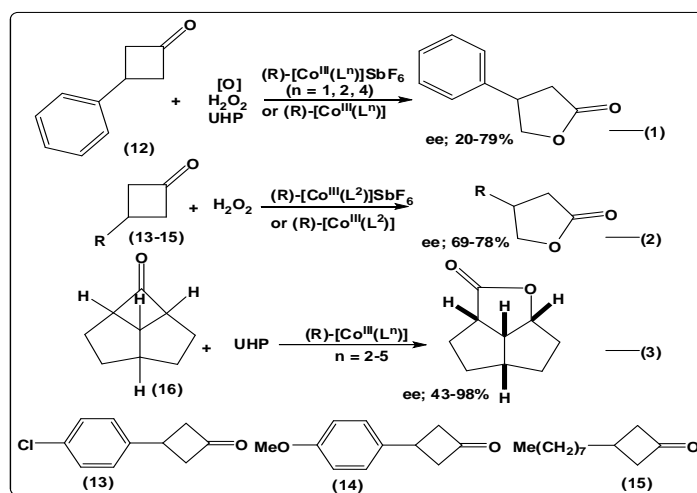
The oxidation of phenols and alcohols by employing dioxygen as oxidant was catalyzed by Co(salen) and its analogues (**19-23**)[13]. Literature also revealed the oxidation of olefins[14]. Co(salen) needs an axial ligand for being catalytically active and binding dioxygen (Scheme 5). The square planar coordination sphere of Co(salen) coordinates dioxygen orthogonally. The sixth coordination site is filled by the axial ligand, in contradiction to dioxygen. The Co(salen) catalyzed oxidation reactions mostly involve pyridine as axial ligand. However, pyrimidine and imidazoles are the other bases which have

also been used[15]. The use of modified salen structure is another way to give axial ligand which possesses additional nitrogen for coordinating axially in the frame of ligand (Scheme 5). Literature

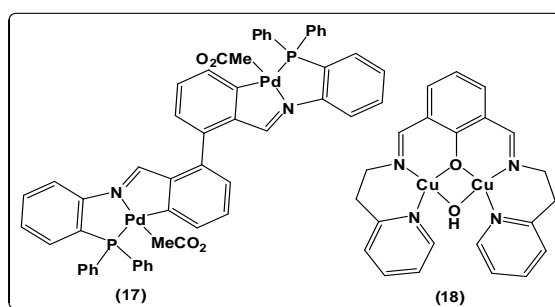
gives noticeably few examples of catalysis of hydrocarbon oxidation by the studies on ruthenium complexes containing salen-type Schiff base ligands[16].



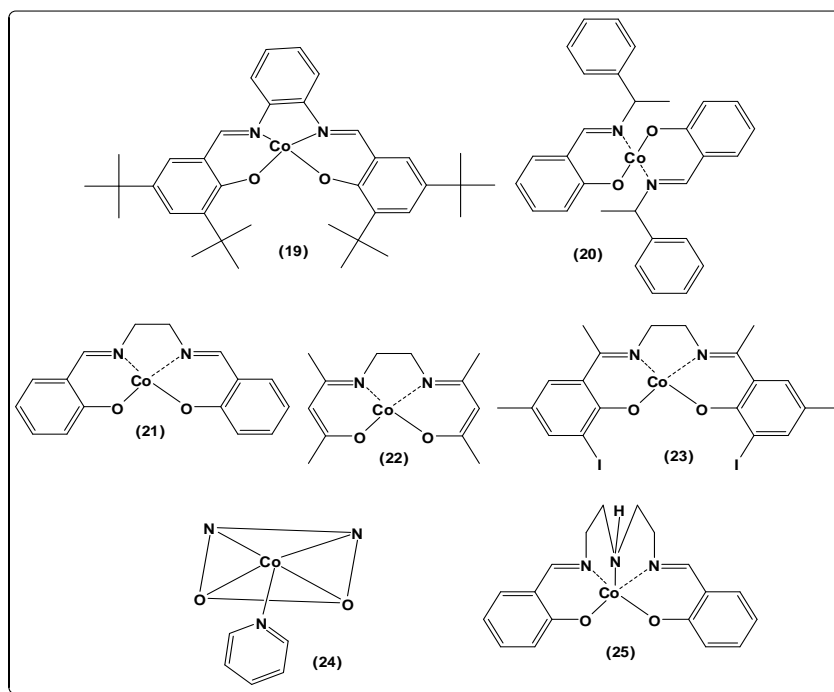
Scheme 2: Structures of Schiff base ligands and metal complexes used as catalysts in oxidation reactions.



Scheme 3: Schiff base complex catalyzed Baeyer-Villiger oxidation [105]. $L^1 = 6$ ($R^1 = R^2 = H$), $L^2 = 6$ ($R^1 = R^2 = F$), $L^3 = 6$ ($R^1 = R^2 = Cl$), $L^4 = 6$ ($R^1 = R^2 = Br$), $L^5 = 6$ ($R^1 = R^2 = I$).



Scheme 4: The complex palladium and copper (II) ions with binuclear Schiff base.

