DIOXOMOLYBDENUM COMPLEXES- SYNTHESIS AND CATALYTIC APPLICATION IN OXIDATION REACTIONS

A THESIS SUBMITTED TO
THE UNIVERSITY OF PUNE

FOR THE AWARD OF
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BY
SWATI L. PANDHARE

RESEARCH GUIDE
Dr. S. B. UMBARKAR

RESEARCH CO-GUIDE
Dr. M. K. DONGARE

CATALYSIS DIVISION
CSIR-NATIONAL CHEMICAL LABORATORY
PUNE-411008, INDIA

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राष्ट्रीय रासायनिक प्रयोगशाला
(वैज्ञानिक तथा औद्योगिक अनुसंधान परिषद)
डॉ. होमी भाभा रोड, पुणे - 411 008. भारत
NATIONAL CHEMICAL LABORATORY
(Council of Scientific & Industrial Research)
Dr. Homi Bhabha Road, Pune - 411008. India

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Certified that the work incorporated in the thesis, **"Dioxomolybdenum Complexes-Synthesis and Catalytic Application in Oxidation Reactions"** submitted by ***Swati L. Pandhare*****,** for the Degree of ***Doctor of Philosophy*****,** was carried out by the candidate under my supervision in the Catalysis Division, CSIR-National Chemical Laboratory, Pune - 411008, India. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

Dr. Shubhangi B. Umbarkar **Dr. M. K. Dongare** Date:

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I, hereby declare that the thesis entitled "***Dioxomolybdenum Complexes- Synthesis and Catalytic Application in Oxidation Reactions***" submitted by me for the degree of ***Doctor of Philosophy*** to the **University of Pune**, is the record of work carried out by me at ***Catalysis Division, CSIR-National Chemical Laboratory, Pune - 411008*** under the guidance of ***Dr. Shubhangi B. Umbarkar*** and has not formed the basis for the award of any degree or diploma to this or any other University. I further declare that the material obtained from other sources has been duly acknowledged in the thesis.

(Swati L. Pandhare) Date:

Signature of the Candidate

Dedicated to…

My beloved Parents and My husband

Mr. Dinanath, who have been a constant source of support and encouragement during my reaserch work.

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CONTENTS

ABSTRACT OF THE THESIS

Dioxomolybdenum Complexes- Synthesis and Catalytic Application in Oxidation Reactions

In chemical industry transition metal based homogenous and heterogeneous catalysts are extensively used for production of wide range of oxygenated compounds per year. Homogeneous catalysts are used in many large scale oxidation processes such as acetaldehyde from ethylene, adipic acid from cyclohexane, terephthalic acid from p-xylene, and propylene oxide from propylene, etc. Special interest arose to use Mo(VI)-oxo-complexes for oxidation when ARCO and HALCON published patents on the olefin-epoxidation by Mo(VI)-catalyst. Several industrial processes such as ammoxidation of olefins, olefin epoxidation and olefin metathesis are performed using molybdenum based catalysts. Most of the catalytic oxidations still use conventional stoichiometric oxidants of low atom economy such as peracids, alkyl hydroperoxides, hypervalent iodine reagent, hypochlorite, and N-oxide compounds. These oxidants generates large amount of waste as by-product which is not acceptable due to environmental concern. Molecular oxygen and hydrogen peroxide overcome these drawbacks hence are preferred oxidants. Molecular oxygen offers a great advantage because it is abundant in air and is inexpensive. Hydrogen peroxide is recognized as a green oxidant due to generation of water as by-product. It is almost as equally atom-efficient as molecular oxygen, and the by-product is safe and clean water. Moreover, its aqueous solution (typically 30-35 %) is inexpensive and easy to handle. Consequently, the development of catalytic oxidations with molecular oxygen or hydrogen peroxide as oxidants is one of the most important issues to be addressed by organic chemists for production of useful oxygenates such as diol, epoxides, alcohols, and carbonyl compounds.

Peroxides of group 4-7 metals with low oxidation potential and high Lewis acidity in their highest oxidation states have proven to be superior catalysts for oxidation with reactivity in the order Mo > W > V > Ti. Ligand environment around the central metal atom directs the selectivity for particular product. Some homogeneous metal complexes are also reported to be recyclable. Generally better catalytic activities of several molybdenum(VI)-oxo complexes in oxidation reactions

make this type of complexes in principle promising candidates for asymmetric catalysis by using chiral ligands. Due to the above mentioned advantages or benefits as well as its industrial interest, Mo catalyzed oxidation has received considerable attention. Owing to the importance of homogenous molybdenum complexes in oxidation, the following objectives have been set for the thesis:

1. Synthesis of achiral and chiral dioxomolybdenum complexes using $MoO_2(acac)_2$ as molybdenum precursor.
2. Synthesis of organometallic molybdenum carbonyl benzyl complex as catalyst precursor for molybdenum dioxo or oxo-peroxo species.
3. Detailed characterization of synthesized complexes using various techniques such as FT-IR, NMR, single crystal X-ray diffraction analysis.
4. Evaluation of complexes for catalytic oxidation of wide range of substrates such as olefins, allylic alcohols and sulfides.

The **first chapter** gives introduction to catalysis, homogeneous catalysis and its various applications in large scale industrial processes. The chapter briefly describes homogeneous and heterogeneous catalysts containing molybdenum in various catalytic applications and its importance. It also gives an overview of the molybdenum catalyzed oxidation reactions especially about achiral, chiral dioxomolybdenum (VI) catalysts in epoxidation reactions and its mechanistic considerations, which helps to understand the role of dioxomolybdenum moiety and ligand in selective oxidation reactions.

The **second chapter** describes the synthesis and characterization of Schiff base dioxomolybdenum complex (**1**), *rac*-salen dioxomolybdenum complex (**2**) and cyclopentadienyl molybdenum tricarbonyl acetylide complex (**3**) (Figure 1) as catalyst precursor of dioxo and oxoperoxo molybdenum species and its application in epoxidations of different allylic alcohols, glycerol and glycerol derivatives.

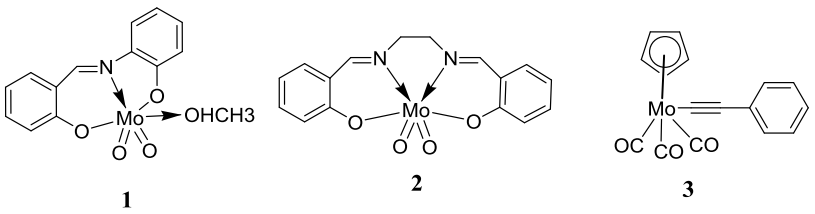
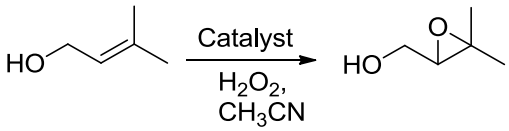


Figure 1. Molybdenum complexes prepared from different ligands

Initially epoxidation of 3-methyl-2-buten-1-ol (Scheme 1) was carried out as model substrate to study the effects of various parameters such as reaction temperature, molar ratio of oxidant and catalysts with respect to substrates to optimize reaction condition for high conversions and selectivity.

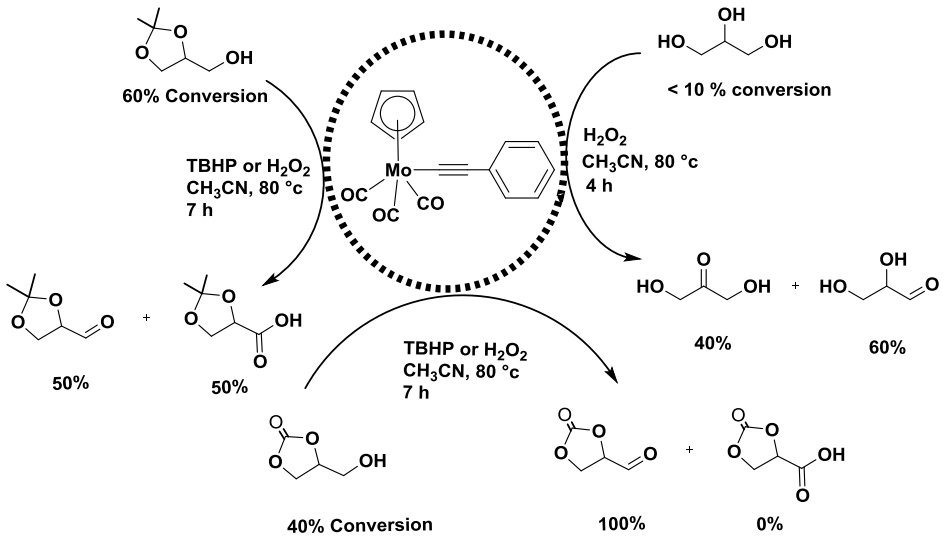


Scheme 1: Epoxidation of 3-methyl-2-buten-1-ol

All the prepared catalysts showed almost similar activity with > 95% conversion and 99% selectivity for epoxy alcohol in 2 h at 80 °C using hydrogen peroxide (2 equiv.) as an oxidant. Decreasing the concentration of catalyst or oxidant decreased the rate of epoxidation of 3-methyl-2-buten-1-ol. A wide range of allylic alcohols including homoallylic alcohols were used to study the epoxidation reaction using optimized reaction conditions.

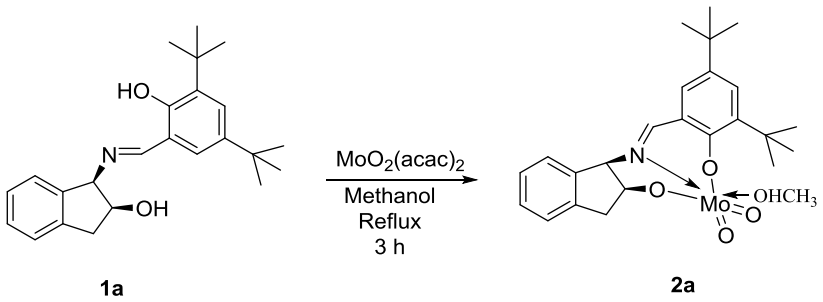
Catalyst **1** showed very high conversion for epoxidation of allylic alcohols compared to homoallylic alcohols. Very high conversion was obtained in case of geraniol (> 99 %) and 3-methyl-2-buten-1-ol (99 %) with 99 % selectivity for epoxy alcohols. No reaction was observed in case of unsubstituted, long chain allylic alcohols and secondary alcohols.

The prepared catalysts **1** and **3** were also evaluated for oxidation of glycerol and glycerol derivatives i.e. glycerol protected with an isopropylidene group (solketal) or a carbonate residue (glycerol carbonate) using H_2O_2 and TBHP as oxidants (Scheme 2). The oxidation ability of all the catalysts was found to depend on protecting group of glycerol as well as oxidizing agent.



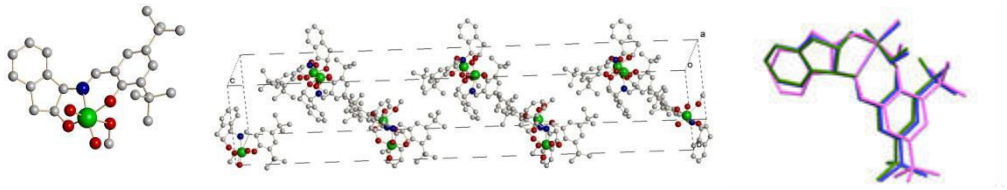
Scheme 2. Oxidation of glycerol and glycerol derivatives by catalyst **3**

Third chapter describes the synthesis of chiral schiff base dioxomolybdenum complex (**2a**) using bis(acetylacetonate) dioxomolybdenum(VI) and (*1R,2S*)-1-[(3,5-di-*tert*-butyl-2-hydroxybenzylidene)amino]-2-indanol (**1a**) as chiral ligand (Scheme 3).



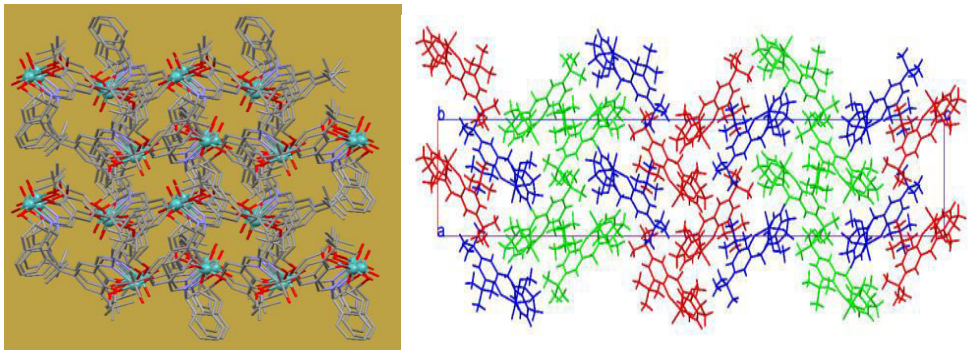
Scheme 3. Synthesis of chiral Schiff base dioxomolybdenum complex

Synthesized complex was characterized by various techniques such as elemental analysis, FT-IR, NMR and single crystal X-ray diffraction analysis. The extensive characterization confirmed the formation of Schiff base dioxomolybdenum complex (**2a**). Single crystal study of the complex confirmed orthorhombic space group $P2_12_12_1$ with 3 molecules in the asymmetric unit. There are 6 molecules in the unit cell.



(**A**) (**B**) (**C**)

Figure 2. (**A**) PLUTON diagram (**B**) Six molecules in unit cell and (**C**) Overlapping of the 3 conformers of complex **2a**



(A) (B)

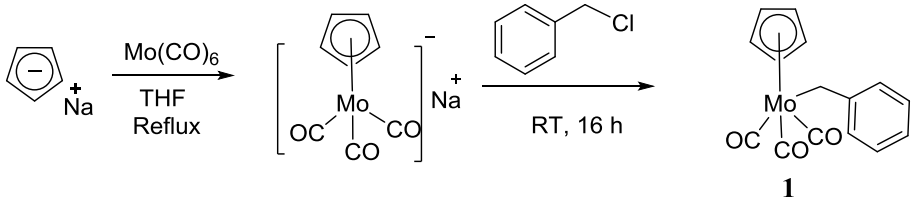
Figure 3. Packing diagram of complex **2a** (**A**) as viewed down c-axis. (**B**) as viewed down a-axis

The packing diagram of complex **2a** when viewed down c-axis showed supramolecular assembly [Figure 3 (**A**)]. When viewed down a-axis molecules B and C were found to entangled and sandwiched between molecules of A [Figure 3 (**B**)].

Asymmetric epoxidation and sulfoxidation reactions were carried out to evaluate catalytic activity of chiral schiff base dioxomolybdenum complex (**2a**). The effect of various parameters such as temperature, solvent, substrate to oxidant molar ratio was studied to achieve high enantioselectivity for epoxide and sulfoxides. Catalyst showed more than 90% epoxides and sulfoxides selectivity, however with no enantioselectivity. Obtained products were confirmed by ^{1}H NMR and enantiomeric excess (*ee)* was measured by GC or HPLC using chiral columns.

Fourth chapter describes the synthesis and characterization of cyclopentadienyl tricarbonyl molybdenum benzyl complex as precursor of dioxo and

oxo-peroxo molybdenum complex (Scheme 4). Synthesized complex was characterized by FT-IR and NMR spectroscopy. FTIR and NMR spectroscopy confirmed the formation of molybdenum benzyl complex. ^{1}H NMR spectrum showed characteristic signal of $\eta^5(C_5H_5)$ at δ 4.86, phenyl ring at δ 6.9-7.4 and CH_2 group at δ 2.87 of approximate relative intensities 5:5:2 corresponding to five π-cyclopentadienyl protons, five phenyl protons and the two methylene protons, respectively.



1

Scheme 4. Synthesis of cyclopentadienyl molybdenum tricarbonyl benzyl complex

The dioxomolybdenum and oxo-peroxo molybdenum benzyl complex obtained *in situ* by the treatment of cyclopentadienyl tricarbonyl molybdenum benzyl complex **1** with TBHP or H_2O_2 has been used as a catalyst for oxidation of various substrates such as ethyl lactate to ethyl pyruvate, alcohols to aldehydes and sulfide to sulfoxides.

Oxidation of ethyl lactate to its pyruvate ester is one of the most important reactions because pyruvate ester is widely used in production of perfumes, food additives and electronic materials. It also used as raw material in synthesis of anticancer drugs. By considering importance of pyruvate ester, effective production of pyruvate at low temperature with an inexpensive catalyst would be desirable. Hence, cyclopentadienyl tricarbonyl molybdenum benzyl complex **1** was screened for this reaction and it showed 80% conversion with very high selectivity (99%) for ethyl pyruvate in 8 h at 80 °C using anhydrous TBHP (~5.5 M in decane) as an oxidant. Same catalyst was screened for oxidation of 1,3-diphenyl-2-propyn-1-ol and benzyl alcohol and excellent conversion of 1,3-diphenyl-2-propyn-1-ol (> 90%) with 99% selectivity for 1,3-diphenylprop-2-yn-l-ones was obtained under similar reaction conditions. Oxidation of benzyl alcohol has been carried out with or without solvent. In presence of solvent (CH_3CN) benzyl alcohol showed very poor activity, whereas, without solvent better conversion was obtained. In case of sulfide oxidation using

hydrogen peroxide as an oxidant catalyst (**1**) showed excellent conversion (> 90%) at room temperature. Scope of substrates has been studied by using range of sulfides.

The **fifth chapter** gives an overall summary and conclusions with respect to the synthesis and characterizations of molybdenum complexes and successful attempts to use of dioxomolybdenum complexes as catalyst in the oxidation of wide range of allylic alcohols to epoxy alcohols, olefins to epoxide, sulfides to sulfoxides with excellent conversions and selectivity.

Chapter 1

Introduction

1. Introduction

1.1. Catalysis

Catalysis word was introduced first by Berzelius in 1850's though catalytic phenomena were practiced much before that. Later on in 1985, Ostwald proposed a detailed description of catalyst: *A substance which changes the rate of a chemical reaction without itself consumed in the reaction.* Substances which act as catalysts are transition metals, organometallic complexes, chemical compounds (e.g. metal oxides, sulfides, nitrides), and enzymes. A catalyst provides an alternative pathway of lower activation energy (E_a) for reaction without altering the energies of reactant and products. In Arrhenius equation, activation energy (E_a) term usually describe the energy which is necessary for reaction to proceed and reach the transition state. Similarly, Eyring equation describes rate of reaction. Instead of using E_a, Eyring used concept of Gibbs free energy (ΔG) to indicate the energy of transition state. If activation energy is lower, the reaction is catalyzed by providing an alternative path which involves a different transition state with lower activation energy (Figure 1.1).

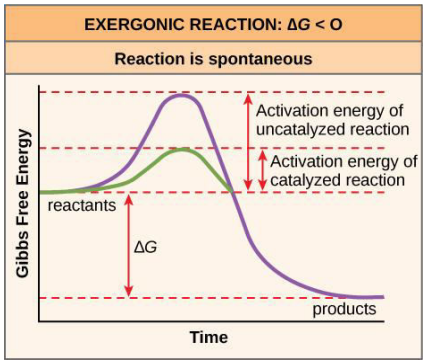


Figure 1.1. Energy profile diagram

Depending on the reactions Gibbs free energy (ΔG) of the reaction can be negative or positive. If ΔG of the reaction is negative that means reaction releases energy and called as exergonic reaction and if ΔG is positive which means reaction consumes energy is called an endergonic reaction. Exergonic reactions are spontaneous due to less energy of the products than their reactants and endergonic reactions are nonspontaneous due to higher energy of their product compared to the reactants. However, all reactions require an initial energy input to proceed, which is called as activation energy. The role of catalyst is very specific under ideal conditions, gives selectivity for particular product and avoids side reactions. Further catalyst in

reaction shows advantages like reduced time and energy. Hence, overall process becomes environmentally sustainable.

Steps of catalytic cycles are shown in Figure 1.2. Reactant **A** and **B** are reacted to give desired product **P.** In the first step molecule A and B bind to the catalyst. If catalyst is heterogeneous, **A** and **B** molecules are adsorbed on catalyst surface. In case of homogeneous catalysis **A** and/or **B** reacts with catalyst forming reactive intermediate complex which may be unstable. This homogeneous intermediate gives product P liberating the original homogeneous catalyst.

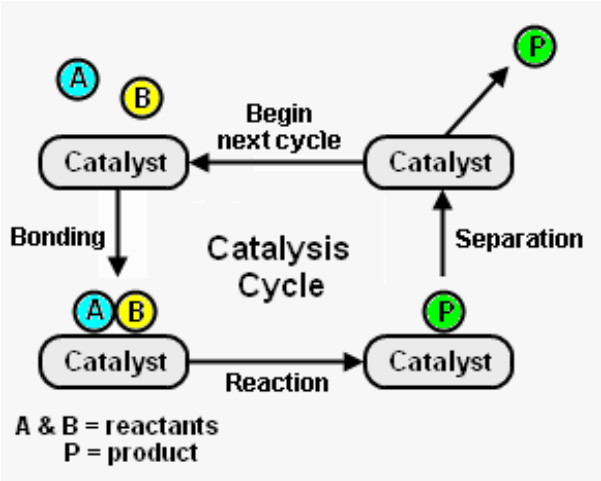


Figure 1.2. The catalysis cycle using heterogeneous catalyst and its elementary steps

Catalysis is divided in to two main types: Homogeneous and Heterogeneous

More than 85% industrial processes are based on heterogeneous catalysts. In heterogeneous catalysis only active site on the surface participates in the catalysis. Catalysis also plays an important role in environmental protection in terms of reducing NO_x coming out from diesel engines. It is one of interdisciplinary field and its exploration in manufacturing field is highly essential to avoid environmental pollution by reducing waste produced in industry by conventional methods. Currently catalysts are used in fine chemicals, fuels, and polymer industries. According to world catalysis study, demand of catalyst is increased per year by 5.8% and global catalysis market is probable to reach a cost of $19.5 billion till 2016. Global catalyst market is an extremely competitive market; day by day new catalysts are being developed by manufacturers to explore the potential of catalysis market to increase their returns. Hence, the investment in R&D terms is increasing for the innovation of new products.

Research efforts also been taken to increase the stability of catalyst and recycle the spent catalysts. Also researchers are involved in solving issues related to life-cycle, selectivity, and recyclability of the catalysts. There is need to develop high performing catalysts which give improved selectivity, longer run-cycles etc. Global catalyst market has demand to increase clean fuels. Automobile industries are growing rapidly and numbers of stringent rules are coming in to effect like decrease in the concentration of sulfur in transportation of fuels. This increased the demand of the catalyst which removes sulfur from gasoline and diesel by hydrotreating applications.

a). Heterogeneous catalysis

In a heterogeneous reaction, the catalyst is in a different phase from the reactants and usually solid. Advantages of heterogeneous catalyst:

- Easier to extract and recycle

Disadvantages are as follows:

- Lower effective concentration of catalyst because reaction occurs only on the exposed active surface

To increase the active site of the catalyst, it is necessary to spread finely on a cheap and sturdy support. In some cases fine mesh is used e.g. Pt mesh used to catalyse the oxidation of ammonia.

Some examples of heterogeneous catalysts are:

- Transition metals
- Transition metal oxides
- Zeolites
- Silica/alumina

Approximately, 95% industrial processes use heterogeneous catalyst because of high thermal stability, lower chance of deactivation and recovery and reusability etc. Some industrially important heterogeneous catalyzed processes are e.g.: Haeber-Bosch process for manufacture of ammonia using heterogeneous iron catalyst, oxidation of ammonia to nitric acid using platinum as catalyst, use of vanadium oxide in Contact process for manufacturing of sulfuric acid, Mobil process for preparation of gasoline from methanol using zeolite (ZSM-5), selective catalytic reduction (SCR) of NO_x with NH_3 to N_2 using V, Ti (Mo, W) oxides (monoliths), oxidation (Sumitomo Chem., two-step process) for production of acrylic acid from propene using (1) Mo,

Bi oxides (2) Mo, V, PO (heteropolyacids), oxidation (Monsanto) for synthesis of maleic anhydride from *n*-butane using vanadylphosphate, oxidation with H_2O_2 (Enichem) using Ti silicalite to get hydroquinone and catechol from phenol, catalytic destruction of N_2O from nitric acid tail gases (EnviNO_x process, Uhde) using Fe zeolite for removal of nitrous oxide and HPPO (BASF-Dow, Degussa-Uhde) by Ti silicalite for preparation of propylene oxide from propene etc.

b). Homogeneous catalysis

In case of homogeneous catalysis reactant and the catalyst present in the same phase. Homogeneous catalysts having disadvantages like more sensitive to permanent deactivation and more difficult product/ catalyst separation which involve distillation. Even though homogeneous catalysts are used over heterogeneous for following advantages:

- Homogeneous catalysts are more selective due to the presence of more complicated sites (chemically and geometrically) which improve selectivity.
- Due to the presence of reactant and catalyst in same phase it is more active and can be easily studied from chemical and mechanistic aspects and modified easily for optimizing selectivity.
- One more advantage of its presence in solution is that catalyst has more effective concentration and there is more contact with reactant and access to the reagent is also easier so there is possibility to increase activity and milder reaction conditions can be used and transfer of heat for highly exothermic or endothermic is not a problem.
- One important thing is at the research and development stage it is simpler to work with homogeneous catalysts to find out path of reaction and further to find out heterogeneous system for industrial applications.

Homogeneous catalysis is not only the study of organometallic complexes but also other catalysts such as

- General acid and base catalysis (alumina–silica catalysts, solid acid catalyst)
- Lewis acids as catalysts (e.g. $AlCl_3$, $ZnCl_2$, BF_3, $SnCl_4$ etc.)
- Organic catalysts (thiazolium ions in Cannizzarro reactions)
- Porphyrin complexes (epoxidations, hydroxylations)
- Enzymatic processes

- Co-ordination complexes (polyester condensations)

In case of transition metal complex catalyzed reactions, ligands plays very important role. Variety of products can be formed from single substrates using one metal by simply changing ligand or substitution on ligands. Organometallic catalysts contain a central metal atom surrounded by organic or inorganic ligands. Metal and ligand determine the property of catalysts. The success of homogeneous catalysts is because it can easily be modified by changing the ligand environment. After the discovery of Zeise's salt $K[PtCl_3(C_2H_4)]\cdot H_2O$, research has been carried out on organometallic complexes and its catalysis. Previously mercury sulfate was used as catalyst in industry for conversion of acetylene to acetaldehyde. Later Wacker introduced a novel method for oxidative conversion of ethylene to acetaldehyde using palladium(II) chloride and copper(II) chloride as a catalysts. After the discovery of hydroformylation in 1938 by O. Roelen, homogeneous catalysts received attention from industrial point of view. Later on more processes started in industries applying homogeneous catalysts namely Ziegler-Natta catalyst for controlled alkene polymerization, nickel catalyzed hydrocyanation (Dupont), cobalt catalyzed carbonylation of methanol (BASF), cobalt catalyzed hydroformylation (Shell) (discovered already in 1938 by Ruhrchemie), and molybdenum catalyzed epoxidation of propene (Halcon Corporation), rhodium catalyzed carbonylation of methanol (Monsanto), rhodium catalyzed hydroformylation (Union Carbide Corporation using Wilkinson's findings), Shell's higher olefins process, asymmetric hydrogenation to L-DOPA (Monsanto), and ring-opening polymerization of cyclooctene using tungsten metathesis catalysts (Huels). Another class of homogeneous catalysts like Bronsted and Lewis acids for e.g. $AlCl_3$, H_2SO_4, *p*-TSA are used in acylation, alkylation, esterification, nitration etc. The main advantages of homogeneous catalysts are-

- High and controllable activity
- Chemo- and regio- and enantioselective
- High TON and TOF
- No mass transfer limitations
- High accessibility to active sites
- Easy catalyst designing and mechanistic understanding, etc.

However, there are major drawbacks like- low thermal stability, isolation problems, recyclability issues, and tedious work up procedures, etc. However, there

are still many important industrial processes carried out using homogeneous catalysts and no alternative heterogeneous catalyst could be developed. One of the most popular and important application of homogeneous catalysis is enantioselective catalysis which is essential for many pharmaceutical applications and so far not many heterogeneous catalysts could replace the homogeneous counterparts as far as required high enantioselectivity is concerned. Asymmetric reactions are normally carried out using preformed or *in situ* prepared chiral homogeneous catalysts. Some commercial processes are Takasago process for asymmetric isomerization, Sumitomo process for asymmetric cyclopropanation, Arco process for asymmetric Sharpless epoxidation and asymmetric hydrogenation to L-DOPA etc. The developments of efficient chiral catalysts or ligands play a crucial role in asymmetric catalysis. Although many chiral ligands/catalysts have been developed in the past decades, the most efficient catalysts are derived from a few core structures, called "privileged chiral catalysts".

