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Coordination Chemistry Reviews 252 (2008) 1420–1450

COORDINATION CHEMISTRY REVIEWS

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Review

Catalytic activities of Schiff base transition metal complexes

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Received 29 November 2006; accepted 7 September 2007
Available online 14 September 2007

Contents

Abstract

Many Schiff base complexes of metal ions show high catalytic activity. Chiral Schiff base complexes are more selective in various reactions such as oxidation, hydroxylation, aldol condensation and epoxidation. The catalytic activity of metal complexes of binaphthyl, binaphthol and their combinations with salen Schiff base is presented in this review. The pyridyl bis(imide) and pyridine bis(imine) complexes of cobalt(II), iron(II)

Abbreviations: FI, phenoxy imine; en, ethylene diamine; MAO, methylaluminiumoxane; ROMP, ring opening metathesis polymerization; TMSD, trimethyl silyl diazomethane; ATRP, atom transfer radical polymerization; LDHs, layered double hydroxides; DTBP, 2,6-di-*tert*-butylphenol; DTBQ, 2,6-di-*tert*-butyl-4,4′-benzoquinone; $ScCO_2$, supercritical carbon dioxide; UHP, urea hydrogen peroxide; *t*-BHP, *tert*-butyl hydro peroxide; ZnTPP, zinc tetraphenylporphyrin; LA, Lewis acid; CMTBS, 3-*t*-Bu-5-(chloromethyl)-2-hydroxybenzaldehyde; MTS, micelles templated silica; SIB, ship in bottle.

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doi:10.1016/j.ccr.2007.09.005

ions have been used as catalysts in the polymerization of ethylene and propylene. The phenoxy-imine (FI) complexes of zirconium, titanium and vanadium and Schiff base complexes of nickel(II) and palladium(II) were also used as catalysts in the polymerization of ethylene. Schiff base complexes of metal ions were catalytic in ring opening polymerization processes at low temperature. Schiff base complexes also catalyzed the oxidation of sulfides, thioanisoles, aldehydes, phenol and styrene. Schiff base complexes in super critical carbon dioxide ($ScCO_2$) and in the presence of polar solvents were active catalysts. Schiff base complexes showed significant activity in catalyzing allylic alkylations, hydrosilation, the decomposition of hydrogen peroxide, isomerization, and annulation and carbonylation reactions. The high thermal and moisture stabilities of many Schiff base complexes were useful attributes for their application as catalysts in reactions involving at high temperature.

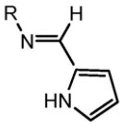
Keywords: Schiff base complexes; Catalysis; Enantioselectivity; Transition metals

1. Introduction

Schiff base ligands are easily synthesized and form complexes with almost all metal ions. Many Schiff base complexes show excellent catalytic activity in various reactions at high temperature (>100 °C) and in the presence of moisture. Over the past few years, there have been many reports on their applications in homogeneous and heterogeneous catalysis, hence the need for a review article highlighting the catalytic activity of Schiff base complexes realized. Schiff base catalyzed reactions are summarized here for the period 1995–2004. The interest in polymerization of olefins has increased recently due to the observed catalytic activity of Schiff base complexes in synthesis of commercially important branched [1,2] and linear polyethylenes [3–14]. The ring opening polymerization of cycloalkenes with transition metals such as tungsten, molybdenum and ruthenium in the presence of alkylating agents such as R_4Sn or $RAlCl_2$ is possible at high temperature without any control on molecular weight of polymers. But Schiff base complex catalyzed ring opening polymerization of cycloalkenes at low temperature provided a control on the molecular weight of the polymers [15,16] without any side reaction. The oxidation of hydrocarbons using Schiff base complexes has been a field of academic and industrial interest to analyze the catalytic activity of various metal complexes [17–21]. The ring opening of large cycloalkanes is usually a difficult process but Schiff base complexes of cobalt(II) [22] and chromium(III) [23] were effective in these reactions with significant enantioselectivity. Phosphine substitution in *N*-heterocyclic carbene Schiff base ligand has enhanced ring closing metathesis reaction to synthesize functionalized olefins [24]. Schiff base complexes showed significant applications in reduction of ketones to alcohols [25] and alkylation of allylic substrates [26–28]. The phosphine Schiff base complexes also showed improved enantioselectivity in hydrosilation reactions [29]. The chiral Schiff base complexes of salen [30] and binaphthyl were used as efficient catalysts in Michael addition reaction. Although the heteroannulation reaction is reported using transition metal complexes [31–33] a new catalytic route for annulation reaction using Schiff base complexes has been an area of current research [34]. Schiff base complexes showed catalytic activity in carbonylation of alcohols and alkenes at low pressure to produce α-arylpropionic acid and their esters [35–38], which are used as non-steroidal anti-inflammatory drugs. In addition to monometallic, the bimetallic Schiff base complexes also showed catalytic activity in carbonylation reactions [39]. The Heck reaction, an industrially useful process to synthesize fine chemicals and pharmaceutical, was successfully catalyzed using Schiff base complexes [40–44]. The complexes of nickel(II) and copper(II) ions have increased enantioselectivity in alkylation of enolates [45–51]. The enantiomeric synthesis of aziridines and amides with chiral metalolloporphyrins was moderate [52–55] but improved in the presence of Schiff base complexes of copper(II) and manganese(III) [56]. The isomerization of norbornadiene to quadricyclane was significantly catalyzed using diimine complexes of rhodium [57–58]. These interconversions were useful for the storage of solar energy. The aluminium–salen Schiff base complexes were also used in catalyzing the addition of hydrogen cyanide to *N*-allylbenzaldimine, which showed significant enantiomeric excess [59]. The enantioselectivity in the cyclopropanation reactions was modest; hence, attempts were also made to improve enantioselectivity in the cyclopropanation reactions using Schiff base complexes as catalysts [60–62]. The optically active cyanohydrins are widely used in the synthesis of drugs and pesticide. These cyanohydrins were synthesized successfully reacting trimethyl silylcyanide (TMSCN) with aldehydes in the presence of Schiff base complexes of transition metal ions [63–65]. Schiff base complexes also played a significant role in desymmetrization of *meso* compounds with significant yield and enantiomeric excess [66]. The homogeneous chiral lanthanum(III) Schiff base complexes showed catalytic activity in asymmetric Diels–Alder reactions [67] and product yield and enantioselectivity were influenced by the nature of catalysts [68]. These studies are indicative that Schiff base complexes are potential catalysts to influence the yield and selectivity in chemical transformations; hence in this review, an attempt has been made to critically analyze and discuss the role of Schiff base complexes in various reactions.

2. Schiff base ligands

Schiff base ligands are typically formed by the condensation of primary amines and aldehydes **1**–**3**. The resultant imines ($R_1HC=N–R_2$) participate in binding with metal ions via nitrogen lone pair electrons. Like aldehydes, the ketones are also able to form Schiff base ligands ($R_1R_2C=N–R_3$), although Schiff base ligand with ketones are formed less readily than with aldehydes.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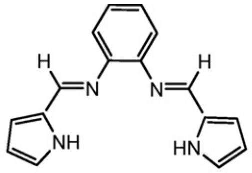
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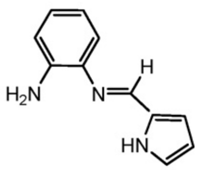
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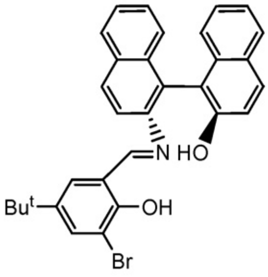
The mono-, di-, tri- and multi-dentate chelating Schiff base ligands are designed according to the binding environments of metal ions. The metal complexes of chiral Schiff base ligands showed stereoselectivity in organic transformation, hence the synthesis of chiral complexes become an important area of current research in coordination chemistry. The chiral binaphthyl Schiff base ligands **4–6** were potentially valuable in various metal mediated catalytic reactions [69].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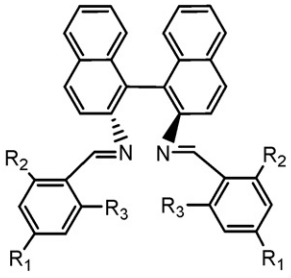
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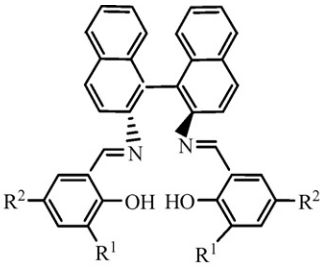
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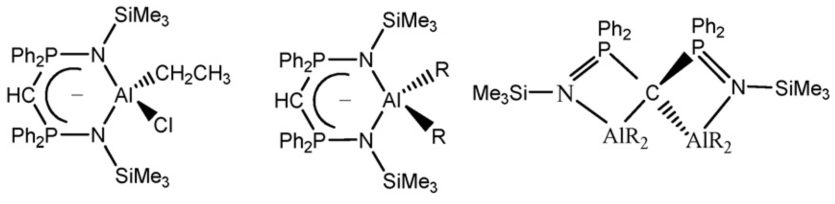
3. Schiff base complex catalyzed reactions

Schiff base complexes of transition metal ions are efficient catalysts both in homogeneous and heterogeneous reactions and the activity of these complexes varied with the type of ligands, coordination sites and metal ions. The catalytic activity of metal complexes has been analyzed critically in various reactions as given below.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8, R = Me; 9, R = ^{i}Bu

10, R = Me; 11, R = ^{i}Bu

Structures of aluminum methandiide **7-11** as polymerization catalyst.

3.1. Polymerization reaction

The polymerization reactions are catalyzed with various catalysts and based on experimental observations; the following conditions apply to the efficient use of catalysts in the polymerization of different monomers.

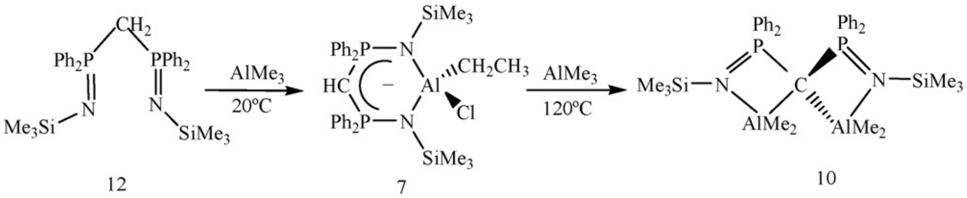
(I) Catalyst must have high olefin-insertion ability.
(II) Catalyst must have two available *cis*-located sites for polymerization.
(III) Catalyst must be stable enough under the usual polymerization conditions.

The polymerization of olefins was catalyzed efficiently using aluminum bis(iminophosphorano) methanide complexes **7–11** [70]. In these complexes **7–11**, the spiro-cyclic carbon center was connected by two AlMe$_2$ units and coordinated further by imino nitrogen. These complexes were formed at high temperature by the reaction of bis(iminophosphorano) methane **12** with AlMe$_3$ (Scheme 1)but low temperature reaction with equimolar stoichiometry yielded bis(iminophosphorano) methanides, which were converted to diide complexes [70–72]. Similarly a butylated aluminum precursor produced complex **11**, which was also used as catalyst to copolymerize ethylene and 1-octene monomers under mild catalytic conditions. The catalytic activity of complex**11** was reduced when substituent R was a butyl group. The observed catalytic activity of complex **11** was indicative that non-transition metal complexes might be used as catalysts in the polymerization of olefins [73].

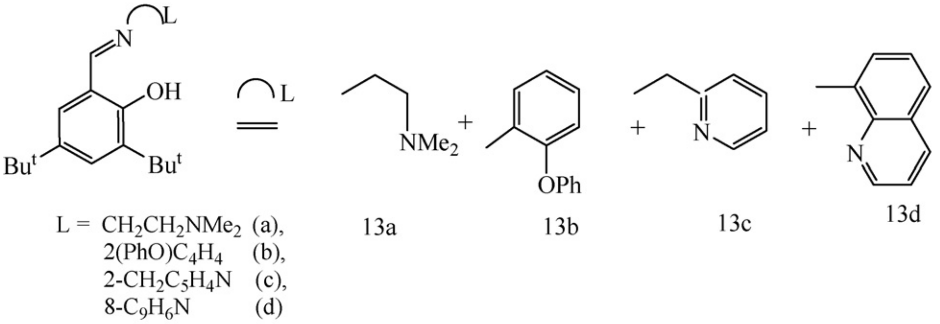
A series of Schiff base ligands **13a–d** were prepared in good yield (>80%) via an imine condensation process (Scheme 2) [74] and used in ethylene polymerization [73].

The tridentate ligand **13** on treating with Me$_3$Al in toluene at room temperature produced dimethyl complexes [3,5-Bu^t-2-(O)C$_6$H$_2$CH = NL] AlMe$_2$ **14** with elimination of methane (Scheme 3), which on reacting with B(C$_6$F$_5$)$_3$ produced the cationic system [(3,5-Bu^t-2-2-(O)C$_6$H$_2$CH = NL)-AlMe]$^+$ **15** able to catalyze the polymerization of ethylene [73].

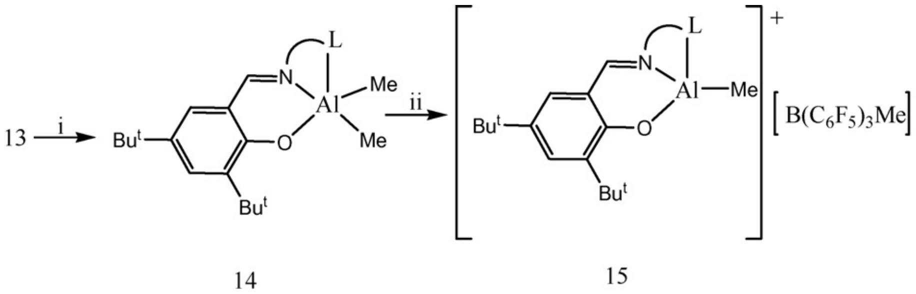
The pyridyl bis(imide) complexes **16–25** (Scheme 4) of cobalt(II) and iron(II) exhibited high activities in the polymer-



Scheme 1. Synthesis of aluminum bis(iminophosphorano) methane catalyst [70].



Scheme 2. Synthesis of Schiff base ligands (**13a**–**13d**) [74].



Scheme 3. Synthesis of aluminum Schiff base complex [73]: (i) $AlMe_3$, toluene; (ii) $B(C_6F_5)_3$, CD_2Cl_2 or toluene.

ization of ethylene [75–77] and the molecular structure of the resulting polyethylenes was influenced by the ortho substitution above and below the metal center [76–78].

Ethylene polymerization with complexes of nickel(II) and palladium(II) produced linear and high-density polyethylenes without molecular chain walking [76]. These catalysts, residing on an inorganic support, were used in the commercial scale polymerization of ethylene [79].

The fourth group of metal complexes **26–30** of phenoxy-imine (FI) were efficient catalysts in the polymerization of ethylene at atmospheric pressure. These complexes showed high activity in the presence of MAO as a cocatalyst. Amongst these catalysts, the zirconium FI catalyst was exceptionally active [80]. The complexes **26–27** were active at 30 min whereas, complexes **28–30** showed their activity within a period of 5 min (Table 1).

Table 1
Polymerization of the ethylene in the presence of FI catalysts [80]

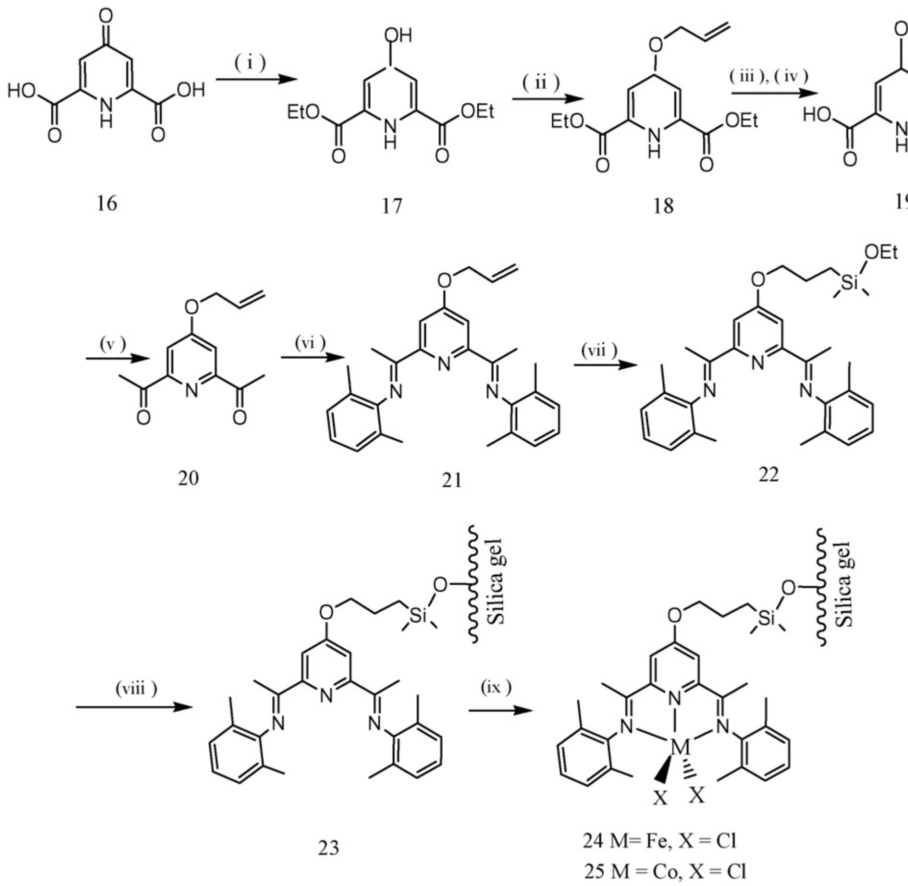
Complex	Complex concentration (μM)	Yield (g)	Activity (kg PE/(mmol cat h))	Mv ($\times 10^4$)
26	20.0[a]	0.18	<0.01	–
27	20.0[a]	3.44	1.4	Oil[c]
28	20.0[b]	1.38	3.3	51
29	0.08[b]	0.87	519.0	1
30	20.0[b]	2.69	6.5	3
Blank	20.0[b]	1.25	3.0	7
Cp_2ZrCl_2	02.0[b]	1.13	27.0	104

Viscometric Mol. wt. (Mv). Conditions: temperature, 25 °C; pressure, 0.1 MPa; solvent, toluene (250 ml); cocatalyst [MAO], 1.25 mmol (Al).

