CYCLOPENTADIENYL MOLYBDENUM ACETYLIDE COMPLEXES AS NOVEL CATALYST FOR OXIDATION REACTIONS

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Research Student
Ankush V. Biradar

Research guide
Dr. Shubhangi B. Umbarkar

CATALYSIS DIVISION
NATIONAL CHEMICAL LABORATORY
PUNE-411008, INDIA

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

CERTIFICATE

Certified that the work incorporated in the thesis entitled ***"Cyclopentadienyl Molybdenum Acetylide Complexes As Novel Catalysts For Oxidation Reactions"*** submitted by ***Ankush V. Biradar*** for the Degree of **Doctor of Philosophy,** in **Chemistry** was carried out by the candidate under my supervision in the Catalysis Division, National Chemical Laboratory, Pune - 411008, India. Materials obtained from other sources have been duly acknowledged in the thesis.

Date :

Dr. Shubhangi B. Umbarkar

(Research Supervisor)

Communication Channels

☎
NCL Level DID : 2590
NCL Board No. : +91-20-25902000
EPABX : +91-20-25893300
+91-20-25893400

FAX
Director's Office : +91-20-25893355
COA's Office : +91-20-25893619
COS&P's Office : +91-20-25893008

WEBSITE
www.ncl-india.org

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Date: Ankush V. Biradar

(Research Student)

Dedicated

to my

Parents
and
Teachers

“I know quite certainly that I myself have no special talent; curiosity, obsession and dogged endurance, combined with self-criticism, have brought me to my ideas.”

-- Albert Einstein

…..Suits me as well !!!

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Ankush V. Biradar

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ABBREVIATIONS

Cp	Cyclopentadienyl anion
CP MAS NMR	Cross Polarization Magic Angle Spinning NMR
EDAX	Energy Dispersive X-ray spectroscopy
FID	Flame Ionized Detector
FT-IR	Fourier-Transform Infrared
GC	Gas Chromatography
GCMS	Gas Chromatography-Mass Spectroscopy
NMR	Nuclear Magnetic Resonance
TBHP	*tert-* Butyl Hydrogen Peroxide
TLC	Thin Layer Chromatography
TON	Turn Over Number
TOF	Turn Over Frequency
TOS	Time On Stream
UV-Vis	Ultra Violet-Visible
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
OsO_4	Osmium Tetroxide
NMO	*N-* Methymorpholine *N*-oxide
Cat	Catalyst, Catalytic
h	Hour (s)
Mol	Mole
THF	Tetrahydrofuran
δ	Chemical Shift
ν	Wave Number

Chapter- 1

Introduction: Organometallic molybdenum complexes and oxidation reactions

1. Introduction: Organometallic molybdenum complexes and oxidation reactions

Abstract: The oxidation of organic compounds with high selectivity is of extreme importance in synthetic chemistry. Important oxidation reactions include the transformation of alkenes to epoxides and diols, oxidation of sulfides to sulfoxides, and alcohols to either the corresponding carbonyl compounds or carboxylic acids. Transition metal complexes play an important role in the selective oxidation. Environmental concerns and regulations have increased in the public, political, and economical world over the last decade as quality of life is strongly connected to a clean environment. The present introductory chapter is not intended to give a complete survey of all published work on oxidation catalysis but rather to give a background and summary of recent important developments in catalytic oxidation reactions. Included is detail literature review on synthetic aspect of mononuclear Mo complexes and catalysis of various reactions such as oxidation of alkenes, amines and sulfide and further objective of thesis.

1.1 Introduction

Chemistry is usually described as the science of matter and its changes at the atomic and molecular levels. It therefore deals primarily with collections of atoms, such as gases, molecules, crystals, and metals; describing, both the composition and statistical properties of such structures, as well as their transformations and interactions to become materials encountered in everyday life. This scientific subject also seeks to understand the properties and interactions of individual atoms, with the purpose of applying that knowledge to macroscopic levels [1]. Chemistry is rightfully described as a "central science" as it links together other sciences such as material science, nanotechnology, biology, pharmacology and geology.

The application of chemistry can be traced back to early human activities such as the use of fire to prepare food, salt to preserve food, use of pigments in cave paintings and dyes to create beautiful clothing. One of the biggest challenges in chemistry is discovering new chemical reactions that will enable society to function in a sustainable manner. Atom economy and waste minimization are at the heart of industrial policy, driven both by governmental incentives and by market considerations [2]. This complicated problem was addressed by various groups and is continuously tried to be solved using novel methodologies, such as catalysis.