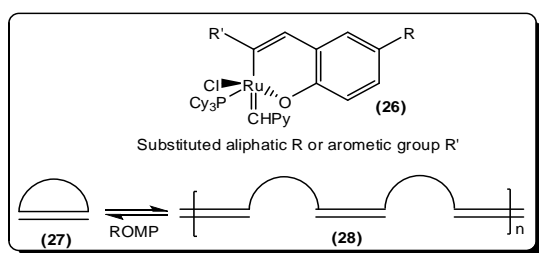


Scheme 5: Cobalt complexes of salen.

Ring opening polymerization reaction

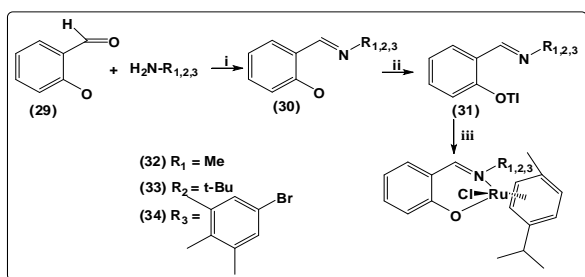
The synthesis of fine chemicals and macromolecular chemistry involve recently the use of ring opening metathesis polymerization (ROMP) (Scheme 6) which has emerged as an important tool. It was noted that olefin metathesis polymerization involved decoordination and coordination of 'onearm' of the bidentate Schiff base ligands [17-18] during the determination of catalytic activity of complexes (26).

During ring opening metathesis polymerization (ROMP) of cyclooctene (27) and norbornene (28), these complexes were found very active.



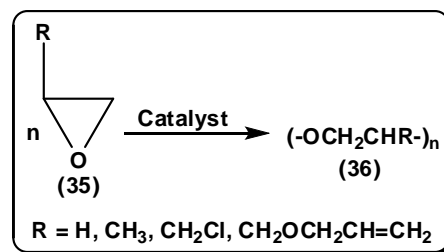
Scheme 6: Ring opening metathesis polymerization (ROMP).

The activity in atom transfer radical polymerization (ATRP) of a series of ruthenium Schiff base complexes (32-34) was carried out [19] in the presence of trimethylsilyldiazomethane (TMSD) (Scheme 7).



Scheme 7: Atom transfer radical polymerization (ATRP)

Similarly ring opening oligomerization or polymerization of epoxides is catalyzed by salen complexes (Scheme 8) [20].



Scheme 8: Ring opening oligomerization or polymerization of epoxides.

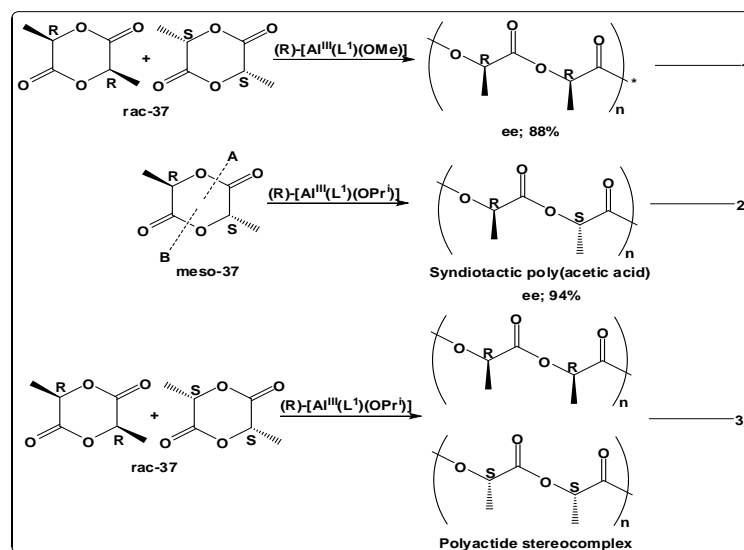
The ring opening polymerization of meso-lactides (37) to produce highly syndiotactic poly(acetic acid) with a 94 % conversion was carried out in a stereoselective manner by employing (Reaction 1 in Scheme 9) aluminium(III) binaphthyl chiral complexes and it has become possible on the basis of their resolution [21] (Reaction 2 in Scheme 9). The cyclic monomer containing two stereo centers can be prepared by this method via stereoselective ring opening polymerization [21]. Stereoselective poly(lactides) (Reaction 3 in Scheme 9) were obtained subsequently by employing aluminium (III) binaphthyl complexes as reported by Radano *et al.* [22]. Stereoselective poly(acetic acid) can be prepared directly from racemic lactides with this process easily which do not require combination of poly(lactides) with enantiopure (*R*)- and (*S*)-poly(acetic acid). Stereoselective polymerization of lactides is carried out by employing aluminium (III) complexes of binaphthyl chiral Schiff bases as catalysts and such type of catalysts opened meso-lactides (37) at site B preferentially. The polymerization produces heterotactic poly(acetic acid) (Reaction 3 in Scheme 9) by employing rac-[Al^{III}(L¹)(OiPr)] instead of (*R*)-[Al^{III}(L¹)(OiPr)] {L¹ = 6 (R¹ and R² = H)}. The mechanism for ring opening polymerization was proposed on the basis of stereochemistry of products [23].