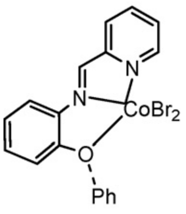
[a] Polymerization time: 30 min.

[b] Polymerization time: 5 min.

[c] GPC Mol. wt.



Scheme 4. Synthesis of supported 2,6-bis(imino)pyridyl iron(II) and cobalt(II) complexes [75–77]. (i) EtOH, concentrated H_2SO_4, 90 °C; (ii) K_2CO_3, allyl bromide, acetone, reflux; (iii) 5N NaOH, THF, 50 °C (iv) $SOCl_2$ DMF, 90 °C; (v) CuI(I), MeLi, Et_2O, THF, 78 °C; (vi) 2,6-dimethylaniline EtOH, AcOH, reflux; (vii) $(CH_3)_2SiHCl$, $H_2PtCl_6 \cdot 6H_2O$ (catalyst), CH_2Cl_2 ($EtOH:Et_3N$) 1:1; reflux; (viii) 5 ml silica gel, toluene, 120 °C; (ix) $FeCl_2$ or $CoCl_2$, THF.



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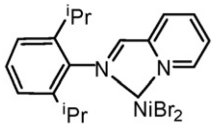

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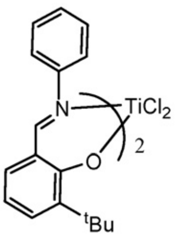

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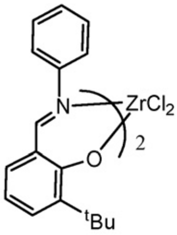

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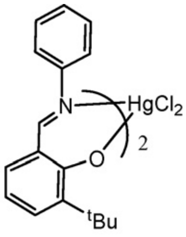

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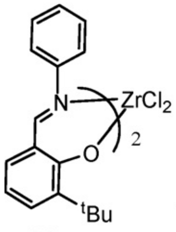
The zirconium, titanium and vanadium complexes of phenoxy-imine **31–34** were also used successfully in the polymerization of ethylene [81]. The zirconium complexes combined with $MgCl_2/R_mAl(OR)_n$ displayed strikingly high activities. The zirconium complex **33** showed a maximum yield in the presence of $MgCl_2/R_mAl(OR)_n$ (14.55 g) and MAO cocatalyst (13.14 g) in comparison to other complexes of zirconium (Table 2).



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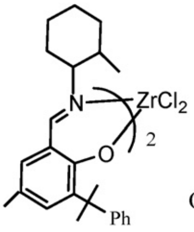

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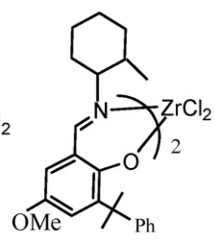

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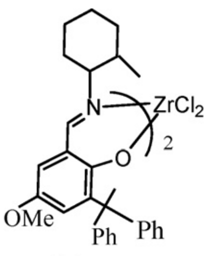

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Table 2
Ethylene polymerization [81] with zirconium complexes **31**–**34** using $MgCl_2/t\text{-}Bu_mAl(OR)_n$ or MAO as a cocatalysts

Complex	Cocatalyst	Amount of cocatalyst (mmol)		Yield (g)	Activity (kg PE/(mmol cat h))	Mv ($\times 10^{-4}$)
		Mg	Al			
31	$MgCl_2/i\text{-}Bu_mAl(OR)_n$	0.20	0.80	1.96	245	9.1
	MAO	0.00	1.25	10.29	1286	7.4
32	$MgCl_2/i\text{-}Bu_mAl(OR)_n$	0.20	0.80	8.67	1084	410.0
	MAO	0.00	1.25	6.02	753	213.0
33	$MgCl_2/i\text{-}Bu_mAl(OR)_n$	0.20	0.80	14.55	1819	509.0
	MAO	0	1.25	13.14	1643	399.0
34	$MgCl_2/i\text{-}Bu_mAl(OR)_n$	0.20	0.80	8.00	1000	460.0
	MAO	0	1.25	11.91	1489	298.0

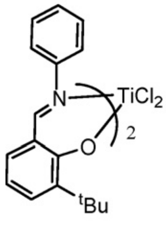
Conditions: temperature, 50 °C; ethylene pressure, 0.9 MPa; solvent, toluene (500 ml); polymerization time, 30 min; complex **31**–**34**, 0.016 μmol; viscometric Mol. wt. (Mv).

Table 3
Ethylene polymerization [81] with titanium complexes **35**–**38** using $MgCl_2/i\text{-}Bu_mAl(OR)_n$ or MAO as a cocatalyst

Complex	Cocatalyst	Amount of cocatalyst (mmol)		Yield (g)	Activity (kg PE/(mmol cat h))	Mv ($\times 10^{-4}$)	M_w/M_n
		Mg	Al				
35	$MgCl_2/i\text{-}Bu_mAl(OR)_n$	0.40	2.40	9.07	36.3	50.9	2.66
	MAO	0.00	1.25	11.16	44.6	46.4	2.38
36	$MgCl_2/i\text{-}Bu_mAl(OR)_n$	0.40	2.40	5.21	20.8	59.6	2.67
	MAO	0.00	1.25	5.35	21.4	62.5	2.74
37	$MgCl_2/i\text{-}Bu_mAl(OR)_n$	0.40	2.40	9.01	36.0	23.1	2.40
	MAO	0.00	1.25	24.77	99.1	22.9	2.07
38	$MgCl_2/i\text{-}Bu_mAl(OR)_n$	0.40	2.40	6.54	26.2	117.0	3.51
	MAO	0.00	1.25	17.01	68.0	42.2	4.74

Conditions: temperature, 50 °C; ethylene pressure, 0.9 MPa; solvent, toluene (500 ml); polymerization time, 30 min; complex **35**–**38**, 0.5 μmol; viscometric Mol. wt. (Mv); M_w/M_n by GPC.

The titanium complexes **35–38** produced polyethylene with a narrow molecular weight distribution (M_w/M_n) and also showed single site catalytic activity in the copolymerization of ethylene and propylene. This was the first example of methylalumoxane (MAO) and borate free single site catalysis in ethylene polymerization [81]. The titanium complexes **35**, **37** also showed catalytic activity in polymerizing of ethylene in the presence of $Bu_mAl(OR)_n$ cocatalyst, whereas, complex **36** showed least activity. The addition of MAO cocatalyst has improved the catalytic activity of complex **37** in comparison to other complexes of titanium (Table 3).



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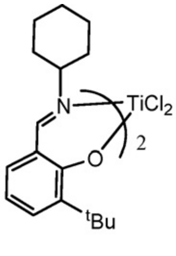

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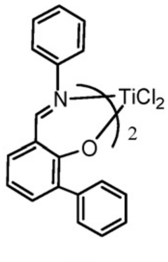

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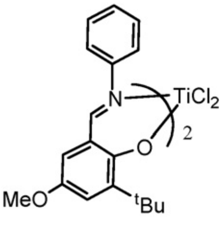

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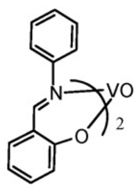
The vanadium complexes **39–42** showed activity at elevated temperatures and were the first examples for vanadium based single site catalysis in the polymerization of olefins [81]. These investigations clearly indicated that $MgCl_2/R_mAl(OR)_n$ not only worked as a cocatalyst but also acted as a suitable support for phenoxy-imine complexes of zirconium, titanium and vanadium [81].



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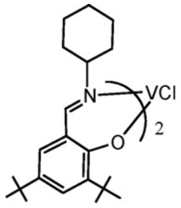

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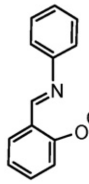

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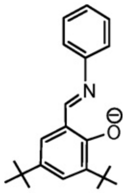

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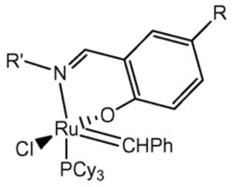
Valency for vanadium in structure 39 is IV and in structure 40 it is III

The iron(III) and cobalt(II) complexes of pyridine bis(imine) ligands **43** showed significant activity in the polymerization of ethylene (Scheme 5). These complexes were also used successfully for copolymerization of ethylene with 1-hexene [82]. The iron(III) Schiff base complexes showed higher yield and activity than the cobalt(II) complexes (Table 4).

The salicylaldiminato complexes of zirconium were long-lived catalysts in ethylene polymerization and promoted radical decomposition in certain cases [83]. Chiral Schiff base complexes were used successfully in the synthesis of crystalline high molecular weight racemic poly(lactic acid) from racemic lactides [84]. These complexes were also used as catalysts in the cyclooligomerization of isoprene and butadiene. The electronic and geometric factors of Schiff base ligands showed pronounced effect on rate of oligomerization.

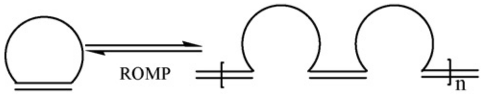
Table 4
Ethylene polymerization with iron and cobalt catalysts [82]

Catalyst		Loading (μmol)	Yield (g)	Activity ($g\,mmol^{-1}\,bar^{-1}\,h^{-1}$)
Metal	Types			
Fe	1	10	4.7	930
	3	9	4.6	1010
	5	10	4.5	980
	7	9	4.9	1110
Co	2	10	3.3	650
	4	9	0.5	100
	6	10	4.3	940
	8	9	1.3	300



44

Substituted aliphatic R or aromatic groups R'

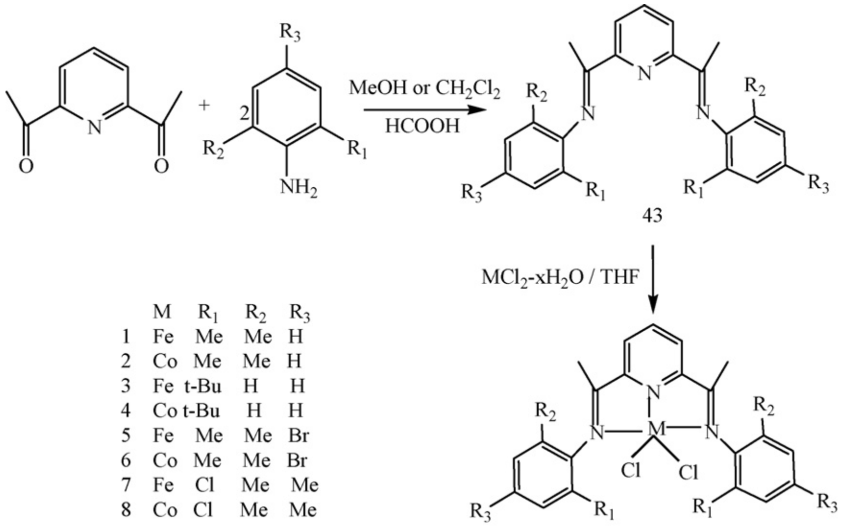


Scheme 6. Schematic representation of ROMP metathesis reaction [85,86].

3.2. Ring opening polymerization reaction

Recently the ring opening metathesis polymerization (ROMP) (Scheme 6) has become an important tool both in synthesis of fine chemicals and macromolecular chemistry. The catalytic activity of complexes **44** was tested in ROMP and it was noted that olefin metathesis polymerization involved decoordination and coordination of 'onearm' of the bidentate Schiff base ligands [85–86].

A series of ruthenium Schiff base complexes **45** were prepared [87] and tested for their activity in atom transfer radical polymerization (ATRP) in the presence of trimethylsilyldiazomethane (TMSD). These complexes were also active in ring opening metathesis polymerization (ROMP) of norbornene and cyclooctene. The percent conversion of norbornene and cyclooctene was increased within 100 min (Figs. 1 and 2) and after that the conversion was almost constant. The activity of complexes in ROMP and ATRP was dependent on steric hin-



	M	R_1	R_2	R_3
1	Fe	Me	Me	H
2	Co	Me	Me	H
3	Fe	t-Bu	H	H
4	Co	t-Bu	H	H
5	Fe	Me	Me	Br
6	Co	Me	Me	Br
7	Fe	Cl	Me	Me
8	Co	Cl	Me	Me

Scheme 5. Synthesis of iron(III) and cobalt(II) complexes [82].

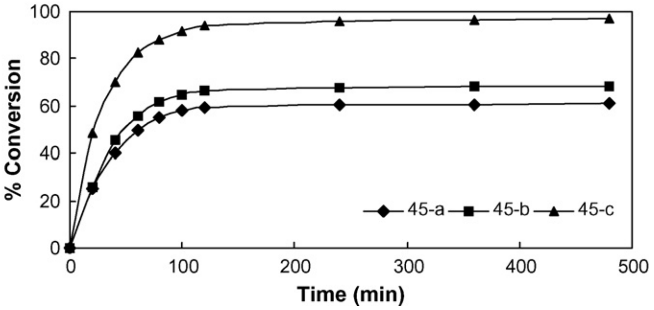


Fig. 1. Plot of percentage conversion vs. time for ROMP of norbornene using catalysts **45-a**, **45-b** and **45-c** [87].

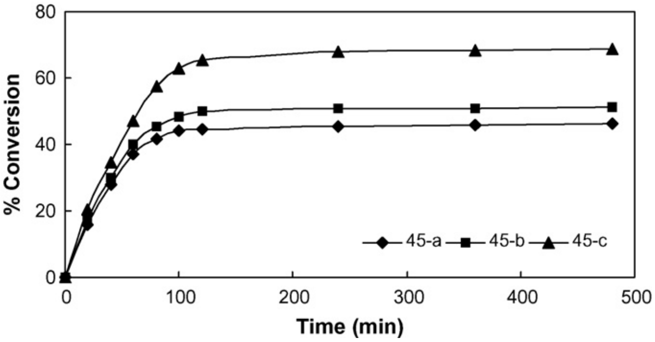


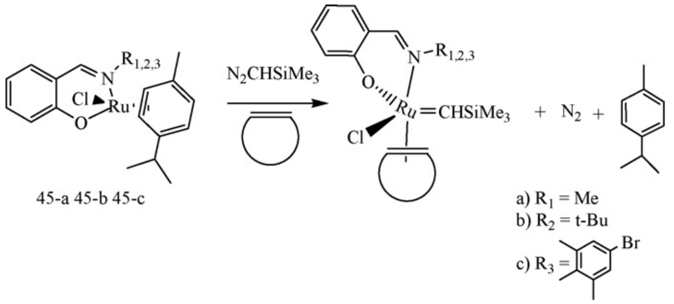
Fig. 2. Plot of percentage conversion vs. time for the ROMP of cyclooctene using catalysts **45-a**, **45-b** and **45-c** [87].

drance and electron donating ability of Schiff base ligands (Scheme 7).

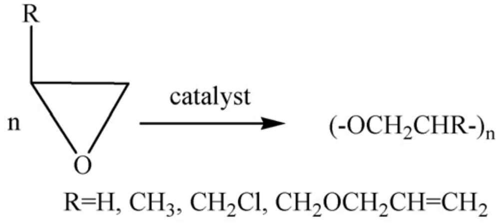
The proposed mechanism depicted in Scheme 8 indicates that the complexes **45-a**, **45-b** and **45-c** were activated with TMSD in ROMP.

Electron-donating alkyl substituent groups at one or both meta positions on arylamine ring facilitate the ring opening/degradation at lower temperatures [88]. The salen complexes also showed activity in ring opening oligomerization or polymerization of epoxides (Scheme 9) [89].

The racemic resolution (Reaction 1 in Scheme 10) of aluminium(III) binaphthyl chiral complexes [90] has allowed their application as catalysts in the ring opening polymerization of

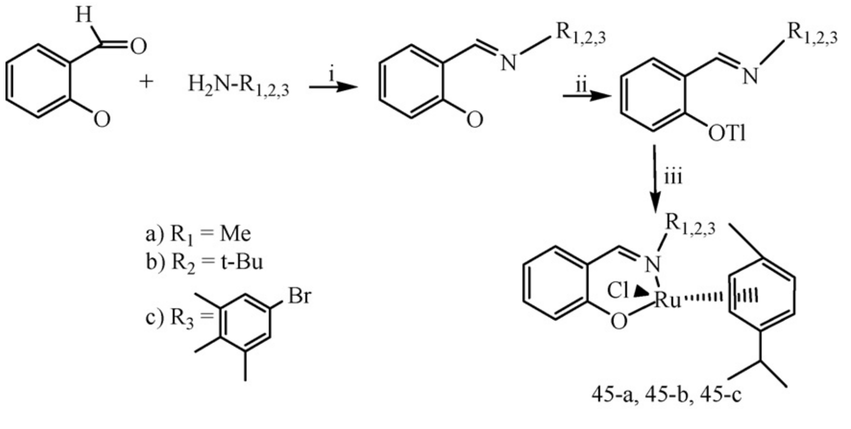


Scheme 8. Possible mechanism for the formation of the catalytically active species in ROMP reactions [86,87].