1.2 Catalysis

The word catalysis came from two Greek words, the prefix, *cata* meaning down, and the verb *lysein* meaning to split or break. Catalysis is a widely occurring process in nature. Enzymes catalyze numerous biological transformations and involve complex and large molecular weight structures that are evolved in nature over millions of years to carry out particular reactions very selectively. Man-made catalysts are relatively simple. Historically important examples are the production of H_2SO_4 using V_2O_5 and the production of ammonia using iron-based catalysts. Research on the mode of operation and the synthesis of catalysts, including an improved understanding of thermodynamics due to the pioneering works of Ostwald and Van't Hoff, paved the way for a rational approach in developing more sophisticated and superior catalysts [3].

The term catalysis was coined by Berzelius around 1850 after observing changes in substances when they come in contact with small amount of species called “ferments”. Many years later in 1895 Ostwald came up with a definition “*A catalyst is a substance that changes the rate of a chemical reaction without itself appearing into the products*” according to which a catalyst could also slow down a reaction. Now a days, the definition in use is “*A catalyst is a substance which increases the rate at which a chemical reaction approaches equilibrium without becoming itself permanently involved.*” The effect of the catalyst is purely kinetic; catalysts work by providing an alternative mechanism that involves a different transition state at lower activation energy (Figure 1.1).

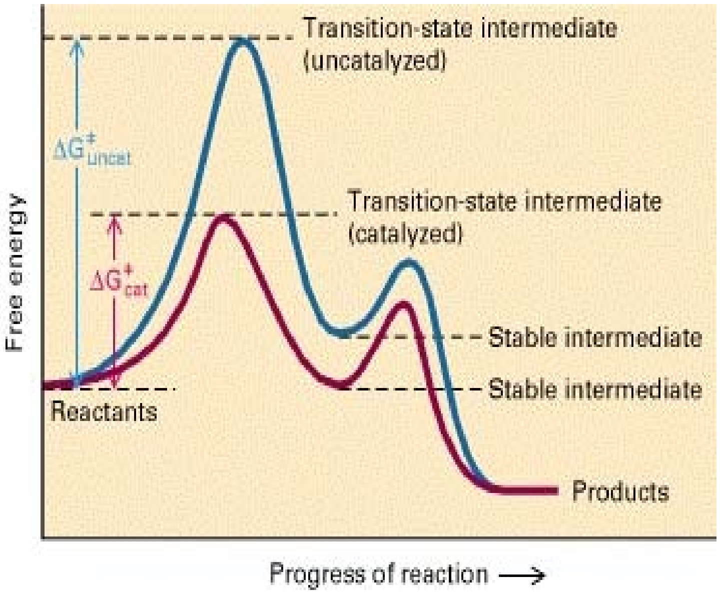


Figure 1.1: Effect of the catalysts on a thermodynamically favorable reaction

The basic principle of all catalysts is that they lower the activation energy by offering an alternative reaction path [4]. A catalyst decreases the activation energy of a reaction ($\Delta G^{\neq}$ is lowered), thereby increasing the rate of the reaction, but has no effect on the chemical equilibrium of the reaction (ΔG remains the same). The action of a catalyst can be very specific, which under ideal conditions, results in selective formation of the desired product and avoids side reactions. Further advantages of the use of catalytic reagents are reduced time and energy requirements, which results in an overall process with increased environmental sustainability. A catalyst can be poisoned when another compound binds to it irreversibly or chemically alters it. This effectively destroys the usefulness of the catalyst. Catalysis plays a key role in production of such a wide variety of products, which are having applications in food, clothing, drugs, plastics, agrochemicals, detergents, fuels etc. [5]. In addition to these, it plays an ever-expanding role in the balance of ecology and environment by providing cleaner alternative routes for stoichiometric technologies [6], by conversion of polluting emissions to harmless streams. Thus the importance of catalysis to society is obviously based on its great economic impact in the production of broad range of commodity products that improve our standard of living and quality of life. Usually, catalysts are categorized depending on the physical form in which they are used.

There are mainly three types of catalysis processes: biocatalysis, homogeneous catalysis, and heterogeneous catalysis. In biocatalysis the catalyst is a biologically active molecule like enzyme. In homogeneous catalysis the catalyst is a transition metal with various ligand, which is in the same phase as that of the reactant and product whereas in heterogeneous catalysis the catalyst is a metal supported on various inorganic supports, which form a separate phase from reactant and product. Table 1.1 highlights major advantages of both homogeneous and heterogeneous catalytic processes.