Epoxidation reactions

A detailed discussion of chromium and manganese-salen complexes catalyzed asymmetric and achiral epoxidations of alkenes is reported by McGarrigle and Gilheany [24]. The mode of selectivity,

mechanism, intermediates and catalytic cycle were mainly addressed by them. Enantioselective epoxidation of unfunctionalised olefins can be carried out effectively by employing Mn-(salen)-type complexes, (Jacobsen's complex)[25-26]. Anyhow, Jacobsen's catalyst has been surpassed by the second-generation Mn-(salen) catalysts (**38**) launched by Katsuki and co-workers[27-29], in terms of activity and selectivity, but their applications are limited due to non-accessibility on synthetic scale. Zhao *et al.* synthesized manganese Schiff base chelate (**39**) which showed asymmetric

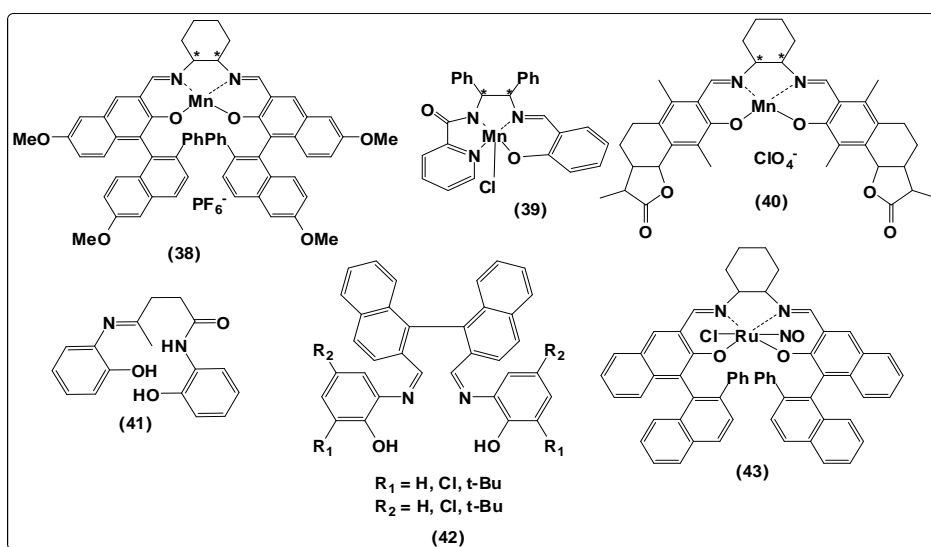
induction of moderate level (31-74 % ee) with higher turnover number upon epoxidation of dihydronaphthalene[30]. Manganese Schiff base complex (**40**) lead to poor asymmetric induction and very high yield upon epoxidation of various unfunctionalized olefins by Fernandez *et al.*[31]. Epoxidation of cyclohexene in the presence of iodobenzene was catalyzed by ruthenium complexes of Schiff base N,N' -bis(7-methyl-2-pyridylmethylene)-1,3-diiminopropane (bpydip) such as $\text{trans-[RuCl}_2(\text{bpydip})]$ and $\text{trans-[Ru(OH)}_2(\text{bpydip})](\text{PF}_6)_2$.



Scheme 9: The ring opening polymerization of racemic lactides.

Schiff bases, N,N' -(2-hydroxyphenyl)acetylaldimine and N -(2-hydroxyphenyl)acetamide were used by Kureshy *et al.*[32] for the preparation of nickel (II) complexes (**41**), which perform a catalytic role for the epoxidation of olefins like *cis*- and *trans*-stilbenes, cyclohexene, indene, 1-hexene with sodium hypochlorite. The condensations of aromatic aldehydes with amines like 2,2'-diamino-1,1'-binaphthyl or 2-amino-2'-hydroxy-1,1'-binaphthyl was

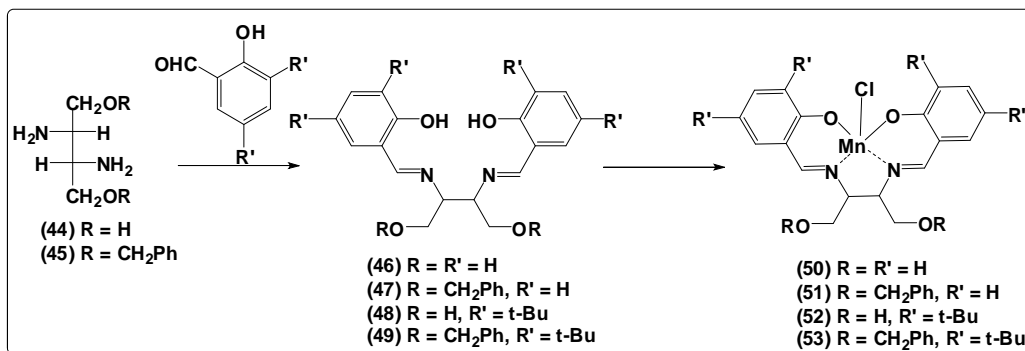
potentially carried out by employing tetradentate binaphthyl N_2O_2 Schiff bases (**42**). Asymmetric epoxidation of unfunctionalized alkenes is wide application of metal complexes in the field of catalysis. The synthesis and catalytic application of ruthenium (II) complex (**43**) was first reported by Katsuki and coworkers[33-34], possessing chiral tetradentate (N_2O_2) Schiff base ligand in the presence of various terminal oxidants (Scheme 10).