Some privileged chiral ligands are given below (Figure 1.3):

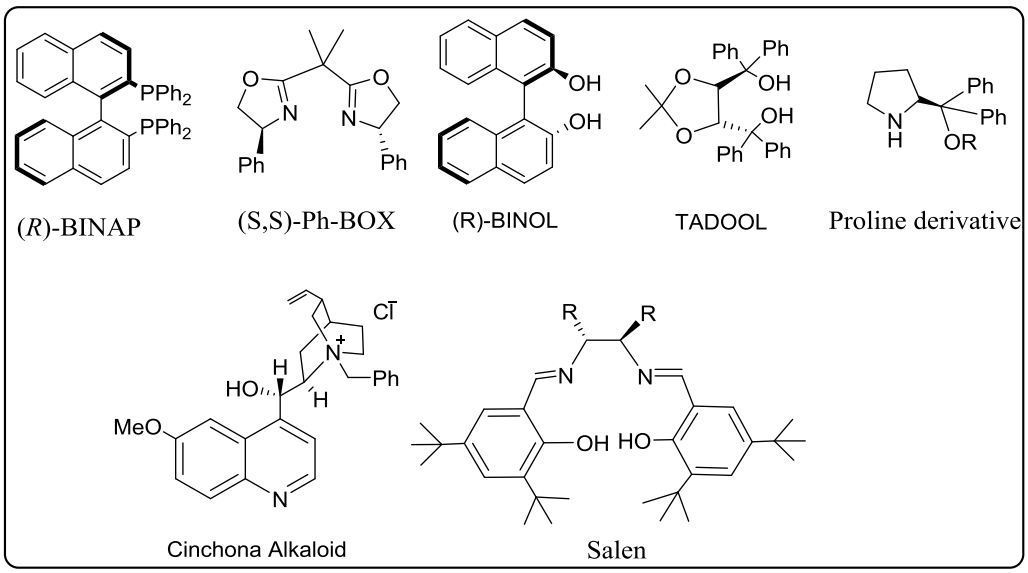


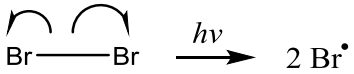
Figure 1.3. Privileged chiral ligands

1.2. Importance of oxidation

Oxidation is one of the industrially important processes for production of oxygenated compounds.[1] The concept of oxidation was initiated by Lavoisier's in 1773 by rejecting the phlogiston hypothesis. Oxidations usually involve homolytic/heterolytic pathways. In case of hemolytic cleavage radical formation takes

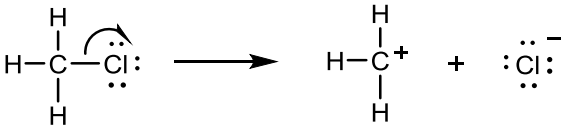
place by cleavage of interatomic bonds (Bond breaking in which the bonding electron pair is split evenly between the products).

For example:



Heterolytic cleavage: In case of bond breaking, bonding electron pair is split unevenly and it produce at least one ion.

For example:



Industrially catalytic oxidation corresponds to huge market for production of fine chemicals. Especially epoxides are highly reactive intermediates due to ring strain and acts as precursor to complex molecule. Epoxides are widely used intermediates in organic synthesis. Transition metal based catalysts are best to improve efficiency of oxidations, normally used in hydrocarbons oxidation with environmentally green oxidants such as oxygen and hydrogen peroxide for the conversion of oil- and natural gas based feedstocks to industrial organic chemicals.[2] Epoxides synthesized in transition metal catalyzed olefins epoxidation are important industrial raw materials used in broad range of products from pharmaceuticals to plastics and paints to adhesives and are also useful in production of other chemicals. Epoxides are typically prepared in batch reactions using stoichiometric oxidants such as dichromate, permanganate and peracids such as peracetic acid and meta-chloroperbenzoic acid (*m*-CPBA) typically produces equivalent amounts of acid as by-product which is not environmentally green process. Due to increasingly stringent environmental constraints it is necessary to develop green route for oxidation or epoxidation which provides many advantages to potential users such as flexibility in feedstock, flexibility in production, cost reduction, efficiency and better returns.

1.3. Choice of oxidant

Several main group elements and virtually all transition metal complexes catalyze oxidation reactions using range of oxidants. Some of the important criteria for selecting oxidant are:

- Cost effective
- Easily accessible
- Selective and easy to handle
- By-product formed after sacrificing oxygen should be environmentally green
- High weight percentage of available oxygen

Though oxygen or air is the most preferred oxidant for all oxidation processes, activation of oxygen is very difficult and many times not feasible under mild conditions of homogeneous catalysis. Hence hydrogen peroxide is the next option because it contains 47% active oxygen and co-product is water. Other oxidants such as alkyl hydroperoxides, hypochlorite or iodosylbenzene etc. can be used in transition metal based oxidation systems but these oxidants have some drawbacks such as low active oxygen content, co-products are not environmentally green etc. Hence, from an environmental and economic point of view, molecular oxygen or H_2O_2 should be the preferred oxidant, as it generates no waste product or only water as byproduct. Another major limitation of using molecular oxygen as oxidant is poor selectivity. Therefore hydrogen peroxide is an attractive oxidant which is cheap and can be used to prepare other oxidant such as sodium perborate, potassium hydroperoxysulfate, and many organic peroxy acids.

Table 1.1 lists the active oxygen content of some common oxidants along with the by-product.

Table 1.1. Active oxygen content of common oxidants

Oxidant	% Active oxygen	Coproduct
Oxygen (O_2)	100 or 50	Nothing or H_2O
H_2O_2	47	H_2O
N_2O	36.4	N_2
O_3	33.3	O_2
NaOCl	21.6	NaCl
CH_3CO_3H	21.1	CH_3CO_2H
t-BuOOH (TBHP)	17.8	t-BuOH
$KHSO_5$	10.5	$KHSO_4$
$NaIO_4$	7.5	$NaIO_3$
PhIO	7.3	PhI

Numerous liquid phase processes were developed during 1950's and 1960's. *e.g.* Wacker process for ethylene oxidation to acetaldehyde, the Celanese process for n-butane oxidation to acetic acid and the Amoco Mid-Century process for the production of terephthalic acid from *p*-xylene. Most important process is production of acetic acid, *e.g*. rhodium catalyzed carbonylation of methanol developed by Monsanto.[3]

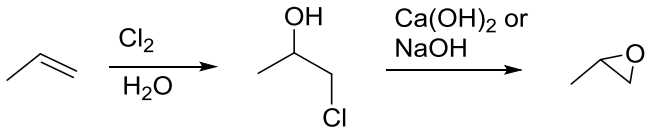
Some important industrial processes for production of oxygenates by heterogeneous reactions are given below in Table 1.2.

Table 1.2. Important industrial processes

Reactant	Product	Catalyst	Conditions	Yield (%)
Methanol	Formaldehyde	Iron molybdates or Silver/support	250-300 °C	90-95
Propylene	Acrolein	Bi, Mo, Co, Fe oxide	350-400 °C	90-95
Acrolein	Acrylic acid	V_2O_5/MoO_3	400-450 °C	90
Cyclohexane	Caprolactam	Pd/Al_2O_3	-	-
o-Xylene	Phthalic anhydride	V_2O_5/TiO_2	420 °C	95
Ethylene	Ethylene oxide	Ag/Al_2O_3	200-300 °C (10-30 O_2 atm)	70-75

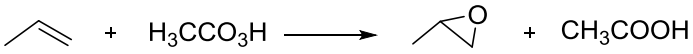
Out of these ethylene and propylene oxidation is important due to its wide range of applications. Ethylene oxide is important raw material for many important products such as detergents, thickners, solvents, plastics and various organic chemicals e.g. ethylene glycol, ethanolamines and higher alcohols etc. Ethylene oxide is prepared commercially by gas-phase oxidation of ethylene with air or oxygen using silver catalyst supported on α-alumina.[4] To replace the chlorohydrin process for production of ethylene oxide, this process was first introduced in 1937 by Union Carbide and in 1958 by Shell. But, this method is limited only for simple olefins and not applicable for olefins which possess allylic C-H bond. Allylic double bond gave

low yield of expected product due to formation of by-products by oxidizing allylic C-H bond.[5] Propylene oxide is an important product for the chemical industries because of its wide range of applications that are predominantly used in the polyurethane and solvent industries. It is highly reactive chemical used as an intermediate for the production of numerous commercial materials. Industrially it is prepared by reacting propylene with hypochlorous acid to form propylene chlorohydrin as intermediate which further treated with base to form propylene oxide (Scheme 1.1).



Scheme 1.1. Chlorohydrin route for propylene oxidation

But Chlorohydrin route is expensive, toxic and environmentally hazardous. Hence, peracid route (Scheme 1.2) was developed[6] to replace chlorohydrin route to epoxidized olefins using peracid such as per acetic acid but this route also has disadvantages such as expensive, corrosive and low efficiency and this method is restricted for special olefins such as acid labile olefins due to side reaction of acid.

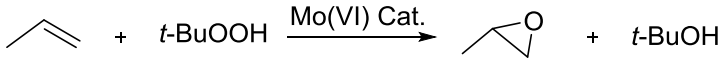


Scheme 1.2. Peracid route for propylene oxidation

Several studies on epoxidation of olefins using hydrogen peroxide and in presence of MnO_2, W or Mo oxides as catalysts showed the process to be economically not viable.[7] First report on epoxidation of olefin with an alkyl hydroperoxide using cumene hydroperoxide (CHP) and V_2O_5 as catalyst showing 30% yield of cyclohexene oxide was developed by Hawkins.[8] Subsequently, Brill[9] reported the use of *tert*-butyl hydroperoxide (TBHP) with catalytic amount of acetylacetonate of Mo, V, Cr.

The most important industrial epoxidation process for production of propylene oxide was developed by SHELL and ARCO/HALCON using high valent transition metal catalyst and alkyl hydroperoxides as an oxidant.[10] ARCO[11] and HALCON[12]

independently developed this process using homogeneous metal (Mo, W, Ti, Re, Cr, V etc.) catalysts. Later on, ARCO and HALCON developed a joint-venture, the Oxiranes Corporation, for the preparation of propylene oxide using Mo(VI) catalyst and organic hydroperoxides. Molybdenum gave excellent reaction rate and selectivity with TBHP.[13] The resulting "oxirane process" was used for almost 45 % of the production of propylene oxide in 2002[14] (Scheme 1.3).



Scheme 1.3. Oxirane process for propylene oxidation

Another successful partnership between the German BASF, the US company DOW and Belgium's Solvay, laid the foundation of the first plant for production of propylene oxide using hydrogen peroxide as an oxidant.[15] The HPPO process makes use of titanium(IV)-silicate (TS-I) as catalyst, first introduced by chemists at Enichem in 1983.[16]

There are other successful large scale processes catalyzed by homogeneous catalyst are acetaldehyde from ethylene, adipic acid from cyclohexane, terephthalic acid from *p*-Xylene etc. Variety of oxidant can be used in oxidation reactions. Several studies have been carried out on development of selective oxidation catalyst.[17]

Asymmetric epoxidation is highly important to prepare enantiopure epoxides which are useful in synthesis of pharmaceuticals compounds, specialty materials, agricultural chemicals etc. and transition metal based catalytic systems are useful for synthesis of chiral compounds.[18] Enantiopurity is extremely important in pharmaceuticals as enantiomers of a chiral compound can have intensely different biological activities.[19] Asymmetric catalysis is an efficient method to introduce chiral epoxides into larger organic compounds.[20] Asymmetric epoxidations are known using Sharpless system,[21] it converts allylic alcohols into epoxides with more than 90 % *ee* using titanium(IV) catalyst and TBHP as oxidant. Jacobsen and Katsuki's system[22] with Mn-Salen provided an efficient method for epoxidation of unfunctionalized and particularly *cis*-olefins etc. Manganese(III) chiral Schiff base complex/NaOCl combination developed by Jacobsen and co-workers[23] in 1990 achieve yield as high as 97% with *ee*'s of 98%. This process is only applicable for the epoxidation of *cis*-olefins, due to geometry of the catalyst and the mechanism of oxo transfer. But the

stoichiometric amount of oxidant used produces equivalent amount of undesirable byproducts giving a low atom economy. For example oxidant such as sodium hypochlorite or iodosylbenzene, oxone etc. produce large amount of waste materials which is not acceptable from environmental point of view. Hence, development of new method for selective oxidation using transition metal based catalyst is extremely necessary.

The non-chiral organomolybdenum(VI) complexes showed excellent activity in epoxidation reactions.[24] Hence, chiral derivatives of these oxo-molybdenum complexes might be applied as chiral catalysts to produce chiral epoxides. Chiral porphyrins of Mo=O catalyzed asymmetric epoxidation of *cis*-*β*-methylstyrene gave up to 29% ee.[25] Other chiral ligands such as bis(oxazoline),[26] bidentate alcohol[27] and sugar derived Schiff base ligands[28] with Mo oxo have been developed. This type of *cis*-MoO_2 moiety with chiral Lewis base ligands has reported to give low or moderate *ee* for the epoxidation of *trans* or *cis*-*β*-methylstyrene.

1.4. Molybdenum chemistry and its catalysis

The outstanding feature of molybdenum is its chemical versatility:

- Oxidation states from (−II) to (VI);
- Coordination numbers from 4 to 8;
- Varied stereochemistry;
- The ability to form compounds with most inorganic and organic ligands, with a particular preference for oxygen, sulfur, fluorine and chlorine donor atoms;
- Formation of bi- and polynuclear compounds containing bridging oxide or chloride ligands or molybdenum-molybdenum multiple bonds up to Mo-Mo quadruple bonds.
- Having as its principal ore molybdenum disulfide, MoS_2;
- Its binding by sulfur ligands in molybdenum-containing enzymes;
- Application of MoS_2 as an important industrial catalyst;
- Low cost

Molybdenum is present in several enzymes such as aldehyde oxidase, sulfite oxidase and xanthine oxidase and catalyzes metabolic reactions.[29] The molybdenum has ability to withstand at extreme temperature without expanding and softening. Hence it is used in manufacture of armor, aircraft parts, electrical contacts, industrial motors and filaments. It is less toxic than other metal, and has ability to resist poisoning by

sulfur. Hence, Mo-based catalysts have a major application in the hydrodesulfurization (HDS) reactions and in conversion of coal to liquids hydrocarbon. Mo(VI) based catalysts are generally used in variety of organic transformation and stabilized through formation of MoO_2^{2+} unit. Molybdenum(II) based complexes also has an extensive application in catalysis. Especially molybdenum hexacarbonyl forms stable organometallic complex in its lower oxidation states which contain molybdenum carbon bond. Some compounds which contain molybdenum in its higher oxidation state like MoO_3, $MoO_2Cl_2.(DMSO)_2$, $Na_2MoO_4.2H_2O$ etc. are used as precursor to prepare molybdenum complexes as well as they are directly used as catalysts. Due to its outstanding characteristics, molybdenum based homogeneous and a heterogeneous catalyst are widely used in variety of catalytic applications and becomes attractive substitute.

Several industrial processes are executed over molybdenum catalysts. Some of these are summarized in Table 1.3.

Table 1.3. Molybdenum compounds in catalysis

Catalyst	Application	Reaction	Importance
Sulfided Co-Mo or Ni-Mo on alumina	Hydrotreating, hydrodesulfurisation	Remove sulfur from crude petroleum	Oil and petroleum refining
Bi-Mo oxides	Propene selective oxidation, ammoxidation	Synthesis of acrolein, acrylonitrile	Polymers and plastics industry
Mo-V oxides	Acrolein oxidation	Synthesis of acrylic acid	Polymers and plastics industry
Fe-Mo oxides	Methanol oxidation	Synthesis of formaldehyde	Making formalin, polymers, resins
Mo oxide on alumina	Olefin metathesis	Propene to ethene and butene	Olefin synthesis

Mo complexes	Epoxidation	Olefin to epoxide	Polyether synthesis
Heteropolyacids-phosphomolybdate	Propene hydration	Propene to alcohol	Alcohols synthesis

Bismuth molybdates catalyzed oxidation reactions; molybdenum participates in the selective oxidation and ammoxidation of propene to acrylonitrile and other chemicals which are used as raw materials in the plastics and fiber manufacturing industries. In case of iron molybdates molybdenum catalyzes the selective oxidation of methanol to formaldehyde.

The technically important reactions of methanol oxidation to formaldehyde and propene to acrolein and acrylonitrile are shown in Figure 1.4.

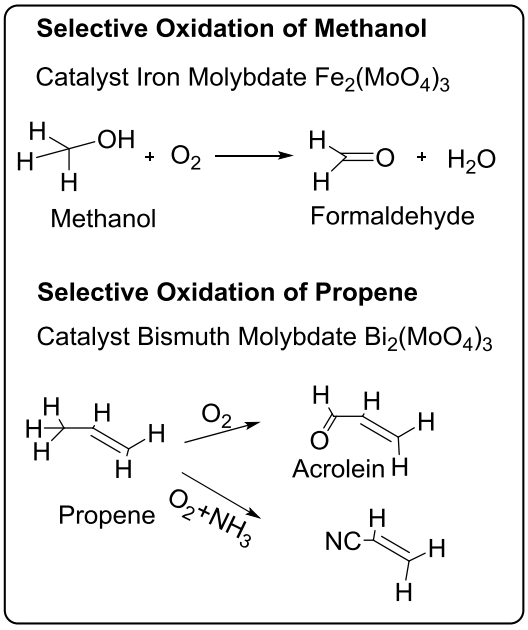


Figure 1.4. Methanol and propene oxidation by molybdenum containing catalyst

In case of two step propene oxidation catalyzed by bismuth molybdates, in the first step breaking of C-H bond take place by bismuth oxide and in the next step molybdenum gets reduced to activate second hydrogen and insertion of oxygen atom. Reduced molybdenum gets reoxidized by oxygen from the feed and catalyst regenerated back. Catalytic activity depends on the ability of oxo-molybdenum

species to change its oxidation state between IV and VI by releasing and transferring oxygen atom (Figure 1.5).

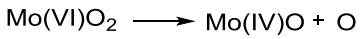


Figure 1.5. Oxidation state of oxo-molybdenum species

After this discovery special interest arose to use Mo(VI) catalysts in oxidation reactions. As we know chemistry of molybdenum is dominated by dioxomolybdenum unit. Dioxomolybdenum catalysis is important in industry.[30] Co-ordination chemistry of Mo(VI) has received considerable attention because of its catalytic ability in epoxidation and hydroxylation of olefins,[31] oxidations of alcohols[32] and in oxygen transfer reactions.[33] Molybdenum complex containing Mo(VI) moiety generally involves O^{2-} oxo ligand. Especially octahedral transition metal complexes can have two orientation, *cis*-dioxo and *trans*-dioxo due to presence of two oxo groups. *Cis*-orientation is possible for transition metal having d^0 electronic configuration. However, in case of d^2 electronic configuration oxo-groups are present in *trans* form. Molybdenum complexes are also present in tetrahedral geometries. Jurison has reported the *cis* and *trans*-orientation of dioxomolybdenum complexes (Figure 1.6).

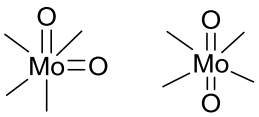


Figure 1.6. Molybdenum *cis* and *trans*-orientation

Dioxomolybdenum complexes can be prepared directly using dioxomolybdenum precursors such as $MoO_2(acac)_2$ and $MoO_2Cl_2(DMSO)_2$ using reported procedures. $MoO_2(acac)_2$ is prepared using sodium molybdates and acetylacetonate by adjusting pH with conc. HNO_3.[34] MoO_2Cl_2 was prepared in 1826 by J. J. Berzelius but is not stable as MoO_2Cl_2 in air and dimerizes quickly. Hence, starting material was stabilized by co-ordinating solvent molecule which forms solvent adducts, $MoO_2X_2L_2$ (X = THF, CH_3CN, DMF, DMSO).[35] Solvent adduct of MoO_2Cl_2 are stable for longer period of time and much easier to handle. This is very important precursor to synthesize variety of dioxomolybdenum complex due to electron deficiency of $MoO_2Cl_2(Solv)_2$ which reacts readily with oxygen and nitrogen donor ligands and it is also used as oxidation catalyst. Replacing chlorides in

MoO_2Cl_2 by organic fragments increases the stability of molybdenum oxide. Varieties of organic fragments are used to synthesize several dioxomolybdenum complexes to tune the catalytic activity. $MoO_2(Mes)_2$ was the first oxide synthesized in 1976 by Heyn and Hoffmann[36] by replacing the chlorides using Grignard reagents MesMgBr. Mo=O groups are labile and a number of reactions are known in which the MoO_2 act as a catalyst for oxygen atom transfer. Due to the strong Lewis acidity and weak basicity of the oxo group, the $Mo(VI)O_2$ units have short Mo(VI)=O bond distances. Realizing the importance of dioxomolybdenum compound in oxidation reactions, Bergmann and co-workers[37] first reported the derivatives of cyclopentadienyl dioxomolybdenum(VI) complex as catalysts for the olefin epoxidation using TBHP as an oxidant. No reaction was observed when Ph_3COOH and hydrogen peroxide was used as an oxidizing agent. In 1970, Mimoun *et al.*[38] synthesized bisperoxo complexes $MoO(O_2)_2$.hmpt (hmpt = hexamethylphosphorus triamide) which oxidized olefins at room temperature. Special interest arose to use Mo(VI)-oxo-complexes for oxidation when ARCO and HALCON published patents on the olefin-epoxidation by Mo(VI)-complexes using *tert*-butyl hydroperoxide (TBHP) as an oxidant.[11,12] Cousin and Green[39] synthesized first high oxidation state organometallic dioxomolybdenum complex containing cyclopentadienyl ligand ($CpMoO_2Cl$) in 1963 by air oxidation of $CpMo(CO)_2(\pi{-}C_3H_5)$ in the presence of HCl but yield obtained was very low. Later on, Legzdins *et al.*[40] synthesized $Cp'MoO_2R$ (R= alkyl) in high yield by oxidation of $Cp'Mo(NO)R_2$ with molecular oxygen in water. Almost at the same time, Faller and Ma[41] synthesized the $Cp'MoO_2Cl$ by oxidizing the $[Cp'Mo(CO)_2]_2$ dimer with oxygen in chloroform to form intermediate μ- oxo bridged compound which was further treated with PCl_5 to get mononuclear dioxo compound. In 1994 Bottomley *et al.*[42] modified the synthesis of dioxomolybdenum compound using hydrogen peroxide as an oxidant followed by an addition of HCl which gave desired product quantitatively. In 1991 Bergmann[37] have reported the oxidative decarbonylation to prepare dioxomolybdenum chlorides. Kuhn and Romao[43,44] applied the oxidative decarbonylation method to prepare dioxomolybdenum complexes containing Cp ligand, alkyl groups and chloride. Several studies of these complexes proved that stability of complexes depends on the ligand, e.g. $(CpBz_5)MoO_2Cl$ being more stable than its Cp and Cp' counterparts.[45] Martins, Romao and Poli[46] reported the different method for preparation of $(CpBz_5)MoO_2Cl$ by treating different carbonyl precursors with excess of TBHP in DCM.

Several mononuclear oxomolybdenum(VI) and oxomolybdenum(IV) compounds have been synthesized[47] to model the oxomolybdenum enzymes. These achievements by inorganic chemists provided a better understanding for the reactivity of the molybdenum cofactors and mechanisms of oxygen atom transfer reactions. The mechanism proposed for the oxygen atom transfer reaction involves a transition state where the molybdenum atom and the substrate are bridged by the oxygen atom that is either entering or leaving the coordination sphere of the molybdenum atom.[48]

Generally better catalytic activities of several oxomolybdenum(VI) complexes in oxidation reactions make this type of complexes -in principle - promising candidates for asymmetric catalysis by using chiral ligands. $MoO_2(Mes)_2$ was used as a precursor for synthesizing chiral molybdenum compounds by exchanging the mesityl ligands with H_2BINOL, yielding MoO_2(S−BINOL)(THF) which showed excellent results in epoxidation of *cis*-cyclooctene, *trans*-*β*-methylstyrene and limonene at room temperature with TBHP as an oxidant but unfortunately no *ee* was observed in all the cases.[49] In 1979, Mimoun *et al*.[3850] have reported asymmetric epoxidation of olefins using chiral Mo(VI) complex but with low *ee*. Molybdenum(VI) complexes prepared from $MoO_2(acac)_2$ as MoO_2 precursor and chiral ligands also becomes attractive catalyst for the asymmetric epoxidation of olefin with hydroperoxides as oxidant. In asymmetric epoxidation of allylic alcohols, Yamada and co-workers[51] used a mixture of $MoO_2(acac)_2$ and *N*-alkylephedrin in catalytic amount and showed 33% *ee* and chiral *N*-methylprolinol increased enantiomeric excess up to 50%.[52] Several attempts have been made to achieve high *ee* in asymmetric epoxidations by Mo based catalyst but unfortunately poor to moderate enantiomeric excesses were observed in typically all the cases.

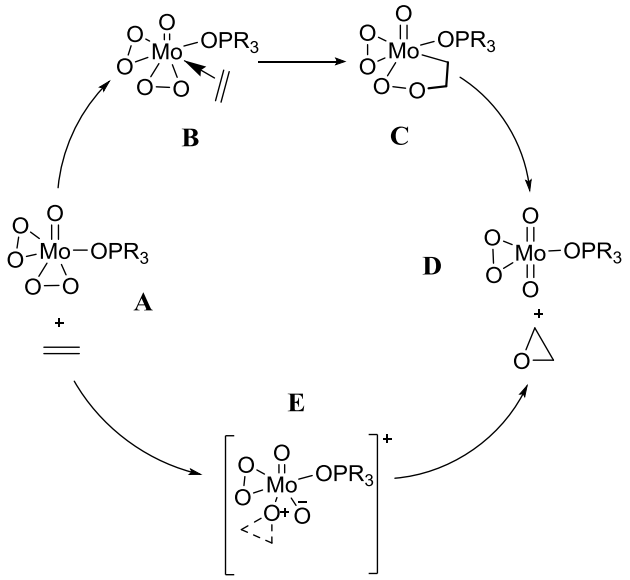
1.5. Mechanistic Considerations for the Epoxidation with Mo(VI) Complexes

Mimoun and Sharpless proposed possible mechanism for olefin epoxidations catalyzed by dioxomolybdenum(VI) initiated a scientific debate about accuracy of the mechanism.

Mo(VI) are well known for epoxidation of olefins with hydroperoxides. Formation of Mo-oxo peroxo or oxo diperoxo species is the accepted first step after reaction of MoO_2 with hydroperoxide as oxidant (**A**). Two different pathways have been proposed for the reaction of olefin with the Mo peroxo species. According to Mimoun *et al*.[38,53] after insertion of the olefins five membered peroxo metallocycles is formed.

These results were further confirmed by olefins epoxidation catalyzed by dioxomolybdenum complex containing bidentate ligand. In the first step olefins coordinates to vacant coordination site of metal atom (**B**) which further inserts in Mo-peroxo bond forming five membered metallacycle (**C**). Which undergo cycloreversion to form epoxide (**D**). In 1977 Sharpless *et al*.[54] prepared the ^{18}O marked peroxo - intermediate of the $MoO_2(acac)_2$ complex and reacted with different olefins. Incorporation of labeled oxygen was not observed in epoxide product. On the basis of this and already established theories from Sheldon and Zajacek, Sharpless proposed a concerted oxygen-transfer pathway involving a three-membered transition state (**E**) instead of the metallacycle (Scheme 1.4).[55]

Mimoun 1970



Sharpless 1972

Scheme 1.4. Mimoun and Sharpless mechanistic pathway for epoxidation of olefin

Rosch *et al*.[56] carried out quantum chemical calculation on these systems and had drawn following conclusions:

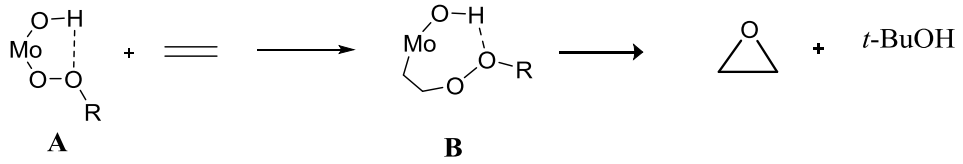
• The oxygen transfer proceeds via concerted mechanism postulated by Sharpless.

• The oxygen attacks the olefin in an electrophilic manner, forming a five-membered transition state.

• In the catalytic reactions, an intra or inter molecular proton transfer to the η^2-peroxo species had the lowest energies. The resulting η^1-peroxo species was superior in the catalytic epoxidation; this assumption was later proven experimentally by Thiel *et al.*

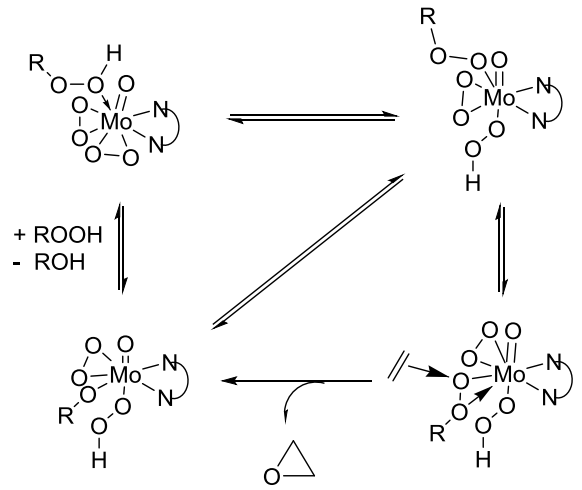
• The epoxidation can be carried out stereoselectively as well.

Calhorda *et al.*[57] had shown similar result by theoretical calculation for epoxidation of olefin with dioxomolybdenum(VI) complex using TBHP as an oxidizing agent. According to his studies, TBHP first transfers a proton to oxygen atom of the complex, coordinating itself in a η^1-fashion (**A** in Scheme 1.5). Later on olefin inserts between Mo - oxygen bond forming a seven membered transition state (**B**, Scheme 1.5) which finally disintegrate and gives two products, *tert* -butanol and epoxide, regenerating the catalyst.



Scheme 1.5. Formation of C-O bond first by co-ordinating olefin to metal

Thiel[58] proposed new mechanism for these reactions, where in the first step alkyl peroxide co-ordinates to metal center. This was activated by giving a proton to one of the peroxide ligands on the molybdenum simultaneously altering its position from η^1 to η^2 (Scheme 1.6). Remaining mechanism was similar to Sharpless mechanism. Like Mimoun, Thiel also observed that strong basic ligand or donor solvents slow down the reaction by blocking the co-ordination sites and making it unavailable to form peroxo co-ordination.



Scheme 1.6. Thiel mechanism for olefin epoxidation

Different complexes showed different mechanistic pathway for olefin epoxidation. Hence we cannot predict plausible mechanism for epoxidation reaction. But certain study can be carried out such as tests with radical scavengers in order to exclude a radical mechanism. Isolation of intermediate species to confirmed the mechanistic pathway.

Studies confirmed that peroxo species are active in olefin epoxidation and can be obtained from the reaction of oxometal groups with alkylhydroperoxides; peroxo complexes were considered active intermediates.