Table 1.1. Advantages of homogeneous and heterogeneous catalytic processes

Homogeneous	**Heterogeneous**
▪ High and controllable chemo-, regio-, and enantio-selectivity	▪ Easy separation of the catalyst from the product
▪ High activity in terms of TON and TOF	▪ Excellent reuse of the catalyst (high total TON)
▪ Excellent accessibility of catalytic sites, no mass transfer limitations, no pressure drop	▪ Continuous operation frequently applied
▪ Use of complex ligand systems to modify the catalyst	▪ Resistance to drastic operational conditions
▪ Excellent catalyst description, mechanistic understanding	▪ Choice of a large variety of supports, *e.g.* silica, alumina, zeolites, carbon *etc.*

Many homogeneous catalysts contain a metal ion that is surrounded by a ligand system, which stabilizes it in a certain oxidation state and offers coordination sites for substrates and reagents. By ingenious designing of ligands, more active and selective catalysts can be obtained. Transition metal catalysts are the largest class of homogeneous catalysts available to the synthetic chemist. In heterogeneous processes, the catalytic sites are part of an insoluble inorganic solid or are distributed on the surface of an insoluble support like silica, alumina or carbon. One of the limiting factors of the catalytic activity of heterogeneous catalysts is the number of active sites, *i.e.* the surface area of the bulk material or of the supported species. Without surrounding organic ligands, it can be difficult to achieve high product selectivity; moreover, achieving enantioselectivity is generally difficult. On the other hand the big advantage of this kind of process is the easy separation of the catalyst from the reaction mixture. This allows easy purification of the product and facile reuse of the catalytic material. Hence, most of the industrial catalysts are heterogeneous in nature. In spite of this, there are a lot of important industrial processes based on homogeneous catalysis [7]. It is estimated that 85% of all chemical processes are run catalytically, with a ratio of applications of heterogeneous to homogeneous catalysis of approximately 3:1 [8].

In general, the advantages of the two systems are complementary to each other. The Nobel prizes [9] awarded in 2001 to ***Sharpless, Noyori*** and ***Knowles*** for their discovery of chirally catalysed oxidation and hydrogenation reactions, and in 2005 to ***Chauvin, Grubbs*****,** and ***Schrock*** for their discovery of metathesis catalysts exemplify how a new catalyst can cause a paradigm shift in the chemical industry. However, the basic concept used for exploring the catalyst in homogeneous catalysis has not changed the **catalyst productivity,** defined as turnover number (TON), i.e. the number of moles of product produced per mole of catalyst. This number determines the catalyst costs. If a catalyst can be re-used, its productivity increases. The **catalyst activity,** often defined as turnover frequency (TOF), i.e. how many moles of product one mole of the catalyst produces per unit time, determines the production capacity of a given catalyst**.**

1.3 Organometallic chemistry and homogeneous catalysis

Organometallic compounds are defined as materials, which possess direct, more or less polar bonds between metal and carbon atoms [10]. Since Zeise synthesized in 1827 the first organometallic compound, $K[PtCl_3(CH_2{=}CH_2)]$, the organometallic chemistry has grown enormously although most of its applications have only been developed in recent decades. Some of the key points in the fast expansion of organometallic chemistry are the selectivity of organometallic complexes in organic synthesis (discovered with Grignard reagents at the end of the 19th century) [11], and the interesting role that metals play in biological systems (e.g. enzymes, hemoglobin, etc.) [12]. One of the important aspect of organometallic compounds is that they can be used as homogeneous catalysts in processes where all the reacting partners are present in one phase, usually the liquid [13].

Transition metal complexes act in different ways within the catalytic reaction: they bring the substrates together, activate the substrates by coordinating to the metal and lower the activation energy of the transition state. In general the use of a homogeneous catalyst in a reaction provides a new pathway, because the reactants interact with the metallic complex. These interactions make it possible for thermodynamically favored reactions, which need long times to reach equilibrium, to be accomplished within hours. Therefore, homogeneous catalysts can be used to synthesize compounds, which can hardly be obtained by conventional methods.

The success of organometallic catalysts lies in the easy modification of their environment by ligand exchange. A very large number of different types of ligands can coordinate to transition metal ions. Once the ligands are coordinated, the reactivity of the metals may change dramatically. In fact the rate and selectivity of a given process can be optimized to the desired level by controlling the ligand environment. Understanding the role played by the different ligands coordinated to a metal is one of the main themes in homogeneous catalysis [14]. Because organometallic complexes are highly soluble in organic solvents, their behavior throughout the catalytic reaction can be studied using different *in-situ* techniques. Fundamental knowledge about the catalytic systems and studies about the steps of the catalytic processes can help to improve the efficiency of the catalysts.

1.4 Application of organometallic catalysts in the chemical industry

A large variety of organometallic compounds are being used in the industry. More common metals used in industrial process are nickel, cobalt, rhodium, titanium and palladium. Although the majority of reactions are still catalyzed by heterogeneous catalysts, the development and application of homogeneous catalysts are of increasing importance, and such catalysts are now being used in almost all areas of the chemical industry (Scheme 1.2) [15].