Scheme 10: Epoxidation of unfunctionalized compounds.

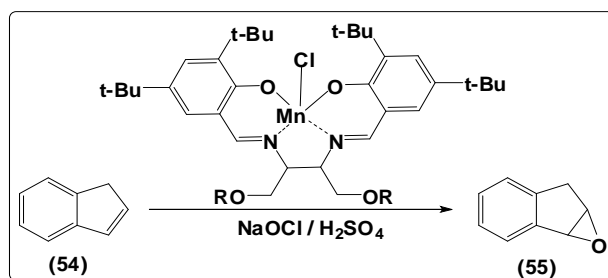
The enantioselective epoxidation of alkenes is also catalyzed by chiral manganese (II) complexes of 1,2-bis(salicylideneamino) cyclohexane. Similarly, olefin epoxidation involves the use of manganese (II) complexes of bis(2-pyridinaldehyde) propylenediamine and bis(2-pyridinaldehyde)ethylenediamine ligands but the presence of PhIO oxidant leads to a reasonable selectivity. A new class of salen type

Schiff base ligands for complexation with transition metals and heavy metals was provided by compounds (**46-49**) which were achieved from compound (**44-45**). The complexes (**50-53**) corresponding to the complexes of Schiff base ligands (**46-49**) with manganese (III) (Scheme 11) were employed in asymmetric epoxidation of indene as chiral catalysts (Scheme 12).

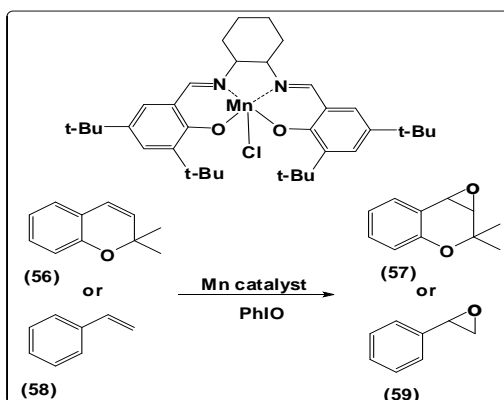


Scheme 11: Chiral catalysts of Mn (II) complexes with salen type Schiff base ligands.

The asymmetric epoxidation of conjugated olefins was catalyzed by manganese (III) (Scheme 13).

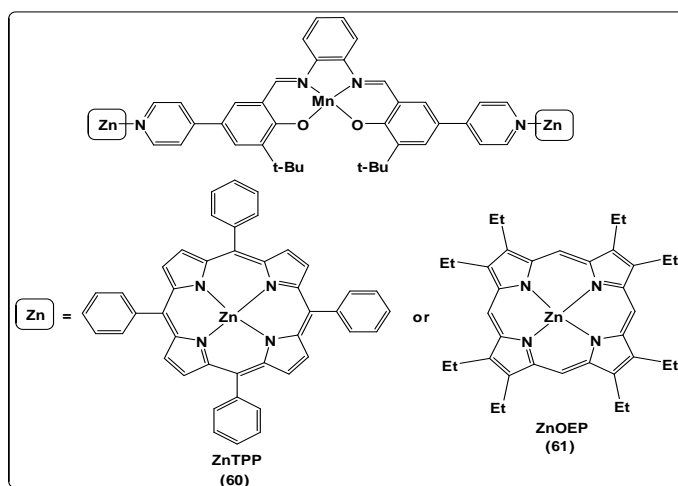


Scheme 12: Asymmetric epoxidation of indene.



Scheme 13: Asymmetric epoxidation of conjugated olefins.

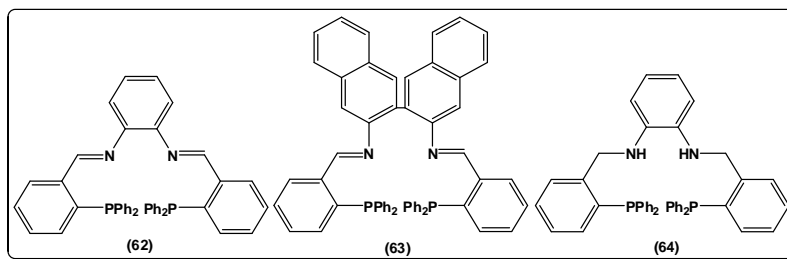
The stable supramolecular complexes were obtained by the addition of bulky Lewis acids such as zinc tetraphenylporphyrin (ZnTPP) (60) or (ZnOEP) (61) and as a consequence manganese (III) salen complexes showed enhanced activity[35] (Scheme 14).



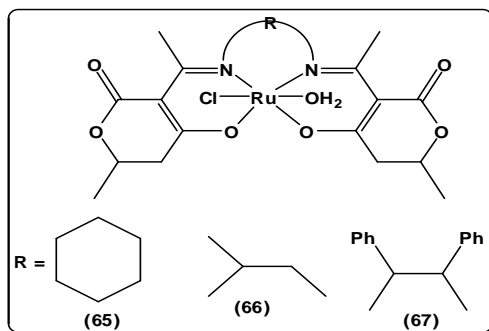
Scheme 14: Structures of (ZnTPP) (60) and (ZnOEP) (61).