1.6. Research scope and objectives of the thesis

The synthesis and characterization of all kinds of molybdenum complexes are already reported in the literature, but only a few of them were employed as epoxidation reaction. Heterogeneous catalyst has advantages over homogeneous but still homogeneous complex has its own importance in industry. Furthermore, the fact that molybdenum(VI) species are known to act as catalysts in a large variety of oxidation reactions inspired us to concentrate on this topic and we have set some objective of the thesis:

- Synthesis of achiral and chiral dioxomolybdenum complexes
- Synthesis of organometallic molybdenum carbonyl complex as catalyst precursor for molybdenum dioxo or oxo-peroxo species
- Detailed characterizations of synthesized complexes by various techniques
- Applications of molybdenum complexes in oxidation of important substrates

The research described in this thesis has mainly been focused on the development of high-valent dioxomolybdenum complexes and evaluated for various oxidation reactions using either H_2O_2 or TBHP as oxidants.

Furthermore, new chiral dioxomolybdenum complex based on salen ligand has been synthesized and used for epoxidations of alkene, allylic alcohols and sulfide oxidations. The second part of this research has been aimed *in situ* preparation of dioxomolybdenum benzyl complex for oxidation of sulfides.

1.7. Outline of the thesis

This section gives the chapter wise distribution of the work done during the Ph.D. tenure.

Chapter 1: Chapter describes in details about industrial important process catalyzed by homogeneous and heterogeneous catalysts. Importance of oxidations, especially asymmetric epoxidation and sulfoxidation has been discussed in detail. Role of molybdenum in catalysis especially carbonyl and dioxomolybdenum complexes as oxidation catalyst has been discussed in brief. Choice of oxidant, its advantages and disadvantages and mechanistic investigation on formation of epoxide has been discussed thoroughly.

Chapter 2: This chapter describes the synthesis of salen, semi-salen ligands and their corresponding dioxomolybdenum complexes. The detailed characterization of all ligands and complexes using NMR, FT-IR spectroscopy has been discussed. Synthesized dioxomolybdenum complex successfully used as catalyst for epoxidations of a range allylic alcohols. Various reaction parameters were studied to optimize reaction conditions so as to achieve high conversion and selectivity for desired product. Catalysts were found to be active in epoxidation of various allylic alcohols with excellent selectivity for epoxides. Oxidations of glycerol and its derivative were also studied to explore catalyst for broad range of substrates and results were compared with standard cyclopentadienyl tricarbonyl molybdenum acetylide complex as catalyst precursors.

Chapter 3: The third chapter deals with the synthesis of chiral dioxomolybdenum complex and its detailed characterizations using elemental analysis, FT-IR, NMR, single crystal X-ray diffraction analysis has been discussed in this chapter. Synthesized chiral complex has been evaluated for asymmetric epoxidation of olefins, allylic alcohols and sulfoxidation of thioanisole. Various reaction parameters were studied to optimize reaction conditions so as to achieve high conversion and enantioselectivity. Asymmetric epoxidation was carried out using different types of olefins so as to study the scope of substrates.

Chapter 4: The fourth chapter deals with the synthesis of cyclopentadienyl tricarbonyl molybdenum benzyl complex. Followed by detailed characterization using FT-IR, NMR spectroscopies has been discussed. The prepared catalyst was evaluated as catalyst precursor for oxidation of range of sulfides. Characterization of *in-situ* formed catalytically active species during reaction has been discussed in details.

Chapter 5: This chapter presents the summary and conclusions of the thesis work.

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Chapter 2

Selective Oxidation of Allylic and Benzylic Alcohols by Molybdenum Salen Complexes

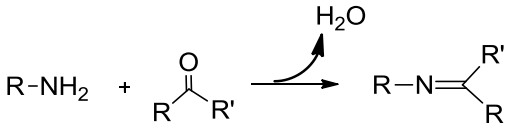
Abstract

*Schiff base dioxomolybdenum complexes (**1**, **2**) and cyclopentadienyl tricarbonyl molybdenum acetylide complex (η^5-C_5H_5)$Mo(CO)_3$($C{\equiv}CPh$) (**3**) were prepared and characterized by FT-IR, NMR spectroscopy. Epoxidation of various allylic alcohols including homoallylic alcohol was studied with hydrogen peroxide using dioxomolybdenum(VI) complex (**1**) as catalyst; excellent conversion of allylic alcohols with 99% selectivity for epoxy alcohols was observed. Under identical conditions cinnamaldehyde was obtained instead of epoxide in oxidation of cinnamyl alcohol showing the selectivity varied according to type of substrate. Results clearly suggested that type of substrates and position of the double bond affected the conversion, selectivity pattern and the reaction pathway under similar reaction conditions. Additionally, oxidation of glycerol and glycerol derivative i.e. glycerol protected either with an isopropylidene group (solketal) or a carbonate residue (glycerol carbonate) was studied in details to achieve maximum conversion of glycerol and its derivatives.*

2.1. Introduction

2.1.1. Schiff Bases

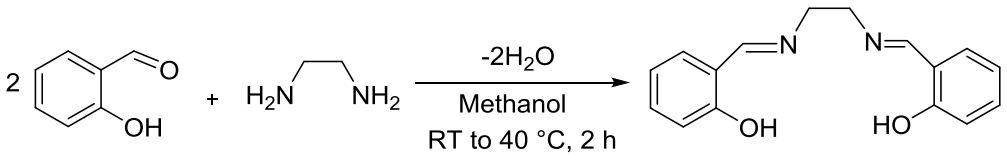
The simple condensation of aldehydes or ketones with primary amines gives imines (Scheme 2.1). Imines that contain -C=N group attached to an aryl or alkyl group, is also called as Schiff bases, since they were first reported by Schiff in 1864.[1]



Scheme 2.1. General scheme for formation of Schiff base

Due to presence of C=N group, Schiff base possess biological properties and are active against wide range of organisms such as; *Candida Albicans, Escherichia coli Staphylococcus aureus, Bacillus polymxa, Trychophytongypseum, Mycobacteria, Erysiphegraminis and Plasmoporaviticola.* Series of Schiff bases were reported by varying range of amines or aldehydes. *O*-phenylenediamine Schiff bases show clinical properties.[2] Isatin Schiff bases showed antiviral, anti-HIV, antiprotozoal and anthelmintic activities.[3] Several studies have shown that due to presence of a lone pair of electrons on nitrogen atom of the azomethine group, Schiff bases have considerable chemical and biological importance. When functional groups like –OH or –SH are present closer to the azomethine group, the Schiff base are capable of forming coordinate bonds with various metals ions through both azomethine group and/or phenolic group and stabilize them in different oxidation states. Various Schiff base ligands have been used as cation carriers in potentiometric sensors as they have shown excellent selectivity, sensitivity, and stability for specific metal ions such as Ag(II), Al(III), Co(II), Cu(II), Gd(III), Hg(II), Ni(II), Pb(II), Y(III), and Zn(II).[4] The applications of Schiff base complexes have been studied in bioinorganic chemistry, biomedical, supramolecular chemistry, catalysis and material science.

Tetradentate Schiff base ligand was first reported by P. Pfeiffer in 1933 by condensation of two equivalents of salicylaldehyde with ethylene diamine (Scheme 2.2); is also called as salen ligand.



Scheme 2.2. Synthesis of salen ligand

Salen term is generally used to describe [O,N,N,O] tetradentate bis-Schiff base ligands. Structure of salen can be varied by changing substituents on amine or aromatics. Salen ligand becomes attractive as chirality can be introduced in to the structure by introducing variety of chiral amines, which gives diverse interesting structures. Syntheses of corresponding metal complexes are easy and importantly ligand retains its chirality during synthesis of metal complexes.

Metal salen complexes can adopt different conformations such as umbrella, stepped, or planar molecular conformation. Most common forms are umbrella (**A** in Figure 2.1) and stepped forms (**B** in Figure 2.1) and rarely planar conformation can be seen. Square planar geometry is observed in metal salen complexes because of imine moieties, which forces the *cis*-configuration around the metal centre. In some cases a slightly distorted geometry exists. In square-planar geometry, the metal ion is in the plane formed by the N_2O_2-donor atoms and the two axial positions of metal are free for coordination with solvent or other molecules.

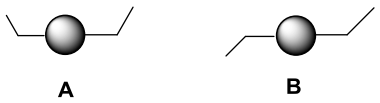


Figure 2.1. Conformations of salen ligands

Introducing the different groups on aldehyde fragment of Schiff base alters the electronic configuration of Schiff base, which subsequently changes the properties of metal complexes. Therefore, catalytic activity of metal complexes can be tuned by altering the substituent on aldehyde fragments. In case of Mo complexes, if the electron withdrawing substituent (X) such as X = NO_2 is present; it draws electron density away from molybdenum centre making it easily reducible. This fact was confirmed experimentally by electrode reduction potential value showing Mo(VI)

reduction potential (Ep,'s) shifted in the anodic direction indicating increased reducibility of the Mo(VI) complexes.

Metal salen complexes have ability to act as both electrophile and nucleophile in certain reaction. Different possible approaches of substrates to salen are shown in Figure 2.2 is well explained in literature by Cozzi.[5]

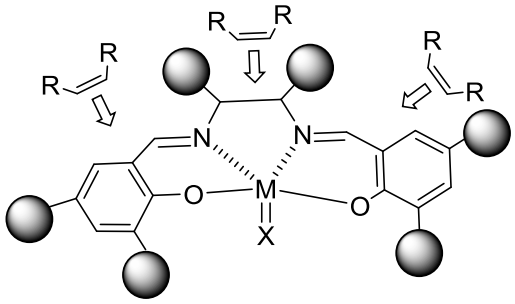


Figure 2.2. Different approaches of a substrate to the salen complex

2.1.2. Transition Metal complexes

Metal coordination complexes have a wide range of scientific and industrial applications ranging from catalysis to anticancer drugs.[6]

Schiff base metal complexes are efficient catalysts both as homogeneous and heterogeneous and are extensively used in literature for variety of applications such as reduction of ketones to alcohols, alkylation of allylic substrates, polymerization of olefins, decomposition of hydrogen peroxide, hydrosilylation of acetophenone, Michael addition reaction, annulation reaction, Heck reaction, carbonylation reaction, aldol condensation, isomerization, oxidations etc. Activity and selectivity of catalyst depends mainly on the structure of ligand and metal precursors. Catalytic properties can be easily tuned by changing reaction conditions or metal precursors.

Tsumaki in 1938 reported that the cobalt(II) salen complex reversibly bound O_2, which led to extensive research on cobalt complexes of salen and related ligands for their capacity as oxygen storage and transport potential as synthetic oxygen carriers. First report on achiral Cr(III)-salen complex catalyzed epoxidation reaction was reported by Kochi *et al.*[7] in 1985. Peptide Schiff base ligand libraries with Ti(O*i*-Pr)$_4$ were used by Hoveyda, Snapper and coworkers[8] for addition of Me_3SiCN to epoxides and imines. Zirconium Schiff base complexes are well known and easily prepared by exchange with Zr(O*i*-Pr)$_4$ or by the addition of $ZrX_4(THF)_2$ to the sodium

or potassium salt of the Schiff bases. Though chiral zirconium salen was rarely used in catalysis, chiral $Zr(salen)Cl_2$ catalyst showed high enantioselectivity for Baeyer-Villiger oxidation.[9] Bolm *et al.*[10] reported *in situ* prepared tridentate Schiff base iron catalyst using $Fe(acac)_3$ as metal precursor for enantioselective oxidation of sulfide. Bolm reported *in situ* preparation of a tridentate Schiff base iron catalyst from $Fe(acac)_3$, which could promote the enantioselective oxidation of sulfides to sulfoxides. The studies on the use of dimeric μ-oxo Fe(salen) complex reported by Nguyen[11] have found an interesting application as stable precursors for the generation of iron carbene complexes. These complexes showed high catalytic activity for enantioselective cyclopropanation of olefins with ethyl diazoacetate. Schiff bases were used as catalysts in polymerization reactions. The pyridyl bis(imide) complexes of iron(III) and cobalt(II) showed substantial activity in the polymerization of ethylene.[12] Cobalt(II) salen complexes showed 93% *ee* for asymmetric nucleophilic ring opening of meso epoxides in the presence of benzoic acid.[13] Chromium(III) salen complexes showed 93-95% *ee* in ring opening reaction of cyclohexa-1,4-dienemonoepoxide.[14]

Schiff base transition metal complexes also showed promising activity in the asymmetric reduction of dialkyl ketones to alcohols, which is known to be difficult.[15] Chiral Schiff base complex showed 99% yield of (S)-1-phenylethanol with 51% *ee* in reduction of ketone.[16] The cobalt(II) complexes of salicylidene diaminocyclohexane encapsulated in zeolites by ship-in-bottle (SIB) method were evaluated for hydrogenation of acetophenone to 1-phenylethanol. These catalysts showed a selectivity of 95% at a conversion of 98%.[17]

Schiff base transition metal complexes were active in catalyzing decomposition of hydrogen peroxide. Solid supported Schiff base transition metal complexes improved its activity in hydrogen peroxide decomposition. Transition metal Schiff base complexes were also effective in sensitizing the conversion of norbornadiene to quadricyclane, because of its capacity in storage of solar energy. Manganese salen complexes were successfully applied for epoxidation of olefins. The epoxidation of norbornene, cycloheptene and cyclohexene were reported using ruthenium(III) bidentate Schiff base complexes as catalyst. Manganese(II) complexes of binaphthyl Schiff base were evaluated for epoxidation of 1,2-dihydronaphthylene in presence of sodium hypochlorite with *ee* of 13–15%.[18]

2.1.3. Molybdenum catalysis

Molybdenum based catalysts have number of important application such as hydrodesulfurization (HDS) of petroleum, petrochemicals, coal-derived liquid. Molybdenum based catalyst have been used successfully for different transformations such as ethylene dimerization, hydrogen generation from water, asymmetric allylic alkylation,[19] olefin metathesis, propene hydration and ammoxidation, oxidation of methanol and acrolein, epoxidation of olefins etc. Molybdenum oxo complexes have received considerable attention because of their reactivity and selectivity under mild reaction conditions. Schiff base dioxomolybdenum complexes were successfully used for epoxidation of olefins with TBHP as oxidant. Molybdenum dioxo or peroxo complexes with chiral ligands such as 2'-pyridyl alcohols[20] and phosphinoalcohols[21] have been studied for the epoxidation and showed 20-40% *ee* for functionalized olefins. The promising catalytic activities of several molybdenum(VI)-oxo complexes in oxidation reactions makes this type of complexes in principle promising candidates for asymmetric catalysis by using chiral ligands. In 1979 Mimoun *et al*. did enantioselective epoxidation of prochiral alkyl-substituted olefins utilizing a Mo(VI) complex bearing a chiral ligand though with low enantioselectivity. Molybdenum(VI) complexes of $MoO_2(acac)_2$ and chiral ligands have also been used for the asymmetric epoxidation of olefin with hydroperoxide as oxidant. For example, Yamada *et al*.[22] applied mixture of $MoO_2(acac)_2$ and *N*-alkylephedrin for the epoxidation of allylic alcohols with up to 33% *ee*.

In industrial processes, transition metal based catalysts are important tools for the production of millions of tons of oxygenated compounds per year.[23] Homogeneous catalysts are widely used in large scale oxidation processes such as acetaldehyde from ethylene [Wacker process ($PdCl_2$-$CuCl_2$)], adipic acid from cyclohexane (Co or Mn catalyst), terephthalic acid from *p*-xylene (cobalt-manganese-bromide catalyst), and propylene oxide from propylene [HPPO- process (TS-1 catalyst) or Pd/TS-1 or Au/TS-1catalyst], synthesis of fine chemicals etc. Synthesis of fine and intermediate chemicals are still widely produced via traditional oxidation methods which needs stoichiometric oxidants such as dichromate, chromium oxides, permanganates, periodates, which generates large amount of waste which is undesirable from environmental point of view. Hence, much attention has been paid for transition metal catalyzed oxidations to achieve the effective oxidation using mild and environmentally benign oxidant. There are several oxidants available for

transition metal catalyzed oxidation reactions like alkylhydroperoxides; iodosylbenzene but these oxidants have low oxygen content. Considering the nature of waste produced, there are further drawbacks of these oxidants. From economic and environmental point of view molecular oxygen is one of the best oxidant, though activation of molecular oxygen is very difficult and it has poor selectivity for desired product. On the other hand hydrogen peroxide is better alternative, it provides 47% active oxygen and the reduction product is environmentally benign H_2O.

Epoxidation of allylic alcohols to its epoxy alcohols is important because it is starting material for the synthesis of biologically important compounds. There are several methods developed for epoxidation of allylic alcohols. Tungsten based catalysts have been described for allylic alcohol using hydrogen peroxide as oxidant. In 1973, Michaelson *et al*.[24] have overcome the regioselectivity problem in geraniol epoxidation. Previously epoxidation of geraniol catalyzed by transition metal based catalyst with alkyl hydroperoxides was highly selective for 2, 3-position compounds. In 1980's Sharpless *et al*.[25] reported asymmetric epoxidations of allylic alcohols using $Ti(O\textit{i}\text{-}Pr)_4$ as catalyst and diethyl tartrate as a chiral ligand and *tert*-butyl hydroperoxide (TBHP) as an oxidant. It was proven to be one of the most important methods of asymmetric catalysis. However, Sharpless epoxidation was not efficient for homoallylic alcohols. Later on catalytic systems developed by Yamamoto and co-workers[26] based on zirconium and vanadium is capable of oxidizing homoallylic alcohols in an enantioselective manner. First attempts of titanium catalyst for asymmetric epoxidation of allylic alcohol with chiral hydroperoxides afforded < 20% *ee*, but sugar derived hydroperoxides showed higher enantioselectivities (up to 50% *ee*).[27] In 1997, Adam *et al*.[28] showed Ti-mediated asymmetric epoxidation of variety of prochiral allylic alcohols with optically active hydroperoxides as oxygen donors and multidentate ligands as achiral additives to achieve up to 50% *ee* with 63-97% yield. In the same year, Lattanzi *et al*.[29] reported the application of several furyl hydroperoxide in the Sharpless asymmetric epoxidation of allylic alcohols. The results showed that the enantioselectivity was strongly dependent on the substitution present near the reactive sites, consistent with the observation made by Corey[30] and Sharpless[31]. In 2003, Lattanzi *et al*.[32] first synthesized an enantiopure tertiary hydroperoxide from camphor via a stereospecific nucleophilic substitution of hydroxyl group bound to the chiral carbon center of alcohol molecule by hydrogen peroxide, in which the reactive peroxo (-OOH) group is directly bound to the

stereogenic carbon center. However the so prepared chiral tertiary hydroperoxide only offered a moderate *ee* up to 46% and yield up to 59% for the asymmetric epoxidation of allylic alcohols.

A number of vanadium(V) complexes have been reported using TBHP as an oxidant for asymmetric epoxidations, in which the epoxidation of allylic alcohol is well-known.[33] Vanadium alkyl peroxo complexes were extensively recognized as intermediate in the catalytic systems of $VO(acac)_2$/ TBHP[34] and $VO(acac)_2$/ ligand/ TBHP.[35] Prior to the appearance of titanium based catalysts the Sharpless group had first developed asymmetric epoxidation catalyzed by chiral vanadium hydroxamate complex.[36] Later on, they found that use of proline derived hydroxamic acid as the chiral ligand showed high *ee* (80%).[37] Though Sharpless asymmetric epoxidation is efficient for the oxidation of allylic alcohols, there is need for improved catalyst. In literature very few catalysts are known for epoxidation of homoallylic alcohols and alcohols with olefin located far from hydroxyl group. There are only few reports on catalytic enantioselective epoxidation of challenging substrate such as homoallylic and bishomoallylic alcohols. Although epoxidation of allylic alcohols are well established using Zr catalyzed asymmetric epoxidation,[38] Nb salen catalyzed asymmetric epoxidation,[39] Shi's reported procedure for epoxidation using chiral ketone,[40] and Sharpless asymmetric epoxidation, could not epoxidized homoallylic alcohols with satisfactory enantioselectivities using the same system.[41] The protocol reported by Yamamoto's group for asymmetric epoxidation of homoallylic alcohols using vanadium and α-amino acid-based hydroxamic acid ligands showed excellent enantioselectivity.[42] Later on Yamamoto and co-workers have shown Zr(IV) and Hf(IV) catalyzed highly enantioselective epoxidation of homoallylic and bishomoallylic alcohols with high enantioselectivity. The major drawbacks of Sharpless epoxidation were overcome by Yamamoto groups using the hindered hydroxamic acid ligand and $VO(O\text{-}i\text{-}Pr)_3$. This system was capable of oxidizing both *cis* and *trans*-homoallylic alcohols.

Salen and salalen complexes of niobium and tantalum have been reported to give high enantioselectivity for asymmetric epoxidation of allylic alcohols by Egami and Katsuki. Recently Susan K. Hanson reported more than 90% yield by vanadium catalyzed oxidation of the benzylic, allylic, and propargylic alcohols using air as an oxidant.[43]

Most of the catalytic system used *tert*-butyl hydroperoxide (TBHP) or cumene hydroperoxide (CHP) as an oxidant and generated *tert*-butanol or methyl styrene, acetophenone and cumyl alcohol as undesired byproduct. However, H_2O_2 is an ideal oxidant from economic and environmental points of view. Though much metal based catalyst with H_2O_2 showed disadvantages, especially low reactivity, low selectivity due to the rearrangement of epoxy alcohols to triols or five membered bicyclic products, over the past few decades, homogeneous and heterogeneous transition metal catalyst such as Ti, V, Mn, Fe with H_2O_2 have been developed for epoxidation.

The use of molybdenum carbonyl complexes as catalyst precursors for oxidation reactions has increased considerably from last decades. Some principal oxidation reactions are sulfides, cis-dihyroxylation and alcohol oxidation etc. According to literature reports Schiff-base metal catalysts are known as potential homogeneous and heterogeneous catalyst in oxidation reactions. Considering this promising performance of these catalysts and continuation of our efforts in molybdenum catalysed selective oxidation reactions, we have developed a new method for selective oxidation of allylic and benzylic alcohols with aqueous H_2O_2 using schiff base dioxomolybdenum complexes $[MoO_2L]$ (**1, 2**) and (η^5-C_5H_5)$Mo(CO)_3(C{\equiv}CPh)$ (**3**) as catalyst precursor of dioxo and oxo-peroxo molybdenum catalyst.

2.2. Experimental Section

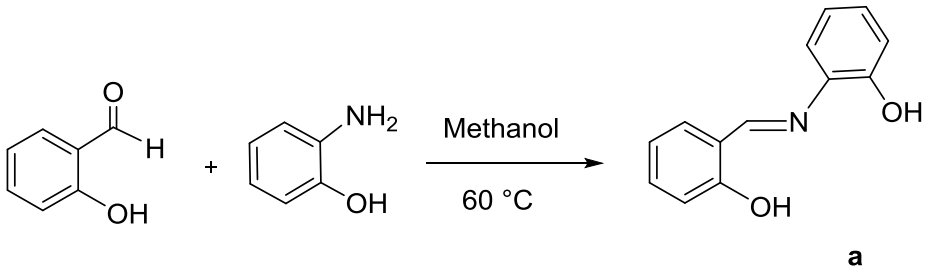
2.2.1. Materials

All reagents of commercial grade (Aldrich) were used as received unless stated otherwise. Hydrogen peroxide used was 35% w/w in water. THF was dried according to standard method and freshly distilled prior to use. Cyclopentadiene was obtained by freshly cracking dicyclopentadiene (Aldrich make) at 60 °C. Phenyl acetylene, diethyl amine was purchased from Aldrich, $MoO_2(acac)_2$ was purchased from stream chemicals. $CpMo(CO)_3Cl$ was prepared according to literature method.[44] CuI was freshly prepared by addition of Cu powder to hydroiodic acid and refluxing for 4 h, followed by filtration and washing with water and ether. Complexes (**1**, **2** and **3**) were prepared according to literature reports.[45] ^1H NMR and ^{13}C NMR was recorded on Bruker AV-200 (50 MHz) or Bruker AV-400 (100 MHz) or Bruker DRX-500 (125 MHz).Tetramethylsilane was used as the internal standard. NMR values are expressed in δ (ppm). FT-IR spectra were recorded on Nicolet Nexus IR 6700 with KBr pellet in

the range of 400-4000 cm^{-1}, with resolution 4 and averaged over 100 scans.

2.2.2. Catalyst Preparation

a) Preparation of schiff base (a)



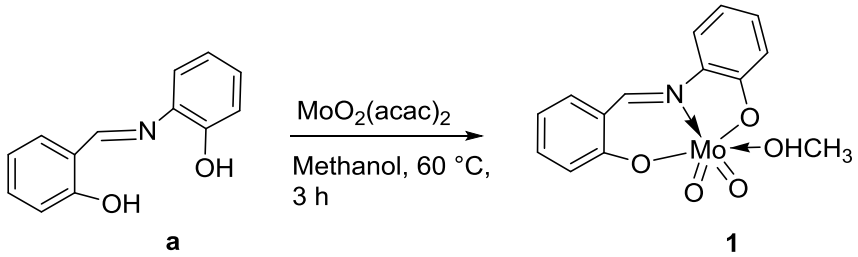
Scheme 2.3. Synthesis of Schiff base ligand **a**

In Schlenk tube under inert atmosphere a solution of salicylaldehyde (2 g, 0.0163 mol) in methanol (5 mL) was added dropwise to a stirred methanol (5 mL) solution of 2-aminophenol (1.78 g, 0.0163 mol) at room temperature. After complete addition the mixture was heated at 40 °C for 2 h and yellow solid was obtained which was filtered off, washed with cold methanol and dried in vacuo.

Yield: 2.96 g, 85%.

^{1}H NMR ($CDCl_3$): δ 3.92 (4H, s, -N=CH), 6.87 (2H, t, *J* = 7Hz), 6.96 (2H, d, *J* = 8Hz), 7.22-7.33 (4H, m), 8.35 (2H, s, -N=CH), 13.28 (2H, s, -OH).

b) Preparation of schiff base dioxomolybdenum complex (1)



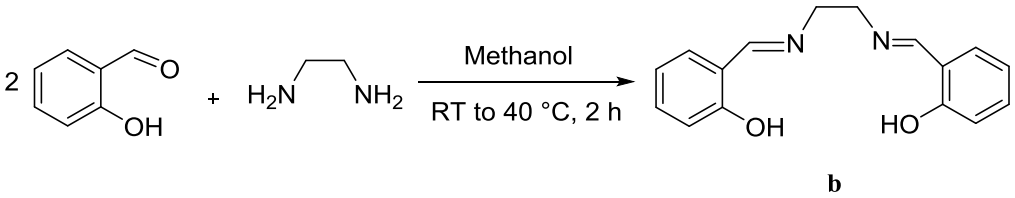
Scheme 2.4. Synthesis of Schiff base dioxomolybdenum complex **1**

In Schlenk tube under inert atmosphere a solution of schiff base **a** (1 g, 0.0046 mol) in methanol (10 mL) was added dropwise to a stirred methanol (10 mL) solution of $MoO_2(acac)_2$ (1.52 g, 0.0046 mol) at room temperature. After addition the reaction mixture was refluxed for 3 h to get yellow solid which was filtered off, washed with cold methanol and dried in vacuo.

Yield: 1.39 g, 80%.

^{1}H NMR (DMSO-d_6): 6.8-7.51(8H, Ph), 8.4 (1H, HC=N-), 3.23 (s, 3H, CH_3OH).

c) Preparation of salen ligand (b)



b

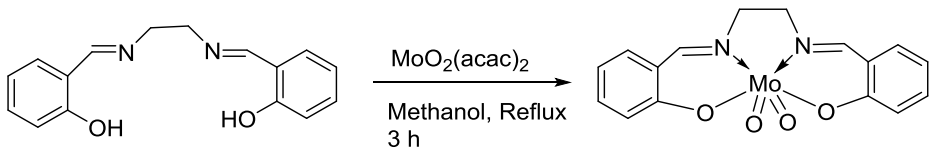
Scheme 2.5. Synthesis of salen ligand **b**

In Schlenk tube under inert atmosphere a solution of salicylaldehyde (2 g, 0.0163 mol) in methanol (5 mL) was added dropwise to a stirred methanol (5 mL) solution of ethylenediamine (0.49 g, 0.0081 mol) at room temperature. After complete addition the mixture was heated at 40 °C for 2 h and yellow solid was obtained which was filtered off, washed with cold methanol and dried in vacuo.

Yield: 3.73 g, 85%.

^{1}H NMR ($CDCl_3$): δ 3.92 (4H, s, -NCH_2), 6.87 (2H, t, J = 7Hz), 6.96 (2H, d, J = 8Hz), 7.22-7.33 (4H, m), 8.35 (2H, s, -N=CH), 13.28 (2H, s, -OH).

d) Preparation of salen dioxomolybdenum complex (2)



b **2**

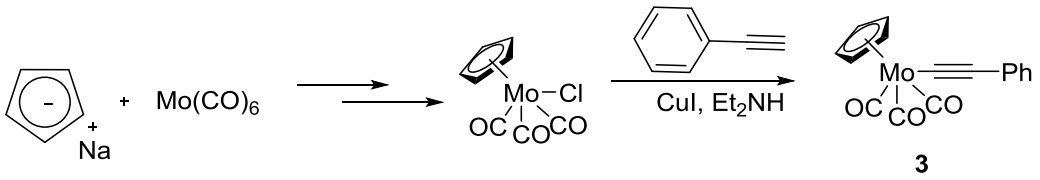
Scheme 2.6. Synthesis of salen dioxomolybdenum complex **2**

In Schlenk tube under inert atmosphere a solution of salen ligand (1 g, 0.0037 mol) in methanol (10 mL) was added dropwise to a stirred methanol (10 mL) solution of $MoO_2(acac)_2$ (1.21g, 0.0037 mol) at room temperature. After addition the reaction mixture was refluxed for 3 h to get yellow solid which was filtered off, washed with cold methanol and dried in vacuo.

Yield: 0.58 g, 40%.