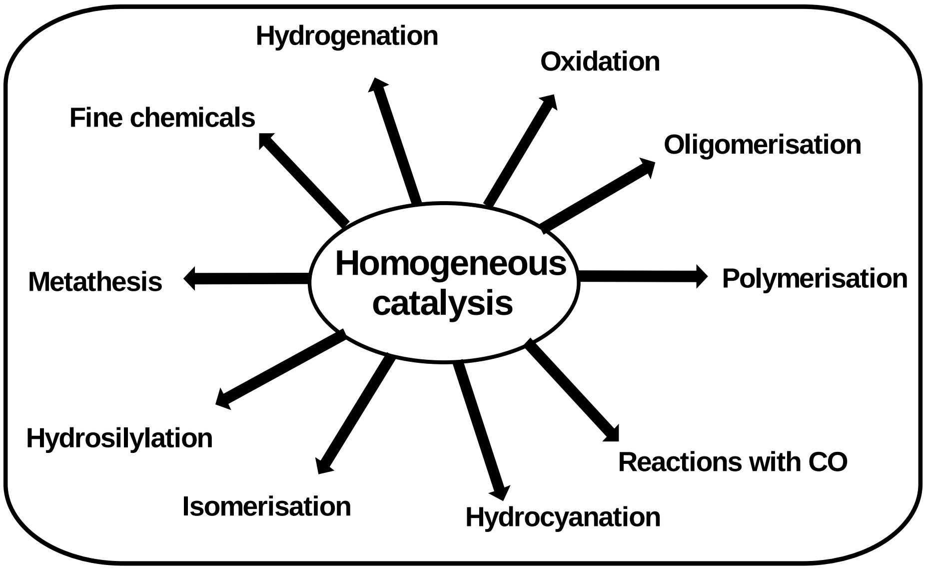
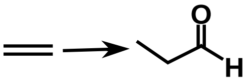
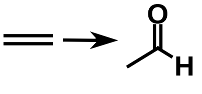
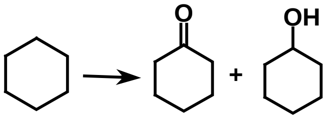
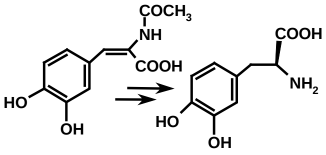
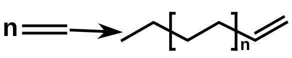


Figure 1.2: Multiple applications of homogeneous catalysts in industrial processes

Many of the processes that have been developed over the past century have been fine tuned to well-known industrial processes by careful selection and development of homogeneous catalysts. These include the hydroformylation reaction, hydrogenation of alkenes, the Monsanto acetic acid process, the use of Ziegler-Natta catalysts in polymerization of alkenes, the Shell higher olefin process and several others. Some of the industrial process that uses homogeneous catalysis are summarized in Table 1.2.

Table 1.2. Major homogeneous catalytic processes based on organometallic chemistry

Process	Type of conversion	Catalyst	Industry
Oxo synthesis hydroformylation		$[Co_2(CO)_8]$; $[HRh(CO)(PPh_3)_3]$	Hoechst; BASF
Monsanto process	$CH_3OH \longrightarrow CH_3COOH$	$[RhI_2(CO)_2]^-$	Monsanto
Wacker process		$PdCl_2$ / $CuCl_2$	Wacker Consortium for Industrial Electro chemistry
Oxidation of cyclohexane		Co (radical mechanism) V, Cr, Mo, Mn	BASF; Bayer; DuPont; ICI *etc.*
Monsanto synthesis of L-dopa		Rh, similar to Wilkinson's catalyst	Monsanto
Oligomerisation of ehylene (SHOP process)		Co, Ti, Ni	SHELL

1.4.1 Molybdenum as an oxidation catalyst

Compared to other transition metals, molybdenum complexes have gained relatively little attention in oxidation chemistry; it has been extensively studied metal in organometallic chemistry because it is versatile and catalyzes a considerable number of organic reactions. The most important molybdenum catalyzed reactions are those leading to C-C bond formation such as oligomerization and polymerization of alkenes, etc. [16]. Apart from this molybdenum is an essential trace element in biological systems. e.g. in plants, enzymes which catalyses nitrogen fixation (nitrogenase) and nitrate reduction (nitrate reductase); in animals, enzymes involved in, e.g., nitrogen metabolism (e.g., xanthine oxidase) and sulphur metabolism (sulfite oxidase) contains molybdenum [17]. For human beings molybdenum features as a component of vitamin and mineral supplements. Molybdenum is generally regarded as nontoxic for humans [18]. The vital role of molybdenum in biology is derived from its affinity for sulfur, its finely balanced oxidation states, and its ability in its higher oxidation states to transfer oxygen. Considering these basic properties of molybdenum it has been used in early days synthesis of bulk chemical such as holcon process and desulphurization.