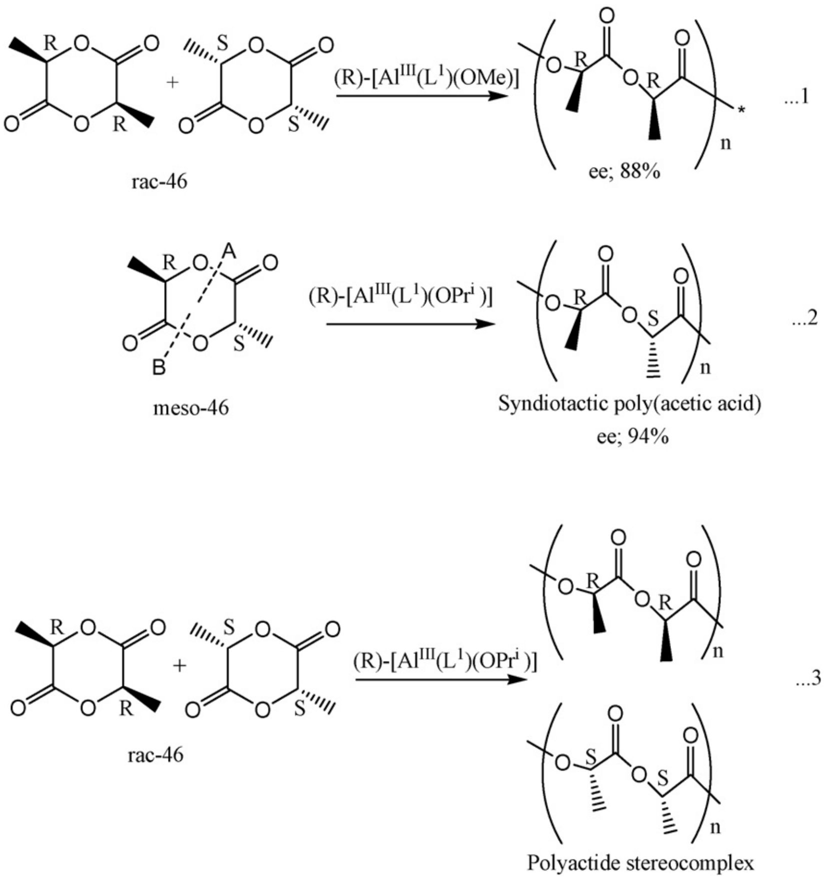


Scheme 9. Ring opening oligomerization or polymerization of epoxides [89].

meso-lactides **46** in a stereoselective manner to produce highly syndiotactic poly(acetic acid) with a 94% conversion [91] (Reaction 2 in Scheme 10). This provided a new method to obtain syndiotactic polymers by stereoselective ring opening polymerization of a cyclic monomer containing two stereo centers [91]. Subsequently Radano et al. [92] used aluminium(III) binaphthyl complexes [91] to obtain stereoselective polylactides (Reaction 3 in Scheme 10). This process has provided an easy way to synthesize stereoselective poly(acetic acid) directly from racemic lactides, unlike other methods, which required enantiopure (*R*)- and (*S*)-poly(acetic acid) combination with polylactides. The aluminium(III) complexes of binaphthyl chiral Schiff base were also used as catalysts in the stereo selective polymerization of lactides in which, catalysts opened *meso*-lactides **46** preferentially at site B. Using rac-[Al^{III}(L^1)(O^{i}Pr)] in place of (*R*)-[Al^{III}(L^1)(O^{i}Pr)] {L^1 = **6** (R$_1$ and R$_2$ = H)}, the polymerization produces heterotactic poly(acetic acid) (Reaction 3 in



Scheme 7. Reaction sequence for the synthesis of three different Schiff base substituted ruthenium catalysts. (i) THF, RT, 2 h for $H_2NR_{1,2}$ and EtOH, 80 °C, RT, 2 h for H_2NR_3; (ii) TlOEt, THF, RT, 2 h; (iii) [RuCl$_2$(*p*-cymene)]$_2$, THF, RT, 6 h [87].

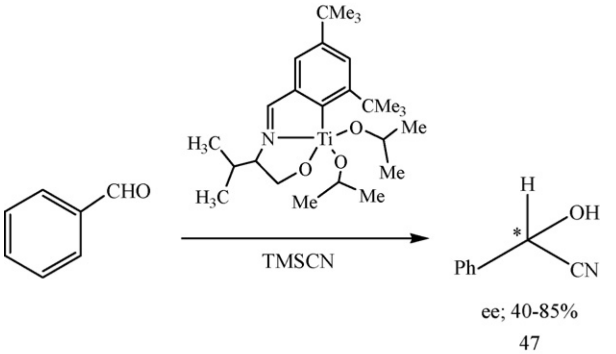


Scheme 10. Ring opening polymerization of lactides [93].

Scheme 10). Based on stereochemistry of the products, the mechanism of ring opening polymerization was proposed [93].

3.3. Oxidation reaction

Chiral Schiff base ligands of –O–N–O– 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 in the presence of titanium(IV) ions resulted in trimethylsilyl cyanohydrins **47** in 40–85% enantioselectivity (Scheme 11) [94,95].



Scheme 11. Chiral Schiff base catalyzed synthesis of trimethylsilyl cyanohydrins [94,95].

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 oxidation of cyclohexane to cyclohexanol and cyclohexanone [96]. The reaction was catalyzed more successfully with Schiff base complexes of manganese(II) ions than other Schiff base complexes.

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 [96]. The manganese(III) complexes of *N*,*N*′-ethylene bis-(salicylidene aminato)salen; *N*,*N*′-ethylenebis-(5-chloro-salicylidene aminato)Cl salen; *N*,*N*′-ethylene bis-(5-bromo-salicylidene 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 [97].

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 [98]. These complexes showed high catalytic activity in the oxidation of phenols in ScCO$_2$ (super critical CO$_2$), which suggested that this high activity of cobalt(II) salen complex in ScCO$_2$ would expand the range of substrates for oxidation. The oxidation resistant substrates such as hydrocarbons and lignins could be oxidized using these catalysts in ScCO$_2$ [99,100]. The iron, manganese and chromium ions complexes of *meso*-tetrakis(2,6-

Table 5
Comparison of DTBP conversion and DTPQ selectivity during DTBP oxidation with cobalt(II) salen complex in CH_2Cl_2 and $ScCO_2$ [101,102]

P_{total} (bar)	Temperature (°C)	Time (h)	CH_2Cl_2 (ml)	Molar O_2	Conversion (%)	Selectivity of DTPQ (%)
2.8	25	2.0	10.0	2.0	17	88
207	70	21.0	0.0	10.0	80	70
62	70	2.0	5.0	10.0	99	98

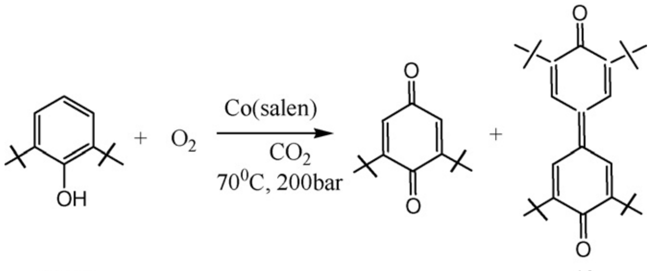
dichloro-3-sulfophenyl)-porphyrin chloride Schiff base were used as catalyst in the presence of hypochlorite as terminal oxidant [100]. Cobalt(II) salen complexes were also used as catalyst in oxidation of DTBP and 35-DTBP in $ScCO_2$ [101]. The conversion and catalyst selectivity were studied as a function of temperature, pressure, and concentration of catalyst and terminal oxidant. Selectivity in favor of oxygen transfer product DTBQ **48** over self-coupling phenoxy radicals (Scheme 12) was observed [101] on varying the concentration of oxygen and total pressure. The selectivity in oxidation remained unaffected over a wide range of temperature and concentration of catalyst (Table 5). 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 behavior of radicals has provided support for the mechanism proposed for these reactions (Scheme 13) [101,102].

The chitosan supported cobalt(II) complexes of bis(salicylidene ethylene diamine) [103] catalyzed the oxidation of DOPA in the presence of oxygen and the activity was compared with unsupported monomeric complexes. The catalytic activity of cobalt(II) salen complex in $ScCO_2$ was evaluated for oxidation of phenols in the presence of organic peroxides as oxidant [101].

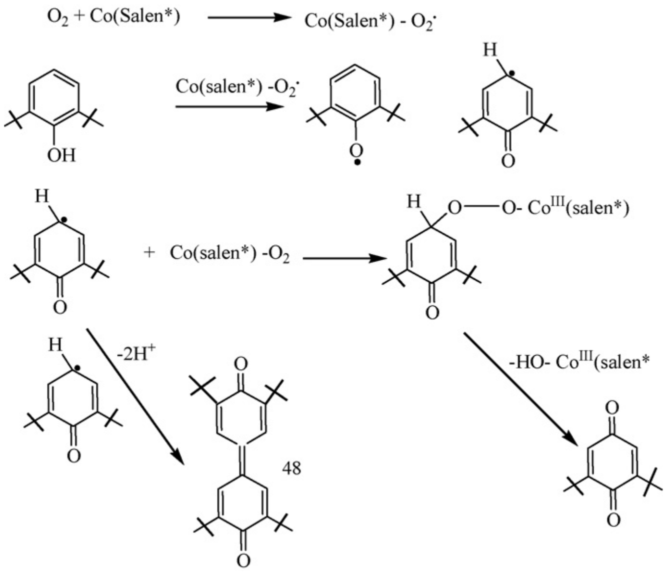
Although $ScCO_2$ is useful over conventional solvents in homogeneous catalysis, it requires high pressures to ensure adequate solubility of salen complexes in CO_2 [98]. However, the addition of fluorocarbon has enhanced the solubility of metal complexes in $ScCO_2$ at moderate pressures but is expensive. Recently poly-ether-carbonate copolymers were used as suitable substitutes to enhance the solubility of complexes in $ScCO_2$ at low pressure [104]. The cobalt(III) complexes of binaphthyl chiral Schiff base (*R*)-[Co(III)(L^n)]SbF_6 ($n = 1, 2, 4$) and (*R*)-[Co(III)(L^n)I] ($n = 2, 3$) were active catalysts in Baeyer–Villiger oxidation of 3-phenyl cyclobutanone **49** with H_2O_2 or urea hydrogen peroxide (UHP) adduct (Reaction 1 in Scheme 14) [105]. These reactions produced (*S*)-3-phenylbutano-4-lactone with 69% ee in dichloromethane. The application of polar solvents such as ethers and alcohols has improved the efficiency of catalysts with high enantioselectivity (60–79%) except with [Zr(salen)] catalysts [106]. The catalysts also showed activity in Baeyer–Villiger oxidation of cyclobutanone derivatives **50–52** to produce lactones in 75–99% yields and 69–78% ee in the presence of H_2O_2 as an oxidant (Reaction 2 in Scheme 14). On taking UHP as oxidant in place of H_2O_2 and replacing catalyst (*R*)-[Co(III)(L^2)I] with (*R*)-[Co(III)(L^n)I] ($n = 3$–5), the enantioselectivity in Baeyer–Villiger oxidation reaction was enhanced significantly (Reaction 3 in Scheme 14).

Manganese(III) complexes of salen, Br_2salen and (*tert*-butyl)$_4$ salen Schiff base ligands encapsulated in zeolites were active catalysts in the oxidation of styrene using molecular oxygen as oxidant [107]. The cobalt(II) complex of *N*,*N*′-bis(salicylidene)-1,2-phenylenediamine was used as a catalyst in oxidation of benzyl alcohol but zeolite encapsulated complexes showed high catalytic activity in comparison to the homogeneous catalyst [108]. Manganese(II) complexes of tetradentate bis(2-pyridinaldehyde) ethylenediamine and bis(2-pyridinaldehyde) propylenediamine entrapped in zeolites were also used as catalysts [109] in the selective oxidation of hydrocarbons with PhIO or *tert*-butylhydroperoxide (*t*-BHP).

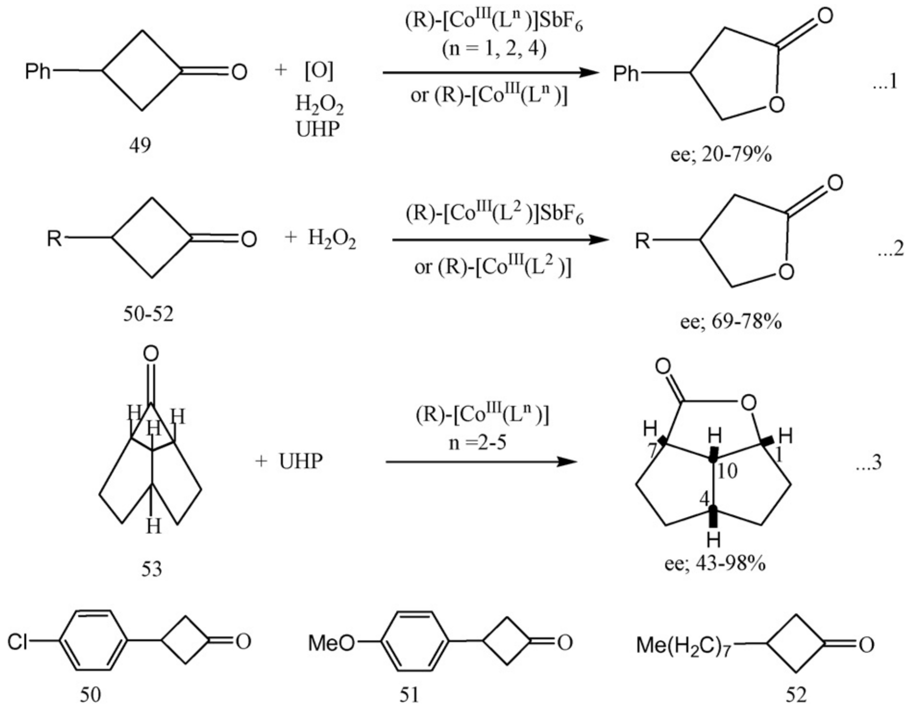
The alkyl aryl sulfides were oxidized in an asymmetric fashion using manganese(III) salen complexes with ee of 94%. The oxidation of sulfides was carried out using equimolar amount of iodosylbenzene and 1% of catalyst.



Scheme 12. Cobalt(II) salen catalyzed aerobic oxidation of DTBP [101].



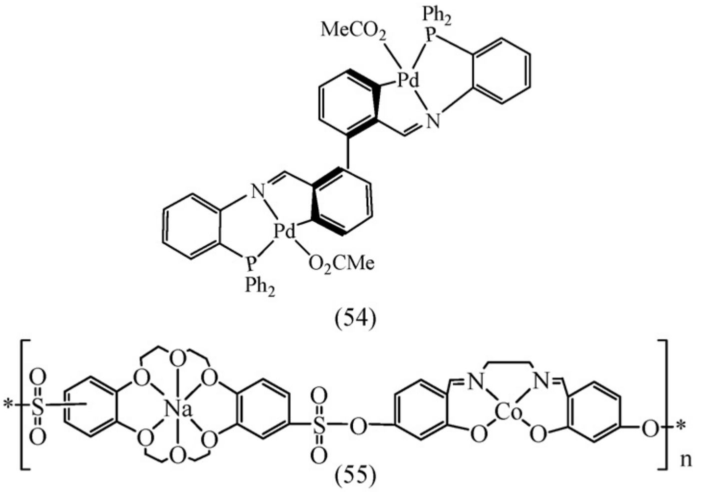
Scheme 13. Proposed reaction mechanism for the oxidation of DTBP by cobalt(II) salen [101,102].



Scheme 14. 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** ($R_1 = R_2 = I$).

Solvents influenced the enantioselectivity of reaction. The manganese(II) salen complexes showed catalytic activity in asymmetric oxidation of silyl ketone acetals with high enantioselectivity (>81%). The yield and enantioselectivity was dependant on the type of oxygen donor, pH of the medium, additives and substitution pattern of the enol substrate [110]. Schiff base ligands prepared with (*S*)-*tert*-leucinol and chiral and racemic salicylaldehyde were used in vanadium-catalyzed asymmetric sulfoxidation of thioethers in the presence of hydrogen peroxide [111]. The enantioselectivity of the product was dependant on the structures of salicylaldehydes. The catalyst showed significant activity in oxygenation of thioanisole and 2-bromo-thioanisole with 78% ee [111].

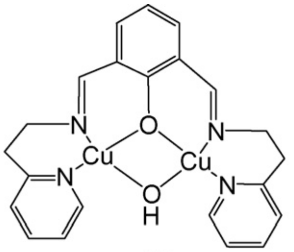
Dinuclear Schiff base complexes of transition metal ions were more efficient catalysts than mononuclear complexes probably due to the synergic effect of two metal ions [112]. A variety of homo [113,114] **54** and hetero **55** dinuclear Schiff base complexes of transition metal ions were used as catalysts in various reactions [115–117]. The dinuclear Schiff base complexes of copper(II) were used as catalysts in oxygen activation [118]. The homo and dinuclear complexes of transition metal ions were effective catalysts in direct oxygenation of unfunctionalized hydrocarbons and phenols.


(54)

(55)

Homo **54** and hetero **55** dinuclear Schiff base complexes used as catalyst.

Dinuclear Schiff base complexes of copper(II) ions **56** were used successfully in hydroxylation of (Scheme 15) phenol [114].



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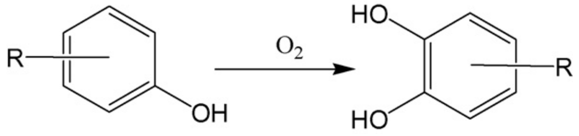
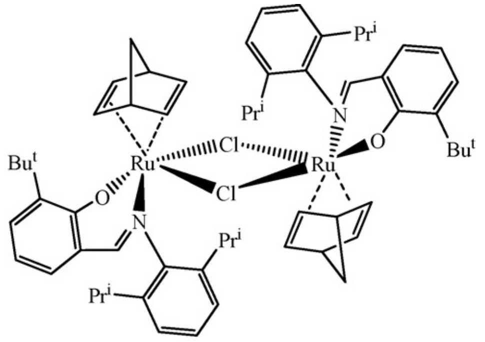


Scheme 15. Hydroxylation of arene with dinuclear complexes [114].