^{1}H NMR (DMSO-d_6): δ 4.1 (4H, -CH_2), 6.8-7.5(8H, Ph), 8.4 (2H, HC=N-).

e) Preparation of CpMo $(CO)_3$(C≡CPh) (3)



Scheme 2.7. Synthesis of cyclopentadienyl molybdenum acetylide complex **3**

The $CpMo(CO)_3$(C≡CPh) was synthesized by reported procedure.[45b] In brief, a 100 mL two necked round bottom flask was charged with $CpMo(CO)_3Cl$ (2.0 g, 0.0071 mol), (H-C≡CPh) (1.05 g, 0.010 mol), catalytic amount of CuI (5 mg) and diethyl amine (10 mL) as solvent. The reaction mixture was stirred at room temperature for 15 min. The progress of the reaction was monitored by TLC using hexane: dichloromethane (80:20) as solvent system. After completion of reaction, diethyl amine was removed in vacuum. The compound (**3**) was purified by column chromatography (silica gels 60-120 mesh) using hexane: dichloromethane (80:20) as solvent system.

Yield: 2.2 g, 92%.

^{1}H NMR ($CDCl_3$): δ 5.5 (s, 5H of Cp), 7.15-7.38(5H of Ph).

IR (KBr, ν cm^{-1}): 2958 (C-C of Cp), 2109 (C≡C), 1940, 1980 and 2038 (CO).

2.2.3. Catalytic activity

Epoxidation of allylic alcohols catalyzed by molybdenum complexes with H_2O_2 was carried out as follows: A Schlenk flask was charged with mixture of substrate (1 mmol), solvent (1 mL), catalyst (1 mol%) and oxidant (2 mmol). The resultant mixture was stirred at 80 °C or 30 °C. The progress of reactions was monitored by GC and products were confirmed by ^{1}H NMR spectroscopy.

2.3. Results and Discussion

2.3.1. FT-IR spectroscopy

Schiff base complexes of **1** and **2** were prepared as reported in literature and characterized by various spectroscopic techniques. IR spectra of Schiff base ligand and corresponding complex is given in Figure 2.3. The IR absorption at 1631 cm^{-1} was attributed to $\nu_{(C=N)}$, which is characteristic of the azomethine group in the Schiff base shifted considerably to lower frequency (1611cm^{-1}) indicating the coordination of azomethine nitrogen atom with molybdenum.[46] The coordination of the imine nitrogen is expected to shift the $\nu_{(C=N)}$ band to lower wave numbers after complexation indicating donation of the nitrogen electrons of azomethine to metal. Complex formation was further confirmed by band observed in low frequency region. The presence of medium intensity bands at 550 cm^{-1} and 468 cm^{-1} were attributed to formation of $\nu_{(Mo–O)}$ and $\nu_{(Mo–N)}$ bands.[47] The IR spectrum of complex **1** in the solid state showed two absorption bands at 909 cm^{-1} and 928 cm^{-1}, characteristic of asymmetric and symmetric $\nu_{(Mo=O)}$ stretches respectively. Disappearance of the broad OH absorption on complexation indicated a coordination of the phenolic oxygen to the metal. Further confirmation of participation of phenolic oxygen in the complex formation was proved by shift in position of band from 1365 $cm^{-1}$to 1392 cm^{-1}. The other series of weak band between 3100 $cm^{-1}$and 2800 cm^{-1} are related to (C-H) modes of vibration. Also, some weak bands located between 2000 $cm^{-1}$and 1750 cm^{-1} can be assigned to overtones of the aromatic rings.

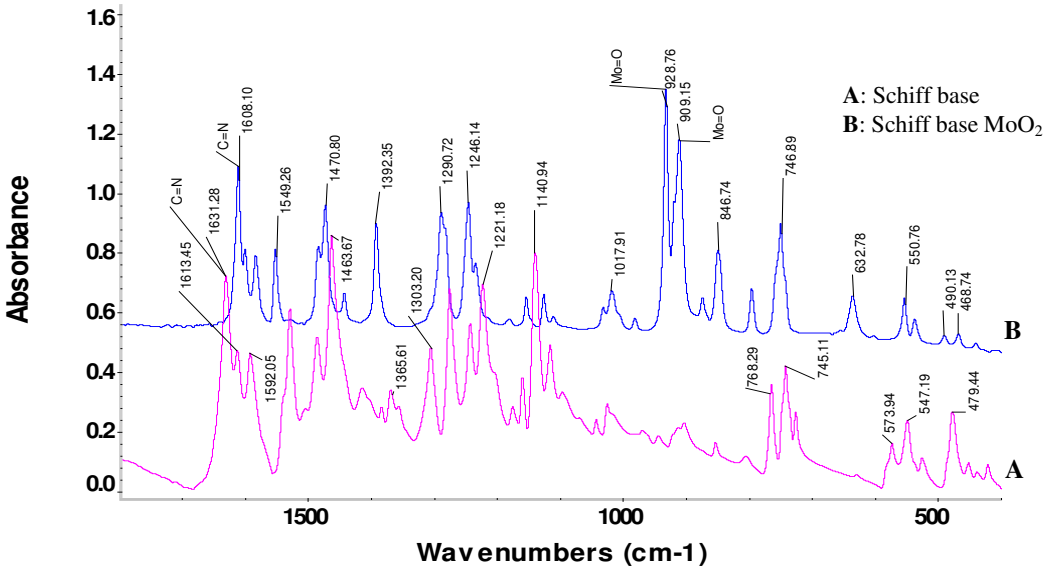


Figure 2.3. IR spectra of [A] Schiff base ligand **a** [B] Schiff base MoO_2 complex **1**

In the complex **2** as shown in Figure 2.4 IR absorption at 1634 cm^{-1} due to $\nu_{(C=N)}$, which is characteristic of the azomethine group shifted to lower wavenumber and appeared at 1630 cm^{-1} indicating the coordination of molybdenum with azomethine nitrogen atom. The bands at 934 and 881 cm^{-1} due to $\nu_{(Mo=O)}$ are characteristic of the cis-dioxo structure. The peaks observed at 484 cm^{-1} and 582 cm^{-1} are assigned to $\nu_{(Mo-N)}$ and $\nu_{(Mo-O)}$, respectively. Disappearance of the broad -OH absorption on complexation indicated a coordination of the phenolic oxygen to the metal. Further confirmation of participation of phenolic oxygen in the complex formation was proven by shift in position of band to 1382 cm^{-1}.

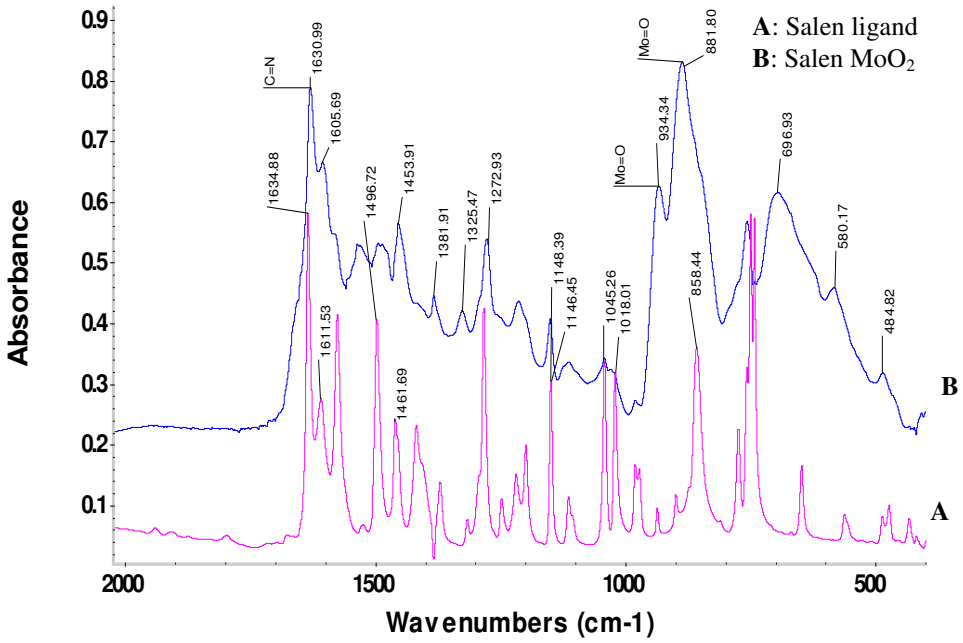


Figure 2.4. FT-IR spectra of [**A**] Salen ligand **b** [**B**] SalenMoO_2 complex **2**

FT-IR spectrum of complex **3** showed strong CO vibrations at 1935, 2017 cm^{-1} and C-C stretching vibration of Cp ring at 2917 cm^{-1}. IR band at 2106 cm^{-1} was due to C≡C stretching.

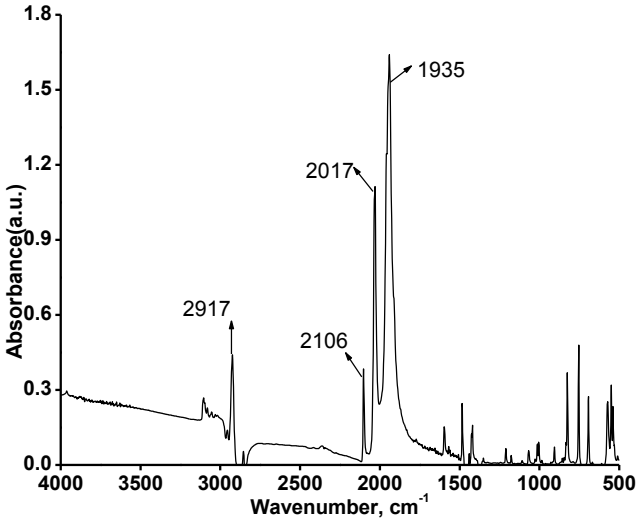


Figure 2.5. FT-IR spectrum of molybdenum acetylide complex **3**

2.3.2. NMR Spectroscopy

The ^{1}H NMR spectrum (Figure 2.6) of Schiff base ligand **a** showed signal at δ 9.74 (s, 1H), characteristic of the aromatic -OH group. The ^{1}H NMR spectrum (Figure 2.7) of complex **1** indicated the binding of ligand through the phenoxy and imine group. A signal at δ 9.17 in the spectrum of ligand showed downfield shift by 0.29 ppm upon complexation. This is attributed to the proton on the azomethine carbon. The range of chemical shift observed for the aromatic proton did not show any appreciable change upon complexation. Two signals appeared at δ 3.12 (s, 3H of CH_3) and 4.07 (s, 1H of –OH) in the spectrum due to coordinated methanol molecule.

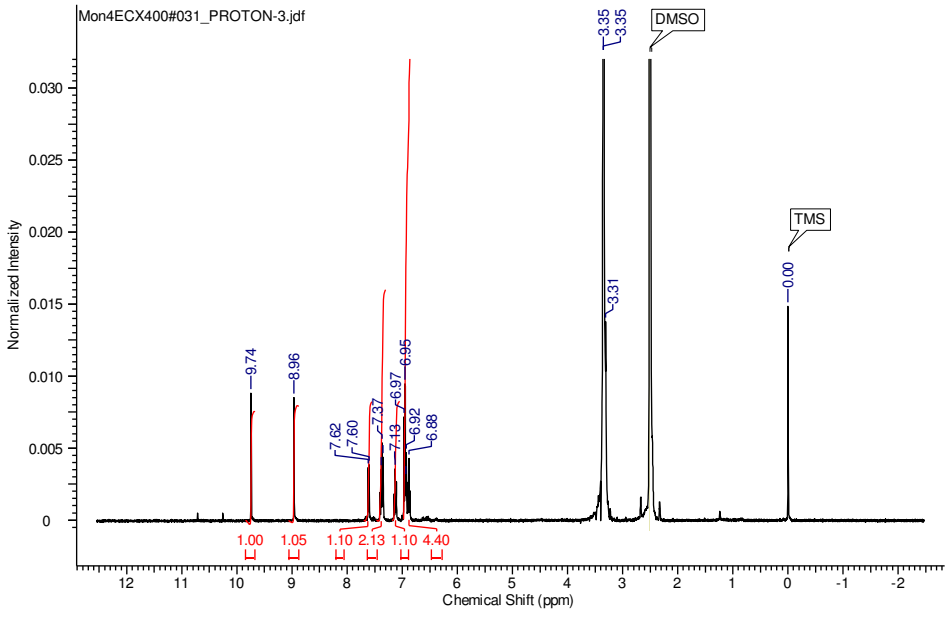


Figure 2.6. ^{1}H NMR spectrum of Schiff base ligand **a**

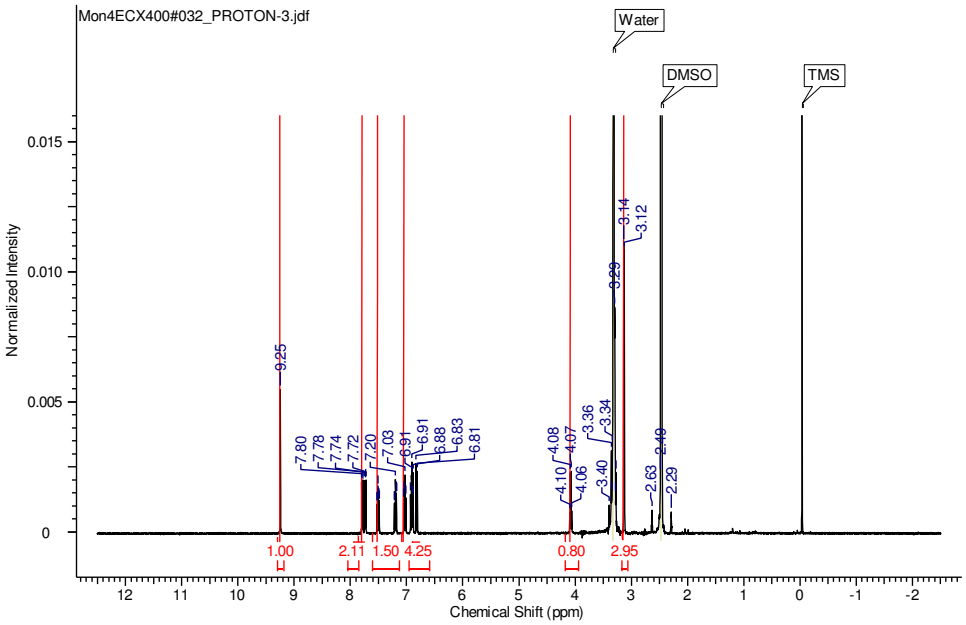


Figure 2.7. ^{1}H NMR spectrum of Schiff base dioxomolybdenum complex **1**

The ^{1}H NMR spectrum (Figure 2.8) of salen ligand **b** showed a signal at δ 8.60 (s, 1H of CH=N), characteristics of the proton on azomethine carbon, which shifted downfield upon complexation and showed splitting of signal in salen dioxomolybdenum complex **2** (Figure 2.9) for CH=N at δ 8.70 and δ 8.81 indicate the non-equivalence of both chelate rings. The range of chemical shift observed for the aromatic proton did not show any appreciable change upon complexation. The ligand showed signal of ethylene diamine (CH_2 groups) proton at δ 3.92 (s, 4H of CH_2-CH_2) which shifted downfield upon complexation to δ 4.41 (s, 2H of CH_2) and δ 4.14 (s, 2H of CH_2).

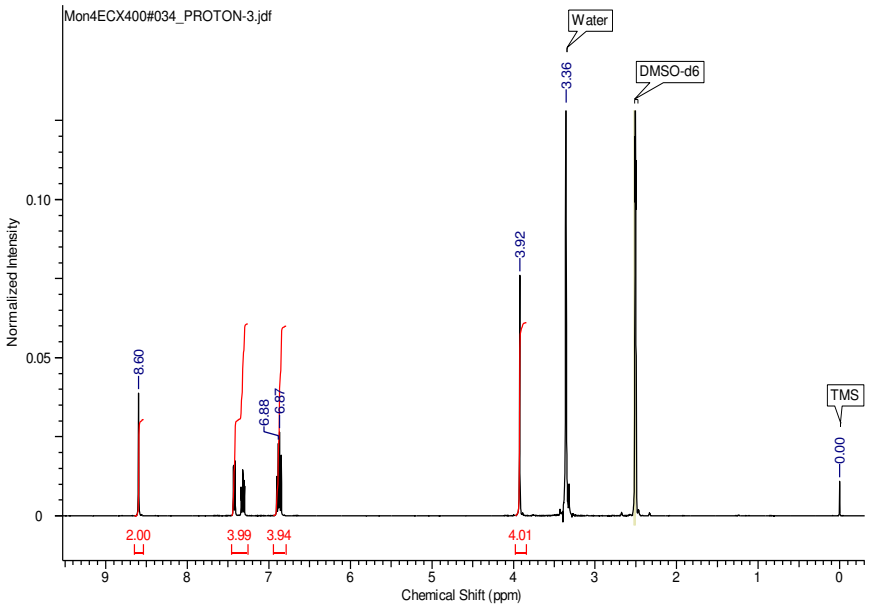


Figure 2.8. ^{1}H NMR spectrum of salen Ligand **b**

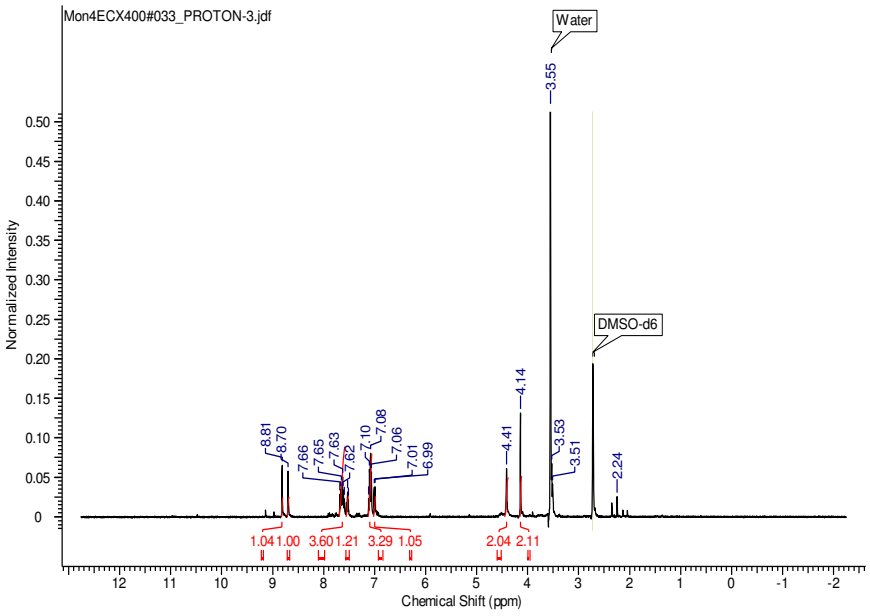


Figure 2.9. ^{1}H NMR spectrum of salen MoO_2 complex **2**

^{1}H NMR spectrum of complex **3** (Figure 2.10) indicated signal at δ 5.56 (s, 5H) due to protons of cyclopentadienyl ring and signal at δ 7.0-7.23 (m, 5H) indicate presence of phenyl proton. In ^{13}C NMR spectrum (Figure 2.11) signal at δ 93.02 was due to the carbon of Cp ring. Peaks at δ 126.1, 127.9, 128, 129.5, and 131.1 were due to carbon of phenyl ring and peak at δ 222.0 indicate the presence of CO group.

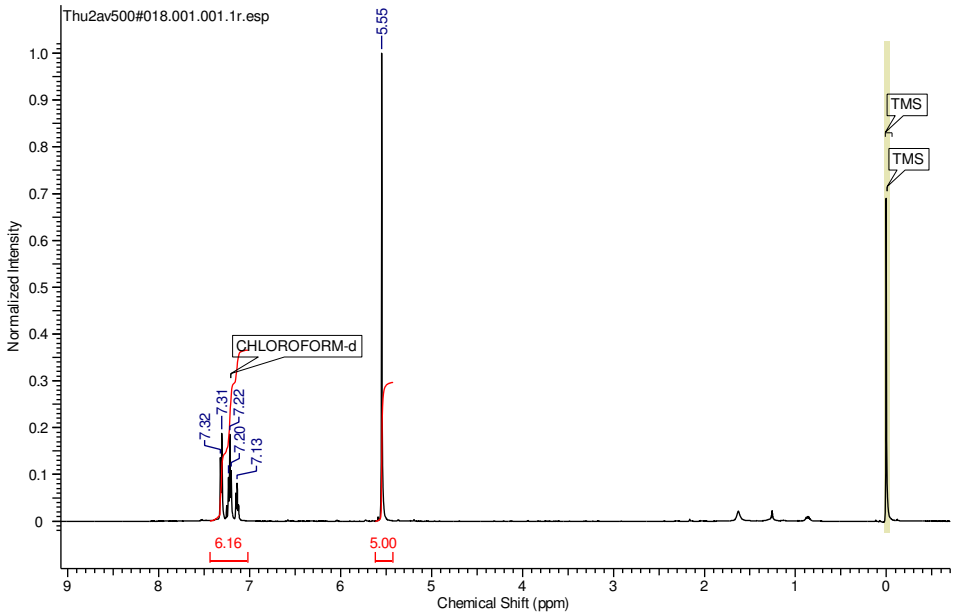


Figure 2.10 ^{1}H NMR spectrum of CpMo(CO)3C≡CPh **3**

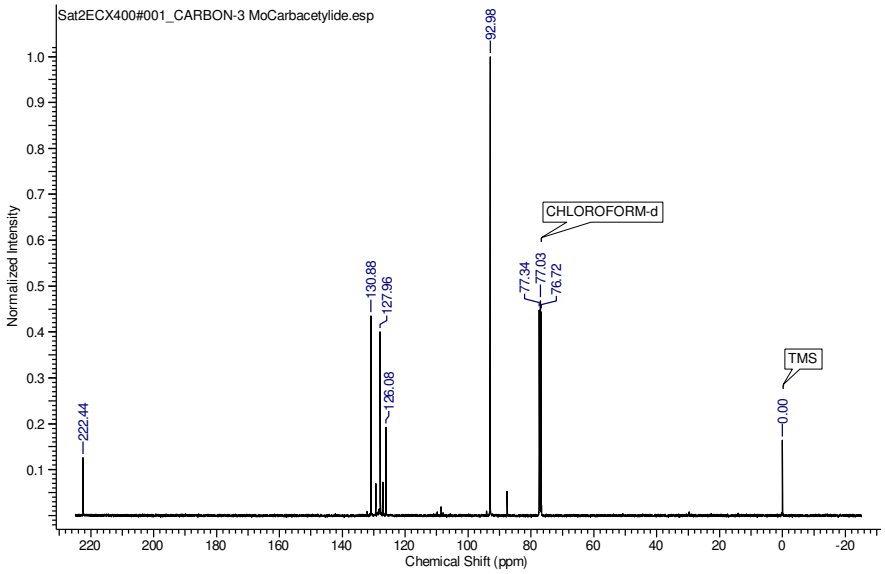
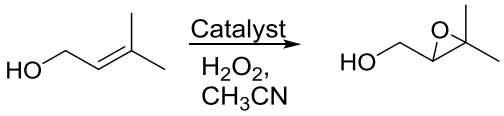


Figure 2.11. ^{13}**C** NMR spectrum of CpMo(CO)3C≡CPh **3**

2.3.3. Catalytic activity



Scheme 2.8. Epoxidation of 3-methyl-2-buten-1-ol

The catalytic activity of molybdenum complexes **1**, **2** and **3** was evaluated for

epoxidation of allylic alcohols using 3-methyl-2-buten-1-ol (Scheme 2.8) as model substrate and hydrogen peroxide as an oxidant and results are shown in Table 2.1. All three catalysts showed almost similar activity with ~ 95% conversion and 99% selectivity for epoxy alcohol. Hence, catalyst **1** was used further to study the effect of different reaction parameters so as to achieve maximum conversion and selectivity.

Table 2.1. Epoxidation of 3-methyl-2-buten-1- ol by molybdenum complexes

Entry	Catalyst	Conversion (%)	Selectivity, (%)	
			Epoxy alcohol	Aldehyde
1	**1**	95	99	1
2	**2**	94	99	1
3	**3**	95	99	1

***Reaction Conditions**:* Substrate (0.1g, 1.1 mmol): Oxidant (0.078 g, 2.3 mmol), Catalyst (2.5 mol%), Temp. (80 $^{\circ}$C), Solvent (CH_3CN, 1.5 g), Time (2 h).

The effect of various parameters such as reaction temperature, molar ratio of substrate: oxidant and catalyst loading on conversion and selectivity was studied to optimize reaction conditions so as to achieve the high selectivity for epoxy alcohols and the results are shown in Table 2.2. Maximum conversion of 3-methyl-2-buten-1-ol was obtained in 2 h at 80 °C with 99% selectivity for epoxy alcohol when 1 mol% catalyst **1** and 2 equivalent of hydrogen peroxide was used. Rate of epoxidation of 3-methyl-2-buten-1-ol decreased when catalyst loading or quantity of oxidant was decreased and hence required more time for completion of the reaction. All three catalysts showed similar activity. Hence, catalyst **1** was used further to examine the scope of substrates.

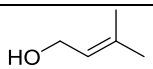
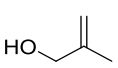
Table 2.2. Effect of catalyst and oxidant concentration on epoxidation of 3-methyl-2-buten-1-ol using catalyst **1**

Entry	Reaction Parameters	Conc.	Time (h)	Conversion (%)	Selectivity, (%)	
					Epoxy alcohol	Aldehyde
1	Catalyst conc.[a] (mmol)	0.0023	5	70	99	1
		0.029	2	95	99	1
		0.029[$]	12	30	99	1
2	Oxidant conc. [b] (mmol)	0.5	18	28	99	1
		1	2	95	99	1
		2[#]	2	96	99	1

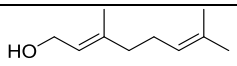
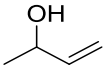
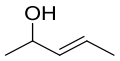
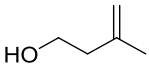
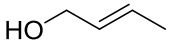
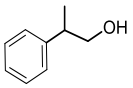
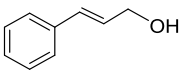
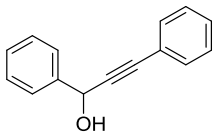
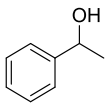
***Reaction conditions**:* [a] Substrate (1.0 mmol), H_2O_2 (2.0 mmol), Catalyst **1** (1 mol%), CH_3CN (1.5 g), Temp. (80 °C). [b] Substrate (1mmol), Catalyst **1** (2.5 mol%), CH_3CN (1.5 g), Temp. (80 °C).[$] Reaction was carried out at 30 °C for 12 h. [#] Reaction was carried out using **3** as catalyst.

After this interesting preliminary result, potential of catalyst **1** was further explore for epoxidation of various allylic alcohols including homoallylic alcohols and results are summarized in Table 2.3.

Table 2.3. Epoxidation of allylic alcohols using catalyst **1**

Entry	Allylic alcohol	Time (h)	Conversion (%)	Selectivity, (%)	
				Epoxy alcohol	Aldehyde
1	 3-methyl-2-buten-1-ol	2	99	99	1
2	 2-methylprop-2-en-1-ol	2	50	100	-

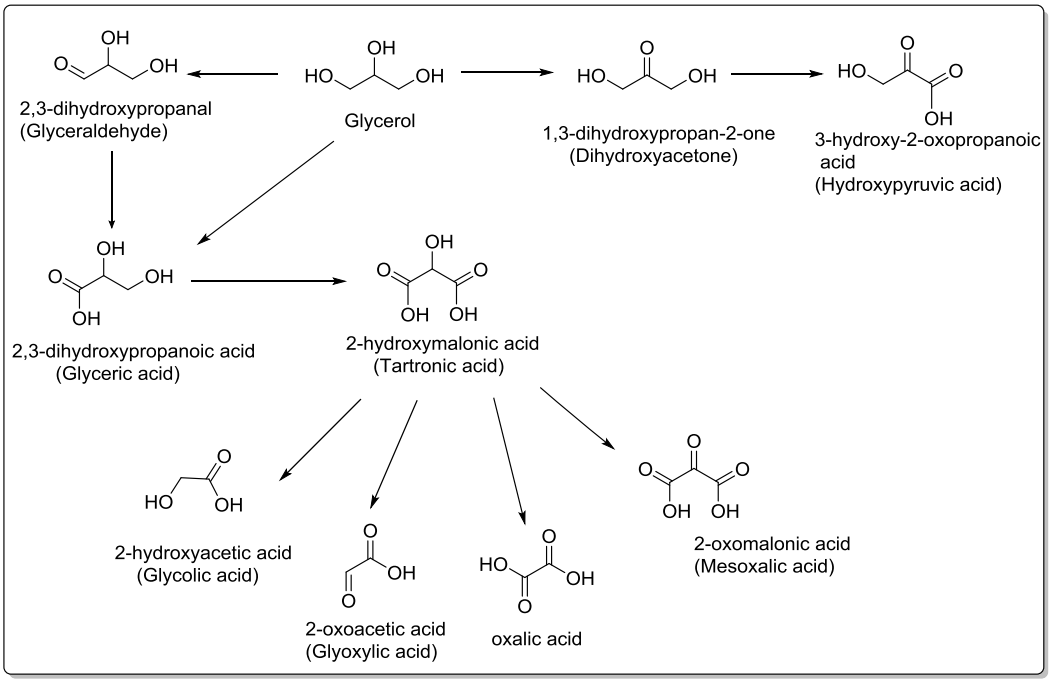
Continued..

3[#]	 (*E*)-3,7-dimethylocta-2,6-dien-1-ol	12	90	99	1
4	 but-3-en-2-ol	2	NR	-	-
5	 (*E*)-pent-3-en-2-ol	2	70	59:41 (*erythro: threo*)	-
6	 3-methylbut-3-en-1-ol	2	NR	-	-
7	 (*E*)-but-2-en-1-ol	2	90	99	-
8	 2-phenylpropan-1-ol	12	NR	-	-
9	 propane-1,3-diol	12	NR	-	-
10	 (*E*)-3-phenylprop-2-en-1-ol	12	98	-	50
11	 1,3-diphenylprop-2-yn-1-ol	12	NR	-	-
12	 1-phenylethan-1-ol	12	NR	-	-

***Reaction Conditions**:* Substrate (1.0 mmol), Oxidant (2.0 mmol), solvent (CH_3CN, 1.5 g), Catalyst (1 mol%), Temp. (80°C). [#] Reaction was carried out at 30 °C with 2.5 mol% catalyst loading.