Organometallic chemistry of molybdenum has been extensively studied in its lower oxidation states. A well known example is molybdenum hexacarbonyl, $Mo(CO)_6$ [19]. These compounds are difficult to prepare and may decompose on exposure to air. They have specialized small volume uses as for example catalysts in fine chemicals synthesis. Materials made from molybdates are oxidation catalysts, photoactive, and semi conducting [3]. 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 bonds.

1.4.2 Structural aspects

There are some readily available starting materials for the synthesis of dioxomolybdenum complexes with the MoO_2^{2+} core, e.g., $MoO_2(acac)_2$, which is easily prepared by the acidification of an aqueous ammonia solution of molybdic anhydride by adjusting the pH [20]. Dioxomolybdenum complexes are readily prepared by ligand exchange. This reaction proceeds in THF or MeOH, sometimes with an amine, such as triethylamine, to assist the ionization of the incoming ligands. MoO_2X_2bipy, an important complex because of its use in the preparation of organometallic complexes, was prepared by the oxidation of $Mo(CO)_4bipy$ with Br_2 or Cl_2 in $EtOH-CH_2Cl_2$ [21]. Another possible starting material for the preparation of this type of complexes are MoO_2Cl_2 and MoO_2Br_2. These two starting materials are much easier to use when transformed to solvent adducts, $MoO_2X_2L_2$ (X = THF, CH_3CN, DMF, DMSO) [22]. When stored free of moisture they can be kept for a long period of time and are much easier to handle than the flurry MoO_2Cl_2 or MoO_2Br_2. Molybdates [23], polymolybdates or even MoO_3 [24] are also used in the preparation of complexes with the MoO_2^{2+} core.

1.4.3 Mononuclear molybdenum complexes

The η^5-cyclopentadienyl (Cp) ligand is used extensively in organometallic chemistry. Complexes containing this ligand exist for all the transition metals and many of the f-block metals. The σ-donor and π-acceptor abilities of the cyclopentadienyl ligand stabilizes transition-metal complexes in low and high oxidation states. Thus, the cyclopentadienyl group is one of the most important ligands in organometallic chemistry. More than 80 % of all known organometallic complexes of transition metals contain cyclopentadienyl fragment or a derivative thereof.

1.4.4 Preparation of molybdenum oxo complexes

The first metal oxo molecular fragment was probably the oxyhalide complex MoO_2Cl_2 described by J. J. Berzelius in 1826. Interest in these inorganic molecular fragments continued in the 19th and 20th centuries. These complexes were thought to be good candidate for molecular models of metal oxides, but could not be used due to their highly unstable nature. Addition of organic molecules to a metal center of a metal oxide with creation of a metal carbon interaction, thus generating an *organometallic oxide*, has proven to be an interesting way to synthesize the desired models for metal oxides. Besides creating more tangible models for metal oxides, organometallic oxides can also be considered as useful models for the interaction between the metal oxides and the organic substrates of catalytic reactions and as a way of avoiding the presence of alkyl co-catalysts. Mononuclear organomolybdenum (VI) dioxo complexes with cyclopentadienyl ligands, a class of ligands, which can form Mo-C σ or π bonds, that has been extensively studied for metal oxides [25].

1.4.5 Metal acetylides Complex

Transition-metal acetylides can be viewed as the HC≡C- ligand, which is isoelectronic with CN^-, CO, and N_2. These are regarded as pseduohalides because of the many similarities in the chemical and physical behavior of the corresponding compounds. This is the reason why transition metal acetylides are often viewed as coordination compounds rather than organometallic. The acetylide organometallic complexes having a linear structure of M-C≡C-R generating a strong coupling between metal and π-conjugation and have consequently strong optical non-linearities [3]. Moreover, these π-conjugated chains containing organometallic carbon-rich complexes are interesting materials for the study of electron transfer [26], liquid crystal formation [27], and for the design of molecular components [28] or for applications in nonlinear optics [29]. Indeed, organized in molecules or polymers, they can become materials having remarkable nonlinear optical properties. The M-C≡C- unit allows the existence of a strong mesomery within the complexes and improves the intramolecular charge transfer between the organometallic group donor and the organic conjugated part that lies in the same plane as this unit. Theoretical and experimental studies on these complexes showed that the strong hyperpolarisability of the second order (β) characterizing the nonlinear optical efficiency of the molecule depends on the length of the π-conjugation and the force on the donor (metal) and acceptor groups. Moreover, it was observed that the nonlinear response of the second-order increases due to the multiple metal-carbon bonds present in this type of complexes [30]. More particularly, beside unidimensional compounds, complexes of transition metals and multipolar two- and three-dimensional systems were also developed [31].