The asymmetric epoxidation was carried out by Mezzetti and co-workers[36-37] by making use of ruthenium (II) complexes of chiral tetradentate Schiff base ligands possessing N_2P_2 donors like compounds (62-64) and terminal oxidant employed during the reaction was hydrogen peroxide (Scheme 15).

The catalytic activity of styrene and substituted styrenes in the asymmetric epoxidation was performed by ruthenium (III) complexes (65-67) of the tetradentate Schiff base ligands achieved by condensing various diamines and 3-acetyl-6-methylpyran-2,4-dione[38] (Scheme 16).



Scheme 15: N_2P_2 -Chiral tetradentate Schiff base ligands.

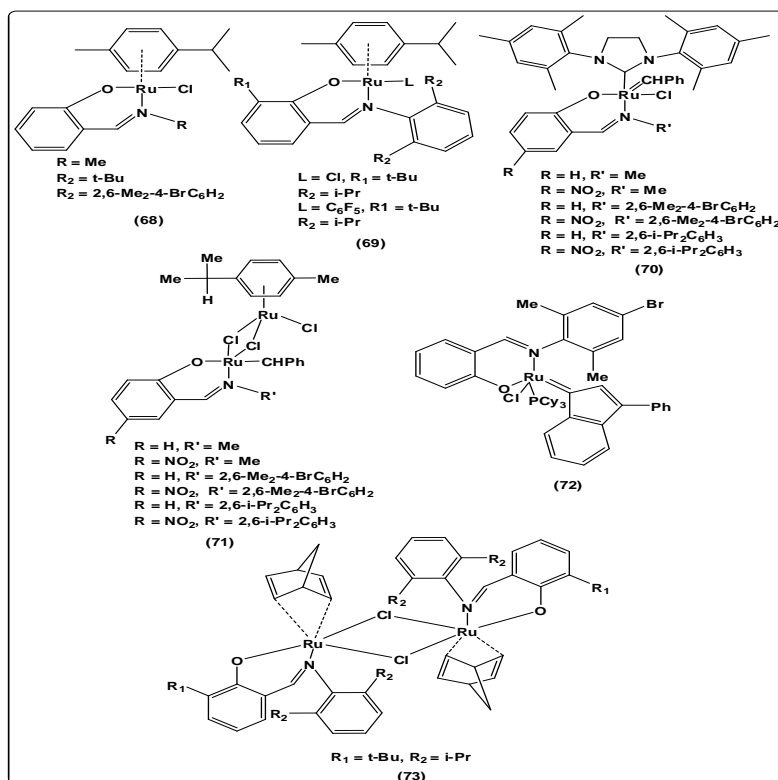


Scheme 16: Ru (III) complexes of tetradentate Schiff base ligands.

Polymerization reactions

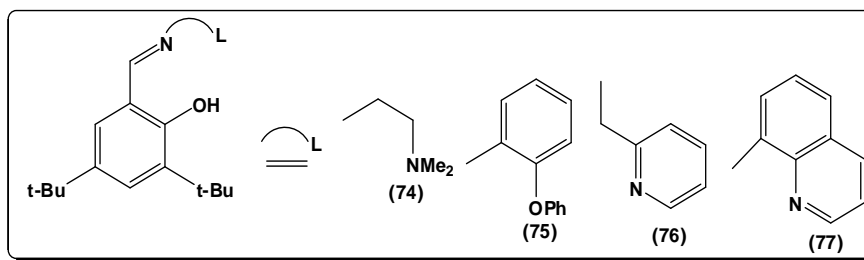
Literature is full of examples in which complexes of Schiff base ligands were employed as catalysts especially in case of polymerization reactions. A detailed discussion of ring opening

metathesis polymerization and atom transfer radical polymerization of various substrates using Ru-catalysts possessing Schiff base ligand of salicylaldiminato-type (68-73) was given by Verpoort *et al.*[39] (Scheme 17).



Scheme 17: Ru-catalysts of salicylaldiminato-type Schiff base ligand.