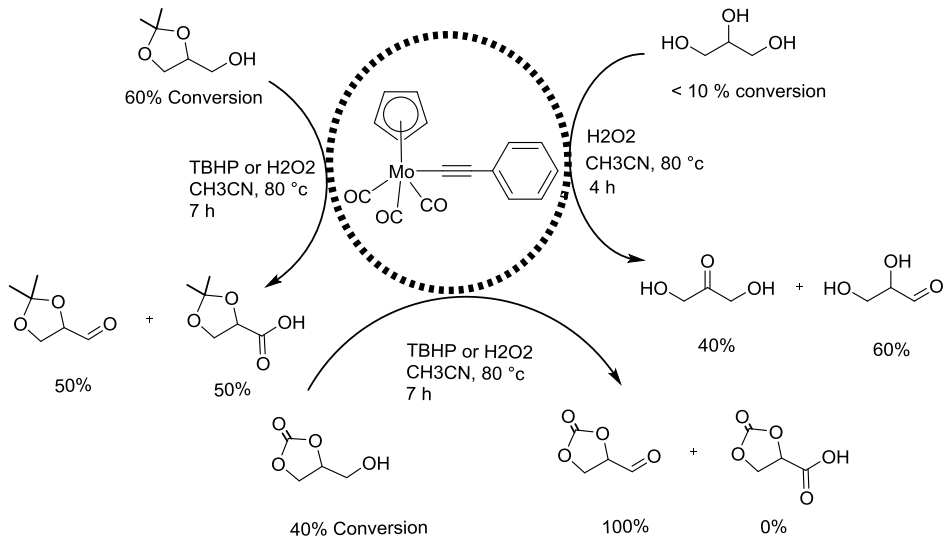
Catalyst **1** showed excellent activity for substituted allylic alcohols than homoallylic alcohols. This behaviour of substrates may be attributed to the presence of electron donating group at the olefinic double bond which increases the electron density on the double bond. No reaction was observed in case of unsubstituted, long chain allylic alcohols and secondary alcohols such as 2-phenyl-1-propanol, 1-phenyl ethanol, 1,3-diphenyl-2-propyn-1-ol. 2-methylprop-2-en-1-ol (Table 2.3, entry 2) showed 50% conversion in 2 h. Chemoselective epoxidation of geraniol (Table 2.3, entry 3) to epoxygeraniol was obtained in which the allylic double bond was epoxidized. The epoxidation of 3-penten-2-ol (Table 2.3, entry 5) showed 100% selectivity for epoxy alcohol however diastereomeric mixture of threo and erythro isomers in a ratio of 40:60 was obtained. (*E*)-2-buten-1-ol (Table 2.3, entry 7) gave very high conversion of 90% with 99% selectivity towards epoxy alcohol. When cinnamyl alcohol was oxidized using **1**, cinnamaldehyde was obtained with 50% selectivity without formation of any epoxide. It indicates that selectivity varied with the type of substrates used for reactions. In literature it is already reported that complex **3** forms oxo-peroxo species in presence of hydrogen peroxide and showed > 80% conversion of benzyl alcohol and substituted benzyl alcohol with excellent selectivity for aldehyde[48] but in case of allylic alcohols, epoxidation is favoured as compare to oxidation of hydroxyl group.

The increasing global demand for biodiesel has spawned an increase in the supply of glycerol. Hence, valorization of glycerol to valuable chemicals is necessary. There are many reactions which give industrially important product from glycerol but out of all oxidation of glycerol are important and can lead to large variety of products as shown in Scheme 2.9.



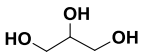
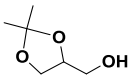
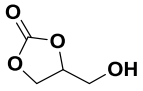
Scheme 2.9. Glycerol oxidation possible products

All the oxidized products have multitude of applications in various fields like pharmaceuticals, cosmetics etc. These products are results of oxidation of primary or secondary –OH group. However, it is difficult to get selective oxidation at primary –OH group due to presence of three reactive -OH groups. The oxidation of primary –OH group of glycerol leads to the formation of glyceraldehyde and further to glyceric acid, which are commercially important due to their industrial applications. Hence, two hydroxyl group of glycerol can be protected by different protecting groups such as isopropylidene group or carbonate residue so as to get selective oxidation at primary –OH group. Protecting groups also help to increase solubility in organic solvents which increased chance to get selective product either glyceraldehyde or glyceric acid. On the other side, molybdenum complexes found to be active and selective in epoxidation reactions. Hence the catalytic efficiency of molybdenum complexes **1** and **3** were explored for oxidation of glycerol and glycerol derivatives (solketal and glycerol carbonate) in the presence of H_2O_2 and TBHP as an oxidants in acetonitrile as solvent and results are shown in Table 2.4 (Scheme 2.10).



Scheme 2.10. Oxidation of glycerol and glycerol derivatives using catalyst **3**

Table 2.4. Oxidation of glycerol and its derivatives using catalyst **1**

Entry	Substrates	Oxidant	Time	Conversion	Selectivity, (%)		
			(h)	(%)	Aldehyde	Acid	DHA
1		H_2O_2	7	< 10	60	-	40
		TBHP	7	NR	-	-	-
2		H_2O_2	7	60	50	50	
		TBHP	7	NR	-	-	
3		H_2O_2	12	< 10	50	50	
		TBHP	3	40	100		
		TBHP[#]	3	60	100		

***Reaction Conditions**:* Substrate (1.0 mmol), Oxidant (4.0 mmol), solvent (CH_3CN, 1.5 g), Catalyst (2.5 mol%), Temp. (80 °C).[#] Reaction was carried out by catalyst **1**

According to results we could observe that both the catalytic activity and the selectivity of catalyst varied with the oxidizing agent as well as with the type of substituents on glycerol. Glycerol (Table 2.4, entry 1) itself was not very active and could be oxidized with a low conversion and poor selectivity in the presence of both

oxidizing agents. Indeed, dihydroxyacetone (DHA) and glyceraldehyde were obtained in a 4:6 ratio accompanied by a glycerol conversion below 10%. When solketal was oxidized using catalyst **1** and hydrogen peroxide, higher conversion of 60% was obtained nevertheless with equal selectivity for corresponding aldehyde and acid (Table 2.4, entry 2). Interestingly no conversion was obtained in presence of anhydrous TBHP (Table 2.4, entry 2). The reactivity pattern was exactly reverse for glycerol carbonate. Glycerol carbonate gave very poor conversion (< 10%) when H_2O_2 was used as oxidant with 50:50 selectivity for aldehyde and acid (Table 2.4, entry 3). However 40% conversion was obtained with 100% selectivity for aldehyde in presence of anhydrous TBHP as an oxidant (Table 2.4, entry 3). Due to presence of water in aq. H_2O_2, over oxidation of formed aldehyde to acid was observed loading to 50:50 selectivity for aldehyde and acid. The formation of products (aldehyde and acid of solketal and glycerol carbonate) was confirmed by ^{1}H NMR of the reaction mixture. Confirmation of the isolated product was not possible due to instability of the products. In ^{1}H NMR spectrum (Figure 2.12) we could clearly see the peak at δ 9.92 corresponds to aldehyde. Whereas, aldehyde peak was absent in ^{13}C NMR spectrum showing the instability of product.

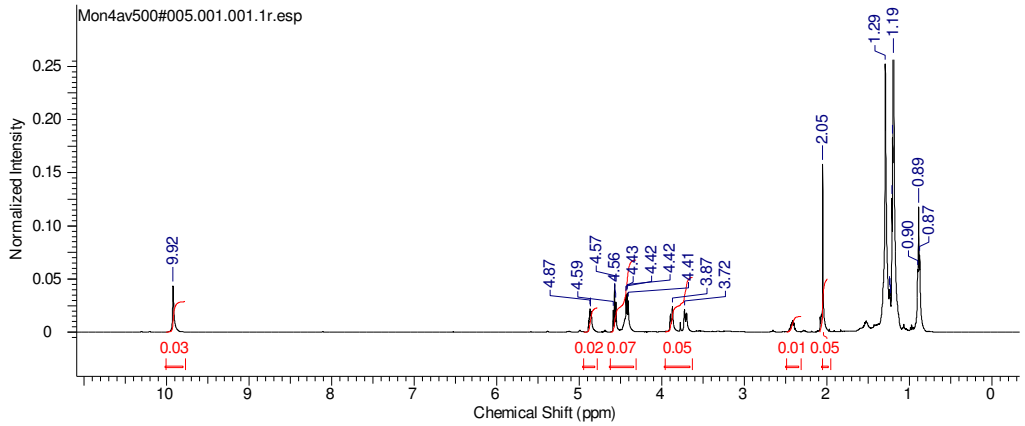


Figure 2.12. ^{1}H NMR spectrum of glycerol carbonate reaction mixture

Kamata *et al.*[49] have reported epoxidation of 3-methyl-2-buten-1-ol using selenium containing dinuclear peroxotungstate with maximum 94% yield. They also evaluated the epoxidation of geraniol in water showing a mixture of 2,3 and 6,7-epoxy geraniol in a ratio of 82:18. Yamamoto and co-workers[50] have reported the epoxidation of geraniol by molybdenum complex in presence of TBHP with very high yield, though selectivity obtained was 1:1 mixture of 2,3-epoxy geraniol and 6,7-

epoxygeraniol. Lattanzi *et al.*[51] have reported the vanadium catalyzed epoxidation of geraniol and showed 98% conversion in 12 h at 0 °C in toluene. However catalyst loading used was very high *i.e.*10 mol%. Solvent used for reaction was not very friendly from environmental viewpoint. Malkov *et al.*[52] have reported the vanadium catalyzed epoxidation of geraniol using 2 mol% of catalyst at -20 °C in 48 h with aq. TBHP and showed 69% conversion. However time required for reaction to reach maximum conversion was high. Katsuki and co-workers[53] reported niobium salen complex for epoxidation of geraniol using urea-hydrogen peroxide as oxidant and showed 83% yield in 24 h in toluene at 40 °C. However reaction rate was slower though oxidant (4 equiv.) used was high. Coleman-Kammula and co-workers[54] reported dioxomolybdenum complex using *in situ* prepared L-methylprolinol as ligand and showed more than 80% conversion of 3-methyl-2-buten-1-ol. However experimental conditions used for reaction were not environmental friendly as reaction was carried out using cumene hydroperoxide as oxidant and cyclohexane as solvent at 60 °C. Corma *et al.*[55] have reported homogeneous and zeolite-heterogenised dioxomolybdenum catalysts prepared using (*2S*,*4R*)-4-hydroxyproline for the epoxidation of geraniol and nerol with > 90% conversion and up to 99% selectivity of epoxy alcohols. Mandelli *et al.*[56] reported tetracopper(II) triethanolaminate complex as catalyst for oxidation of glycerol with H_2O_2/TBHP as oxidant with maximum 18% conversion of glycerol and 40-90% selectivity for dihydroxyacetone (DHA). Waymouth *et al.*[57] have reported 97% conversion of glycerol with 99% selectivity for DHA using homogeneous Pd catalyst. Ikunaka *et al.*[58] reported $RuCl_3$/TCCA (trichloroisocyanuric acid) mediated oxidation of solketal with 96% yield of 2,2-dimethyl-1,3-dioxolane-4-carboxylic acid. Hence it is clear that the present catalyst has shown much superior performance for epoxidation of various allylic alcohols under mild reaction conditions.

2.4. Conclusions

Synthesized molybdenum(VI) salen complexes have shown to be highly efficient catalyst for epoxidation of various allylic alcohols with excellent conversion and selectivity under mild reaction conditions. Selective epoxide obtained in epoxidation of allylic alcohols could be correlated to geometry of catalyst and type of substrates. Cinnamaldehyde was obtained in case of cinnamyl alcohol oxidation showing variation in selectivity pattern according to substrates. Promising results were

obtained in oxidation of protected glycerol; however both the catalytic activity and the selectivity varied with the oxidizing agent as well as type of substituents present on glycerol.

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Chapter 3

Molybdenum(VI) Cis-Dioxo Complex with Chiral Schiff Base Ligand and Their Catalytic Applications in Asymmetric Oxidation Reactions

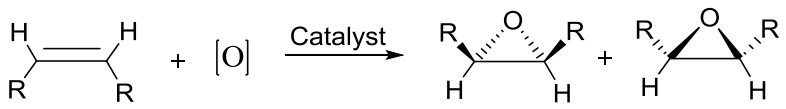
Abstract

*Chiral Schiff base dioxomolybdenum complex (**2a**) was prepared and extensively characterized by various spectroscopic techniques viz., elemental analysis, FT-IR, NMR, single crystal X-ray diffraction analysis. Single crystal X-ray diffraction studies showed that crystal of the complex belongs to orthorhombic space group and there are three molecules in slightly different conformations. Catalyst **2a** was evaluated for asymmetric epoxidation of olefins with tert-butyl hydroperoxide (TBHP) as an oxidant showing conversion in the range of 20-70% with excellent selectivity for epoxides (99%). Catalyst was also evaluated for sulfoxidation of thioanisole using H_2O_2 as an oxidant. A very high conversion of thioanisole and > 80% selectivity for sulfoxide was observed. However there was no asymmetric induction observed.*

3.1. Introduction

3.1.1. Transition metal Schiff base complexes for oxidation reactions

Epoxides are important intermediates and selective oxidation is dominated by epoxidation studies (Scheme 3.1). Epoxides are three membered cyclic rings composed of two carbon atoms and a bridging oxygen atom. Bond angle of epoxides are 60 °, which is different than normal sp^3 hybridized bond angle of 109 °. Due to this huge deviation ring undergoes substantial Baeyer strain and acts as reactive electrophile due to presence of δ^+ charge on two carbon atoms by electronegative oxygen atom and easily undergo ring opening reactions. Especially in chiral epoxides due to presence of two stereogenic centers, it is valuable intermediate in pharmaceutically active compounds and also useful in synthesis of natural products.[1]



Scheme 3.1. Catalytic asymmetric epoxidation of alkenes

During past few years research has been devoted to develop a method for enantioselective epoxidation of olefins using transition metal catalysts or organocatalysts, which are two main classes of catalysts. In this section we have mainly focused on transition metal based catalysts for asymmetric oxidation reactions.

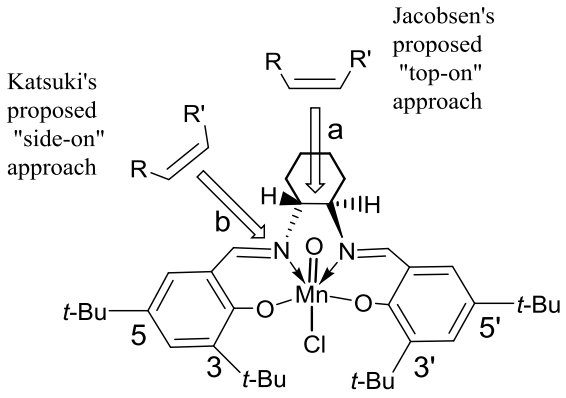
Chiral epoxides were first reported in 1965. After this great discovery significant attention has been paid to use chiral transition-metal complexes for enantioselective epoxidation of different organic substrates. In 1980, Sharpless and Katsuki[2] developed a first method on epoxidation for variety of allylic alcohols and showed excellent enantiomeric excess using titanium(IV) alkoxide, an enantiomerically pure tartrate ester and *tert*-butyl hydroperoxide as oxidant. This reaction became one of the most widely applied reactions in asymmetric synthesis.[3]

Asymmetric epoxidation of olefins using transition metal Schiff base complexes has been studied extensively in literature.[4, 5, 6] Activity of transition metal Schiff base complexes totally depends on metal ion and ligand used for the reaction. In 1990, Jacobsen and Katsuki modified a procedure reported by Kochi and evaluated for asymmetric epoxidation of olefins using chiral Mn(III) salen complexes. This method showed excellent activity and selectivity for epoxide with NaOCl as oxidizing

agent. However, this method is restricted to *cis*-olefins; it could not epoxidized trans-olefins. This method showed high enantioselectivity for cis-olefins, it also worked for a small number of conjugated trisubstituted and tetrasubstituted olefins and electron deficient olefins but requires high catalyst loading and longer reaction time. However, Katsuki's catalysts showed high enantioselectivity only for *trans*-olefins. Both catalysts showed high *ee* only for substrates containing alkene bond in conjugation with an aryl moiety.[7]

There are two rationales for the observed enantioselectivity in the epoxidation process, the difference between them being the approach of the substrate to the active catalyst. Jacobsen has proposed a 'top-on' approach to the axial oxygen, whereas Katsuki has suggested a 'side-on' approach (Figure 3.1).[8] DFT studies showed the stepwise mechanism of epoxidation, led to the formation of a variable amount of trans-epoxide when the radical intermediate was stabilized by polar substituents on the alkene. Jacobson and co-workers has also studied another manganese(III) Schiff base complex for epoxidation of olefins in the presence of additives.[9] Later on Katsuki showed the epoxidation of 6-acetoamino-7-nitro-2,2-dimethylchromene by chiral manganese(III) salen complexes in the presence of chiral additives and showed yield of 5–65% with 73% *ee*.[10] These complexes were also evaluated for enantioselective epoxidation of unfunctionalized olefins[11] showing lower *ee* than Jacobsen catalyst.[12] Chromium(III) salen complexes showed 83% *ee* for epoxidation of *trans* olefins.[13] More recently, chromium oxo complexes of salen ligands were studied for the asymmetric epoxidation of *trans*-*β*-methylstyrene and found *ee's* up to 90%.[14] Chiral binaphthyl Schiff base metal complexes were studied in the epoxidation of alkenes.[15] The binaphthyl Schiff base manganese(II) complexes were studied for the first time by Bernardo *et al*.[16] for epoxidation of 1,2-dihydronaphthalene in the presence of sodium hypochlorite showing *ee* up to 13–15%. Palladium(II) complexes of binaphthyl Schiff base were also studied for the epoxidation of styrene and 4-fluorostyrene with TBHP as oxidant showed 17–71% *ee*.[17] Molybdenum complexes bearing chiral ligands such as 2'-pyridyl alcohols[18] and phosphine alcohols[19] have been used for the epoxidation of olefins and reported moderate *ee* of 20-40% for functionalized olefins. Lots of efforts have been taken to synthesize variety of cis-MoO_2^{2+} catalysts containing chiral ligands such as bis-oxazoline, cis-diol, cis-8-phenylthiomenthol[20] and sugar derived chiral ligands[21] to achieve high *ee* in

asymmetric epoxidation but unfortunately less to moderate *ee* were achieved in all cases.



Model to explain enantioselectivity

Figure.3.1. Top-on approach and side-on approach to Mn- salen complex

Varieties of hydroxamic acid ligands have been introduced by several groups in recent years. Yamamoto and co-workers[22] designed hydroxamic acid bearing axially chiral binaphthyl group as ligand (Figure 3.2) and vanadium as transition metal for asymmetric epoxidation of allylic alcohol. *In situ* synthesized catalysts showed for the first time that very high enantioselectivity up to 94% can be achieved.

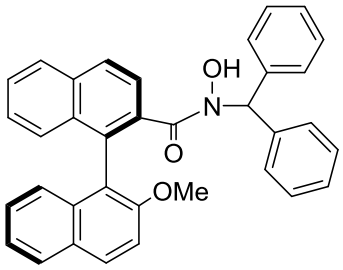


Figure. 3.2. Hydroxamic acid bearing axially chiral binaphthyl group

In situ prepared vanadium complexes using α-amino acid based hydroxamic acids such as *tert*-leucine derived ligand (Figure 3.3) and $VO(O\text{-}iPr)_3$ showed very high enantioselectivity for epoxides.[23]

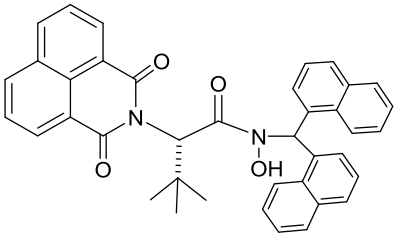


Figure 3.3. *α*-amino acid based hydroxamic acids

Yamamoto and co-workers[24] also studied the use of chiral C_2-symmetric bishydroxamic acids as ligand with vanadium. The $VO(O\text{-}iPr)_3$/BHA (bis-hydroxamic acid) system showed high yield and enantioselectivity in asymmetric epoxidation of homoallylic alcohols, as well as *cis* and *trans*-substituted homoallylic alcohols. Recently, Egami and Katsuki[25] have reported niobium salen complexes as a catalyst for epoxidation of allylic alcohol with high enantioselectivity.

In 1999, Bellemin-Chaponnaz *et al.*[26] have reported $[MoO_2L_2]$ complex using 2-[(-)-menthol-pyridine] as the chiral ligand for oxidation of 1-hexene showing 20% conversion and an *ee* of 15%. Optically active pyridyl alcoholates were synthesized by Herrmann *et al.*[18a] using chiral monoterpenes (-)-camphor, (+)-camphor, (-)-fenchone, and (-)-menthone as synthetic ligand precursors and prepared molybdenum complexes, which showed conversions in the range of 60-70% and asymmetric induction in case of *trans-β*-methylstyrene in the range of 4-26% *ee*. Chiral 2-pyridinyl alcohols derived from isopropylidene-protected carbohydrates were also reported with MoO_2^{2+}moiety showing conversion of 58% at 50-70 °C with *ee* of 23% in epoxidation of *trans-β*-methylstyrene using tert-butyl hydroperoxide (TBHP) or cumene hydroperoxide (CHP) as an oxidant. The higher *ee's* were observed with cumene hydroperoxide as oxidant.[27] In 2001, Goncalves *et al.*[28] evaluated dioxomolybdenum(VI) complexes ligated with one or two pyridyl alcoholate ligands for epoxidation of olefins. The monosubstituted complex was found to be more active than the complex containing two chiral ligands. A variety of dioxomolybdenum complexes with tetradentate bis(oxazoline) ligand, containing a $C(CH_3)_2$ bridge, or two bidentate pyridyl alcoholate ligands were synthesized by Romao *et al.*[29] and used for epoxidation of trans-β-methylstyrene with TBHP as oxidant at 55 °C. The bis(oxazoline) complexes showed very good activity (up to 86% conversion) but unfortunately with very low *ee* (4–6%). Chiral dioxomolybdenum(VI) complexes

$[MoO_2Cl_2(L^*)]$ and $[MoO_2Cl(THF)_2L^*]$ containing 8-phenylthioneomenthol, 8-phenylthioisoneomenthol have been prepared using $[MoO_2Cl_2(THF)_2]$ as metal precursor with the appropriate ligands . These complexes showed conversions in the range of 63-82% with poor *ee* for *cis-β*-methylstyrene using TBHP as an oxidant in toluene at 55 °C.[20]

Rao *et al.*[30] have reported the complexation of sugar-derived chiral ligand with $(MoO_2)^{2+}$ moiety. This complex was evaluated later on for olefin epoxidation by Kuhn *et al*.[21] Another methodology to achieve high *ee* with dioxomolybdenum(VI) directed to the application of tetradentate chiral salen ligands. Although dioxomolybdenum(VI) complexes have already been prepared and spectroscopically characterized in past 20 years.[31] Recently, researchers have shown interest in using its chiral derivative for asymmetric reactions. Shi *et al*.[32] reported epoxidation of cis-1-propenylphosphonic acid with 30% aqueous hydrogen peroxide using chiral tetradentate molybdenum(VI) complex affording (*1R,2S*)-(-)-(1,2-epoxypropyl) phosphonic acid showing that reaction strongly dependent on ligand and reaction conditions.

In asymmetric synthesis, chiral sulfoxides are also valuable and efficient reagents. Chiral sulfoxides have various applications in organic synthesis. Zhu and co-workers[33] examined tetradentate ligands with vanadium for asymmetric sulfide oxidation. Salen ligand (Figure 3.4) was used to catalyze the oxidation of a range of sulfides, affording sulfoxides in good yields (up to 86%) and excellent enantioselectivities (up to 95% *ee*), in certain cases.

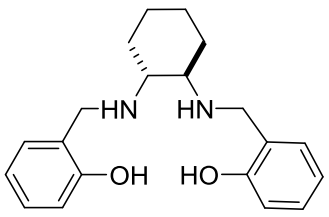


Figure 3.4. Salen ligand

In situ prepared niobium based complexes with chiral ligand (Figure 3.5) was reported by Miyazaki and Katsuki[34] showing very high enantioselectivity for asymmetric oxidation of sulfides in presence of urea hydrogen peroxide (UHP).

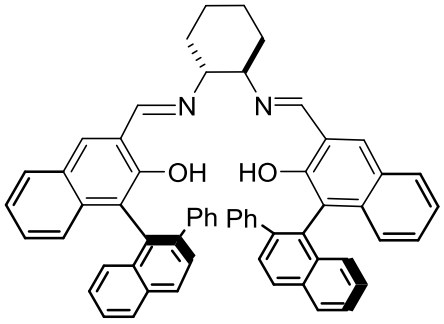


Figure 3.5. Chiral ligand

Since 1984, Schiff base metal complexes with chiral ligands have shown very good activity for enantioselective oxidation of sulfides. Kagana and Modenab[35] reported moderate to high *ee* for alkyl aryl sulfoxides and dialkyl sulfoxides by modified Sharpless reagent. Uemura and co-workers[36] have reported chiral BINOL as a ligand with titanium. Titanium complex with (*1R*,*2R*)- or (*1S*,*2S*)-1,2-diphenylethan-1,2-diol as a ligand was reported by Rosini and co-workers.[37] Both systems showed high *ee* for alkyl aryl sulfides. *In situ* prepared catalyst from vanadyl acetylacetonate and chiral Schiff bases reported by Bolm and Bienewald[38] showed high *ee* for sulfoxidation of different sulfides. After this report several group have successfully described the modification of Schiff base ligand for sulfide oxidations.[39]

Considering this background we have synthesized chiral Schiff base dioxomolybdenum(VI) complex and characterized by various spectroscopic techniques. The prepared complex was used as catalyst precursor for asymmetric epoxidation of alkenes, sulfides and allylic alcohol and results are discussed in this chapter.

3.2. Experimental Section

3.2.1. Materials

All reagents of commercial grade (Aldrich) were used as received unless stated otherwise. Hydrogen peroxide used was 35% w/w in water. Preparation of catalyst was performed under inert atmosphere using Schlenk technique. Solvents were dried according to standard procedures. (*1R*,*2S*)-1-[(3,5-di-*tert*-butyl-2-hydroxybenzylidene)amino]-2-indanol (**1a**), (*1S,2S,4S*)-1,7,7-trimethyl-3-morpholinobicyclo[2.2.1]heptan-2-ol (**1b**), L-(+)-prolinol (**1c**), (*R*)-2-(4-isopropyl-

4,5-dihydrooxazol-2-yl)propan-2-ol (**1d**) and $MoO_2(acac)_2$ was purchased from Aldrich and Stream chemicals and used as received without further purifications.

Elemental analysis (carbon, hydrogen and nitrogen) were performed on a Perkin–Elmer 2400 CHNS/O elemental analyzer. Optical rotation was recorded on P-2000 Jasco polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AV-200 (50 MHz) or Bruker AV-400 (100 MHz) or Bruker DRX-500 (125 MHz). Tetramethylsilane was used as the internal standard. NMR values are expressed in δ (ppm). FT-IR spectra were recorded on Nicolet Nexus IR 6700 with KBr pellet in the range of 400-4000 cm^{-1}, with resolution 4 and averaged over 100 scans.

3.2.2. Synthesis of Schiff base dioxomolybdenum (VI) complex (2a)

In Schlenk tube under inert atmosphere a solution of the (*1R,2S*)-1-[(3,5-di-tert-butyl-2 hydroxybenzylidene)amino]-2-indanol (**1a**) ligand (1 g, 0.0027 mol) in methanol (5 mL) was added dropwise to a stirred methanol (5 mL) solution of $MoO_2(acac)_2$ (0.89 g, 0.0027 mol) at room temperature. After complete addition the mixture was heated at 40 °C for 2 h and yellow solid was obtained which was filtered off, washed with cold methanol and dried in vacuo.

Yield: 1.15 g, 80%.

^{1}H NMR: δ 1.45 (18H, d, $-CH_3$), 3.2-3.3 (2H, d, CH_2), 5.6 (s), 7.15-7.35 (6H, $-C_6H_5$), 8.9 (1H, s, -NCH)

^{13}C NMR: δ 34.4-35.3 ($-CH_3$), 39.7($-CH_2$), 77.02 (-CH), 119-144 ($-C_6H_5$), 168 (-CH=N)

IR (KBr) (cm^{-1}): v 3439, 2963.1, 1618.3, 1460 (s), 1301.8 (m), 1254.4 (m), 1073.5 (m), 1012.1 (m), 899.9 (s) (Mo=O), 876.1 (s, Mo=O), 754.1 (m).

Elemental analysis of $C_{25}H_{33}MoNO_5$

Calculated C (%) 57.36, H (%) 6.35, N (%) 2.68.