The dinuclear ruthenium(III) Schiff base complexes of pyridine 2-carboxaldehyde and diamines were efficient catalyst in epoxidation of alkenes [119]. The ruthenium dinuclear Schiff base complexes **57** also showed activity in ROMP of norbornene and ATRP of methyl methacrylate and styrene [120].



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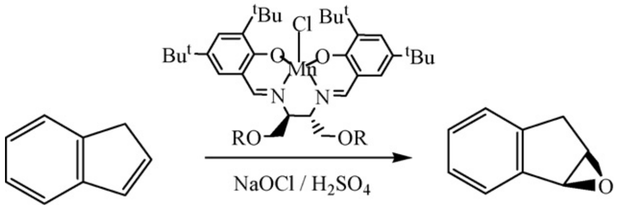
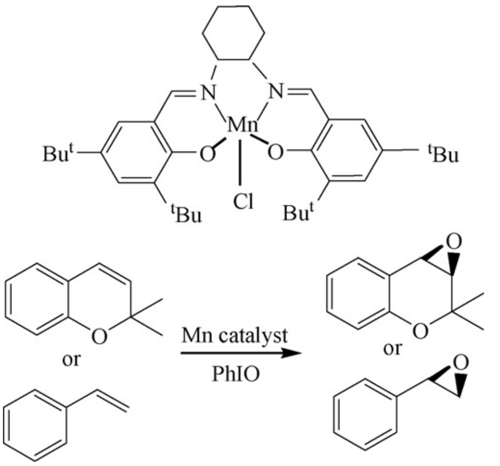


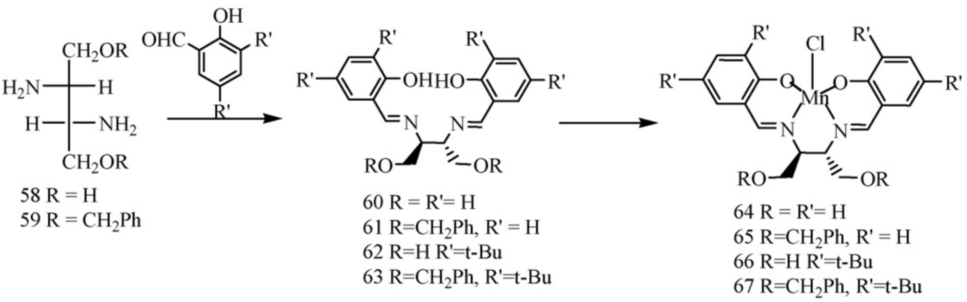
Scheme 17. The epoxidation of indene [121] using the manganese(III) complexes of D-2,3-bis(di-*t*-butyl-salicylideneamino)-1,4-butanediol and-dibenzyl ether.



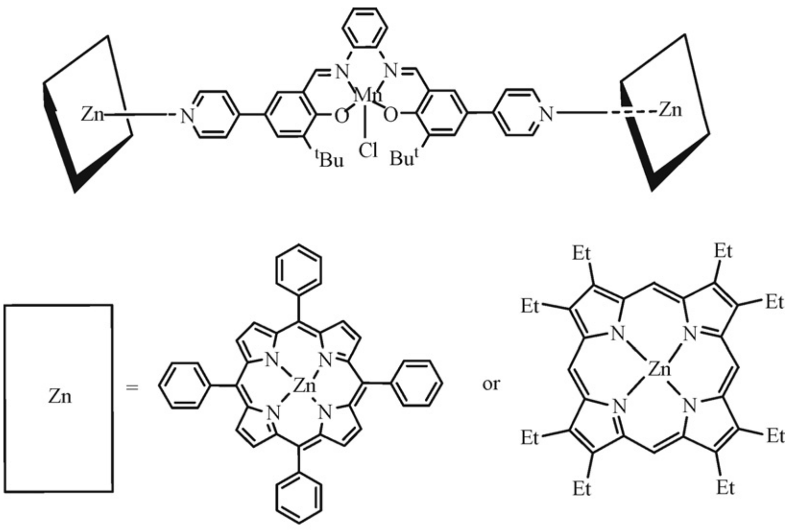
Scheme 18. Epoxidation of conjugated olefins by manganese(III) complex [122].

3.4. Epoxidation reaction

Chiral manganese(II) complexes of 1,2-bis(salicylideneamino) cyclohexane entrapped in zeolite showed catalytic activity in the enantioselective epoxidation of alkenes [109]. 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 PhIO oxidant [109]. Compounds **60–63** obtained from **58** and **59** constituted a new class of salen based Schiff base ligands to form complexes with transition and heavy metal ions [121]. The manganese(III) complexes (Scheme 16) **64–67** corresponding to Schiff base ligands **60–63** were chiral catalysts and used in asymmetric epoxidation of indene (Scheme 17) [121]. The manganese(III) salen complexes catalyzed the asymmetric epoxidation of conjugated olefins (Scheme 18). The addition of bulky Lewis acids such as zinc tetraphenylporphyrin (ZnTPP) **68a** or (ZnOEP) **68b** formed stable supramolecular complexes, which showed enhanced catalytic activity of manganese(III) salen complexes [122].



Scheme 16. The synthesis of D-2,3-bis(arylideneamino)-1,4-butanediol derivatives [121] (**60–63**) and of their manganese(III) complexes (**64–67**).



ZnTPP

68a

ZnOEP

68b

Structures of ZnTPP and ZnOEP supramolecular complexes.

The enantioselective epoxidation of styrene, indene and 2,2-dimethyl-6-nitro chromene was carried out using dicationic chiral manganese(III) salen complexes [123], which were prepared reacting 1*S*,2*S*-(+)-1,2-diaminocyclohexane/1*S*,2*S*-(−)-diphenyldiamine with 2-hydroxy-3-*t*-Bu-5-(triisooctylaminomethyl)benzaldehyde chloride/2-hydroxy-3-*t*-Bu-5-(triethylaminomethyl)benzaldehyde chloride [124].

The 3-*t*-Bu-5-(chloromethyl)-2-hydroxybenzaldehyde (CMTBS) was prepared from 3-*t*-Bu-2-hydroxy benzaldehyde [125], which on interactions with an appropriate tertiary amine, viz., triisooctylamine, triethylamine, yielded quaternary ammonium salt of salicylaldehyde, QATBS (Scheme 19) [124]. Under similar epoxidation conditions, the epoxide selectivity was higher with styrene compared to indene. The catalytic activity of these montmorillonite-immobilized catalysts was compared with their homogenized counter part, indicating significant enhancement in ee (69–70%) for the former (ee: 41–52%). These manganese(III) salen catalysts were recovered easily and recycled efficiently several times [124].

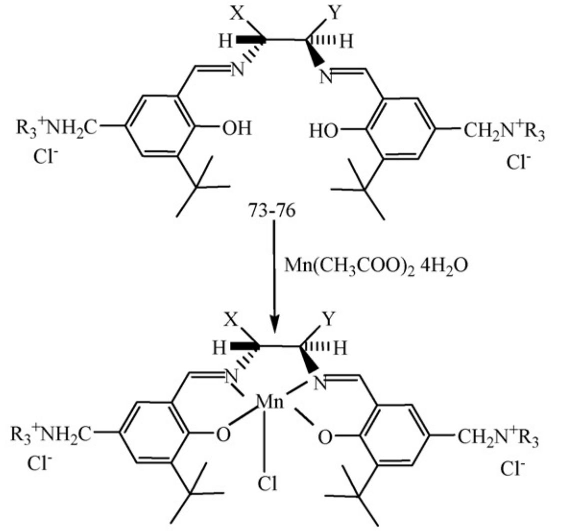
Ruthenium complexes of *trans*-[$RuCl_2$(bpydip)] and *trans*-[$Ru(OH)_2$(bpydip)]$(PF_6)_2$ with tetradentate Schiff base ligand *N*,*N*′-bis(7-methyl-2-pyridylmethylene)-1,3-diiminopropane were used as remarkable catalysts in the epoxidation of cyclohexene in the presence of iodosobenzene [126].

Condensation of aromatic aldehydes with 2,2′-diamino-1,1′-binaphthyl or 2-amino-2′-hydroxy-1,1′-binaphthyl produced tetradentate chiral binaphthyl Schiff base ligands [100], which formed complexes with various metal ions. These chiral metal complexes showed catalytic activity in epoxidation, hydroxylation, aldol, Diels–Alder and ring opening polymerization reactions [126].

Epoxidation of alkenes **77–80** catalyzed by (*R*)-[Cr(III)(L^4)Cl]-MCM-41(m) (Scheme 20) is an unique example of heterogenized metal catalysts with chiral binaphthyl Schiff base ligands [127].

Nickel(II) Schiff base complexes of *N*,*N*′-bis(2-hydroxyphenyl)ethylenediimine (H_2L^1) **81** and *N*,*N*′-(2-hydroxyphenyl)acetylaldimine *N*-(2-hydroxyphenyl) acetamide (H_2L^2) **82** were tested for their catalytic activity in the epoxidation of olefins (Table 6) viz., cyclohexene, 1-hexene, *cis*- and *trans*-stilbenes, indene with sodium hypochloride [125].

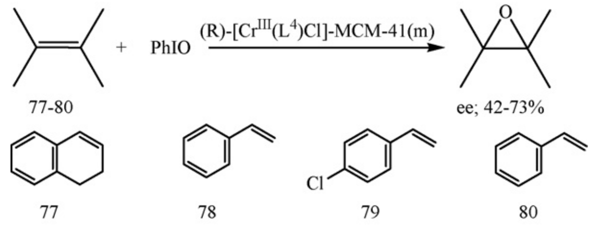
Manganese(II) Schiff base complexes [128] of 1,3-diamino-2-hydroxypropane with salicylaldehyde, 2-hydroxynaphthaldehyde or 2-hydroxyacetophenone ligands were excellent catalysts in the epoxidation of olefins in the



69-72

69 & 73; X=Y Ph, R= isooctyl; 70 & 74; X=Y= -$(CH_2)_4$, R= isooctyl
71 & 75; X=Y=Ph, R= ethyl, 72 & 76; X=Y= -$(CH_2)_4$, R= ethyl

Scheme 19. Preparation of manganese(III) Schiff base complexes (**69–72**) [124]. Condition: (i) $Mn(CH_3COO)_2{\cdot}4H_2O$, EtOH, N_2, reflux, 7–8 h (ii) LiCl, reaction time, 4 h, 88–92%.

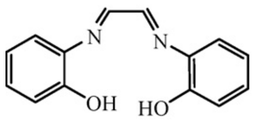


Scheme 20. Epoxidation of alkenes with chiral binaphthyl Schiff base ligands [127]. $L^4 = \mathbf{6}$ ($R_1 = R_2 = Br$).

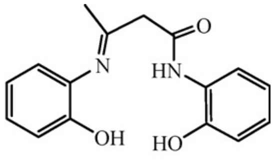
Table 6
NiL catalyzed oxidation of olefins [128]

Catalyst complex	Substrate	Product	Yields (%)
NiL^1 **(81)**	Cyclohexene	Cyclohexene epoxide	16
	1-Hexene	1-Hexene epoxide	29
	cis-Stilbene	*trans*-Stilbene oxide	13
		Benzaldehyde	10
		Benzoic acid	Trace
	trans-Stilbene	*trans*-Stilbene oxide	35
		Benzaldehyde	7
		Benzoic acid	Trace
	Indene	Indene oxide	25
NiL^2 **(82)**	Cyclohexene	Cyclohexene epoxide	14
	1-Hexene	1-Hexene epoxide	21
	cis-Stilbene	*trans*-Stilbene oxide	11
		Benzaldehyde	9
		Benzoic acid	Trace
	trans-Stilbene	*trans*-Stilbene oxide	31
		Benzaldehyde	7
		Benzoic acid	Trace
	Indene	Indene oxide	21

presence of idosylbenzene as an oxidant. The extent of olefins epoxidation was dependent on OH substitution on Schiff base ligand. The chiral metal porphyrins and Schiff base catalysts introduced significant enantioselectivity into the epoxidation of olefins but the mechanism for enantiomeric induction in the epoxidation of olefins is not yet clear; hence, chiral copper(II) porphyrins were used as proton NMR relaxation agents to test the mechanism of enantioselectivity in asymmetric epoxidation [128]. The epoxidation of norbornene, cycloheptene and cyclohexene involving carbocation intermediates was reported using ruthenium(III) bidentate Schiff base complexes as catalyst. The epoxidation was studied in the presence of surfactants viz., SLS, CTABr and Triton X-100.



(H_2L^1)
81



(H_2L^2)
82

Manganese(II) salen complexes on soluble and insoluble supports were also used as catalysts in various asymmetric epoxidation reactions [129]. Poly(ethylene glycol) monoethyl ether and non-crosslinked polystyrene were used as soluble support, whereas, Janda Jel and Merrifield resins were used as insoluble supports. These supports were linked to salen complexes through a glutarate spacer. The soluble supports were recovered by precipitation with suitable solvents, while insoluble catalysts were simply filtered from the reaction mixture. These catalysts were

Table 7
Epoxidation of olefins with supported M salen complexes [130]

Catalyst	Oxidant	Substrate	Product	Yield (%)
Ni(salen)Y	NaOCl	Cyclohexene	Cyclohexene epoxide	13
			Cyclohexenol	Trace
		Cyclooctene	Cyclooctene epoxide	10
			Cyclohexenol	Trace
		1-Hexene	1-Hexene epoxide	17
Ni(salen)Y	$KHSO_3$	Cyclohexene	Cyclohexene epoxide	11
			Cyclohexenol	Trace
		Cyclooctene	Cyclooctene epoxide	8.5
			Cyclohexenol	Trace
		1-Hexene	1-Hexene epoxide	14
Mn(salen)$^+$Y	NaOCl	Cyclohexene	Cyclohexene epoxide	9
			Cyclohexenol	2
		Cyclooctene	Cyclooctene epoxide	7.4
			Cyclohexenol	1.4
		1-Hexene	1-Hexene epoxide	11
Mn(salen)$^+$Y	$KHSO_3$	Cyclohexene	Cyclohexene epoxide	8
			Cyclohexenol	Trace
		Cyclooctene	Cyclooctene epoxide	6.8
			Cyclohexenol	Trace
		1-Hexene	1-Hexene epoxide	
Mn(salen)$^+$-clay	$KHSO_3$	Cyclohexene	Cyclohexene epoxide	9.2
			Cyclohexenol	Trace
		Cyclooctene	Cyclooctene epoxide	7.6
			Cyclohexenol	Trace
		1-Hexene	1-Hexene epoxide	12

used in epoxidation of styrene, *cis*-β-methylstyrene and dihydronaphthalene [129]. The zeolite encapsulated manganese(III), nickel(II) complexes of salen were synthesized and examined for epoxidation of cyclohexene, cyclooctene and 1-hexene in the presence of terminal oxidants, viz., NaOCl, $KHSO_5$ (Table 7) [130].

The epoxidation of olefins in homogeneous and heterogeneous catalytic conditions was compared and evaluated [130]. The linear olefins such as hexene 1 showed high selectivity for epoxidation than cylic olefins [103]. Polymer-supported manganese(II) salen complexes were used as catalysts in the enantioselective epoxidation of 1,2-dihydronaphthalene, *cis*-β-methyl styrene and styrene. The heterogenized catalyst was more selective to form *trans*-epoxide with *cis*-β-methyl styrene. The supported salen complexes were produced by sequential treatment of polymer with 2,4,6-trihydroxy benzaldehyde and chiral *trans*-1,2-diaminocyclohexane and 3,5-di-*tert*-butyl salicylaldehyde and then manganese(II) ions were loaded [131]. The polymer supported salen ligand was also prepared by polymerization of 4-(4-vinyl benzyloxy) salicylaldehyde with styrene and vinyl benzene then reacting subsequently with 1,2-diamino-cyclohexane. The prepared polymer supported salen after reacting with manganese(II) was used as a catalyst in the asymmetric epoxidation of dihydroxy naphthalene and indene in the presence of *m*-chlorobenzoic acid as activator. The immobilized catalyst showed high chemical activity and modest enantioselectivity [132]. The $ScCO_2$ manganese(II) salen complexes [101] were used as catalyst in the epoxidation of olefins using *t*-BuOOH as terminal oxidant (Table 8). Similarly, the substituted $Mn[(5,5\text{-}NO_2)_2salen]$ catalyst in CH_3CN was used in the epoxidation of alkenes in the presence of iodobenzene as terminal oxidant (Table 9) [101].

Chiral binaphthyl Schiff base metal complexes were used for first time in the epoxidation of alkenes [127,133–136]. The manganese(II) complexes of binaphthyl Schiff base epoxidized 1,2-dihydronaphthylene **83** in the presence of sodium hypochlorite with 13–15% ee (Reaction 1 in Scheme 21) [136]. Similarly Che et al. [127,133–136] epoxidized *cis*-β-methylstyrene **84** and 4-chlorostyrene **85** with PhIO, employing the manganese(II) complexes of binaphthyl Schiff base (Reaction 2 in Scheme 21), which produced the highest ee 58%. The epoxidation of styrene **86**, 3-chlorostyrene **87**, 3-nitrostyrene **88** and 4-methylstyrene **89** was studied using similar catalysts in the presence of PhIO as oxidant [133]. Subsequently, manganese(III) binaphthyl Schiff base complexes were also used in epoxidation of styrene (Reaction 3 in Scheme 21). The palladium(II) complexes of binaphthyl Schiff base were also catalytic in the epoxidation of alkenes [137]. The epoxidation of styrene **86** and 4-fluorostyrene **90** with *t*-BuOOH in the presence of palladium(II) complexes [137] produced epoxides with 17–71% ee (Reaction 4 in Scheme 21). Chiral binaphthyl Schiff base complexes of chromium(III) on MCM-41 epoxidized alkenes [137] in the presence of PhIO and produced epoxides with 42–73% ee (Reaction 5 in Scheme 21). Although unsupported catalysts showed higher reusability than heterogenized Mn-salen-MCM-41 catalysts heterogenized catalysts were more enantioselective than homogenized analogue [137].