1.5 Heterogenization of homogeneous catalysts

The heterogenization of homogeneous transition metal catalysts has received considerable attention in recent years, since such heterogenized homogeneous catalysts (surface organometallic catalysts) may combine the most advantageous properties of both homogeneous and heterogeneous systems [32], easier product/catalyst separation and high activity and selectivity. Many attempts have been made to enhance the activities of heterogenized complexes, which are usually lower than those of homogeneous systems due to low loadings and problems concerning the accessibility of catalytic sites. The term heterogenization refers to a process, whereby a homogeneous transition metal complex (including free metal particles, biological molecules, organic species etc.) is either immobilized, anchored, incorporated or encapsulated in an inert organic (polymer) or inorganic support. These heterogeneous catalysts have a lot of advantages over their homogeneous analogues:

- Fixed-bed and continuous flow through operations,
- Complete commercial utility on a large scale owing to the economic debits of batch type operations and/or expense of catalyst recovery and recycle,
- Maintaining high selectivities and conversions (turn over frequency) of their homogeneous analogues for many reactions, and
- Preventing other side reactions e.g. dimerization, alkylation and aggregate formation of the catalyst complex, which normally occurs in solution.

Leaching occurs in some cases, where the activity in fact results from a homogeneous catalyst. It is therefore important to check the true nature of the process. In particular, recyclability is important for industrial applications but is often not easy to obtain. This contribution deals with the particular case for heterogenization of organomolybdenum (VI) complexes, which are very important catalysts for many reactions in the homogeneous phase.

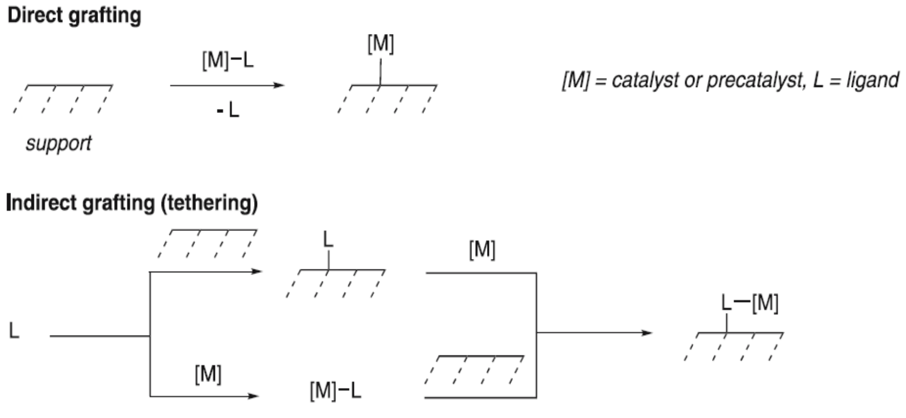
1.5.1 Immobilization Techniques

In spite of the fact that homogeneous catalysis is undoubtedly one of the most promising methods for complicated syntheses, industrial applications are still underdeveloped. The main reason is not associated with qualitative aspects of the transformations where high selectivity and conversions are obtained for a wide variety of reactions but to rather high costs of the ligand or metal. These drawbacks could be avoided if the catalyst is separated and reused after reaction. An evident way for achieving this is the use of heterogeneous catalysis, allowing easy work-up procedures and possible recycle.

One promising strategy to combine the best properties of the homogeneous and heterogeneous catalysts is the heterogenization or immobilization of active metal complexes on supports, which may be separated by filtration or precipitation [33]. Polymers (linear, noncrosslinked polymers; swellable, slightly cross linked polymers; and highly cross linked polymers) or inorganic materials (amorphous oxides such as silica, alumina, zirconia, and ZnO; clay minerals, pillared clays, and LDHs; zeolites such as zeolite and Y-zeolite; regular mesoporous structures such as MCM-41 and MCM-48) are normally used as supports [34].

The synthetic procedure to attach the currently available catalysts onto a support involves either surface modification or metal complex modification in order to connect both *via* a covalent interaction. Comparison with their homogeneous counterparts in catalysis reveals an increased activity in some of the cases. Comparison amongst various supports shows an advantage of using structured, mesoporous support.

The two main immobilization techniques on a mesoporous material are direct grafting and indirect grafting (tethering), as shown in Scheme1.1. In the former case, the complex interacts directly with the matrix. In the latter case, the complex is tethered to the supporting material via a spacer ligand, which is either introduced first on the support or integrated into the complex before being anchored onto the support.



Scheme 1.1: Immobilization of homogeneous catalysts on the support

Organometallic compounds have found useful applications in a variety of catalytic processes mostly related but not limited to oxidations processes. In particular, the catalytic activity of organometallic oxo molybdenum compounds in olefin epoxidation [35] has recently attracted renewed interest [36].