Obtained C (%) 57.09, H (%) 6.225, N (%) 3.27

[α]20/D= -12.7 (CH_2Cl_2, 3mM)

3.2.3. Single Crystal X-ray diffraction analysis of 2a

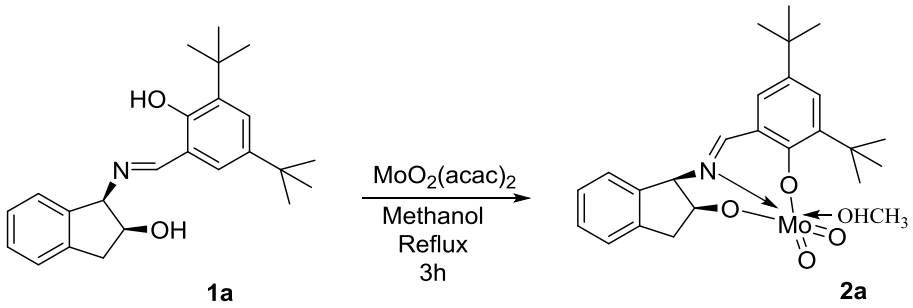
Crystal Data for $C_{25}H_{35.33}MoNO_5$ (2a) compound: Single crystals of the complex were grown by slow evaporation of the solution of methanol. Data was collected on SMART APEX-II CCD using Mo-Kα radiation (λ = 0.7107 Å) to a maximum θ

range of 25.00°. Yellow colored plate like crystal of approximate size 0.33 x 0.26 x 0.15 mm^3, was used for data collection. Crystal to detector distance 5.00 cm, 512 x 512 pixels /frame, Oscillation / frame -0.5 °, maximum detector swing angle = -30.0 °, beam center = (260.2, 252.5), in plane spot width = 1.24, Multirun data acquisition. Total scans = 2, total frames = 657, exposure / frame = 10.0 sec / frame, θ range = 0.66 to 25.00 °, completeness to θ of 25.00 °, is 99.1%. $C_{25}H_{35.33}MoNO_5$, M = 525.82. Crystals belong to Orthorhombic, space group $P2_12_12_1$, a = 10.4720(1) Å, b = 11.3588(2) Å, c = 61.7106(9) Å, V = 7340.44(18) $Å^3$, Z = 12, D_c = 1.427 g /cc, μ (Mo–Kα) = 0.571 mm^{-1}, 31275 reflections measured, 12743 unique [I > 2σ(I)], R value 0.0930, wR2 = 0. 1959. Largest diff. peak and hole 4.198 and -2.935 e. $Å^{-3}$. All the data were corrected for Lorentzian, polarisation and absorption effects. SHELX-97 (ShelxTL)[40] was used for structure solution and full matrix least squares refinement on F^2.

3.2.4. Catalytic activity

The oxidation of olefins and sulfides was carried out using TBHP (5.5 M in decane)/ aq. H_2O_2 (35% solution) were carried out in a 50 mL two necked round bottom flask fitted with reflux condenser and a magnetic stirrer. The flask was charged with substrate (1 mmol), dichloromethane/ tetrachloroethane/ CH_3CN as solvent, TBHP/H_2O_2 (1.5 mmol) as oxidants and catalyst **2a** (1 mol%/ 5 mol%). The reaction was stirred at 0 °C or 30 °C or reflux temperatures and monitored by TLC and ^{1}H NMR spectroscopy.

3.3. Results and Discussion



Scheme 3.2. Synthesis of chiral Schiff base dioxomolybdenum complex **2a**

The formation of the complex **2a** was initially confirmed by elemental analysis which showed C (%) 57.09, H (%) 6.225, N (%) 3.27 contents in agreement

with the structure given in Scheme 3.2. The optical rotation of the purified complex was found to be -12.7 which confirmed the chirality of the complex.

3.3.1. FT-IR spectroscopy

Schiff base complex **2a** was further characterized by FT-IR spectroscopy and the spectra of Schiff base ligand and corresponding complex is given in Figure 3.6. The IR absorption at 1622 cm^{-1} is attributed to $\nu_{(C=N)}$, characteristic of the azomethine group in the Schiff base which is shifted to lower frequency and appeared at 1614 cm^{-1} indicating the coordination of azomethine nitrogen atom with metal ion.[41] The coordination of the imine nitrogen is expected to shift the $\nu_{(C=N)}$ band to lower wave numbers after complexation indicating donation of the nitrogen electrons of azomethine to metal. Complex formation was further confirmed by band observed in low frequency region. The presence of medium intensity bands at 550 cm^{-1} and 478 cm^{-1} were attributed to the formation of $\nu_{(Mo–O)}$ and $\nu_{(Mo–N)}$ bands.[42] The IR spectrum of complex **2a** in the solid state showed two absorption bands at 898 cm^{-1} and 936 cm^{-1}, characteristic of asymmetric and symmetric $\nu_{(Mo=O)}$ stretches respectively. Disappearance of the broad O–H absorption on complexation indicated a coordination of the phenolic oxygen to the metal. Further confirmation of participation of phenolic oxygen in the complex formation was proven by shift in position of band to 1365 cm^{-1}. The other series of weak band between 3100 $cm^{-1}$and 2800 cm^{-1} are related to C-H modes of vibration.

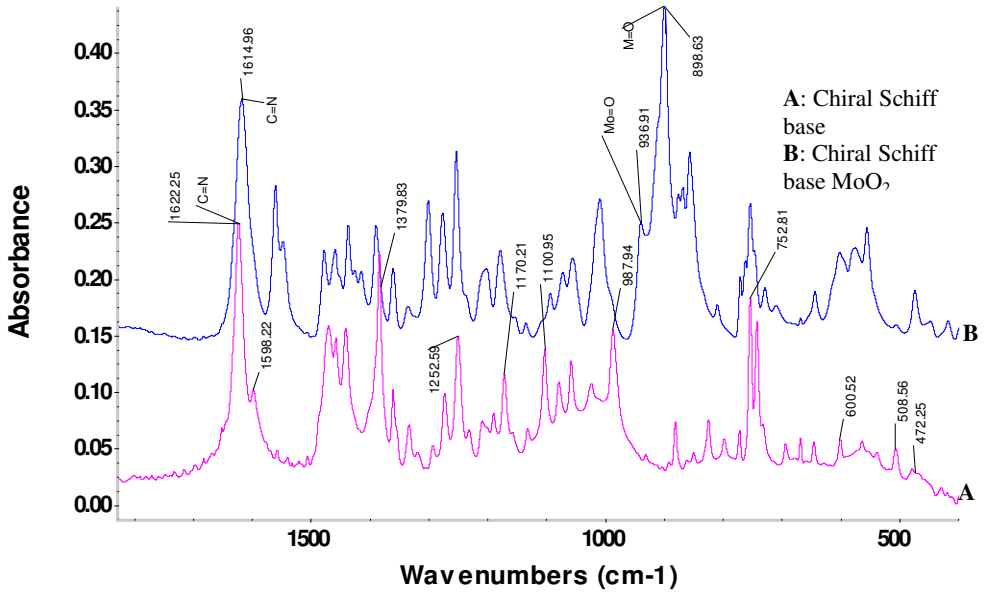


Figure 3.6. FT-IR spectra of (A) Schiff base ligand **1a** (B) chiral Schiff base MoO_2 complex **2a**

3.3.2. NMR Spectroscopy

NMR spectra of Schiff base ligand and corresponding complex is given in Figure 3.7. Nuclear magnetic study was used to investigate the exact binding of ligand with metal atom. In ^{1}H NMR spectrum of ligand signal observed at δ 8.62 corresponds to H of -N=CH which shifted downfield by 0.23 ppm upon complexation. Signal at δ 11.65 corresponded to 2H of –OH disappeared after complexation. All the aromatic proton signals expected from the ligand and complex are clearly observed in the region at δ 7.20–7.65, which clearly indicates complex formation.

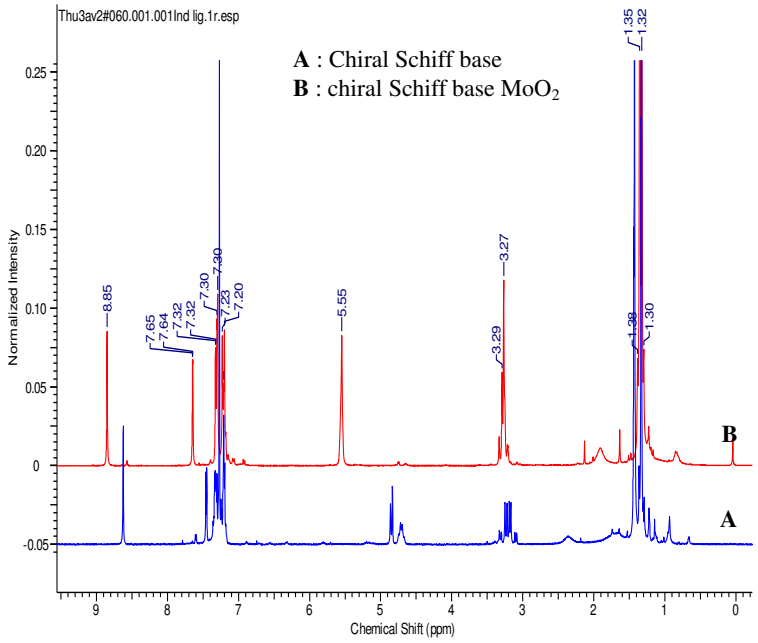


Figure 3.7. ^{1}H NMR of [**A**] chiral ligand **1a** [**B**] chiral dioxomolybdenum complex **2a**

3.3.3. Single crystal X-ray diffraction analysis of 2a

The structure of complex **2a** was unambiguously determined by the single crystal X-ray diffraction analysis. The ORTEP diagram of **2a** is shown in Figure 3.8. Crystal belongs to orthorhombic space group $P2_12_12_1$ with three molecules in different asymmetric unit. The crystallographic details are given in Table 3.1 and selected bond lengths and bond angles are given in Table 3.2 and 3.3. The structure as shown in Figure 3.8 revealed Mo centre to be attached to two oxo groups are not symmetric showing slight variation in bond length of Mo-O(3) and Mo-O(4) in all three molecules 1, A and B. Additionally Mo centre is attached to N-atom of C=N moiety of ligand via co-ordination. In the molecule 1, Mo centre is more strongly co-

ordinated to N-atom as compare to molecule A and molecule B. The structure of the complex indicated the participation of methanol solvent in the form of co-ordination of lone pair of oxygen atom to Mo centre. Structure of the complex showed three molecules have different conformation and that can be seen by overlap. Every molecule has slightly different bond length. A molecule 1 in the complex has disorder in the tert-butyl group (C18, C19, C20) with 0.7 and 0.3 occupancy. An H atom for one of the tert-butyl group was not fixed. Oxygen O1B is disordered in the molecule B. The refinement is converged with isotropic refinement. In case of anisotropic refinement, many of the atoms in all the three molecules show disorder. Hence the refinement is done isotropically.

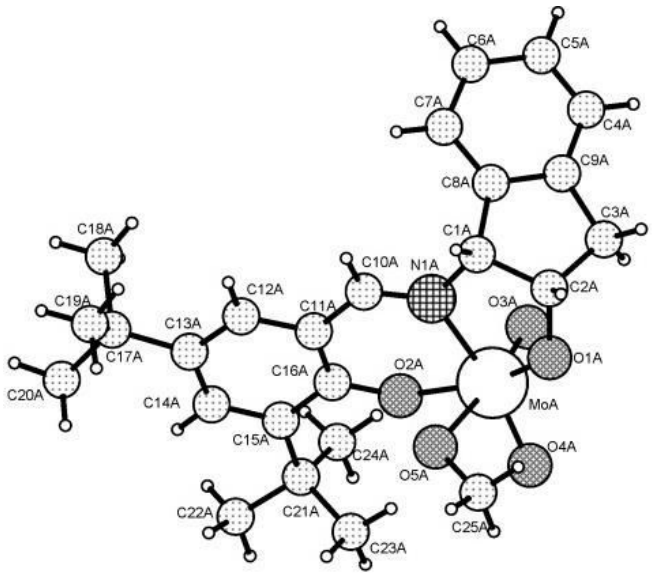


Figure 3.8. ORTEP diagram of molecule A of **2a**

Packing of the molecule in unit cell is shown in Figure 3.9; there are 6 molecules in the unit cell.

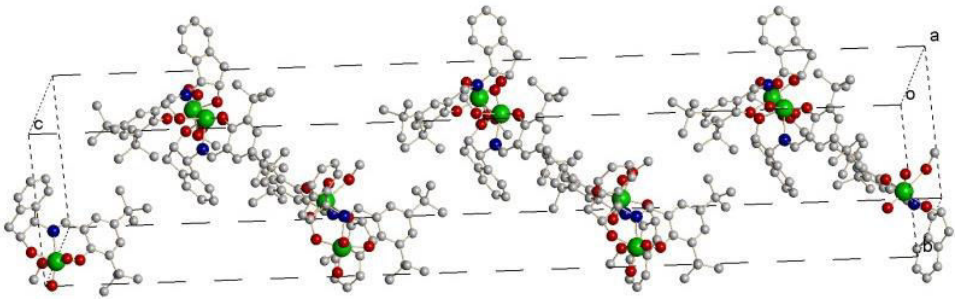


Figure 3.9. Packing of molecule in unit cell of **2a**

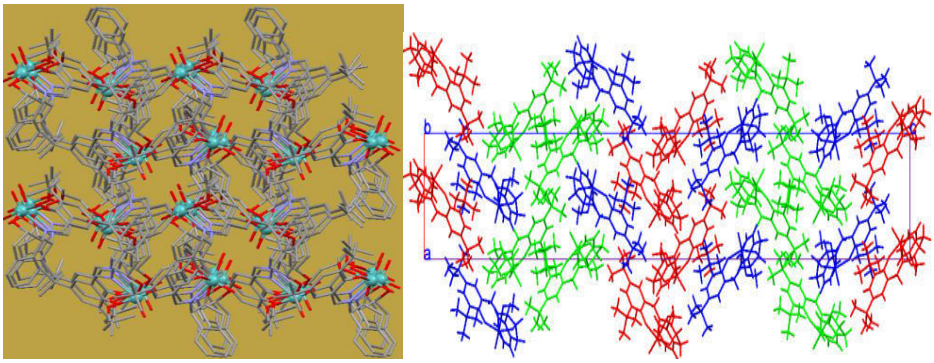


Figure 3.10. Packing diagram of complex **2a** (A) as viewed down c-axis (**B**) as viewed down a-axis

The packing diagram of complex **2a** (Figure 3.10) when viewed down c-axis showed supramolecular assembly [Figure 3.10 (A)]. When viewed down a-axis molecules B and C were found to entangled and sandwiched between molecules of A [Figure 3.10 (B)].

PLUTON diagram of molecules are given below in Figure 3.11.

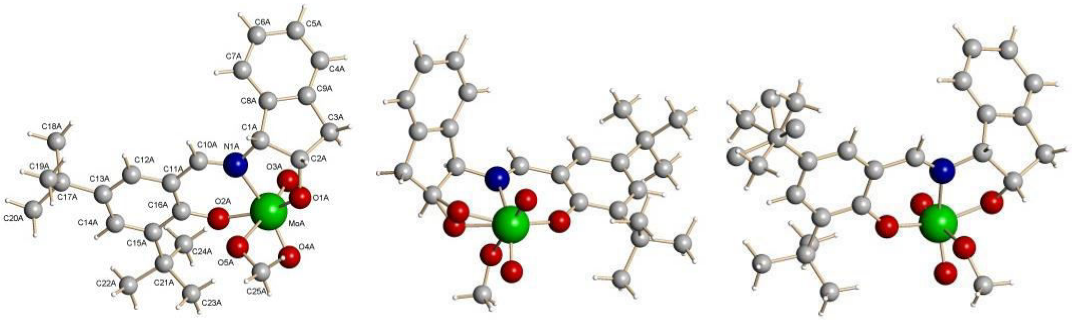


Figure 3.11. PLUTON diagram of molecule A (left), molecule B (middle) and molecule 1 (right)

The three molecules in the unit cell have slightly different conformation which can be seen by the overlaps of three molecules with each other as shown in Figure 3.12.

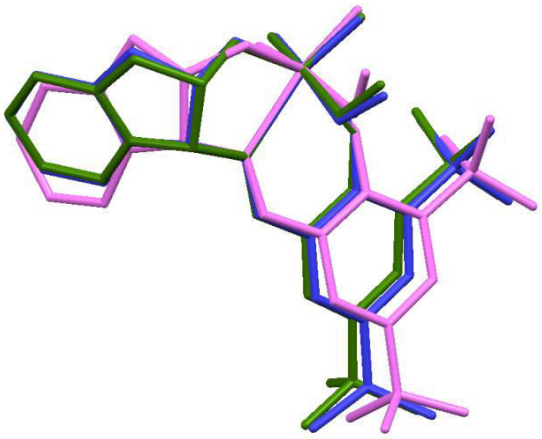


Figure 3.12. Overlapping of three molecule of **2a**

Table 3.1. Data collection and structural refinement details for single crystal X-ray diffraction studies of complex **2a**

Empirical formula	C_{25} $H_{35.33}$ Mo N O_5
Formula weight	525.82
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 10.4720(1) Å α= 90°
	b = 11.3588(2) Å β=90°
	c = 61.7106(9) Å γ=90°
Volume	7340.44(18) $Å^3$
Z	12
Density (calculated)	1.427 g/cc
Absorption coefficient	0.571 mm^{-1}
F(000)	3292
Crystal size	0.33 x 0.26 x 0.15 mm^3
θ range for data collection	0.66 to 25.00°.
Index ranges	-12<=h<=12, -8<=k<=13, -73<=l<=49
Reflections collected	31275

Independent reflections	12743 [R(int) = 0.0358]
Completeness to θ = 25.00°	99.1%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9193 and 0.8362
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12743 / 6 / 423
Goodness-of-fit on F^2	1.201
Final R indices [I > 2sigma(I)]	R1 = 0.0930, wR2 = 0.1959
R indices (all data)	R1 = 0.0955, wR2 = 0.1972
Absolute structure parameter	0.06(6)

Table 3.2. Selected bond lengths [Å] for **2a**

Bond	Molecule 1	Molecule A	Molecule B
Mo-O(3)	1.725(8)	1.745(8)	1.725(11)
Mo-O(4)	1.728(8)	1.760(7)	1.692(8)
Mo-O(1)	1.944(6)	1.878(7)	1.911(11)
Mo-O(2)	1.935(7)	1.944(6)	1.922(7)
Mo-N(1)	2.253(8)	2.267(8)	2.288(9)
Mo-O’	-	-	2.00(2)
Mo-O(5)	2.442(8)	2.398(7)	2.431(10)
O(1)-C(2)	1.441(12)	1.463(13)	1.514(16)
O(2)-C(16)	1.331(12)	1.346(11)	1.37(3)
O(5)-C(25)	1.438(13)	1.447(13)	1.332(12)
N(1)-C(10)	1.322(13)	1.302(13)	1.287(13)
N(1)-C(1)	1.491(12)	1.500(12)	1.498(13)

Table 3.3. Selected bond angles [°] for **2a**

Bond	Molecule 1	Molecule A	Molecule B
O(3)-Mo-O(4)	103.9(4)	106.0(4)	104.4(5)
O(3)-Mo-O(2)	97.5(3)	98.5(3)	94.5(4)
O(4)-Mo-O(2)	99.0(3)	100.7(3)	99.5(4)
O(3)-Mo-O(1)	94.6(3)	98.5(3)	93.3(5)
O(4)-Mo-O(1)	101.5(3)	97.0(3)	101.6(4)
O(3)-Mo-N(1)	106.0(3)	95.5(3)	106.6(4)
O(4)-Mo-N(1)	150.0(3)	158.0(3)	149.0(4)
O(2)-Mo-N(1)	79.6(3)	79.9(3)	79.6(3)
O(1)-Mo-N(1)	73.7(3)	75.1(3)	75.3(4)
O(3)-Mo-O(5)	176.9(3)	172.7(3)	175.3(5)
O(4)-Mo-O(5)	77.7(3)	81.2(3)	79.8(4)
O(2)-Mo-O(5)	84.8(3)	79.7(3)	82.7(3)
C(2)-O(1)-Mo	124.8(6)	123.7(6)	123.2(8)
C(16)-O(2)-Mo	141.8(7)	140.7(6)	144.0(7)
C(10)-N(1)-C(1)	116.0(8)	119.3(8)	119.2(9)

Table 3.4. Selected torsion angles [°] for **2a**

Bond	Molecule 1	Molecule A	Molecul B
O(3)-Mo-O(1)-C(2)	132.9(7)	65.1(8)	130.1(10)
N(1)-Mo-O(1)-C(2)	27.6(7)	-28.3(7)	23.8(9)
O(5)-Mo-O(1)-C(2)	-46.1(7)	-107.6(8)	-45.3(10)
O(1)-Mo-O(2)-C(16)	28.7(14)	10.2(13)	7.5(17)
O(3)-Mo-O(1)-C(2)	132.9(7)	65.1(8)	130.1(10)
C(10)-N(1)-C(1)-C(8)	-85.4(11)	-83.5(12)	-84.4(12)

3.3.4. Catalytic activity

Asymmetric epoxidation of olefins was normally carried out in literature using *in situ* prepared chiral complexes. To study the effect of *in situ* prepared chiral dioxomolybdenum complexes on olefin epoxidation of 1-phenyl-1-cyclohexene, experiments were carried out using $MoO_2(acac)_2$ with different chiral ligands namely **1a**, **1b**, **1c**, **1d** (listed below) in a molar proportion of 1:1.5 and results are compared with *in situ* prepared chiral vanadium complex using $VO(acac)_2$ as metal precursor with similar ligands. But surprisingly no reaction was observed with both the metals (Scheme 3.3).

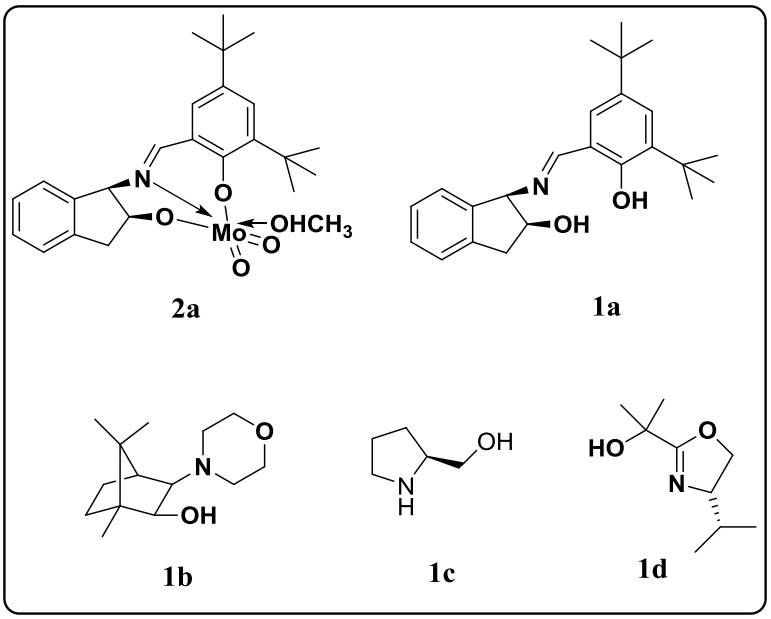
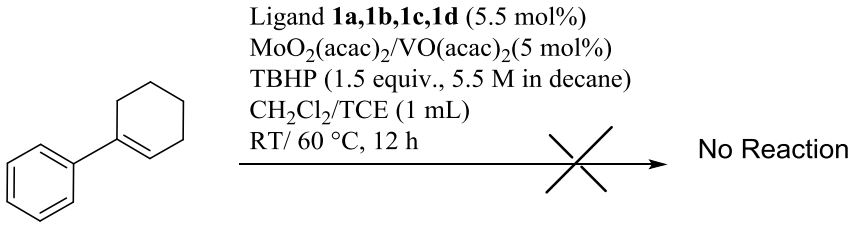


Figure 3.13. Chiral ligands studied for epoxidation reactions



Scheme 3.3. Epoxidation of 1-phenyl-1-cyclohexene

Hence to study the ability of preformed complex **2a** for oxidation of various organics as well as ability to induce chirality was studied by oxidation of variety of prochiral molecules. Initially **2a** was used for oxidation of olefins using TBHP as

oxidant. Oxidation of 1-phenyl-1-cyclohexene as a model substrate was carried out using complex **2a** as catalyst and TBHP as oxidant and results are shown in Table 3.5.

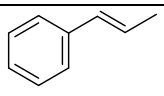
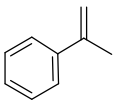
Table 3.5. Epoxidation of 1-phenyl-1-cyclohexene using **2a**

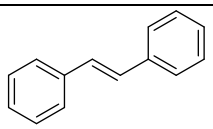
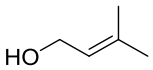
Entry	Solvent	Temp. (°C)	Conversion (%)	*ee*[a] (%)
1	DCM	RT	NR	-
2	DCM	40	NR	-
3	TCE	60	55	0

Reaction conditions: Substrates (1 mmol), TBHP (1.5 mmol, 5.5 M in decane), Time (12 h), NR (no reaction).[a] *ee* measured by chiral GC: chiral column CHIRASIL-DEX CB with 110°C iso for 5 min then 5°C/min to 170°C, then 170°C for 20min, 250°C detector and injector.

When reaction was carried out using dichloromethane (DCM) as solvent, there was no reaction at RT or even at 40 °C. Whereas using tetrachloroethane (TCE) as solvent 55% conversion was obtained in 12 h. However no enantiomeric excess was observed. Hence we further investigated the ligand effect on the asymmetric epoxidation of styrene derivatives and trans-stillbene using catalyst **2a** and results are given in Table 3.6.

Table 3.6. Epoxidation of olefins by chiral dioxomolybdenum(VI) catalyst **2a**

Entry	Substrate	Conversion (%)	Selectivity for epoxide (%)	*ee* [a] (%)
1		77	100	0[$]
2		20[c]	100	n.d.[b]

3		19[c]	100	n.d.[b]
4[#]		60	99	0

***Reaction Conditions**:* Substrate (1.0 mmol), TBHP (1.5 mmol, 5.5 M in decane), Catalyst **2a** (5 mol%), Solvent (TCE, 1 mL), Temp. (60 °C), Time (12 h). [#] Substrate (1.0 mmol), H_2O_2 (1.0 mmol), Catalyst (1 mol%), Temp. (30 °C), Time (15 h). [b] n.d.: Not determined, [a] *ee* measured by chiral GC: [$] Chiral column G-TA with 80 °C iso, 1mLmin^{-1}, 170 °C detector and injector., 28.8 min and 34.1 min. [c] Yields measured by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard.

Catalyst **2a** showed good to excellent activity for epoxidations of olefins. The reaction of *trans-β*-methyl styrene gave very high conversion of 77% with 100% selectivity for epoxide (Table 3.6, entry 1). Whereas, exactly reverse trend was observed in case of *α*-methyl-styrene (Table 3.6, entry 2) and bulky substrate like *trans*-stilbene (Table 3.6, entry 3), where catalyst showed very poor conversions (< 20%) but 100% selectivity for epoxides**.** The reaction was also carried out using 3-methyl-2-buten-1-ol as substrate, and high conversion and selectivity for epoxide was observed but in no case asymmetric induction could be observed.

Rao *et al*.[30] have reported molybdenum complexes coordinated to chiral imino N,O,O'-tridentate ligands containing a carbohydrate backbone for asymmetric epoxidation of olefins. However maximum 30% *ee* was obtained for *cis-β*-methylstyrene using *tert*-butylhydroperoxide as an oxidant. Kuhn *et al*.[43] have reported Mo(II) complexes of cyclopentadienyl-based chiral ligands for alkene epoxidations. However, low selectivity was observed in all the cases. The highest enantiomeric excess of 25% was obtained when chiral ansa-bridged cyclopentadienyl molybdenum(II) tricarbonyl chloride complex was evaluated for the epoxidation of *trans-β*-methylstyrene. Yoon *et al*.[44] have reported 81% *ee* for (*E*)-Ph–CH=CH–Me; however, the asymmetric induction remained low (less than 40%) for *cis*-styrene.

Several *cis*-dioxo molybdenum(VI) complexes bearing sugar derived chiral Schiff-base ligands have been reported by Zhao *et al*.[21] for asymmetric epoxidation of olefins and showed a moderate enantiomeric induction of about 30% *ee* for *cis-β*-

methyl styrene. Zhang *et al.*[45] also screened D_2-symmetric chiral trans-dioxoruthenium(VI) porphyrin based catalysts for enantioselective epoxidation of *trans-β*-methylstyrene showing 70% *ee*. Collman *et al.*[46] have reported threitol-strapped manganese porphyrins with bulky co-catalysts such as 1,5-dicyclohexylimidazole, for epoxidation of *cis-β*-methylstyrene with 77% *ee*. Pezet *et al.*[47] have reported the catalytic application of chiral ruthenium sulfoxide for the asymmetric epoxidation of olefins and showed 94% *ee* for *trans-β*-methyl styrene. Park *et al.*[48] have reported heterogenised chiral Mn(III) salen catalysts for epoxidation of styrene and *cis*-stilbene. This experiment showed enhanced enantioselectivity (43-51% *ee*) at low-temperature, slightly higher than that of the homogeneous counterpart (35-46% *ee*). Xiang *et al.*[49] have reported a new heterogenised chiral Mn-salen complex for the epoxidation of *R*-methylstyrene with NaClO as an oxidant in CH_2Cl_2. Gbery *et al*[50] developed a novel method to heterogenize homogeneous manganese salen complex within the supercages of zeolite MCM-22 and used as catalyst for the enantioselective epoxidation of *R*-methylstyrene with NaClO. Lattanzi *et al.*[51] used vanadium acetylacetonate and *N*-hydroxy-*N*-phenylbenzamide as ligand for epoxidation of 3-methyl-2-buten-1-ol and showed 98% conversion with 44% *ee*.

To study the scope of catalyst in asymmetric oxidations, catalyst has also been evaluated for asymmetric oxidation of sulfides and results are shown in Table 3.7.

Table 3.7. Oxidation of thioanisole using catalyst **2a**

Entry	Catalyst (mol%)	Oxidant (Equiv.)	Time (h)	Yield (%)	Selectivity for sulfoxides (%)	*ee* [a] (%)
1	**2a** (5)	H_2O_2 (1.1)	2	84	72	0
2	**2a** (1)	TBHP (2)	22	17	99	0
3[#]	**2a** (1)	H_2O_2 (1.1)	2	25	98	0

***Reaction conditions**:* Substrate (1.0 mmol), Solvent (DCM, 1 mL), Temp. (0 °C).
[#] Reaction carried at RT, [a] *ee* measured by chiral HPLC, DAICEL IC, hexane/iso-propanol (8/2), 1 mL min^{-1}.