Table 8
Oxidation of alkenes by Mn (salen) in *t*-BuOOH/*t*-BuOH [101]

Alkenes	Product
Cyclohexene	Cyclohexene oxide 1,2-Cyclohexenediol
Styrene	Styrene oxide Benzaldehyde
cis-Stilbene	*cis*-Stilbene oxide Benzaldehyde
trans-Stilbene	*trans*-Stilbene oxide Benzaldehyde

Catalyst, 5.0 M; pressure, 83 bar; temperature, 50 °C; Mn (salen), 70 wt% in *t*-BuOOH/*t*-BuOH.

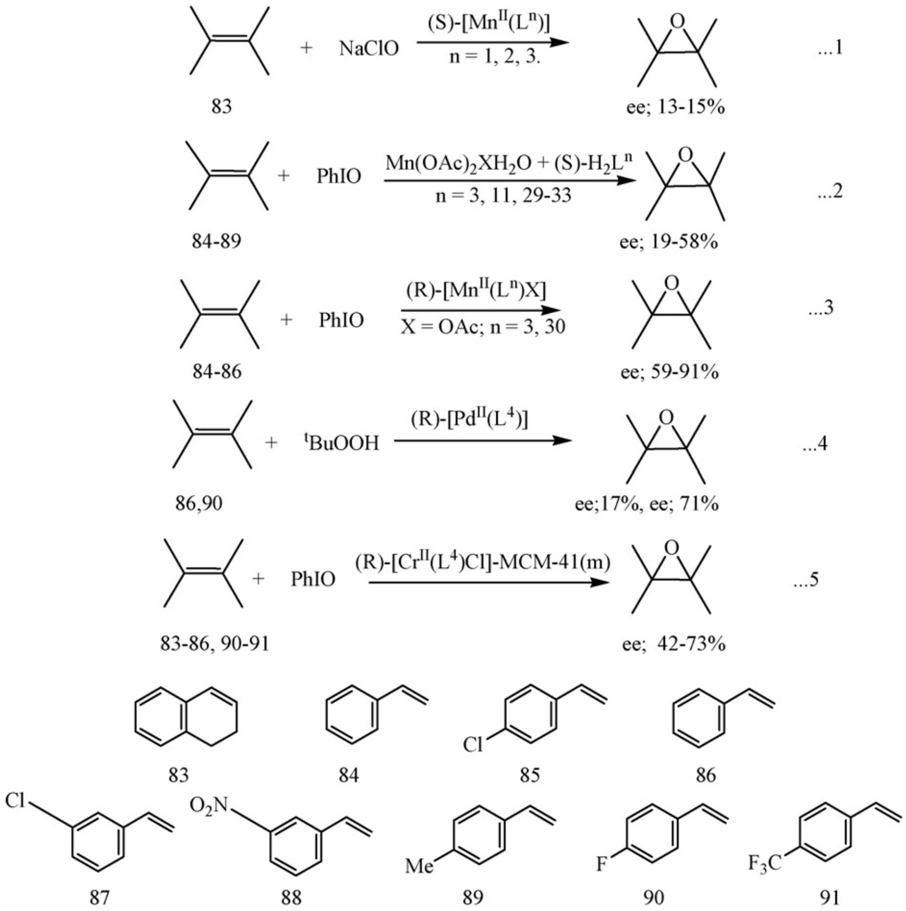
Table 9
Oxidation of alkenes by $Mn[(5,5'\text{-}NO_2)_2salen]$ and PhIO [101]

Alkenes	Product
Cyclohexene	Cyclohexene oxide
Styrene	Styrene oxide Benzaldehyde
cis-Stilbene	*cis*-Stilbene oxide Benzaldehyde
trans-Stilbene	*trans*-Stilbene oxide Benzaldehyde

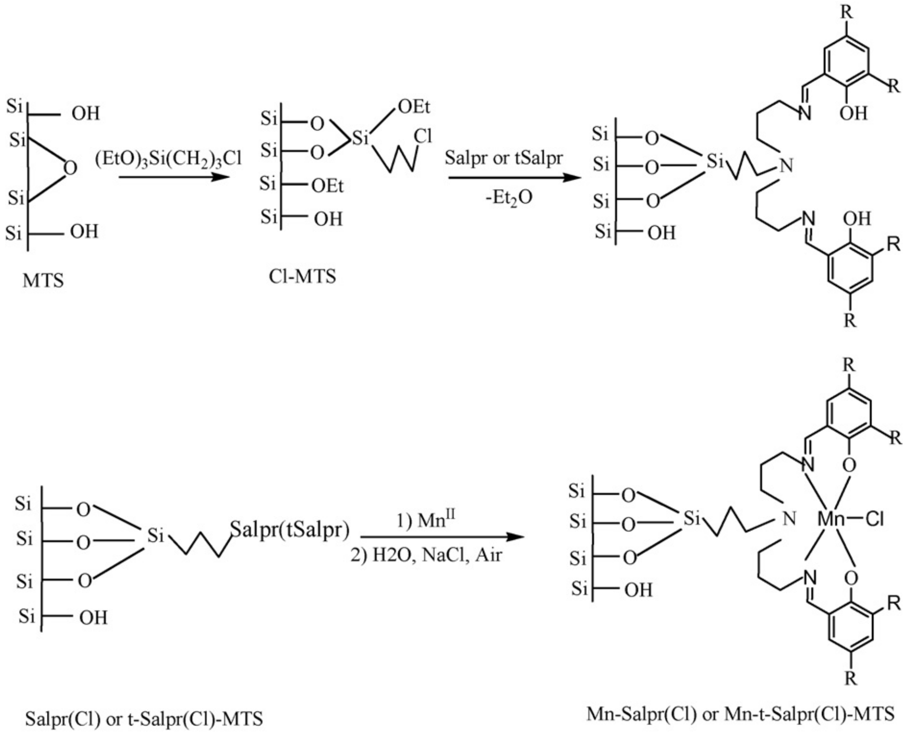
Solvent, 5 ml CH_3CN; catalyst, 0.01 mmol; iodosylbenzene, 0.15 mmol; olefin, 0.30 mmol.

The zeolite encapsulated chiral manganese(II) complexes of *trans*-(*R*,*R*′)-1,2-(salicylidene amino)cyclohexane were active catalysts in the epoxidation of alkenes [138]; the importance of chiral catalysts in the epoxidation of unfunctionalized alkenes was highlighted. The polymer supported chiral manganese(II) salen Schiff base complexes were more enantioselective in the epoxidation of alkenes. The polymer supports were designed for high enantioselectivity in epoxidation of alkenes by anchoring manganese(II) complexes on a single flexible linkage of polymer to mimic the structure of Jacobson catalysts. The active sites were made accessible to alkenes and no mass transfer limitation was allowed to affect the epoxidation of alkenes [139].

Intra-zeolite chiral salen complexes of manganese(III) provided the benefit of shape selectivity of zeolites and stereo control of chiral manganese(III) complexes [138,140] in the epoxidation of olefins. The high catalytic activity of intra-zeolite combination is a special case of salen complexes, which is not possible when these complexes were used in homogeneous conditions. Complexes reacted freely with substrates and were prevented from leaching by restricted pore openings in the zeolites. The activity of catalysts on zeolites was high in comparison to free catalysts [141]. The micelle templated silica (MTS) supported complexes of manganese(III) also were used as catalysts [142]. The 3-chloropropylsilane grafted MTS reacted with Salpr or *tert*-Salpr pentadentate ligands [142] to produce suitable support for anchoring of Schiff base complexes (Scheme 22).



Scheme 21. Epoxidation of alkenes by binaphthyl Schiff base metal complexes [127,133–146]. 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^{11} = **6** ($R_1 = H$, $R_2 = NO_2$), L^{29} = **6** ($R_1 = Me$, $R_2 = NO_2$), L^{30} = **6** ($R_1 = Et$, $R_2 = NO_2$), L^{31} = **6** ($R_1 = Pr^i$, $R_2 = NO_2$), L^{32} = **6** ($R_1 = Bu^t$, $R_2 = NO_2$), L^{33} = **6** ($R_1 = Cl$, $R_2 = NO_2$).

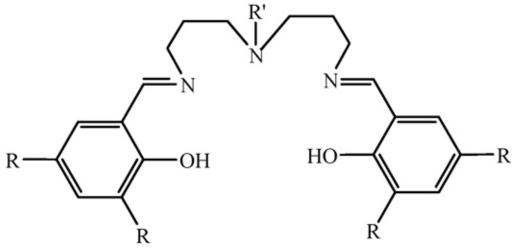


Scheme 22. Manganese(III) Salpr complex grafting on MTS materials [142].

Table 10
Epoxidation of styrene using various oxygen donors on MTS-based catalysts [144]

Catalyst	Solvent	Oxygen donor	Conversion (%)	Selectivity (%)
Mn(III)-Salpr-MTS	Buffered solution	NaOCl	0	–
Mn(III)-Salpr-MTS	Acetonitrile	H_2O_2	0	–
None	Acetonitrile	PhIO	0	–
Mn(III)-Salpr-MTS	Acetonitrile	PhIO	53	58
Mn(III)-*t*-Salpr-MTS	Acetonitrile	PhIO	44	24

The pentadentate ligands **92** with secondary amines contributed significantly to improve the catalytic activity of metal complexes in epoxidation reactions [143]. The activity was tested on the epoxidation of styrene in the presence of different oxidants (Table 10) [144]. The activity of the catalysts in homogeneous conditions decreased due to the collapse of the mesoporous skeleton [145]. The grafting of salen-type complexes on MTS surfaces allowed the design of new oxidation catalysts, which were an alternate to encapsulate transition metal complexes in the microporous voids of zeolites. These supported Schiff base complexes showed better loading for heavy metals [146–147]. The anchoring of chiral ligands on these surfaces produced chiral catalysts for enantioselective epoxidation of olefins.



R' = H, R = H: Salpr
R' = H, R = tBu: tSalpr
R' = CH_3, R = H: Smdpt

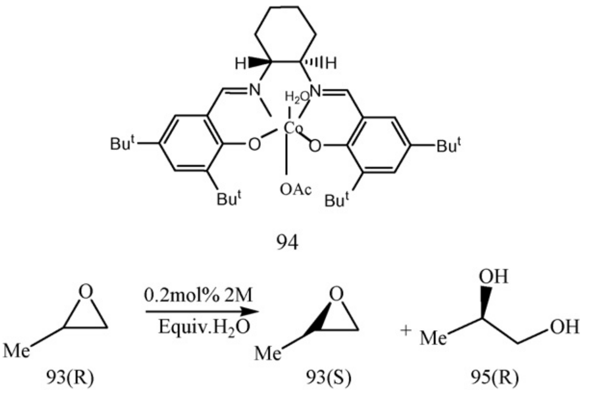
92

Structure of Salpr, t-Salpr and Smdpt ligands.

The polymer-bound (pyrrolidone salene)-manganese(III) Schiff base complexes were excellent enantioselective catalysts for the epoxidation of alkenes [148]. The catalysts showed 92% ee for epoxidation of 2,2′-dimethylchromene, however the activity and enantioselectivity of catalysts was dependent on the epoxidation conditions and degree of decomposition of catalysts; hence, to obtain high degree of epoxidation, the design of supported catalyst and experimental conditions are important. The epoxidation of (*Z*) and (*E*)-stilbene was catalyzed using chiral (*R*,*R*′)-(-)-*N*,*N*′-bis-(3,5-di-*tert*-butylsalicylidene) cyclohexane 1,2-diamine ligand modified and manganese exchanged Al-MCM-41 [149]. The enantioselective epoxidation was also carried out in the presence of iodosylbenzene as oxygen donor. The enantioselectivity of (*Z*)-stilbene to (*E*)-epoxide with heterogeneous catalyst was low (70% ee) in comparison to homogeneous catalyst (77% ee). The effect of reaction temperature, donor ligands and solvents was discussed [149]. The manganese(III) complexes of *N*,*N*′-bis(salicylidene ethylenediamine) catalyzed epoxidation of alkenes. These catalysts were used to study the formation of oxygen transfer agents $[\text{(salen) Mn}=\text{O}]^+$ and $[\text{PhIO(salen)Mn–OMn(salen)OIPh}]^{2+}$, which were intermediates in the epoxidation of alkenes in the presence of PhIO [150].

The effect of additives on enantioselective epoxidation of olefins using chiral manganese(III) complexes was studied in aqueous and non-aqueous media [151]. The presence of additives in both cases showed a significant effect on the activity of the catalysts, product yield and enantioselectivity. The 4-phenylpyridine *N*-oxide was the additive of choice under aqueous conditions, whereas, *N*-methyl morphine N-oxide was effective in non-aqueous conditions. The primary role of additives was to avoid the formation of Me Oxo-Mn(IV) diamines in the reaction mixture [151]. Jacobson has subsequently used another manganese(III) Schiff base complex in epoxidation of olefins in the presence of additives [152]. The epoxidation of 6-acetoamino-7-nitro-2,2-dimethylchromene was studied using chiral manganese(III) salen complexes in the presence of chiral additives, which showed moderate yield (5–65%) with 73% ee [153]. These complexes were also used in the enantioselective epoxidation of unfunctionalized olefins [145] but asymmetric induction was lower than observed by Jacobson [151]. Manganese(III) salen complexes in conjugation with iodosylobenzene showed high yield for epoxidation of olefins (78–99%), but poor ee (5–10%) [154]. Chromium(III) salen complexes catalyzed the epoxidation of unfunctionalized trans olefins with 83% ee [155].

The epoxidation of conjugate alkenes used chromium(III) salen complexes and the effect of solvent on reaction products was analyzed [156]. The monolithic compact block manganese(III) salen polymer supported complexes were used in epoxidation of unfunctionalized alkenes in good yield (65–72%) [157]. The catalysts with spacer arm between polymer support and active sites produced better results. The polymer supported chiral manganese(III) salen complexes were used in the epoxidation of styrene derivatives in the presence of iodosilylbenzene, which produced 16–46% ee [158]. The zeolite encapsulated manganese(III) salen complexes were used successfully in asymmetric epoxidation of *cis*-β-methyl styrene [159] and epoxidation of ethylcinamates in the presence of bleach as oxidant, which produced ee > 4% [160]. A series of mono and binuclear metal complexes of *N*,*N*′-ethylenebis(3-formyl-5-methyl) salicylidimine ligands were used in epoxidation of alkenes in the presence of PhIO as terminal oxidant [161]. Binuclear complexes were less efficient in epoxidation of olefins



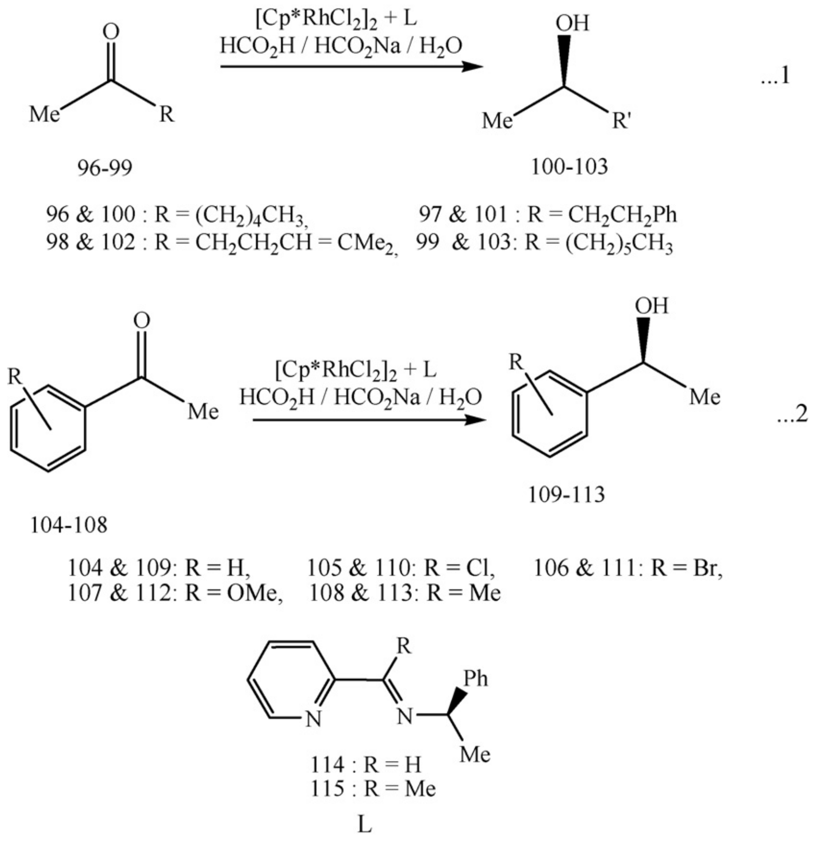
Scheme 23. Ring opening of epoxides using cobalt(II) complexes [162].

than mononuclear manganese(III) complexes. The low activity of binuclear complexes was due to low rate of formation of Mn(V) = O intermediates and transfer of oxygen from intermediates to alkenes. The UV–vis analysis indicated that bimetallic complexes become inactive in the presence of PhIO oxidant [161].