1.6 Oxidation reactions: A challenge

Oxidation and reduction reactions constitute a wide part of chemistry and it is difficult to imagine a synthesis, either in the laboratory or in nature [37], which does not include an oxidation/reduction step. General definition for oxidation is the loss of an electron or an increase in oxidation number. Many oxidation reactions are related to the conversion of a functional group, such as hydroxylation, epoxidation, dihydroxylation, aziridination, hydroxyamination and halogenation. The oxidation of organic substrates by direct oxygen atom transfer from transition metal complexes is of fundamental importance [38]. Reasons for this interest are the necessity for functionalisation of lower alkenes, interest in understanding reactions of biological importance, the need for partial selective oxidation and the preparation of compounds with a specific spatial structure. The transition metal complexes seem to fulfill some of these requirements and many different systems are available that can utilize a variety of oxygen sources for these oxidation reactions. The oxidation of alkenes to epoxides, aldehydes, ketones and glycols is a large and growing part of homogeneous catalysis with direct industrial applications [39]. Although laboratory-scale alcohol and alkene oxidations using chromium (VI) oxide, hypervalent iodine reagents (Dess-martin) and peracids have been reported, use of stoichiometric amount of toxic and reactive oxidants poses severe safety and environmental hazards in large-scale industrial reactions. In addition, oxidation of unreactive substrates such as amines, amides and alkanes are usually not selective or has low conversion rates.

In view of the low selectivity and growing concern on environmental hazards with the currently adopted oxidation technologies in industry [40], there is a growing interest for environmental-friendly and operationally safe protocols for chemo selective organic oxidations. The utilization of transition metal complexes has the origin from biological processes such as flavin and cytochrome P-450 monooxygenases [41] using atmospheric oxygen as terminal oxidant. Biomimetic oxidation studies have been largely focused on metalloporphyrins, in which reactive nature performs the task of biological oxidations at ambient conditions, employing metalloenzyme and protein catalysts, which are remarkably more efficient, specific and particularly selective for producing a specific oxygenated compound [42]. In many of industrial practices, using man-made catalysts, significant amounts of undesired side-products are usually obtained. In order to make the process more economic and green, one of the major challenges in catalysis research is to develop solid, highly efficient and selective oxidation catalysts for reactions at ambient conditions. It is known that during oxidations, different types of active metal-oxo species (peroxo, hydroperoxo and superoxo) are generated [43].

Many transition metal complexes form coordination compounds with oxygen. These complexes can be of superoxo, peroxo, oxo or hydroperoxo type [44]. Upon formation of these complexes, the metal ion donates unpaired electrons to the oxygen and is thus oxidized, formally by one or two electrons. In reality, the electron transfer is not complete, and the metal ion has properties between the lower and the higher oxidation state. This is especially true with reversible oxygen carriers [45]. Superoxo and peroxo complexes are easily formed by reaction of triplet state dioxygen $^3O_2$ and a transition metal ion with unpaired electrons available to donate to the oxygen molecule. Upon complexation, the metal ion also receives and donates electron density (π-back bonding) [46]. On the other hand, formation of the oxo complexes from molecular oxygen requires breaking of the O–O bond, which is achieved by reduction of the dioxygen with four electrons. Thus oxo complexes are mostly observed with metal ions such as manganese [47], iron [48] that are capable of existing in multiple oxidation states. An easier way to prepare oxo complexes is with oxygen transfer reagents and peroxides such as NaOCl, iodosylarenes, H_2O_2, organic hydroperoxides, peroxy acids and peroxysulfates that possess an easily heterolysble O–O bond. Common metals in these kinds of complexes are titanium, vanadium, chromium, manganese, iron and molybdenum. Titanium often forms binuclear bis μ-oxo type [49] or mononuclear μ-oxo type complexes [50], where the vanadium [51], chromium [52], manganese [53] and molybdenum [54] favour mononuclear terminal oxo type coordination. μ-oxo coordination mode is common in iron complexes [55].

1.6.1 Choice of oxidant for oxidation reaction

There are several terminal oxidants available for the transition metal catalyzed oxidation reactions. Typical oxidants compatible with majority of metal based oxidation systems are various alkyl hydroperoxides, hypochlorite or iodosylbenzene. Problems associated with these oxidants are their low active oxygen content. Considering the nature of the waste produced, there are further drawbacks of these oxidants. Hence, from an environmental and economical point of view, molecular oxygen should be the preferred oxidant, considering its high active oxygen content and no waste product or only water as byproduct. One of the major limitations of molecular oxygen as oxidant is poor selectivity for desired product. On the other hand, hydrogen peroxide displays much better properties as the terminal oxidant. The active oxygen content of H_2O_2 is about as high as for typical application of the molecular oxygen and the waste produced by employing this oxidant is plain water. Therefore hydrogen peroxide is an attractive alternative. Hydrogen peroxide has a number of other advantages over other common low cost oxidants such as sodium perborate, potassium hydroperoxysulfate, and many organic peroxy acids, which are prepared from hydrogen peroxide itself. Table 1.3 lists the active oxygen content of some common oxidants along with the byproduct.