Excellent conversion and selectivity was observed for thioanisole (Table 3.7, entry 1) using **2a** as catalyst. However no enantiomeric induction was observed showing the less ability of dioxomolybdenum complexes in asymmetry. In 1995, Bolm and Bienewald[38] reported the efficient sulfoxidation of different sulfides using *in situ* prepared chiral vanadium complex from vanadyl acetylacetonate and chiral schiff base ligand with 30% hydrogen peroxide as oxidant showing chiral sulfoxides with 85% *ee*. Valinol derivative showed 90% yield and 75% *ee* in case of thioanisole oxidation.[52] Jacobsen and co-workers[53] showed high yield and moderate *ee* with manganese salen type ligand using PhIO or H_2O_2 as an oxidant. Zhu *et al*.[54] reported chiral salen copper complex showed 17% *ee* of sulfoxide. Sakuraba and Maekawa[55] reported Cu(II) - complexes containing β-cyclodextrin based ligand showed *ee* in the range of 26-52% in oxidation of thioanisole using aq. hydrogen peroxide. Recently, Yamamoto and co-workers[56] showed very high conversion and enantioselectivity for olefins epoxidation and sulfides oxidation using *in situ* prepared dioxomolybdenum complex using $MoO_2(acac)_2$ and bis-hydroxamic acid and its derivatives as a chiral ligands.

There was no chiral induction when ligand **1a** was used with MoO_2 in preformed catalyst **2a**. However with same ligand $VO(acac)_2$ showed 53% *ee* in case of phenyl methyl sulfoxide.[57] No chiral induction in catalyst **2a** may be due to presence of two oxo group on molybdenum which may transfer either of the oxygen to the substrate very fast which may lead to formation of both the isomers giving no *ee*. In literature, studies have been carried out on behavior of molybdenum in asymmetric catalysis. Carreiro *et al*.[58] studied the asymmetric epoxidation of olefins by Mo-peroxo species and found no *ee*. Therefore, Carreiro and co-workers have given some probable reasons for low or no chiral induction such as

- Presence of other chiral or achiral Mo(VI) peroxy or peroxo species in solution competing with the principal oxo-peroxy complex
- The labile nature of the peroxy appendage, particularly at the high temperature applied for reaction and generation of a number of competing diastereomeric transition states under reaction conditions
- The fast on/off exchange of the ligands or part of the ligands from the coordination sphere of the Mo(VI) peroxy complex.

Thiel and co-workers[59] showed using NMR experiments (temperature-dependent two dimensional NOESY experiments) and DFT calculations that 89-110 KJ/mol activation energy was necessary for ligand to dissociate which is easily provided by reaction temperature under (60-80 °C) which typically molybdenum catalyzed oxidations were carried out. Hence asymmetric induction was found to be low in case of molybdenum catalyzed reactions. Another important reason already mentioned by Stirling and co-workers[19] is that oxygen atom provided by oxo group to olefins is symmetric generating both enantiomers of oxiranes ring leading to very low or no chiral induction.

3.4. Conclusions

Prepared chiral dioxomolybdenum complex **2a** by simple condensation method was successfully used as catalyst for asymmetric epoxidation reactions and found to be highly efficient in case of olefins, allylic alcohols with excellent conversions and selectivity. The catalyst was also evaluated for sulfoxidation of phenyl methyl sulfide showing excellent activity and selectivity for sulfoxides. High conversion and selectivity up to 99% was obtained in all the cases. However, no enantioselectivity was observed in all the reactions showing the geometry of chiral ligand is extremely important for asymmetric induction.

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Chapter 4

Cyclopentadienyl Molybdenum Tricarbonyl Benzyl Complex as Catalyst Precursor for Dioxomolybdenum Complex for Oxidation Reactions

Abstract

*The synthesis and catalytic properties of molybdenum benzyl complex $CpMo(CO)_3CH_2Ph$ (**1**) was studied. The prepared complex (**1**) was characterized by FT-IR and NMR spectroscopies. It forms dioxo and oxo-peroxo species after treatment with TBHP and H_2O_2 respectively. These in situ formed species were found to be active for oxidation of various sulfides with excellent conversion and selectivity for sulfoxide. Surprisingly, no appreciable conversion was observed with refractory sulfides due to competitive decomposition reaction of hydrogen peroxide. Interestingly, even though complex (**1**) was homogeneous; it could be recycled very efficiently for three cycles in case of phenyl methyl sulfides by extracting the catalytically active molybdenum oxo peroxo species in aqueous phase. Complex **1** was also evaluated for oxidation of ethyl lactate to pyruvate with TBHP as an oxidant with excellent conversion (>90%) and selectivity (99%) for ethyl pyruvate. No ethyl lactate conversion was observed in case of hydrogen peroxide as an oxidant. Complex **1** was found to be very active for oxidation and hence led to decomposition of H_2O_2. Due to competitive oxidation and H_2O_2 decomposition excess H_2O_2 was used to achieve high conversion.*

4.1. Introduction

4.1.1. Metal carbonyl complex

Carbonyl is one of the most widely used ligand in organometallic chemistry. After the discovery of $Ni(CO)_4$ by Mond *et al.*[1], the transition metal carbonyls have been used frequently as starting material in the synthesis of other metal complexes. Metal carbonyl derivatives are important intermediates in homogeneous catalysis, e.g. in hydroformylation process.[2] Transition metal carbonyls are used as catalysts in various chemical transformations including industrially important applications such as $HCo(CO)_4$ catalyzed olefin isomerization,[3] hydroformylation of olefin,[4] and the Reppe synthesis of acrylic acids or esters from acetylene.

The thermochemistry of the carbonyl complexes and especially metal-carbonyl bond energies are of great importance in catalyst design. Effect of other ligands on the M-CO bond also plays important role in catalytic activity. The π-donor complexes are characterized by L-M donor as well as L-M acceptor interaction involving ligand orbitals that exhibit π-symmetry with respect to ligand. Probably the most important π-donor ligand is the Cp ligand.

In 1901, Thiele *et al.*[5] reported the first Cp metal compound. After the discovery of ferrocene $[(Cp)_2Fe]$,[6] Cp ligand came in to the picture. Chemistry of Cp complexes was studied widely and the known Cp containing compounds showed high structural diversity. As a π-donor ligand, the hapticity of Cp is usually 5, but it can be η^3 or even η^1 by forming an M-C σ-bond. Cp ligand remains inert to most nucleophile and electrophile and stabilizes organometallic complexes. Cp containing complexes are reported with almost all transition metals for various applications. Metallocenes and their derivatives are widely used as catalysts in polymerization reactions[7] and as precursors in chemical vapor deposition (CVD).[8] Metallocenes are also known to be important nonlinear optical materials and some of the bent metallocenes derivatives have antitumor activity.[9]

4.1.2. Cyclopentadienyl Molybdenum complexes

Dioxomolybdenum complex containing Cp ligand ($CpMoO_2Cl$) was first developed by cousin and green in 1963 by air oxidation of $CpMo(CO)_2(\pi\text{-}C_3H_5)$ in the presence of HCl, though obtained yield was very low. Different methods of preparation of $CpMoO_2Cl$ and $CpMoO_2Br$ were studied by Green and coworkers, very low yield were observed in all cases due to formation of several competing by-

products such as mono-oxo and dimeric complexes.[10] After this report Kuhn and co-workers reported the straight forward synthesis of dioxomolybdenum complex [(η5-C_5R_5)MoO_2Cl] (R=H, Me, CH_2Ph) from [(η^5-C_5R_5)$Mo(CO)_3Cl$] as carbonyl precursor with the treatment of 10 equivalent of 5–6 M TBHP solution in *n*-decane.[11] Later on, molybdenum carbonyl complexes became most widely used precursors to synthesize dioxomolybdenum(VI) complexes or catalysts. Consequently various types of molybdenum carbonyl complexes have been studied, including cyclopentadienyl complexes, η^3-allyl complexes [Mo(η^3-allyl)$Cl(CO)_2$(L)], heptacoordinate tricarbonyl complexes [$Mo(CO)_3I_2$(L)] and tetracarbonyl complexes *cis*- [$Mo(CO)_4$(L)] (where L is a bidentate chelating dinitrogen ligand). Considering the importance of molybdenum(VI) compound in oxidation reactions, synthesis of Cp*MoO_2Cl has been reported by Bergman and Trost[12] by modifying previous reported procedures and used as catalyst precursor (2-5 mol%) in epoxidation of olefins such as cyclooctene, geraniol, *cis*/*trans*-diphenylpropene using alkyl hydroperoxides such as *tert*-butyl hydroperoxide (TBHP), cumene hydroperoxide (CHP), *n*-hexyl hydroperoxide etc as an oxidizing agents. In most cases epoxides were obtained as only product. No epoxidation was observed in case of olefins containing electron withdrawing substituents and *α, β*-unsaturated ketones, whereas olefin containing electron-donating substituents showed better results. Recently, Kuhn *et al.*[13] introduced the use of ansa bridge η^5-cyclopentadienyl ring as ligand (Figure 4.1) for catalytic oxidation reactions. Aim to introduce such type ligand was the prevention of free rotation by steric hindrance and stereoelectronic properties at the metal center. However the catalytic activity was not significantly influenced by an ansa bridge, in fact the reaction was somewhat slower due to increased steric hindrance. The enantiomeric excess was, however, merely at ca. 20% in the case of *trans-β*-methylstyrene.[14]

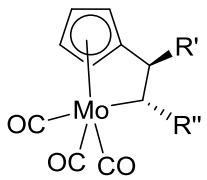


Figure 4.1. *Ansa* bridge molybdenum carbonyl complex

Later on Kuhn and Romao[15] reported menthyl-substituted cyclopentadienyl ring for synthesis of molybdenum complexes and their catalytic activity in epoxidation reaction. Dinuclear cyclopentadienyl molybdenum oxo complexes of the type $[Cp'MoO_2]_2O$ (Cp'=Cp, Cp*, C_5Bz_5, $C_5H^iPr_4$, $C_5H_2{}^tBu_3$) were also investigated as efficient catalysts for cyclooctene epoxidation. As compared to mononuclear species, all investigated bimetallic complexes achieved similar or better conversions with the exception of the C_5Bz_5 derivative.[16] Recently, Poli *et al.*[17] have shown tungsten(VI) and molybdenum(VI) based dinuclear complexes $[Cp^*_2M_2O_5]$ (M=Mo, W) for catalytic epoxidation of *cis*-cyclooctene using 30% aqueous H_2O_2 as an oxidant and showed excellent selectivity for epoxide. These results are different than complexes of type $[Cp'MoO_2X]$ and $[Cp'Mo(CO)_3X]$ (X=Cl, CH_3), in which mononuclear molybdenum complexes are more active than tungsten for epoxidation of olefins using TBHP as an oxidant.[18] Literature reports gave us an idea about *in situ* formation of active dioxo species from carbonyl in presence of hydroperoxides which encourage us to study molybdenum carbonyl complexes as catalyst precursors for oxidation reactions.

The advantages of the molybdenum carbonyls as precursors are:

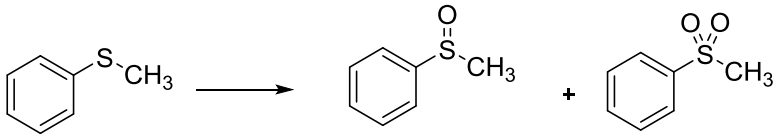
- Straightforward synthesis
- Stability: All compounds are stable under air for a short period of time and indefinitely under inert gas atmosphere.
- Ligand variability: The cyclopentadienyl and the alkyl - ligands can be easily modified, altering the electronic properties of the metal center and thus its catalytic activity. Designing task-specific ligands for immobilization of these compounds is also an important issue.

Recently in our group we have developed a green and easier route to synthesize dioxo or oxo-peroxo species of molybdenum acetylide complex from cyclopentadienyl molybdenum tricarbonyl acetylide complex as carbonyl precursor treated with hydrogen peroxide as green oxidant without addition of HCl and studied the catalytic activity of this complex for oxidation of various organics. The catalyst showed excellent activity and selectivity in all cases and importantly even though it is homogeneous it could recycled efficiently and easily.

In continuation of our work in dioxomolybdenum catalyzed oxidation reactions, herein we have synthesized cyclopentadienyl molybdenum tricarbonyl benzyl complex as catalyst precursor for dioxomolybdenum complex to study the oxidation of various substrates.

4.1.3. Oxidation of sulfides

Catalytic oxidation of sulfides is an important reaction in the synthetic chemistry and has varied applications. The chemoselective oxidation of sulfides to sulfoxides is of current research interest for fundamental research and for variety of applications. These reactions are significant from green chemistry and industrial perspective because organosulfur materials are major pollutants. Organic sulfides have electron-rich sulfur atoms which undergo electrophilic oxidation giving sulfoxide; upon further oxidation sulfones are also formed. The undesired sulfones are a common by-product in sulfide oxidation reactions with H_2O_2 and its formation has to be suppressed (Scheme 4.1).

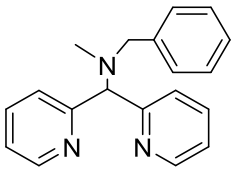


Scheme 4.1. Oxidation of sulfide to sulfoxide and sulfone

Sulfoxides are valuable in synthesis of bioactive molecules, in C-C bond formation, molecular rearrangement and biologically active sulfoxides play an important role as therapeutic agents such as anti-ulcer, antibacterial etc. A wide range of oxidizing systems have been studied for the oxidation of sulfides to the sulfoxides such as H_2O_2/SSA (Silica sulfuric acid), UHP/Mn(III), H_2O_2/$VO(acac)_2$, *N*-bromosuccinimide (NBS) etc. Some of these methods still have disadvantages like overoxidation to sulfones, low selectivity, low yield of desired product, tedious work-up, toxicity and expensive reagent or catalyst. Research efforts have been devoted for the development of catalytic methods for the preparation of selective sulfoxides due to its significance in bioactive products. A catalytic oxidation of sulfides to sulfoxides using hydrogen peroxide as an oxidant under mild reaction conditions is a green attractive system for large-scale processes from economic and environmental points

of view. Practically all catalytic reactions reported for this conversions use hydrogen peroxide or molecular oxygen.

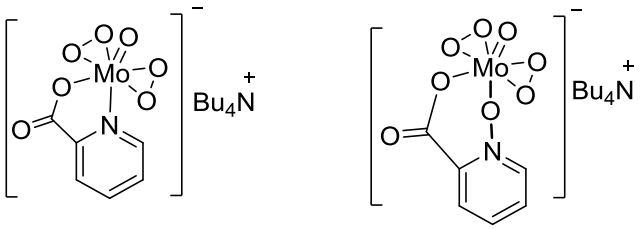
Oae and coworkers reported quantitative yield of sulfoxides within 5-15 min in oxidation of various sulfides by $TiCl_3$ using hydrogen peroxide as an oxidant.[19] Recently, Noyori and coworkers[20] have reported tungsten-based catalytic system for oxidation of sulfide using hydrogen peroxide as an oxidant showing moderate to good selectivity. Feringa *et al.*[21] have reported manganese catalysts with various nitrogen containing ligands for oxidation of sulfides using 30% aq. H_2O_2. The $Mn(OAc)_3.2H_2O$ with bipyridine ligand (**a**) showed 55% yield of phenyl methyl sulfoxide with no sulfone formation.



a

Figure 4.2. *N*-benzyl-*N*-methyl-1,1-di(pyridine-2-yl)methanamine

Oxidations of sulfides to sulfoxides using vanadium and molybdenum based catalyst {$[MoO_2(acac)_2]$, molybdenum hexacarbonyl $[Mo(CO)_6]$ and molybdenum peroxide $[MoO(O_2)_2]$} with H_2O_2 are known for this transformation. Di Furia and Modena have reported $MoO(O_2)_2L$ (L =HMPT, L = HBPT) catalysts for oxidation of p-$ClC_6H_4SCH_3$ to the corresponding sulfoxide using aqueous H_2O_2 in 1,2-dichloroethane at 40 °C. In 1988, Di Furia and coworkers[22] explored the complexes of **b** and **c** for oxidation of sulfides to sulfoxides in quantitative yield.



b **C**

Figure 4.3. Catalysts reported by Di Furia

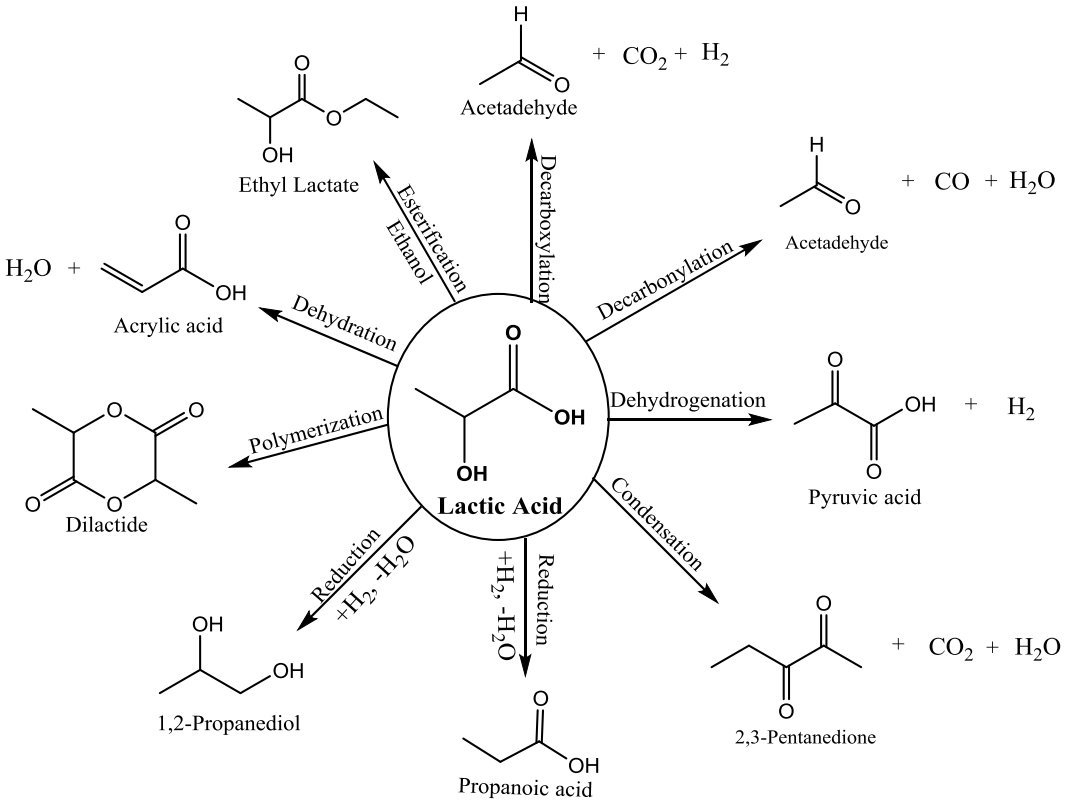
In 2001, Cass and co-worker reported Mo(VI) complexes grafted on silica gel for oxidation of sulfides to sulfoxides showed more than 80% yield of sulfoxide at

−10 °C. The performance of molybdenum peroxo complexes in oxidation of sulfides with H_2O_2 as an oxidant was studied by Bhattacharyya.[23]

In 2012, Bagherzadeh *et al*.[24] reported complex of molybdenum for the oxidation of various types of substrates like aryl alkyl, diaryl, dibenzyl, benzyl phenyl and dialkyl sulfides using urea-H_2O_2 and aq. TBHP as an oxidant. Sulfoxides were obtained in the range of 66–99% yield in 30 min without formation of sulfone even though TBHP was used in excess. Recently in our group we have studied the oxidation of refractory and non-refractory sulfides using cyclopentadienyl molybdenum tricarbonyl acetylide complex as catalyst precursor with H_2O_2 and selectivity was observed either to sulfone or sulfoxide depending on the experimental conditions. To continue our efforts in oxidation of sulfides by molybdenum carbonyl complex as catalyst precursor, in present study we have used cyclopentadienyl molybdenum tricarbonyl benzyl complex as catalyst precursor for oxidation of sulfides.

4.1.4. Ethyl lactate oxidation

In 1780, Swedish chemist Scheele first discovered lactic acid in acid milk.[25] Lactic acid is an α-hydroxyl carboxylic acid with a chiral centre at its second carbon. It is reactive due to presence of two functional groups in a three carbon molecule. Lactic acid acts as a platform chemical to synthesize variety of intermediates in industry,[26] commercially it is produced from sugars on a medium sized scale. Its production is nearly 0.26 million tons per year.[27] A recent survey expects a market of 0.329 million tons in 2015[28] and estimated lactic acid demand in 2020 to be 0.6 million tons per year. Hence production of lactic acid will increase continuously and its price is expected to go down. Therefore valorization of lactic acid to value added chemical is important and bearing a hydroxyl group and an acid function, it undergoes numerous chemical conversions to useful products such as shown below (Scheme 4.2).



Scheme 4.2. Possible pathways of lactic acid valorization

Considering the importance of pyruvic acid as an intermediate of perfume, food, additives, and electronic materials and the significant difference in their prices, the production of pyruvic acid from direct oxidation of the lactic acid under the mild reaction conditions is a valuable process. Direct oxidation of lactic acid to pyruvic acid is difficult due to the competing decarboxylation reaction which gives the side products such as acetaldehyde and CO_2 instead of pyruvic acid. Hence, the protection of carboxylic group of lactic acid is necessary to get selective pyruvate easily. Pyruvate is another important platform chemical used as raw material in the synthesis of pharmaceutical precursors. Commercially it is produced by dehydration and decarbonylation of tartaric acid.[29] This classical process is not cost effective due to some drawbacks like formation of hydrogen peroxide etc. Thus, the catalytic transformations of cheaper substrates, hence the catalytic transformations of lactates have been considered as the more attractive method.

Most of the catalysts convert a lactate to acetaldehyde and CO_2 rather than pyruvate. Biocatalyst could catalyze lactate to pyruvate under relatively mild

conditions. Different enzymes have been used in biotechnological production of pyruvate from lactate.

Several catalysts have been studied for the oxidation of lactic esters in the vapor and liquid phase system. Hayashi and co-workers[30] showed binary oxides (TeO_2-MoO_3, $Co(II)O.TeO_2.MoO_3$) as efficient catalysts for conversion of ethyl lactate with 93% yield of ethyl pyruvate at 300 °C. SiO_2 supported Mo and V phosphates were also found to be very active for this reaction. Gas phase process was more difficult with LA than its esters, according to work done by Ai and co-workers.[31] Fe phosphates at 230 °C showed best results with selectivity of 62% to pyruvic aldehyde (PYR) at 60% conversion. The low selectivity was observed due to formation of acetaldehyde. Later, modification of above catalyst with Pd and Mo especially small quantities of Mo(VI) proved to be valuable as shown by Ai.[32] Hayashi *et al*.[33,34,35] proposed a liquid phase process for ethyl lactate using low O_2 pressures over suspended Ti, Zr, Sn and Mo oxides in low loadings in dimethyl succinate at 130 °C. In case of SnO_2-MoO_3, 50% yield of ethyl pyruvate was obtained in 5 h with 80% selectivity. Pd-Pt/C catalysts in aqueous phase showed conversion of sodium lactate to sodium pyruvate in air at 65 °C giving 81% yield with 90% conversion after 70 min. They also showed process for free LA using Pb-modified Pd/C and pH 8, with 60% yield of PYR at 90 °C. Recently Sugiyama and co-workers[36] reported the conversion of sodium lactate with (Te-) Pd/C. The main advantage of using salt was the absence of pH adjustment, and the maximum yield was found to be 68% at 1 MPa of O_2. Recently, Yasukawa *et al*.[37] have reported homogeneous vanadium oxytrichloride ($VOCl_3$) for conversion of lactate to pyruvate using alkyl hydroperoxides as oxidants.

Novel systems which produce pyruvate under mild reaction conditions are of current research interest.

4.2. Experimental

4.2.1. Materials

All reagents were of commercial grade (Aldrich) and were used as received unless stated otherwise. Hydrogen peroxide was used 50% w/w in water. THF was dried according to standard method and freshly distilled prior to use.[38] Cyclopentadiene was freshly prepared by cracking dicyclopentadiene (Aldrich make) at 60 °C. $Mo(CO)_6$, benzyl chloride was purchased from Aldrich and used as received.

Complex $CpMo(CO)_3(-CH_2Ph)$ (**1**) was prepared according to literature report.[39] A freshly distilled dry THF (10 mL), freshly cracked cyclopentadiene (1 g, 0.015 mol) and sodium (0.45 g, 0.019 mol) was added to an oven dried 250 mL two necked round bottom flask. The solution was stirred at room temperature till complete dissolution of sodium. To this solution molybdenum hexacarbonyl (3 g, 0.011 mol) and additional dry THF (~ 20 mL) was added. Reaction mixture was refluxed at 80 ºC for 4 h and then cooled to room temperature. To the reaction mixture benzyl chloride (1.7 g, 0.013 mol) in THF (2 mL) was added and stirred for 16 h at room temperature. After the removal of the THF, the residue was extracted with three 100 mL portions of diethyl ether. Removal of diethyl ether in vacuo gave yellow crystals of cyclopentadienyl tricarbonyl molybdenum benzyl complex $[CpMo(CO)_3CH_2Ph]$.
Yield: 2.48 g, 65 %.

4.2.2. Complex characterisation techniques: Instrumentation

^1H NMR and ^{13}C NMR were recorded on Bruker AV-200 (50 MHz) or Bruker AV-400 (100 MHz) or Bruker DRX-500 (125 MHz). Tetramethylsilane was used as the internal standard. NMR values are expressed in δ (ppm). FT-IR spectra were recorded on Nicolet Nexus IR 6700 with KBr pellet in the range of 400-4000 cm^{-1}, with resolution 4 and averaged over 100 scans.

4.2.3. Catalytic activity

The oxidation of sulfides was performed in a 50 mL round-bottom flask equipped with a magnetic stirrer. A solution of sulfide (0.2 mol) in CH_3CN (5 mL), 50% (w/w) H_2O_2 and Mo-benzyl complex (**1**) (0.4 mmol) was magnetically stirred at desired temperature. Reaction was monitored by withdrawing the sample at regular intervals of time and analyzed using gas chromatography (Model Agilent 6890 Gas Chromatograph equipped with a HP-5 dimethyl polysiloxane, 60 m length, 0.25 mm internal diameter, 0.25 um film thickness).

4.2.4. Catalyst recycles studies

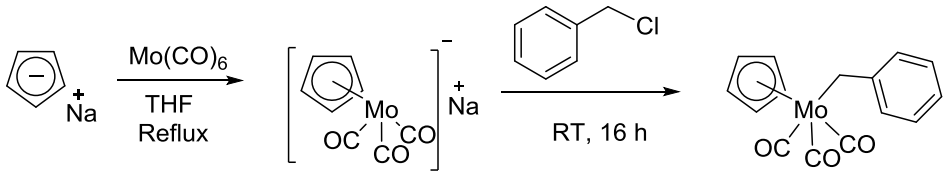
In a typical catalyst recycle experiment, a two necked 50 mL round-bottom flask was charged with thioanisole (1 mmol), 50% hydrogen peroxide (2 mmol), 1 g solvent and catalyst precursor **1** (1 mol%). The reaction mixture was stirred at room temperature till the completion of the reaction was monitored by GC. After the

completion of reaction, solvent was removed in vacuo. Reaction mixture was extracted in ethyl acetate and further organic phase was treated with sodium sulphate and the products were recovered by evaporation of the solvent. Catalytically active species $CpMo(O_2)O(–CH_2Ph)$ which was soluble in aqueous phase was concentrated and used further for recycle studies.

CAUTION: Please note that "The molybdenum oxoperoxo species were found to be pyrophoric if completely dried".

4.3. Results and Discussion

4.3.1. Synthesis of cyclopentadienyl molybdenum tricarbonyl benzyl complex (1)



1

Scheme 4.3. Synthesis of complex **1**

4.3.2. FTIR spectroscopy

FTIR Spectrum of complex **1** is given in Figure 4.4 which showed strong CO vibrations at 1912, 1930 and 2005 cm^{-1} and C-C stretching vibration of Cp ring at 2958 cm^{-1}.

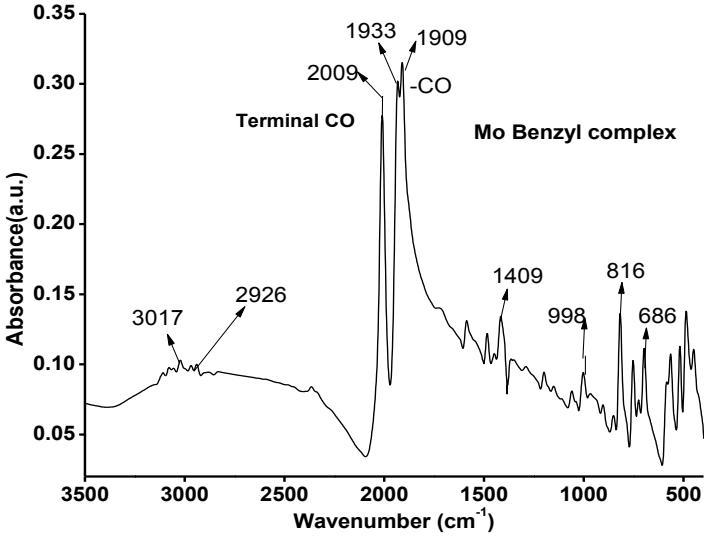


Figure 4.4. FT-IR spectrum of complex **1**

4.3.3. NMR Spectroscopy

^{1}H NMR spectrum of the complex **1** (Figure 4.5) showed characteristic signal of $\eta^5(C_5H_5)$ at δ 4.86, phenyl ring at δ 6.9-7.4 and CH_2 group at δ 2.87 of approximate relative intensities 5:5:2 corresponding to the five π-cyclopentadienyl protons, five phenyl protons and the two methylene protons, respectively.