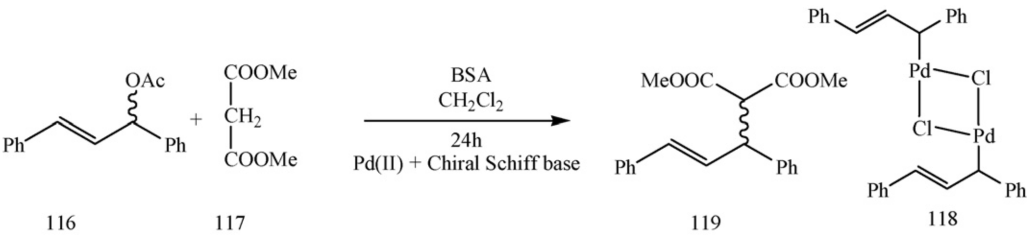
3.5. Ring opening reaction of epoxides

The ring opening reaction of propylene oxide **93**R to form **93**S (Scheme 23) and terminal diol **95** was catalyzed by cobalt(II) complexes **94** [162]. The polymer supported manganese(II) and chromium(III) salen complexes showed catalytic activity in ring opening of epoxides to form azido-silyl ethers [163]. Manganese(II) complexes epoxidized, 1,2-dihydronaphthalene, styrene and *cis*-β-methylstyrene between 46.9 and 79% ee, whereas, chromium(III) complexes were enantioselective in ring opening of epoxyhexane, propylene oxide and cyclohexene oxide with trimethylsilyl azide, which produced yield between 34.36 and 60% ee. Chromium(III) catalyzed ring opening of epoxides was carried out in mild conditions, which allowed the reuse of heterogeneous catalysts without any loss of activity or enantioselectivity upto three runs. In these catalysts, the leaching of chromium(III) was least and catalysts were reused up to hundreds of cycles.

Homogeneous manganese(II) complexes were deactivated due to dimerization but anchoring of these catalysts on polymer support prevented the dimerization of catalysts [163]. In these reactions, the chromium(III) and manganese(II) complexes were based on [*N*,*N*′-bis(3,5-di-*t*-butylsalicylidene)]-(1,2-diamino hexane) Schiff base ligand, which showed exceptionally high enantioselectivity in epoxidation reactions [164]. Cobalt(II) salen complexes were used in the asymmetric nucleophilic ring opening of *meso* epoxides in the presence of benzoic acid [22] with ee 93%. The ring opening of cyclohexa-1,4-dienemonoepoxide was carried out using chromium(III) salen complexes with a yield of 93–95% ee [23].



Scheme 24. Reduction of ketones using chiral rhodium complexes of different types of ligand [173,174].



Scheme 25. Allylic alkylation of 1,3-diphenylallylacetate [178].

3.6. Reduction reaction of ketones

The asymmetric reduction of dialkyl ketones to alcohols [165,166] is a difficult process but Schiff base complexes of transition metals are efficient catalysts in carrying out these reductions [167,168]. Although the presence of formic acid has favored asymmetric reduction of ketones [169,170], the aqueous phase reduction is of great significance [171,172] from an environmental point of view.

The reduction of ketones using iridium and ruthenium analogous was also performed [173,174]. The reduction rate was affected by central metals and decreased in order Rh ≥ Ir ≫ Ru. The reduction of ketones was also carried using chiral complexes in place of bipyridine complexes. The reduction of ketones (Reaction 1 and 2 in Scheme 24) [173,174] were better when carried out in the presence of chiral Schiff base **114**, which produced (*S*)-1-phenylethanol with 51% ee and 99% yield. A variety of ketones **96–99**, **104–108** were examined from which, it was observed that enantioselectivity was influenced by the position and electronic properties of ring substituents in aryl ketones. The ortho substituted acetophenones were more enantioselective than meta- and para-substituted ketones. The reduction of ketones was also carried out using zeolites [175,176] and polymer anchored complexes of transition metals [177]. The cobalt(II) complexes of salicylidenediaminocyclohexane occluded in zeolites as ship-in-bottle (SIB) were highly active in hydrogenation of acetophenone to 1-phenylethanol. These catalysts showed selectivity of 99% at 98% conversion, which was as high as found with homogeneous catalysts.

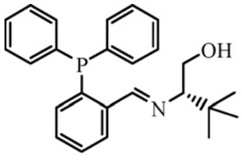
The catalysts showed best ee at 25 °C in comparison to −10 °C with homogeneous catalysts [175]. Platinum(II) salen complexes occluded in zeolites were also used as catalysts in the hydrogenation of ketoacids to hydroxyacids [176].

The hydrogenation of methylpyruvate occurred with a product selectivity of ≤99% at ≤70% conversion [176]. For methyl acetoacetate, the product selectivity was 92% at 52% conversion. The hydrogenation of bulkier pyruvate esters, e.g., isopropylpyruvate or *tert*-butylpyruvate showed low conversion or no conversion at all. The catalytic and spectroscopic results were used to indicate that platinum(II) complexes were occluded in upper cage of zeolites as a SIB [176]. The iridium, cobalt and ruthenium salen complexes anchored on polymer support showed catalytic activity in asymmetric hydrogenation of acetophenone [177]. The iridium salen complexes controlled asymmetric induction but other metal complexes were inactive in induction of enantioselectivity.

3.7. Allylic alkylation reaction

Palladium(II) catalyzed allylic alkylation with soft carbon nucleophiles is an useful process for C–C bond formation [178]. In the reaction of 1,3-diphenylallylacetate **116** with dimethyl malonate **117**, the chiral ligands were able to introduce enantioselectivity in reaction products (Scheme 25).

Palladium(II) complexes of **120** and **121** catalyzed allylic alkylation of barbiturates including methohexital [179]. The activity of imine ligands with amino acid derived backbones was compared with new oxime ethers bearing carbohydrate functionalities [180]. The transition metal complexes anchored on polymer supports and encapsulated in layered structures of zeolitic minerals were synthesized as catalysts [181]. Schiff base ligands on micelle templated silica (MTS) surface showed high activity for epoxidation in the presence of PhIO as oxygen donor [181].



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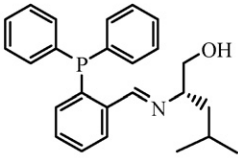

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3.8. Hydrosilation of acetophenones

Rhodium oxime ether complexes were active catalysts in the hydrosilation of acetophenones with diphenylsilanes [29]. The yield was high with in-situ catalysts consisting of $[Rh(cod)Cl]_2$ and ligands containing sufficient phosphorus (>80%). The observed enantioselectivity was 5.6% in the presence of ligand **122** containing phosphorus. The ligands without phosphorus showed low product yields without any enantioselectivity. In $RuCl_2(PPh_3)_3$ catalyzed transfer hydrogenation of acetophenone with 2-propanol at room temperature, the ligand **123** gave 8.2% ee with poor conversion (2.2%). The reaction at elevated temperatures (>83 °C) showed high yield, but the enantioselectivity was dropped as low as 1.2% [182]. The rhodium-catalyzed hydrosilation reactions also showed low enantioselectivity [180].

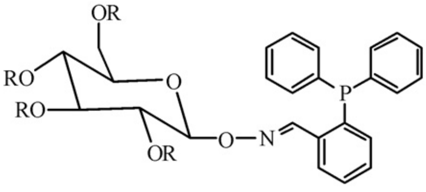
Corrections in Schemes structures of scheme 26

$$H_2O_2 \longrightarrow H^+ + {}^-OOH \qquad ...1$$

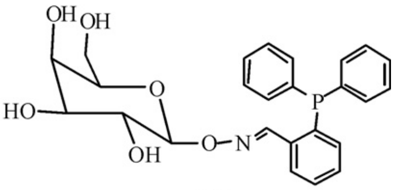
$$\text{Ps-ANBN-Cu(II)} + {}^-OOH \longrightarrow \text{Ps-ANBN-Cu(II)}({}^-OOH) \qquad ...2$$

$$\text{Ps-ANBN-Cu(II)}({}^-OOH) + H^+ \longrightarrow \text{Ps-ANBN-Cu(II)} + H_2O + \tfrac{1}{2}\,O_2 \qquad ...3$$

Scheme 26. Mechanism for decomposition of H_2O_2 [184–186].



122a; R=H
122b; R=Ac



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3.9. Decomposition of hydrogen peroxide

The decomposition of hydrogen peroxide is an activated process, and the presence of catalysts like Schiff base complexes of transition metal ions was effective in catalyzing the decomposition of hydrogen peroxide. Schiff base complexes of transition metals on solid supports showed improvements in decomposition of hydrogen peroxide. The metal complexes immobilized on crosslinked styrene divinylbenzene copolymers with α-nitroso-β-naphthol spacer were very effective catalysts in the decomposition of hydrogen peroxide [183–186]. In the decomposition of hydrogen peroxide, the formation of HOO^- ions was proposed, which was subsequently consumed through formation of a peroxo-copper adduct as shown in Scheme 26. Finally, the adduct was decomposed to form oxygen by reacting with hydrogen ions generated in the first step.

Hydrogen peroxide decomposition in the presence of supported catalysts was dependent on the properties of the polymer supports, but the rate of decomposition of hydrogen peroxide with degree of crosslinking was contradictory [183]. The effect of various transition metal ions on the decomposition of hydrogen peroxide was also studied, but complexes of copper(II) ions were more active in comparison to cobalt(II) and nickel(II) ions. Schiff base complexes of zinc(II) ions showed poor catalytic activity in the decomposition of hydrogen peroxide [183]. The decomposition kinetics of H_2O_2 using polymer supported complexes of cobalt(II) ions of different Schiff base ligands viz. *N*,*N*′-bis(salicylidene)hydrazine, bis(acetylacetone)ethylenediamine and bis(acetyl acetone)-*o*-phenylenediamine were reported [184–186] and the activity of the catalysts was evaluated as a function of crosslinked density and degree of swelling of the polymer support.

A detailed investigation on the decomposition kinetics of hydrogen peroxide taking different concentrations of anchored catalysts and hydrogen peroxide was reported. The efficiency of heterogenized catalysts was compared with homogeneous analogues. There was no leaching and supported catalysts showed high turn over number, which was attributed to low degree of aggregation of metal complexes on polymer supports. The catalysts were able to maintain their activity even at high temperature (>70 °C); hence, investigations suggested their applicability in reactions occurring within a temperature range of 70–100 °C [184–186].

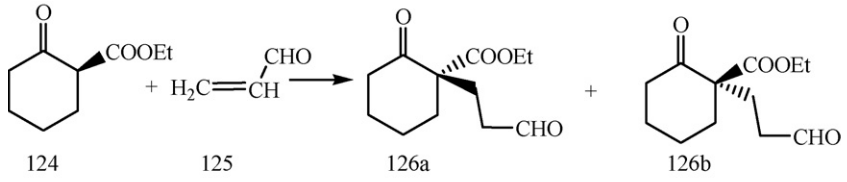
3.10. Michael addition reaction

Nucleophilic addition of carbanions to α,β-unsaturated carbonyl compounds is known as Michael addition, which is useful in formation of C–C bond. Copper(II) complexes of tetradentate ligands derived from salicylaldehyde showed high enantioselectivity (75% ee) [187]. Michael addition of 2-cyanopropionates to α,β-unsaturated ketones with rhodium(I) complexes showed optical induction up to 89% ee, but binaphthyl bisphosphine complexes of rhodium(I) showed 73% ee [188]. Binaphthyl complexes of titanium(IV) catalyzed alkenoyl-1,3-oxozolidine-2-one with *o*-benzyl hydroxylamine in Michael addition reaction up to 42% ee [189]. Chiral bis(oxazoline) copper(II) complexes catalyzed the reaction of propionate silyl ketene acetal to 2-(carbomethoxy) cyclopentanone and showed optical induction upto 63% ee [190]. The acrolein **124** (Scheme 27) with ethyl 2-oxocyclohexanecarboxylate **125** was catalyzed enantioselectively with a number of optically active transition metal complexes or in-situ combinations of transition metal complexes with optically active ligands [30].

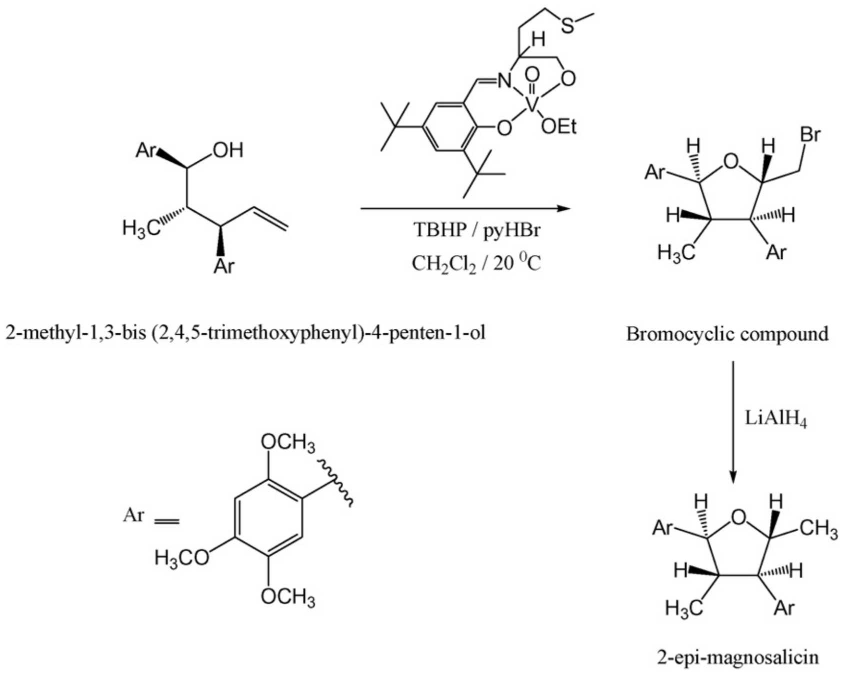
The Co(acac)$_2$ and optically active 1,2-diphenylethylenediamine ligands resulted in 47% ee **126** [30].

3.11. Annulation reaction

Schiff base complexes were mild and efficient catalyst in heteroannulation reaction. The 2-epi-magnosalicin was synthesized



Scheme 27. Michael addition reaction of acrolein [30].



Scheme 28. Annulation of 2-methyl-1,3-bis(2,4,5-trimethoxyphenyl)-4-penten-1-ol with vanadium(V) Schiff base catalyst [191].

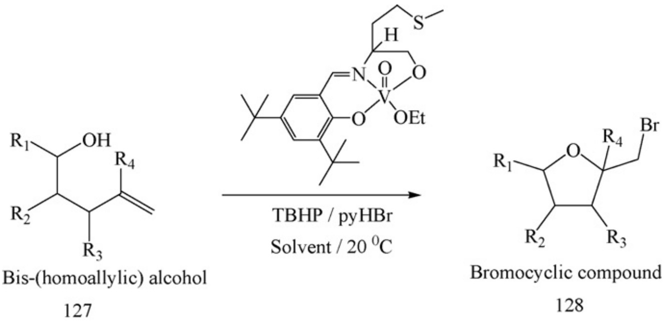
using 2-methyl-1,3-bis(2,4,5-trimethoxyphenyl)-4-penten-1-ol with pyridinium hydrobromide (pyHBr), *t*-butyl hydroperoxide (TBHP) and 5 mol% vanadium(V) Schiff base complex, which produced bromocyclized product at 20 °C [191]. The 2-epi-magnosalicin was obtained by the reduction of bromocyclized product with $LiAlH_4$ (Scheme 28).

Vanadium(V) Schiff base complexes [191] also showed catalytic activity in annulation of bis(homoallylic) alcohol **127** through bromocyclization **128** process (Scheme 29).

The annulation of bis(homoallylic) alcohol showed significant variation with type of substituents and reaction media [191]. The phenyl substituted allylic alcohol ($R_2 = C_6H_5$, $R_1 = R_3 = R_4 = H$) showed high yield (88%) in comparison to other substituents with CH_2Cl_2 (Table 11).

3.12. Carbonylation reaction

Carbonylation reactions showed their importance in organic synthesis. Amongst these reactions, the hydroformylation and hydroalkoxycarbonylations were more predominant. A number of mono and bidentate phosphines were used as both chiral and achiral ligands with transition metals as catalysts in hydroformylation and hydroalkoxycarbonylation reactions [192]. Palladium(II) and platinum(II) complexes modified with enantiopure homoannularly bridged ferrocenyl aminophosphine ligands were catalytic in the hydroformylation of styrene [193]. Aromatic isocyanates were industrially useful intermediates in the field of polymers to produce polyisocyanates. The aromatic isocyanates were produced by catalyzed carbonylations of aromatic nitro compounds using Schiff base complexes of palladium and rhodium metals. The environmentally benign reactions presented many advantages over conventionally used phosgene route for the production of isocyanates in which toxic phosgene is used and hydrolyzable chlorine compounds are unavoidably included in the products, which can be detrimental in further processing of the isocyanates [194].



Scheme 29. Annulation reaction of bis(homoallylic) alcohol by vanadium(V) Schiff base catalyst [191].