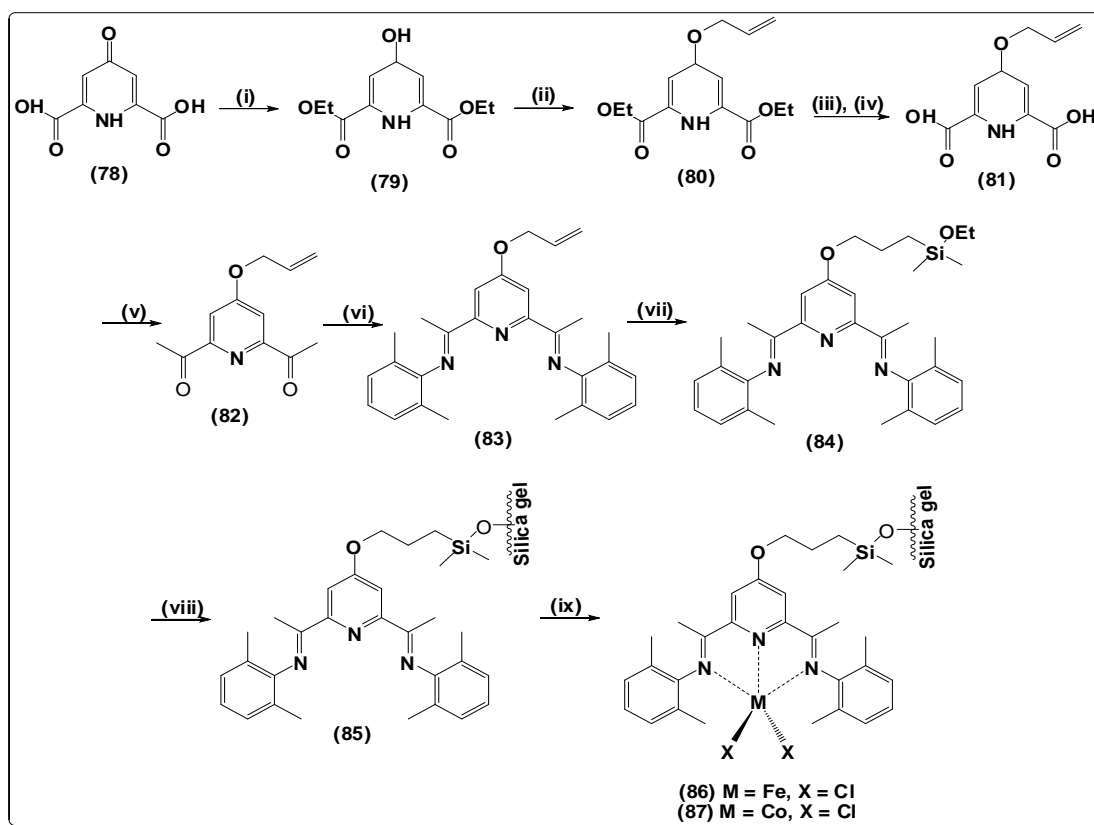
The polymerization of ethylene was catalyzed by a series of complexes of tridentate Schiff base ligands (**74-77**) with aluminium[40] (Scheme 18).



Scheme 18: Tridentate Schiff base ligand complex of aluminium for polymerization of ethylene.

The polymerization of ethylene involve very high activity exhibited by cobalt (II) and iron (II) complexes of pyridyl bis(imide) complexes (**78-87**) (Scheme 19)[41-43] and ortho substitution above or below the central metal atom influenced the molecular structure of resulting polyethylenes[44]. The

polymerization of complexes of nickel (II) and palladium (II) with ethylene lead to molecular chain walking free polyethylenes of high density and linear structure. The polymerization of ethylene on a commercial scale involves these catalysts, residing on an inorganic support[45].



Scheme 19: Polymerization of ethylene by cobalt (II) and iron (II) complexes of pyridyl bis(imide) complexes.

The effective catalysts in ethylene polymerization were salicylaldimino complexes of zirconium which were considered in certain cases as radical decomposition promoters[46]. The controlled radical polymerization of the methylmethacrylate monomer to give polymethylmethacrylate was conducted in presence of Cr (III) and Ni (II) salen complexes as catalysts[47].

Hydrogenation reactions

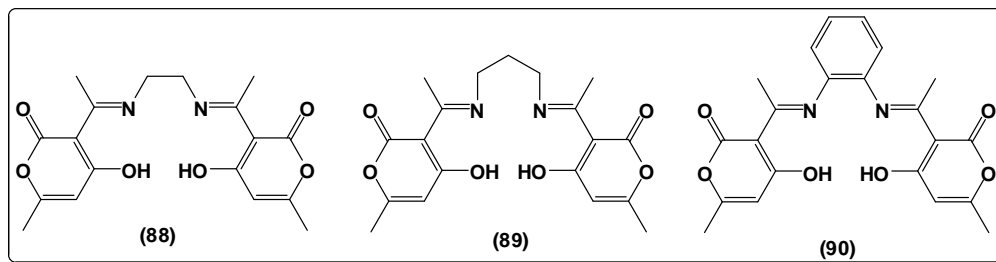
Asymmetric reduction of dialkyl ketones was carried out by transition metal complexes of Schiff base which were proven as efficient catalysts[48]. Ruthenium (III) complexes with Schiff base compounds with general formula $[RuX(EPh_3)(LL')]$, where X = Cl or Br, E = P or As and $LL' = [ONNO]$ donor of the heterocyclic Schiff base ligands (**88-90**) were employed as catalysts in the transfer hydrogenation of aromatic and aliphatic ketones in the presence of potassium hydroxide and isopropanol (Scheme 20)[49].

Ruthenium (III) bis-bidentate Schiff base complexes mediated transfer hydrogenation of imines to amines was reported by Venkatachalam and Ramesh[50].