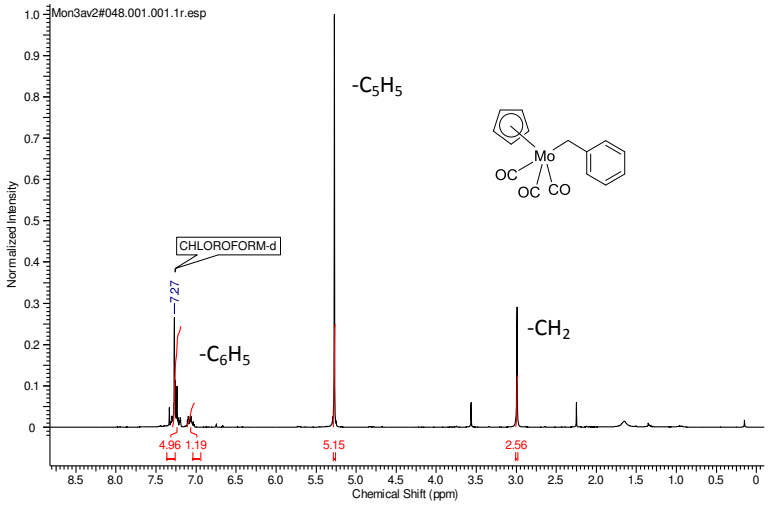


Figure 4.5. ^{1}H NMR spectrum of complex **1**

^{13}C NMR (Figure 4.6) spectrum showed the resonance at δ 93.91 assigned to cyclopentadienyl ring. Aromatic carbons were observed in the range of δ 120-130. The peak at δ 4.78 assigned to -CH_2 group and peak at δ 228 and δ 239 were due to two different CO groups present.

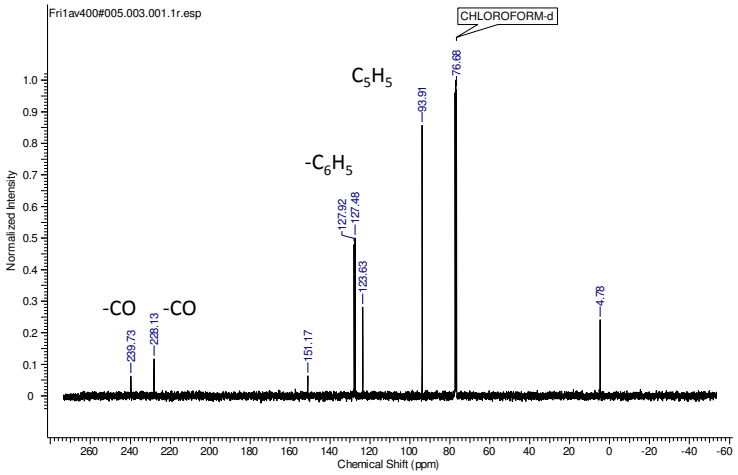


Figure 4.6. ^{13}C NMR spectrum of complex **1**

4.3.4. Catalytic activity

It is known that organic sulfides are oxidized by hydrogen peroxide by heterolytic process involving the nucleophilic attack of the sulfur atom on the oxygen. Generally the reactivity of thioether is correlated to the nucleophilicity and electron density of the sulfur atom. Hence, dipropyl sulfide showed more reactivity than dialkyl or diaryl sulfide. Consequently, the catalytic activity of catalyst precursor **1** was evaluated for sulfide oxidation particularly thioanisole was chosen as the model substrate and hydrogen peroxide as an oxidant (Table 4.1). 99% conversion of the thioanisole was obtained in 1 h at room temperature with very high selectivity for sulfoxide (95%) indicating two step reactions; starting with the oxidation of sulfide to sulfoxide and then further oxidation of the sulfoxide to sulfone. During the reaction it was observed that initially selectivity for sulfoxide was 100%. Later on, sulfoxide selectivity decreased due to further oxidation of sulfoxide to sulfone clearly indicating a two-step process. The progress of reaction is shown in Figure 4.7.

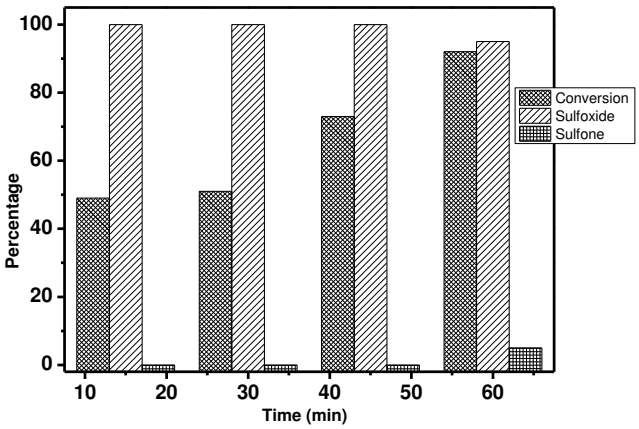


Figure 4.7. Kinetic study of sulfide oxidation to sulfoxide and sulfone

When reaction of thioanisole was monitored with time it was observed that initially the rate of reaction is very high giving high conversion of thioanisole to sulfoxide. However it was observed that after some time (51% Conversion) reaction stopped giving a blue complex formation. However, when the reaction was continued with addition of excess H_2O_2 the original color of the complex was regained. This observation indicated that parallel decomposition of H_2O_2 with simultaneous oxidation of sulfides. To further study the effect of catalyst concentration on the rate of reaction, experiments were carried out using different catalyst loadings and results are shown in Table 4.1.

Table 4.1. Oxidation of sulfides

Entry	Catalyst loading, mol%	Time (min)	Conversion %	Selectivity %	
				Sulfoxide	Sulfone
1	Blank	60	50	60	40
2[#]	2.5	15	90	95	5
3	1	60	99	92	8
4	0.5	80	100	90	10

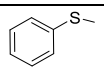
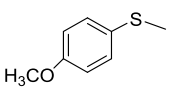
***Reaction conditions**:* Substrate (1mmol), H_2O_2 (5 mmol), Solvent (CH_3CN, 1g), Temp. (RT). [#] H_2O_2 (7 mmol)

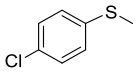
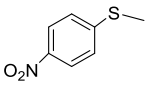
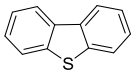
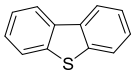
Oxidation of thioanisole without catalyst in acetonitrile even using 5 equiv. of H_2O_2 gave 50% conversion with 60% selectivity for sulfoxide in 1 h. As the catalyst precursor loading was varied gradually from 0.5 to 2.5 mol%, time required to reach maximum conversion was lowered (Table 4.1) but with marginal changes in selectivity were observed. However, the rate of decomposition of hydrogen peroxide increased with increased loading of catalyst precursor with respect to substrate and further high amount of hydrogen peroxide was required for complete conversion. However, 1 mol% catalyst was further used to study the scope of substrates.

4.3.5. Substrate scope

Wider applicability of the catalyst precursor **1** was evaluated for oxidation of a range of sulfides containing various functionalities and results are shown in Table 4.2.

Table 4.2. Oxidation of sulfides using complex **1** as catalyst

Entry	Substrates	Time (h)	Conversion %	Selectivity %	
				Sulfoxide	Sulfone
1		1	99	92	8
2		1	92	80	20

3		1	90	85	15
4		1	90	80	20
5[#]		5	NR	-	-
6*		7	Traces of product		

***Reaction Conditions**:* Substrates (1 mmol), Oxidant (5 mmol), CH_3CN (1 mL), Catalyst **1** (1mol %), Temp. (RT), Time: 1h. [#] Reaction was carried out at 80 °C in CH3CN, * Reaction was carried out at 100 °C in toluene.

Sulfides with electron donating group like -OCH_3 (Table 4.2, entry 2) showed fast conversion from sulfide to sulfoxide but the selectivity for sulfoxide was lower compared to unsubstituted sulfide as reaction goes further to sulfone. No appreciable changes were observed in conversion and selectivity when -OCH_3 group was replaced by electronegative -Cl group (Table 4.2, entry) and electron withdrawing group such as -NO_2 (Table 4.2, entry 4). Surprisingly, no appreciable conversion (a trace of product) was observed in case of dibenzothiophene even though catalyst is very active for range of sulfides. As refractory sulfides are not active at low temperature, the reaction was carried out at higher temperature. However, a trace of product was observed. This can be explained by considering a competitive H_2O_2 decomposition reaction, which is accelerated at high temperature compared to room temperature. Hence, no hydrogen peroxide remained for oxidizing sulfides and formed molybdenum blue species of catalyst. The formed species is catalytically inactive and usually formed in absence of peroxide. Hence, to convert intermediate molybdenum blue to catalytically active oxo-peroxo species, intermittent addition of excess hydrogen peroxide was required during reaction.

Molybdenum blue formation was observed in all cases; nevertheless its formation was rapid at high catalyst loadings however led to high decomposition rate of hydrogen peroxide by the catalyst. Hence, the sulfide oxidation using high catalyst loading required more amount of hydrogen peroxide for complete conversion. In case

of oxidation reaction, oxidation goes on by reducing metal centre to produce molybdenum blue with its typical blue color. Upon addition of hydrogen peroxide, molybdenum blue gets reoxidized and the cycle starts again. Molybdenum blue is molybdenum oxide hydroxide clusters $\{Mo_w^{VI}Mo_x^{V}O_yH\}$ of variable composition and generally produced by reduction of MoO_4^{2-} under the acidic conditions. The color change of the catalyst from yellow to blue indicates the redox behavior of molybdenum centre. Molybdenum blue species are coming from redox process resulting in a mixture of Mo(VI) to Mo(V).[40] Torok *et al*.[41] have reported the formation of molybdenum blue after one electron reduction of Mo(VI) to Mo(V). The change in the valence state of the molybdenum led to the formation of dark blue colored solid. This formation of molybdenum blue in absence of hydrogen peroxide was well studied in the literature by Jensen and co-workers.[42] One important aspect of this study even though the catalyst was homogeneous, but could be recycled for more than three cycles and it was studied by extracting the catalyst in aqueous layer after completion of reaction. As reported earlier in the literature oxo peroxo species is soluble in water so it can be easily separated out from organics and can be used further by removing maximum water at vacuo. In recycle studies conversion and selectivity did not change significantly even after three cycles except the handling losses and results are shown in Table 4.3.

Table 4.3. Catalyst recycle study

Cycle	Conversion	Selectivity	
	(%)	Sulfoxide	Sulfone
1	99	95	5
2	95	94	6
3	92	95	5

***Reaction Conditions**:* Substrate (1.0 mmol), Oxidant (5 mmol), Solvent (CH3CN, 1 mL), Catalyst **1**(1 mol%), Temp. (RT), Time (1 h).

Catalyst recyclability studies and reoxidation of catalyst or resumes yellow species after addition of H_2O_2 indicated the stability of catalyst. To check further *in situ* formed species during reaction and integrity of the ligand in complex during

catalysis, the catalytically active species were characterized after addition of H_2O_2 by FT-IR and UV spectroscopy.

4.3.6. Characterization of *in situ* formed molybdenum species

a). FT-IR spectrum of oxo-peroxo molybdenum complex

The FT-IR spectrum of *in situ* formed oxo-peroxo molybdenum benzyl complex shown in Figure 4.8. The IR band at 948 cm^{-1} indicated the presence of a Mo=O terminal bond. The band at 853 cm^{-1} corresponds to the O–O stretching vibration of the peroxo species. The weak bands at 644 and 576 cm^{-1} are assigned to the Mo–O_2 (peroxo) asymmetric and symmetric stretching vibrations, respectively.

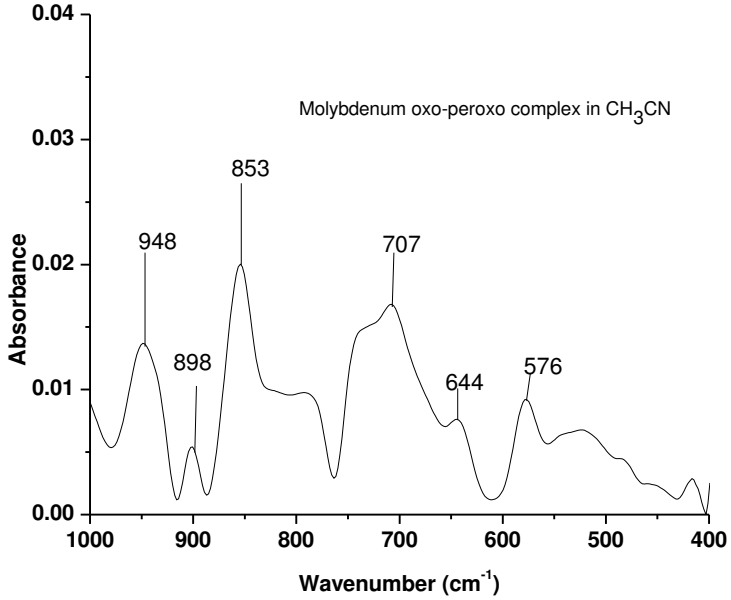


Figure 4.8. FT-IR spectrum of molybdenum oxo-peroxo species of complex **1**

The bands due to the carbonyl stretching vibrations (1933, 2009 cm^{-1}) disappeared after addition of H_2O_2. This clearly indicates the elimination of all the CO ligands and the formation of a higher oxidation state Mo(VI) complex with the retention of the benzyl moiety attached to the Mo center.

b). Electronic Spectra

Electronic spectrum of oxo-peroxo species is shown in Figure 4.9. The high intensity peaks observed in the region 295–360 nm of the dioxo and oxo peroxo molybdenum(VI) complexes seem to appear due to intra-ligand n-π*/π-π* transitions. Additionally, the shoulder at 325 nm indicated the presence of crystal field (d-d)

bands of Mo^{5+} centers as well as the intervallic bands resulting from the optical excitation Mo^{5+}….O….Mo^{6+} to Mo^{6+}….O…. Mo^{5+}.

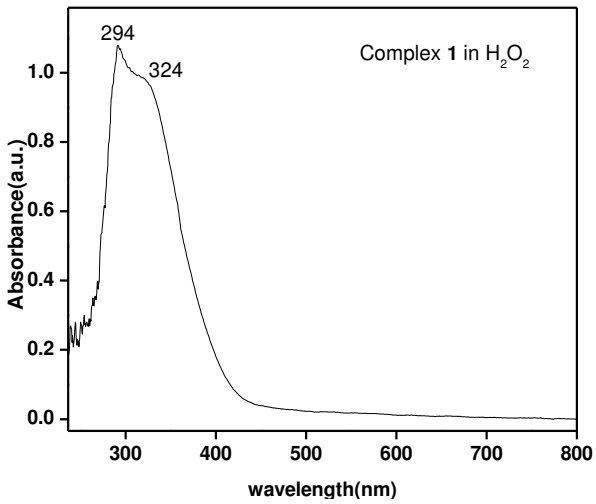


Figure 4.9. UV spectrum of oxo-peroxo species of molybdenum complex **1**

E. Dumitriu *et al.*[43] have reported layered double hydroxide (LDH) as catalyst for sulfoxidation of diaryl sulfide with excellent conversion and selectivity using H_2O_2 as an oxidant and observed the competitive H_2O_2 decomposition reaction in all the cases. Imada *et al.*[44] showed sulfide oxidation using bisflavin as catalyst with H_2O_2 showing > 90% yield of sulfoxides. Jayaseeli *et al.*[45] showed iron (III)-salen ion with H_2O_2 for oxidation of various sulfides and decreased reactivity was observed by changing substituent of aryl ring from H to NO_2. Chand *et al.*[46] showed application of MoO_2Cl_2 as a catalyst for sulfide oxidation with excellent sulfoxide yield (> 90%) in 5 min. However, no appreciable change was observed by changing substituent on aryl from H to NO_2. No decomposition of H_2O_2 was observed. Later on, Chand *et al.*[47] showed ammonium heptamolybdate as Mo(VI) source with H_2O_2 for sulfide oxidation. The reactions provided excellent yields within a short time interval, also sensitive functional groups such as allyl, vinyl, propargyl, alcohol, ketone, ester, pyridine and nitrile were found to be tolerated.

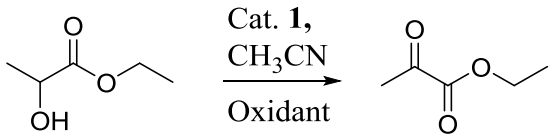
N. Moussa *et al.*[48] have reported vanadium catalyzed sulfoxidation of thioanisole with very high conversion (95%) and selectivity (96%) for sulfoxide at RT and showed that catalytic activity and selectivity of reaction was dependent on the nature of the support and vanadium peroxide species was formed by reaction of vanadium with the oxidant. The differences in activity and selectivity between

VO_x/SiO_2 and VO_x/Al_2O_3 were confirmed by the existence of different vanadium species. In case of silica supported catalyst, V_2O_5 species was present which was more selective than the polyvanadate groups present on alumina. This was related to the presence of unreactive polymerized surface vanadia species and in case of homogeneous *in situ* prepared catalyst by using $VO(acac)_2$ and TBHP/H_2O_2. In case of H_2O_2 peroxovanadium species formation was observed, but with TBHP peroxyvanadium species was found to be more selective in sulfide oxidation. M. Kirihara *et al.*[49] have reported application of tantalum(V) and niobium(V) catalysts for sulfide oxidation using hydrogen peroxide as an oxidant with > 90% yield of sulfoxide. In this case niobium(V) catalyst was found to be more active compared to tantalum because it showed more reactivity with less equivalents of H_2O_2 (3 or 2 equiv.) than tantalum which required 5 equiv. of oxidant with respect to substrate. This shows many metals along with catalyzing oxidation, also catalyzes decomposition of H_2O_2.

Very recently in our group we have developed a method for oxidation of various sulfides including -refractory sulfides with H_2O_2 as an oxidant and cyclopentadienyl molybdenum tricarbonyl acetylide complexes as catalyst precursor and showed that the activity and the selectivity can be tuned by varying the amount of oxidant.[50] Surprisingly no H_2O_2 decomposition was observed in any of cases mentioned above. By changing ligand from acetylide to benzyl it was observed that the stability of the catalyst becomes limited and also activity of catalyst changed due to competitive H_2O_2 decomposition.

4.3.7. Oxidation of ethyl lactate to pyruvate

Considering the activity of catalyst **1** for sulfide oxidation, to further explore its catalytic activity, ethyl lactate was chosen as a substrate. According to previous reports in the literature oxidation of ethyl lactate to ethyl pyruvate is one of the most important transformation due to its importance as a raw material in the manufacturing of cosmetic. Ethyl pyruvate is an important intermediate in organic synthesis which is used in pharmaceutical, agriculture, perfume, fine chemical industry, laser materials etc. They are also attractive raw materials for various bioactive substances such as antiviral drugs.[51]



Scheme 4.4. Ethyl lactate to ethyl pyruvate

Further to study the scope of substrates, catalyst **1** was evaluated for oxidation of ethyl lactate as an important substrate and results are shown in Table 4.4.

Table 4.4. Oxidation of ethyl lactate using complex **1** as catalyst

Entry	Oxidant	Conversion, (%)	Selectivity, (%)
			Ethyl pyruvate
1	TBHP	90	100
2	H_2O_2	NR	-

Reaction conditions: Substrate (1 mmol), Oxidant (2 mmol), Catalyst **1** (2 mol%), Temp. (80 °C), Time (7 h).

Excellent conversion of ethyl lactate (90%) with 100% selectivity for ethyl pyruvate was observed with TBHP as an oxidant (Table 4.4, entry 1). However, no ethyl lactate conversion was observed when hydrogen peroxide was used as an oxidant (Table 4.4, entry 2). Due to the importance of pyruvic acid and its derivatives, these reactions were studied by several groups, using both gas and liquid phases. In gas-phase reactions, various solid acid catalysts were used including MoO_3, TeO_2. These processes gave high yield of pyruvate, but required high temperature. In case of SnO_2-MoO_3, 50% yield of ethyl pyruvate was obtained in 5 h.[33] Pd-Pt/C catalysts were also studied for aqueous phase conversion of sodium lactate to sodium pyruvate in air at 65 °C showing 81% yield with 90% conversion in 1h.[34] Recently, Yasukawa *et al*.[37] have reported liquid phase system for conversion of ethyl lactate to pyruvate using vanadium based catalyst showing up to 39% yield of pyruvate with $VOCl_3$/TBHP system. They also studied the vanadium based other systems like $VOCl_3$/air, $VOCl_3/O_2$, $VO(acac)_2$/TBHP, $VO(acac)_2$/m-CPBA etc. with moderate yield.

Fernandez *et al*.[52] have shown TiO_2 catalyst for conversion of ethyl lactate to ethyl pyruvate with excellent conversion and selectivity. They also observed polymerization of pyruvate in absence of solvent which led to decrease in selectivity of pyruvate with increasing conversion of lactate. Hence, solvent is necessary for reaction to control polymerization. Hence the result obtained with molybdenum benzyl complex **1** was superior under very mild reaction conditions with very high conversion and selectivity for ethyl pyruvate.

4.4. Conclusions

Cyclopentadienyl molybdenum tricarbonyl benzyl complex was proved to be highly efficient catalyst for selective oxidation of various sulfides to sulfoxide using H_2O_2 as an efficient oxidant under mild reaction conditions. Sulfides with various functional groups could be oxidized with equal efficiency. The hard refractory sulfides like dibenzothiophene could not be oxidize efficiently due to competitive decomposition of hydrogen peroxide favored at high temperature required for oxidation. Even though complex **1** was homogeneous catalyst; but was recycled effectively for three recycles without appreciable loss in the conversion and selectivity. Complex **1** also showed excellent catalytic activity in oxidation of ethyl lactate to ethyl pyruvate selectively under mild reaction conditions.

4.5. References

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Chapter 5

Summary and Conclusions

Abstract

This chapter delivers the overall summary of the results and highlights of new findings. Chapter wise important results are briefed to give an overview of the complete thesis.

This chapter gives brief summary of the results discussed in the previous chapters.

Chapter 1: Introduction

Chapter 1 gives a general introduction on catalysis. This chapter also gives a brief discussion on homogeneous and heterogeneous catalysis, its advantages and disadvantages and its industrial processes. Oxidation concept and its importance were discussed in details so as to give brief summary of transition metal catalyzed epoxidation especially asymmetric epoxidation was discussed. Role of molybdenum in catalysis especially carbonyl and dioxomolybdenum complexes as oxidation catalyst has been discussed in brief. Choice of oxidant, its advantages and disadvantages and mechanistic investigations on formation of epoxide has been discussed thoroughly. Scope and objective of the thesis was given in details.

Chapter 2: Selective Oxidation of Allylic and Benzylic Alcohols by Molybdenum Salen Complexes

Chapter 2 describes the detailed synthesis of schiff base and salen ligands and its corresponding dioxomolybdenum complexes. The synthesized complexes were successfully used for epoxidation of allylic alcohols using hydrogen peroxide as an oxidant. The effects of various reaction parameters such as reaction temperature, molar ratio of catalyst and oxidant were studied so as to optimize reaction conditions in order to achieve high conversion and maximum selectivity for epoxide. An appreciably moderate to high conversion of allylic alcohols and selectivity for epoxide was achieved. In continuation of our efforts in oxidation reaction, epoxidation of cinnamyl alcohol was carried out using dioxomolybdenum schiff base complex showing high selectivity for aldehyde instead of epoxide confirmed the selectivity of catalyst varied with the type of substrates used. Catalyst was evaluated for oxidation of glycerol and its derivative like glycerol carbonate and solketal. Promising results were obtained in case of glycerol carbonate with excellent conversion and selectivity for corresponding aldehyde using TBHP as an oxidizing agent. These results also indicated that the activity and the selectivity of catalyst varied with nature of substrate and oxidizing agents. Obtained results were compared with standard cyclopentadienyl molybdenum tricarbonyl acetylide complex as catalyst precursors.

Chapter 3: Molybdenum(VI) Cis-Dioxo Complex with Chiral Schiff Base Ligand and their Catalytic Applications in Asymmetric Oxidation Reactions

Chapter 3 deals with the synthesis of chiral dioxomolybdenum schiff base complex and its detailed characterization using elemental analysis, FT-IR, NMR, single crystal X-ray diffraction analysis. Single crystal X-ray diffraction study confirmed the complex to be chiral with three molecules in different asymmetric unit. Synthesized chiral complex was evaluated for asymmetric epoxidation of olefins, allylic alcohols and sulfoxidation of thioanisole. Various reaction parameters were studied to optimize reaction conditions so as to achieve high conversion and enantioselectivity. Asymmetric epoxidation of olefins showed moderate to good conversion with excellent selectivity for epoxide. The oxidation of thioanisole showed excellent conversion and selectivity for sulfoxide. However no chiral induction could be observed in epoxides as well as sulfoxide.

Chapter 4: Cyclopentadienyl Molybdenum Tricarbonyl Benzyl Complex as Catalyst Precursor to Dioxomolybdenum Complex for Oxidation Reactions

Chapter 4 describes the synthesis and characterization of cyclopentadienyl molybdenum tricarbonyl benzyl complex. The synthesized complex was evaluated as catalyst precursor for oxidation of range of sulfides. Excellent conversion of thioanisole (> 90%) was obtained in 1 h at room temperature using 1 mol% catalyst with > 95% selectivity for sulfoxide. In presence of higher catalyst loading, catalyst deactivation was observed after some time due to formation of molybdenum blue species as intermediate. The formations of molybdenum blue indicate the absence or decomposition of hydrogen peroxide during reaction. This behavior could be explained by considering competitive hydrogen peroxide decomposition reaction. Molybdenum blue species could be reoxidized after addition of hydrogen peroxide to get catalytically active species. Hence, reaction requires excess hydrogen peroxide. To study the substrate scope the reaction was carried out with a range of sulfides using catalyst **1**. Substituted sulfides with electron donating group and withdrawing group led to negligible change in sulfide conversion and selectivity.

Catalyst was also evaluated for oxidation of ethyl lactate using TBHP as an oxidant. A maximum of 90% ethyl lactate conversion was obtained in 7 h at 80 °C with 99% selectivity for the ethyl pyruvate. However there was no reaction in presence of H_2O_2.

List of publications and patents

1. **Swati L. Pandhare**, Rajesh R. Jadhao, Pranaya V. Joshi, Vedavati G. Puranik, Mohan K. Dongare, Christophe Michon, Francine Agbossou-Niedercorn, Shubhangi B. Umbarkar "*Selective oxidations by molybdenum oxo complexes", Manuscript under preparation*

2. **Swati L. Pandhare**, Rajesh R. Jadhao, Ankush V. Biradar, Mohan K. Dongare, Shubhangi B. Umbarkar, "*Cyclopentadienyl molybdenum tricarbonyl benzyl complex as catalyst precursor for oxidation of sulfides", Manuscript under preparation*

Other publications

1. Rajesh R. Jadhao, Prakash Chandra, **Swati L. Pandhare**, Sumeet Kale, Anjali P. Likhite, Shailaja P. Maybhate, Pranaya V. Joshi, Vedavati G. Puranik, Mohan K. Dongare, Kumar Vanka, and Shubhangi B. Umbarkar, "*Synthesis, Characterization and DFT Studies of Formation of Molybdenum η1-S-Propargyl and η3-S-Allyl Mercaptobenzothiazole Carbonyl Complexes", Manuscript under preparation*

2. **Swati L. Pandhare**, Trupti V. Kotbagi, Mohan K. Dongare, Shubhangi B. Umbarkar, *Copper Exchanged SiO_2/Al_2O_3 Catalyst Prepared by Sol-Gel Method for Intermolecular Hydroamination of Terminal Alkynes"*, *Current Catalysis*, 2 (2013), 62.

3. Prakash Chandra, **Swati L. Pandhare**, Shubhangi B. Umbarkar, Mohan K. Dongare, and Kumar Vanka, "*Mechanistic Studies on the Roles of the Oxidant and Hydrogen Bonding in Determining the Selectivity in Alkene Oxidation in the Presence of Molybdenum Catalysts",* Chem. Eur. J., 19 (2013), 2030.

4. Sidhanath V. Bhosale, Mohan B. Kalyankar, Santosh V. Nalage, Dattatry S. Bhosale, **Swati L. Pandhare**, Trupti V. Kotbagi, Shubhangi B. Umbarkar,

Mohan K. Dongare, "*One-Pot Synthesis of 2,4,5-Trisubstituted Imidazoles Using MoO3/SiO2, an Efficient and Recyclable Catalyst "*, *Synthetic Communication*, 41 (2011), 762.

Presentations at symposia

1. *Presented poster in symposium on "The Wonderland of Molecular Structures through the Looking-Glass of X-ray Crystallography" at CSIR-National Chemical Laboratory, Pune on 23rd September 2013*. Topic- "Study of molybdenum dicarbonyl complexes with S-propargyl 2-mercaptobenzothiazole ligand".
2. *Oral presentation at 2nd Indo-French Bilateral symposium on 'Catalysis for Sustainable and Environmental chemistry' at Univ. of Lille, Lille, France (11th-13th July 2012).* Topic-"Synthesis of Schiff base dioxomolybdenum(VI) complex for oxidation reactions."
3. *Presented Poster at CSIR-NCL, Pune on National Science Day, 26th February 2011. Topic--* "Synthesis, characterization and application of Schiff base dioxomolybdenum(VI) complexes for oxidation reactions."
4. *Presented poster in symposium on 'Modern Trend in Inorganic Chemistry (MTIC-XIV)' at school of chemistry, University of Hyderabad, Hyderabad (10th -13th December, 2011).* Topic-"Synthesis, characterization and application of Schiff base dioxomolybdenum(VI) complexes for oxidation reactions."
5. *Presented poster at 20th National Symposium on Catalysis (NSC-2010), NCCR, IIT-Madras, Chennai (19th-22nd December, 2010).* Topic- "Synthesis of cyclopentadienyl molybdenum acetylide complexes for oxidation reactions."
6. *Oral presentation at 2nd Indo-French Bilateral symposium on 'Catalysis for Sustainable and Environmental chemistry' at NCL, Pune, India (11th-13th July 2010).* Topic- "Synthesis of novel molybdenum catalysts for organic transformations."
7. *Presented poster at CSIR-NCL, Pune on National Science Day, 26th February 2010.* Topic- "Copper exchanged SiO2/Al2O3 catalyst prepared by sol-gel method for intermolecular hydroamination of terminal alkynes."