3.13. Heck reaction

Schiff base ligands are synthesized easily in comparison to phosphene ligands. The metal complexes of Schiff base ligands

Table 11
Annulation reaction of bis(homoallylic) alcohol [191]

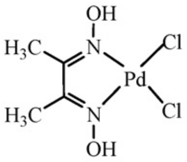
R_1	R_2	R_3	R_4	Solvent	Yield (%)
p-$H_3COC_6H_4$	H	H	H	CH_2Cl_2	69
C_6H_5	H	H	CH_3	CH_2Cl_2	64
H	C_6H_5	H	H	CH_3CN	82
H	C_6H_5	H	H	CH_2Cl_2	88
H	H	C_6H_5	H	CH_3CN	55
H	H	C_6H_5	H	CH_2Cl_2	56
H	H	H	C_6H_5	CH_2Cl_2	66

Table 12
The Heck reaction of 4-iodo anisole and 4-chloro-iodo benzene with ethyl acrylate and styrene by palladium(II) complex **129** [198]

Aryl halide	Olefin	Catalyst	Yield (%)
4-CH_3O-C_6H_4I	$C_5H_8O_2$	Pd (DMG)Cl_2	80
4-Cl·C_6H_4·I	$C_5H_8O_2$	Pd (DMG)Cl_2	68
C_6H_5·Br	$C_5H_8O_2$	Pd (DMG)Cl_2	48
4-HO-C_6H_4·Br	C_8H_8	Pd (DMG)Cl_2	16

$C_5H_8O_2$ (ethyl acrylate), C_8H_8 (styrene).

were stable toward heat, air and atmospheric moisture than metal complexes of phosphene ligands [195]. Palladium(II) complexes of nitrogen Schiff base ligands showed high catalytic activity in Heck reaction than commercially used phosphene Schiff base complexes [196,197]. The palladium(II) complexes of 8-hydroxyquinoline **129** produced high yield of *E*-cinnamates and *E*-stilbenes [197,198]. The palladium(II) complexes of oxime **129** showed high yield (80%) in Heck reaction of 4-iodoanisole with ethyl acrylate but the catalytic activity of these complexes was low (48%) in 4-chloro-iodobenzene and bromobenzene (Table 12). The activity of palladium(II) complexes **129** was low in the Heck reaction of 4-hydroxybenzene with styrene.



Pd(DMG)Cl_2
129

Structures of palladium(II) complexes of DMG.

3.14. Benzylation reaction of alanine

Nickel(II) salen complexes **130** showed catalytic activity in asymmetric benzylation reaction [199–201] of an alanine enolate **131** (Scheme 30). The fourth group transition metal complexes with square planar geometry were catalytic and particularly copper(II) and cobalt(II) complexes showed more catalytic activity.

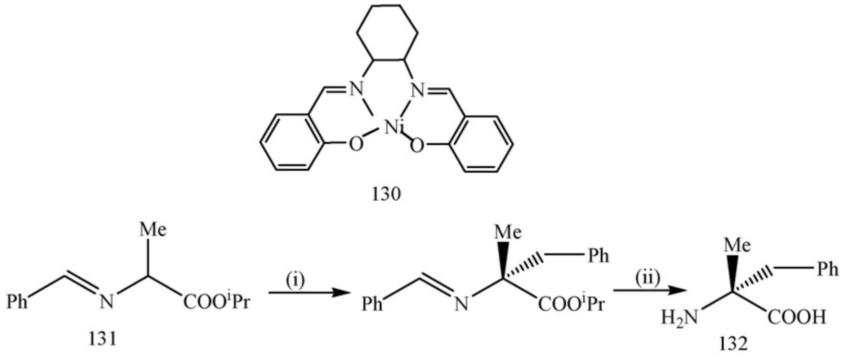
Salen ligands from acyclic chiral 1,2-diamines produced poor catalysts due to the presence of diamine substituents, which adopted anti-conformations in metal complexes, but Schiff base complexes from 5- and 6-membered cyclic 1,2-diamines produced active catalysts with low enantioselectivity [199–201].

3.15. Amidation and aziridination of hydrocarbons

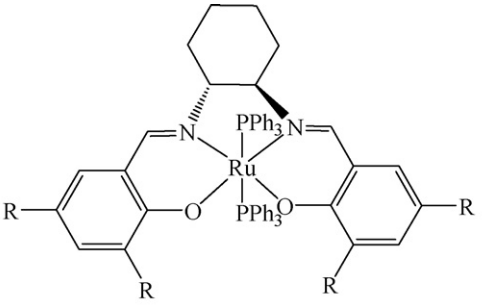
Metal-catalyzed aziridinations and amidations of hydrocarbons provided a useful means to synthese aziridines, amides and amines. Chiral metallo porphyrins also showed catalytic activity in asymmetric nitrine transfer reactions with moderate ee. Since the synthesis of chiral porphyrin ligands is a tedious process; hence, the improvement in ee through structural modifications in chiral metallo porphyrins is a difficult task. In comparison to porphyrin ligands, salen ligands are synthesized easily and are useful in asymmetric aziridination of alkenes and amidinations of saturated hydrocarbons. The asymmetric aziridination of alkenes and amidation of saturated C–H bonds was carried out using chiral ruthenium(II) salen complexes [Ru(II)(Salen)$(PPh_3)_2$] [202]. The aziridination of indene in the presence of these complexes showed 83% ee, whereas amidation of (1-cyclohexenyloxy)-trimethylsilane showed 97% ee. The chiral ruthenium(II)-salen complexes **133** were effective catalysts in the asymmetric amidation of silyl enol ethers and aziridation of alkenes [203]. The catalytic activity in the aziridation of 1-cyclohexenyloxy trimethyl silane **134** was dependant on substrate to catalyst concentration. At 12.5 mol% of catalyst, the conversion, yield and ee of 1-cyclohexenyloxy trimethyl silane **134** to 2-[*N*-(*p*-tolylsulfonyl)amino]cyclohexanone **135** was highest (Scheme 31). The activity of catalyst was lower in acetonitrile [203].

3.16. Isomerization of norbornadiene to quadricyclane

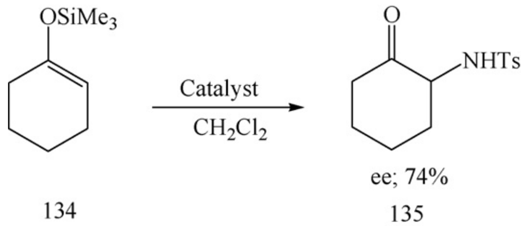
The isomerization of unfunctionalized alkenes has received much attention and has been a subject of extensive mechanistic and synthetic studies. The interconversion of norbornadiene and quadricyclane has attracted considerable efforts due to its potential importance in storage of solar energy. Transition metal Schiff base complexes were effective in sensitizing the conversion of norbornadiene to quadricyclane due to the formation of ground state charge transfer complexes between transition metal and norbornadiene. Isomerization of tetraphosphanorbornadi-



Scheme 30. Nickel(II) salen complex **130** catalyzed asymmetric benzylation of alanine enolate **131** forming α-methyl phenylalanine [199–201].

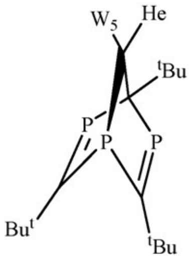


133a- R = NO$_2$, 133b- R = I, 133c- R = Br



Scheme 31. Aziridation of 1-cyclohexenyloxy trimethyl silane with ruthenium(II) salen complexes [203].

ene to quadricyclane isomers is reported [204] in the presence of tungsten Schiff base complexes of phosphinidine **136** and triphosphabenzene **137** at room temperature. The investigations have confirmed that the relative stability of norbornadiene and quadricyclane was inverted when phosphorus changed the framework of the Schiff base.



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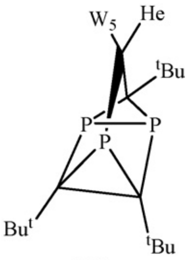


137

The nickel(II) complexes of Schiff base of glycine and pyridine 2-carboxylic acid (2-benzoyl-phenyl)-amide(PBP) were used successfully as catalysts in synthesis of chiral isomers of α-amino acids, which showed 80% ee in the presence of α,α,α′,α′′-tetraaryl-1, 3-diaoxanal-4,5-dimethanol (TADDOL) [205].

Table 13
Asymmetric cyclopropanation of styrene catalyzed by copper(I) [209]

Ligand	mol (%)	Yield (%)	*cis*:*trans*	ee (%cis)	ee (%trans)
115	5.0	52	30:70	8	2
115	2.5	40	46:54	2	1

ee (Enantioselectivity excess).

3.17. Addition reaction of cyanides to imine

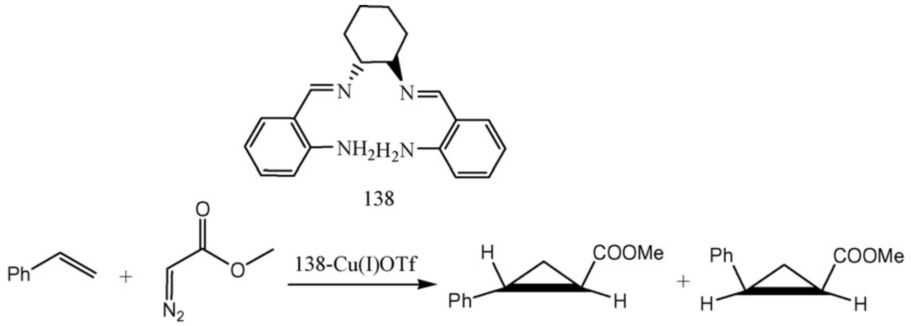
The enantioselective catalytic addition of HCN to ketoimines was carried out using readily accessible and recyclable Schiff base catalysts [206]. The conversion of α-aminonitrile adducts to the corresponding α-quaternary α-amino acid showed high yields through formylation/hydrolysis sequences. The chiral catalysts in formal addition of hydrogen cyanide to imines were effective in various imine substrates and showed >80% ee for Strecker reaction of aliphatic imines [207].

The polymer supported tridentate Schiff base complexes were also prepared as catalysts by sequential addition of linker amino acid, linker diamine and salicylaldehyde components, which showed increased enantioselectivity due to the presence of bulky group on salicylaldehyde [208].

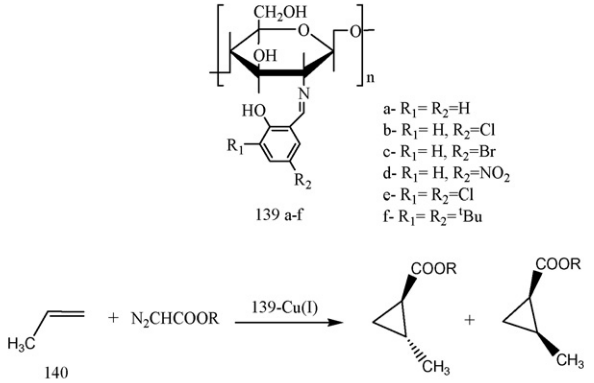
3.18. Cyclopropanation reaction

Copper(I) complexes showed catalytic activity in the cyclopropanation of styrene (Scheme 32) with diazo reagents **138**—Cu(I)OTf [209]. The yield of cyclopropanation of styrene in the presence of Cu(I)OTf catalyst varied significantly on increasing the mol% of catalyst in the reaction mixture (Table 13). The yield and *trans*-selectivity for cyclopropanation of styrene decreased on decreasing the mol% of catalyst [209].

Schiff base complexes of copper(I) from chitosan and substituted salicylaldehydes **139 a–f** also showed catalytic activity in the cyclopropanation of olefins **140** with alkyl diazoacetates (Scheme 33) [210]. These catalysts showed high activity and 56% ee was achieved under optimal conditions. The catalysts were recovered easily and reused in the cyclopropanation reaction. The asymmetric cyclopropanation of olefins was also carried out by slow addition of diazoacetate to a refluxing solution in chloroform containing Schiff base complexes of copper(I) [211,212] and a significant effect on ee was noticed. Substituents on salicylaldehydes influenced the catalytic activity



Scheme 32. Cyclopropanation of styrene with methyl diazoacetate [209].

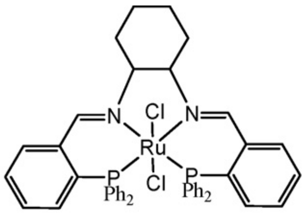


Scheme 33. Cyclopropanation of olefins by Schiff base complexes of Cu(I) [210].

of Schiff base complexes of copper(I) monohydrate in asymmetric cyclopropanation of styrene [213]. The electron withdrawing substituents also enhanced the selectivity, but bulky substituents retarded the selectivity.

Partially heterogenized chiral binaphthyl Schiff base ligands with copper(I) and copper(II) were also used as catalyst [214] in cyclopropanation of several terminal alkenes, which produced cyclopropanes in 60–96% yields (Reaction 1 in Scheme 34). Binaphthyl chiral Schiff base complexes of copper(II) also used as catalysts in the cyclopropanation of styrene [215], which produced cyclopropanes in 32–99% yields on varying trans: *cis* ratio from 65:35 to 80:20 (Reaction 2 in Scheme 34). These binaphthyl complexes also showed catalytic activity in the cyclopropanation [215] of various aromatic alkenes (Reactions 2 and 3 in Scheme 34).

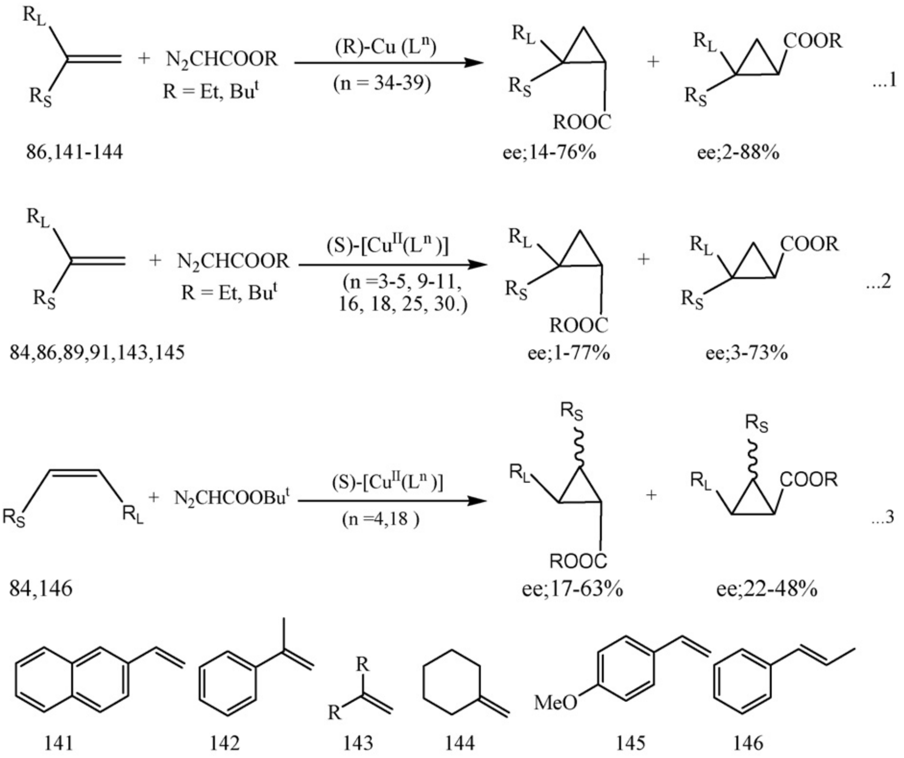
N_2P_2–Ru(II) complexes **147** were activated by silver triflate to catalyze the asymmetric cyclopropanation of styrene with ethyl diazoacetate but observed enantioselectivity was low [216].



147

N_2P_2-Ru(II) Schiff base complex

Cobalt(III) salen complexes were active in the cyclopropanation of styrene with *t*-butyldiazoacetate and showed high *trans*-selectivity (95%) and enantioselectivity (75% ee) [217]. The folded structure of cobalt(III) salen complexes controlled the enantioselectivity and catalytic activity in the cyclopropanation of styrene. Chitosan Schiff base complexes of copper(II) were also catalytic in the cyclopropanation of styrene in the presence of ethyldiazoacetate [218].



Scheme 34. Cyclopropanation reactions [214,215]. $L^3 = \mathbf{6}$ ($R_1 = R_2 = Cl$), $L^4 = \mathbf{6}$ ($R_1 = R_2 = Br$), $L^5 = \mathbf{6}$ ($R_1 = R_2 = I$), $L^9 = \mathbf{6}$ ($R_1 = H$, $R_2 = PhI$), $L^{10} = \mathbf{6}$ ($R_1 = H$, $R_2 = Cl$), $L^{11} = \mathbf{6}$ ($R_1 = H$, $R_2 = NO_2$), $L^{16} = \mathbf{6}$ ($R_1 = OEt$, $R_2 = H$), $L^{18} = \mathbf{6}$ ($R_1 = Cl$, $R_2 = H$), $L^{25} = \mathbf{6}$ ($R_1 = Cl$, $R_2 = Bu^t$), $L^{30} = \mathbf{6}$ ($R_1 = Et$, $R_2 = NO_2$), $L^{34} = \mathbf{5}$ ($R_1 = R_2 = R_3 = Cl$), $L^{35} = \mathbf{5}$ ($R_1 = R_2 = R_3 = Br$), $L^{36} = \mathbf{5}$ ($R_1 = R_2 = R_3 = Me$), $L^{37} = \mathbf{5}$ ($R_1 = R_2 = R_3 = Pr^i$), $L^{38} = \mathbf{5}$ ($R_1 = H$, $R_2 = R_3 = Cl$), $L^{39} = \mathbf{5}$ ($R_1 = H$, $R_2 = R_3 = Me$).