Costa *et al.*[51] studied the catalytic activity of Pd (II) complexes of Schiff bases possessing nitrogen donors during hydrogenation of alkenes and alkynes under mild conditions (with 1 atm dihydrogen pressure at 40 °C). In this regard, two examples of representatives are shown below (**91-92**). A very efficient catalytic activity is exhibited by mono and dinuclear Pd (II) complexes of Schiff bases possessing t-butyl groups on the salicyl ring with steric constraints towards reduction of cyclohexene and nitrobenzene. Asymmetric transfer hydrogenation of methyl aryl ketones with 2-propanol as the hydrogen donor was carried out by employing in situ prepared ruthenium complexes of the chiral PNO Schiff bases (**93**), obtained from (R)-1-[(S)-2-(diphenylphosphino)ferrocenyl], substituted salicylaldehyde and ethylamine and $Ru(DMSO)_4Cl_2$. Karame *et*.

al.[52] synthesized a series of chiral N₄-Schiff bases, having sulfonamide or amine functionalities. The interesting results in the acetophenone hydrogenation were observed by using these Schiff

bases coupled with ruthenium. The hydrogen pressure (30 bar) employed at room temperature for conducting asymmetric hydrogenation in the presence of in situ produced chiral catalyst.



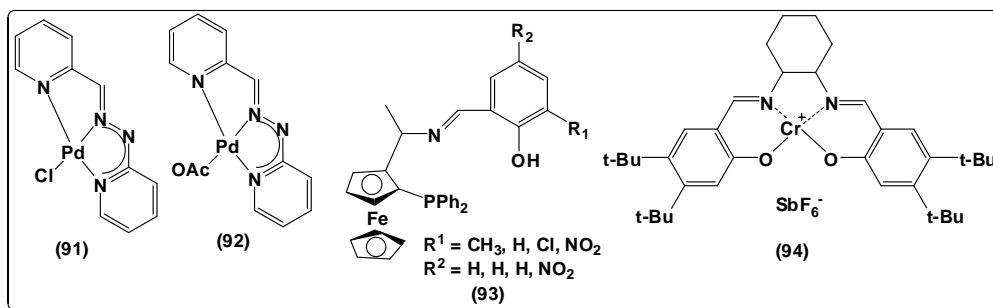
Scheme 20: (ONNO)-donor heterocyclic Schiff base ligands.

Miscellaneous applications

Schiff base complexes are also involved in the catalysis of certain reactions in addition to three major types of above mentioned catalytic reactions. Asymmetric Diels-Alder reaction of 3-(2-propenoyl)-2-oxazolidinone with cyclopentadiene involves the catalytic role of lanthanum (III) complexes of chiral Schiff bases[53]. The acylation of 4-furyl-4-N-benzylaminobut-1-enes with maleic anhydride catalyzed by Schiff bases produced 4-oxo-3-aza-10-oxatricyclo[5.2.1.0]dec-8-ene-6-carboxylic acid through intramolecular Diels-Alder reaction of furan via amide

formation[54]. Chromium (III) complexes of Schiff bases (94) were also used as catalysts in Diels-Alder reactions and are a good addition to new class of enantiomerically enriched Schiff bases (Scheme 21).

The asymmetric hetero-Diels-Alder reaction between [(2-chlorobenzoyl)oxy]-acetaldehyde and 1-methoxy-3-[(trimethylsilyl)oxy]buta-1,3-diene was carried out by Jacobsen *et al.*[55] in the presence of 2 mol % Cr(salen) and a noncoordinating etheral solvent was employed at 230 °C and 4 Å molecular sieves were used for drying.



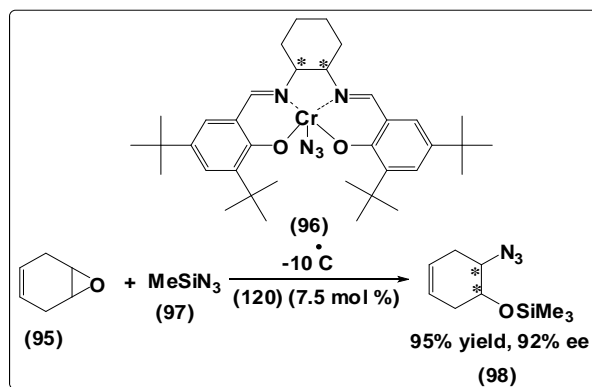
Scheme 21: N-donor complexes of Pd (II) (91-92), PNO-donor Schiff base ligand (93) and ONNO-donor Cr (III) complexes of ligand (94).

The aldol addition/acyl transfer reactions between 5-methoxyoxazoles and aldehydes were performed in the presence of aluminum (III) chiral complexes of binaphthal Schiff base ligand, which resulted in corresponding (4*S*, 5*S*)- oxazoline products with 60 % turnover number and 98 % ee. The reaction between 5-methoxyoxazoles and benzaldehydes actively involves the complexes of Schiff bases with aluminum (III) to produce optically active cis-oxazoline adducts with >99 % ee[56].