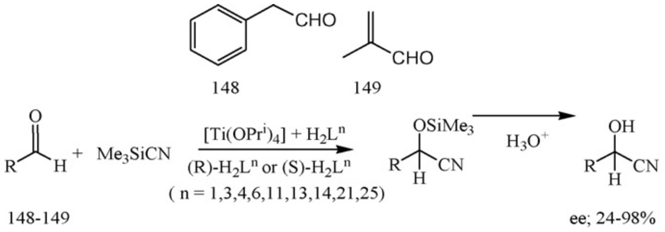
3.19. Silylcyanation reaction of aldehydes

The room temperature addition of trimethylsilylcyanide to aromatic and aliphatic aldehydes was catalyzed by adding 1 mol% of ((2,6-bis(*N*-cyclohexyl)imino)phenyl) aquaplatinum(II) trifluoromethanesulfonate to produce corresponding cyanohydrins. These catalysts were prepared taking 1:1 ratio of aqua [2,6-bis[(cyclohexylimino-*k*N) methyl]phenyl-*k*C]platinum(1+),aqua[2,6-bis[[(1,1-dimethylethyl) imino-*k*N] methyl]phenyl-*k*C]platinum(1+) tetrafluoroborate(1−), aqua [2,6-bis(4,5-dihydro-4,4-dimethyl-2-oxazolyl-*k*N3)phenyl-*k*C] palladium(1+) salts with trifluoro methane sulfonic acid [219]. The trimethylsilylcyanation of (α*S*)-α-methyl-*N*-(phenylmethylene)benzenemethanamine with trimethylsilanecarbonitrile (TMSCN) was catalyzed using platinum and palladiun NCN-pincer complexes as catalyst, which produced (α*S*)-α-[[(1*S*)-1-phenylethyl[amino]benzeneacetonitrile as major stereoisomer [219]. The TMSCN was efficiently added to ketones by using 3 mol% achiral Schiff base complex ($Ti(OCHMe_2)_4$) as Lewis acid and 3 mol% *N*,*N*-dimethylaniline *N*-oxide as Lewis base [220]. The aromatic, aliphatic, cyclic and heterocyclic ketones such as acetophenone, 2-octanone and 2-acetylfuran produced racemic O-TMS cyanohydrins, e.g. α-methyl-α-(trimethyl silyloxy) benzeneacetonitrile showed good to excellent yields (99%) under mild conditions [220]. The chiral titanium(IV) Schiff base catalysts were also used in asymmetric silylcyanation of aldehydes and in asymmetric addition reaction of diketenes with aldehydes [221]. The titanium(IV) complexes of binaphthyl chiral Schiff base were used as catalysts [222–227] in trimethylsilylcyanation of benzaldehyde **148**, which produced cyanohydrins in 42–98% yields and 24–93% ee on treatment with acid (Scheme 35).

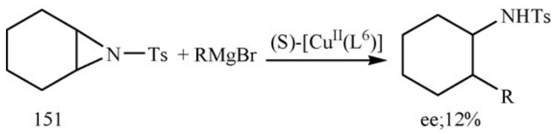
The trimethylsilylcyanation of other aldehydes **149** in the presence of titanium(IV) complexes of binaphthyl chiral Schiff base have produced corresponding cyanohydrins in 63–87% yields with >96% ee [127]. The chiral titanium(IV) salen complexes showed catalytic activity in enantioselective trimethylsilylsilation of benzaldehyde in dichloromethane at room temperature and produced (*S*)-2-phenyl-2-trimethylsiloxyacetonitrile in 86% ee [225].

3.20. Desymmetrization reaction of meso compounds

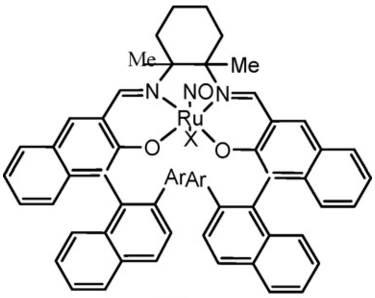
Chiral (nitrosyl)Ru(salen) complexes **150** (X = Cl, OH; Ar = Ph, *p*-C_6H_4Ph) were used as catalyst in aerobic oxidation to desymmetrize the *meso* diols [228]. The activity of the catalyst was dependent on nature of apical ligand. The oxidation of *meso* diols with apical hydroxo ligand complex **150** (X = OH, Ar = *p*-C_6H_4Ph) as catalyst showed moderate to good enantioselectivity (80% ee).



Scheme 35. Silylcyanation reaction [222–227]. L^1 = **6** ($R_1 = R_2 = H$), L^3 = **6** ($R_1 = R_2 = Cl$), L^4 = **6** ($R_1 = R_2 = Br$), L^6 = **6** ($R_1 = R_2 = Bu^t$), L^{11} = **6** ($R_1 = H$, $R_2 = NO_2$), L^{13} = **6** ($R_1 = Et$, $R_2 = H$), L^{14} = **6** ($R_1 = Bu^t$, $R_2 = H$), L^{21} = **6** ($R_1 = Bu^t$, $R_2 = Cl$), L^{25} = **6** ($R_1 = Cl$, $R_2 = Bu^t$).



Scheme 36. Desymmetrization of azabicyclohepatene [66]. L^6 = **6** ($R_1 = R_2 = Bu^t$).



150

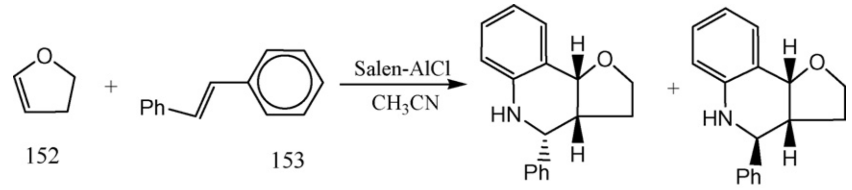
The catalytic activity of copper(II) complexes of binaphthyl chiral Schiff base was also evaluated in the desymmetrization of 7-tosyl-7-azabicyclo [4.1.0] heptanes **151** in the presence of Grignard reagent RMgBr [66], which afforded sulfonamide product in 78% yield and 12% ee (Scheme 36).

The activity of catalyst was similar to 1,2-cyclohexyl analogue of (*S*)-[Cu(II)(L^6)], but high enantioselectivity (12% ee) was observed in the presence of (2,4,6-$Me_3C_6H_2$) MgBr [66].

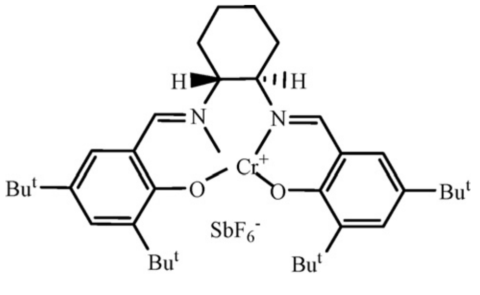
3.21. Diels–Alder reaction

The first target-oriented synthesis of pyranoquinolines as potential antibacterial agents by inverse electron demand Diels–Alder reaction (IED-DA) was accomplished using chiral salen–AlCl complex as catalyst, which resulted in moderate yields and high diastereoselectivity (>90%) [229]. The addition of molecular sieves in the reaction mixture increased the yield and ee. Therefore, the salen–AlCl complex catalyzed IEDDA reaction was studied in the presence of different mol% of molecular sieves in reaction mixture of 2,3-dihydrofuran **152** and 2-azadiene **153**, which showed marginalized increase in diastereomeric excess (Scheme 37).

Chiral Schiff base lanthanum(III) complexes displayed catalytic activity in the asymmetric Diels–Alder reaction of 3-(2-propenoyl)-2-oxazolidinone with cyclopentadiene [230]. 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) [231,232]. The new family of enantiomerically enriched BINAM-derived Schiff base chromium(III) complexes **154** were used as catalysts in Diels–Alder reactions [233].



Scheme 37. Diels–Alder reaction using chiral salen-AlCl [229].



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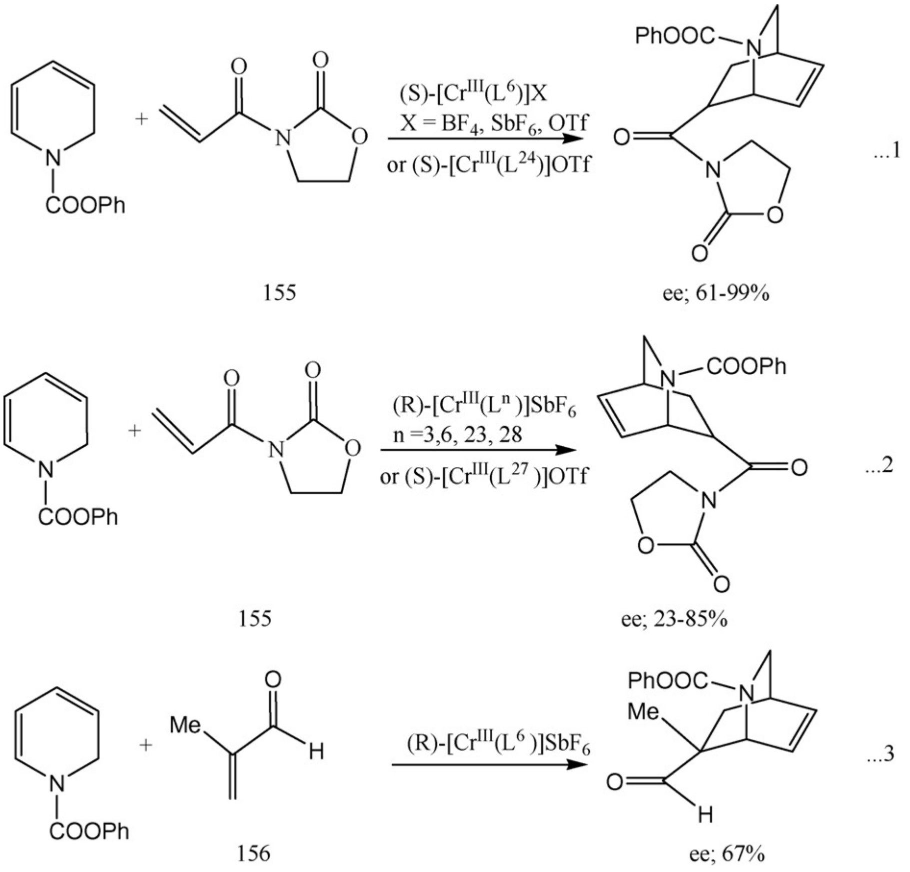
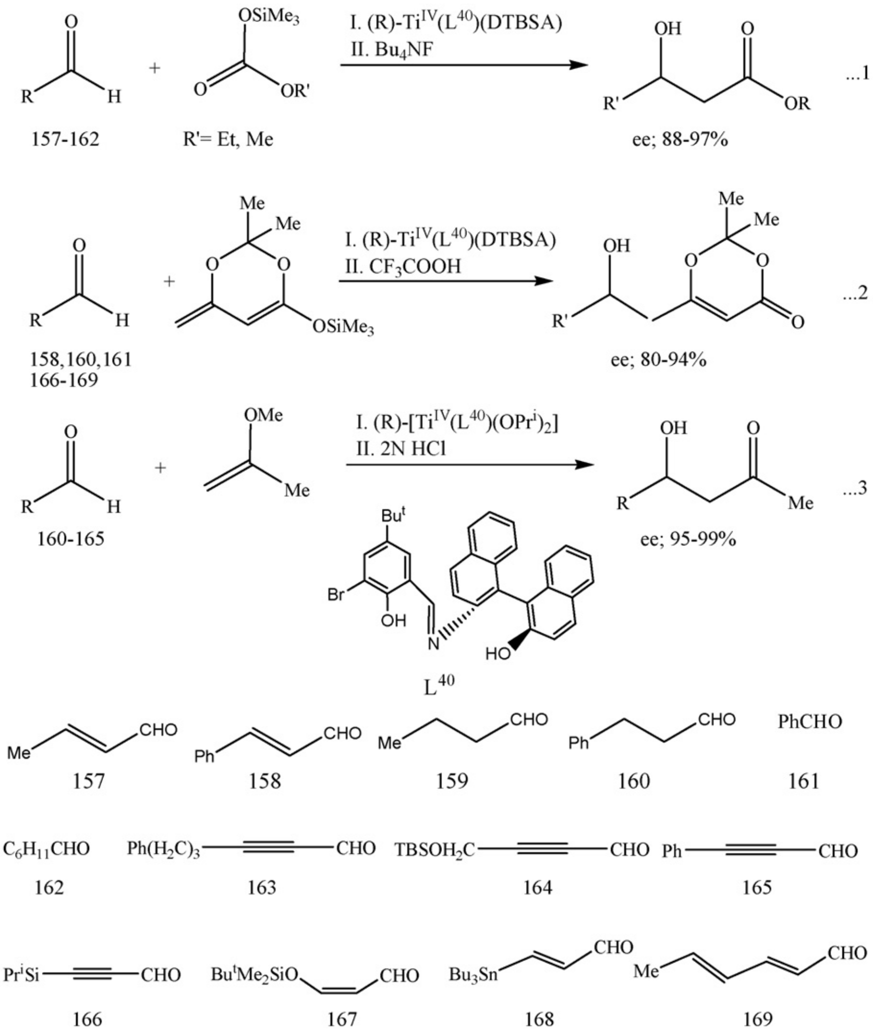
Chromium(III) complexes of binaphthyl chiral Schiff base were efficient catalysts in Diels–Alder reaction of protected 1,2-dihydropyridines. The reaction of 1-phenoxycarbonyl-1,2-dihydropyridine with *N*-acryloyloxazolidinone **155** in the presence of binaphthyl catalysts afforded endo-cycloadduct in 61–99% ee and 23–85% ee (Reactions 1 and 2 in Scheme 38). The activity was improved, when acetone was used as solvent. In acetone, the endo-cycloadduct showed 86–99% yield and 70–85% ee except for (*S*)-[Cr(III)(L^{27})]OTf catalyst. The reaction of 1-phenoxycarbonyl-1,2-dihydropyridine with metha-acrolein **156** in the presence of (*S*)-[Cr(III)(L^6)]SbF_6 catalyst produced endocycloadduct with 89% yield and 67% ee (Reaction 3 in Scheme 38). The enantioselectivity was 10% higher than observed with 1,2-cyclohexyl analogue of (*S*)-[Cr(III)(L^6)]SbF_6 [233].

The asymmetric hetero-Diels–Alder reaction between [(2-chlorobenzoyl)oxy]-acetaldehyde and [(trimethylsilyl)oxy]buta1,3-diene was carried out using chromium(III) salen complexes in non-coordinating ethereal solvent at −30 °C in the presence of 4 Å molecular sieves [234]. The nature of the catalyst showed a significant effect on both yield and enantioselectivity of reaction. The chiral Schiff base complexes of titanium and aluminium were also used as catalyst in Diels–Alder reactions [234].



Scheme 38. Diels–Alder reaction of 1,2-dihydropyridines [233]. $L^3 = \mathbf{6}$ ($R_1 = R_2 = Cl$), $L^6 = \mathbf{6}$ ($R_1 = R_2 = Bu^t$), $L^{23} = \mathbf{6}$ ($R_1 = Bu^t$, $R_2 = Me$), $L^{24} = \mathbf{6}$ (R_1 = Adamantly $R_2 = Me$), $L^{27} = \mathbf{6}$ ($R_1 = SPh$, $R_2 = Bu^t$), $L^{28} = \mathbf{6}$ ($R_1 = Bu^t$, $R_2 = OMe$).



Scheme 39. Aldol condensation reaction with different aldehydes [238,239].

3.22. *Aldol condensation reaction*

Aldol condensation between ketones and aldehydes is an easy way for C–C bond formation. Metal oxides have been used as catalysts in difficult Aldol condensation reactions with acetaldehydes or formaldehydes [235]. Pyridoxal-catalyzed aldol reaction of amino acid with aldehydes or ketones is a biologically important process to add new C–C 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 [236,237].

Titanium(IV) binaphthyl (DTBSA) Schiff base complexes showed activity in enantioselective aldol condensation of dienolate with a variety of aldehydes **157–162**, **166–169** (Reactions 1 and 2 in Scheme 39), which produced about 88–97% ee [238,239]. These complexes were also used as catalysts in the aldol addition reaction between $CH_2{=}C$ (OMe) Me and aldehydes **160–165**, which showed 95–99% ee (Reaction 3 in Scheme 39). 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 [240]. 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 [241], 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 [241].

4. Concluding remarks

Schiff base complexes of transition metal ions have played a significant role in various reactions to enhance their yield and product selectivity. The convenient route of synthesis and thermal stability of Schiff base ligands have contributed significantly for their possible applications in catalysis as metal complexes. Catalytic activity of Schiff base complexes showed significant variations with structure and type of Schiff base ligands as found in oligomerization of isoprene and butadienes. Schiff base complexes with hydroxyl groups have shown high activity in epoxidation of olefins than unsubstituted or aryl substituted ligands. The transition metals in combination with different Schiff base ligands showed high catalytic activity in reaction of industrial importance as described in this review. Enantioselectivity in various reactions was controlled with metal complexes of chiral Schiff base ligands. Metal complexes of binaphthyl ligands showed high enantioselectivity than metal complexes of salen and other Schiff base ligands. The metal ions complexes of chiral Schiff base ligands also used as catalyst in controlling the product molecular weight in ATRP reactions and also induced photodegradation in polyethylenes under mild conditions. The easy electron donating ability of Schiff base ligands also played a significant role in carrying out ROMP and ATRP reactions at low temperatures. The activity of Schiff base complexes of transition metals showed significant improvements on their immobilization on various supports. In addition to high catalytic activity of Schiff base complexes on various supports, the supported catalysts also showed efficient recovery and reuse in various reactions. Schiff base complexes of transition metal ions in supercritical carbon dioxide ($ScCO_2$) have further enlarged the range of substrates, which were difficult to be oxidized in the presence of Schiff base complexes of metal ions alone or other catalysts. The activity of Schiff base complexes has shown dependence on their solubility in $ScCO_2$, which was controlled by adding different additives such as fluorocarbons and copolymers of polyether carbonates. The polarity of reaction media has also influenced the activity of Schiff base complexes of transition metal ions as observed in some reactions described in this review. These studies have clearly demonstrated that Schiff base complexes of transition metals are versatile and efficient catalysts for reactions of commercial importance and suitable to catalyze various reactions under mild experimental conditions. Further research and developments in the area of Schiff base complexes transition metal ions would be highly useful to industries and academia.

Acknowledgements

Authors are thankful to I.I.T. Roorkee for providing facilities to carry out these investigations. One of the authors, Mr. Alekha Kumar Sutar is thankful to MHRD New Delhi for financial assistance ship.

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