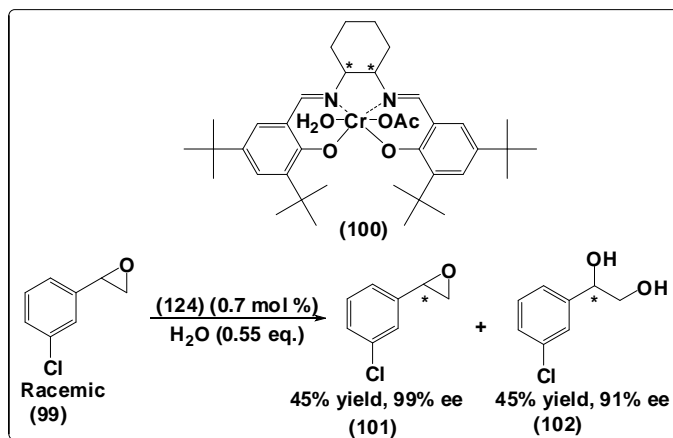
Jacobsen's group[57]carried out the ring-opening of cyclohexa-1,4-diene monoepoxide (95) in 92 % enantiomeric excess in the presence of 7.5 mol % of compound (96) under solvent free

conditions and azidotrimethylsilanolate (97) to produce azido silyl ether (98) (Scheme 22).

The Co(salen) complex (100) was discovered by Jacobsen[58] which was active in the kinetic and hydrolytic resolution of racemic epoxides that provides an access in high enantiomeric purity for terminal epoxides and diols (Scheme 23). It was not easy to realize the synthesis of Ru(salen) without the nitrosyl group until it was reported by Nguyen *et al.*[59]that very efficient catalysts for cyclopropanation of olefins are ruthenium (II) salen complexes. The nitrosyl precursors were utilized for realizing the synthesis of Ru(salen)[60].

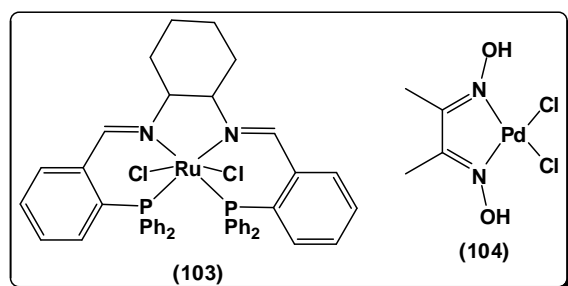


Scheme 22: Ring opening of cyclohexa-1,4-diene monoepoxide.



Scheme 23: The kinetic and hydrolytic resolution of racemic epoxides by Co(salen) complex.

Asymmetric cyclopropanation of styrene with ethyldiazo acetate was carried out by activating N_2P_2 -Ru (II) complexes (**103**) with silver triflate but it was observed that it resulted in very low enantioselectivity (Scheme 24).



Scheme 24: N_2P_2 -Ru (II) complex (**103**) and N_2 -Pd (II) complex (**104**).

The complexes of nitrogen Schiff base ligands with Pd (II) exhibited higher catalytic activity than that of commercially used phosphene Schiff base complexes in Heck reaction[61]. In this regard, Mizoroki-Heck reaction was employed to get high yields of the *E*-cinnamates and *E*-stilbenes with dimethyl glyoxime, complexes of Pd (II) (**104**) salen, 8-hydroxyquinoline and other ligands like picolinic acid (Scheme 24).

The transition metal complexes of Schiff base also find wide application in catalysis, in addition to the homogeneous catalytic reaction[62-64]. Among these zeolites encapsulated Schiff base complexes and polymer supported play a key role in heterogeneous catalysis[65-68]. Most of the salicylaldehyde derived Schiff base complexes have been mentioned above. It seems that the field of catalysis is based on various metal complexes including complexes of Schiff base with metals. The most important aspect of Schiff bases complexes is based on the fact that changes in properties are observed by changing the portion of Schiff base. The petroleum refining process involves transition metal complexes with 2,2-bipyridine and 1,10-phenanthroline[69]. The level of copper in blood and urine influences the pregnancy disorders, nephritis leprosy, hepatitis, anemia and leukemia in children and this fact was reported by Popova and Berova[70]. Non linear optical (NLO) properties were exhibited by metal complexes of Schiff base obtained from *o*-hydroxy benzaldehyde or its phenylazoderivative and tetradentate precursor 1-phenylbutane-1,3-dione mono *S*-methylisothiosemicarbazone. It was observed that NLO response strongly depends upon the electronic configuration of the metal center by a comparison between complexes of a variety of metals with the same ligand i.e., phenylazo-substituted ligand. The use of Schiff bases type chelating ligands with Zn (II) complexes as an effective emitting layer has been reported by researchers[71]. Moreover, complexes of benzothiazoles, which are composed of benzothiazolines in oxidized forms, with Zn (II) exhibit

luminescence[72]. The complexes of N_2S_2 -Schiff base ligands with Zn (II) and Cd (II) constitute a new class of luminescent compounds and fine tuning of the emission wavelength can be achieved by careful derivatization of the substituents on the pendent phenyl rings. A benzofuran derivative is found in Baker's yeast which prevents haemolysis of red cells in vitamin E deficiency and haemorrhagic liver necrosis in rats[73]. In nuclear medicine, amino acid Schiff base complexes obtained from 2-hydroxy-1-naphthaldehydes are very effectively used as radiotracers[74]. Many fundamental biological functions are due to macrocyclic Schiff bases of dithiocarbamic acid like transport of oxygen and photosynthesis in respiratory systems of mammals and other species[75].

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