Table 1.3. Active oxygen content of common oxidants

Oxidant	Active oxygen content	Waste product
Oxygen (O_2)	100	Nothing or H_2O
Oxygen (O_2)/reductor	50	H_2O
H_2O_2	47	H_2O
NaOCl	21.6	NaCl
CH_3CO_3H	21.1	CH_3CO_2H
t-BuOOH (TBHP)	17.8	*t*-BuOH
$KHSO_5$	10.5	$KHSO_4$
PhIO	7.3	PhI

Figure 1.3 summarizes the different ways H_2O_2 can be activated by metal complex or organic moiety [56].

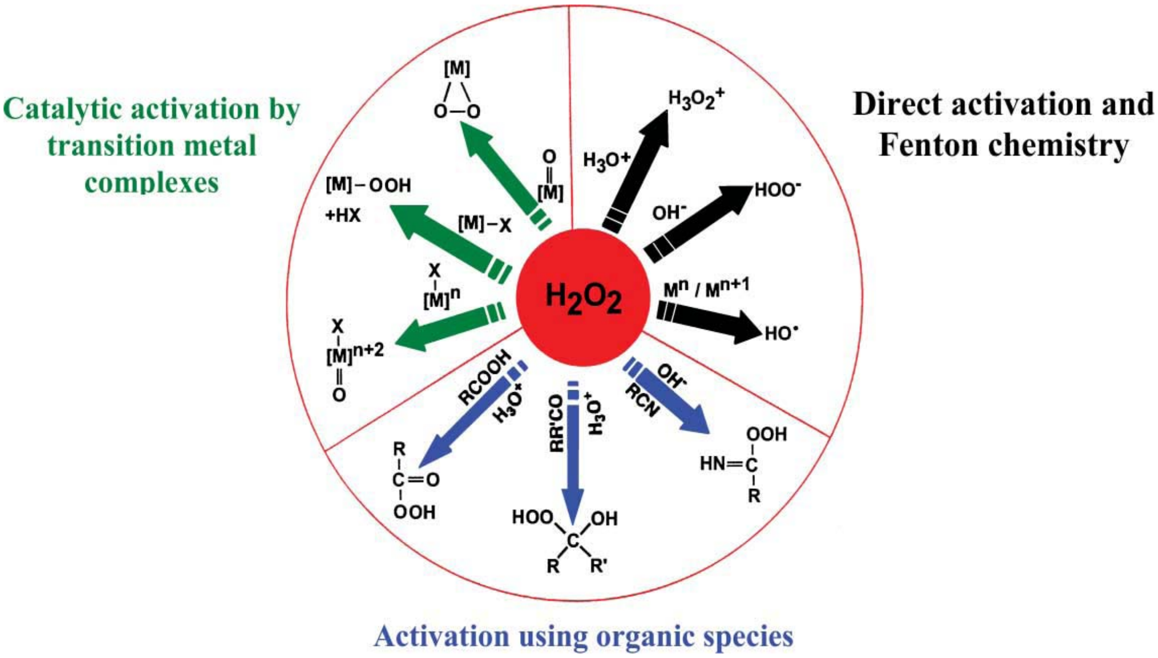
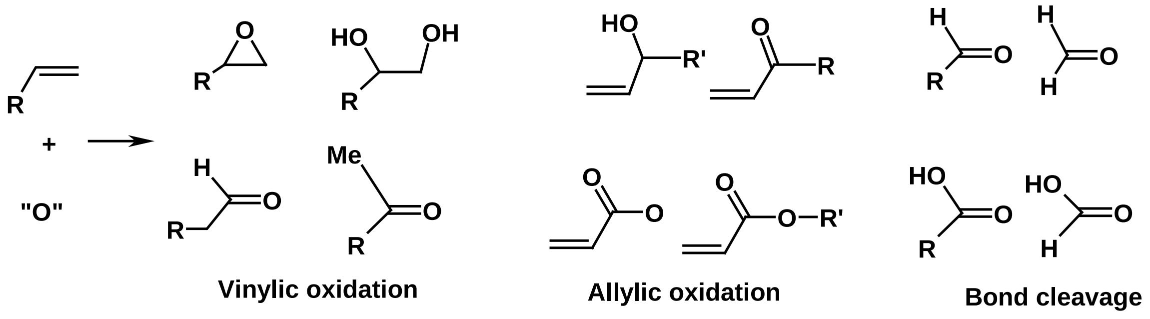


Figure 1.3: Activation of hydrogen peroxide

1.6.2 Metal catalyzed olefin oxidation

Metal catalyzed oxidation of olefins can give rise to a whole variety of organic products, as illustrated for terminal olefins in Scheme1.3. Cleavage of the double bond results in aldehydes or carboxylic acids. In the absence of cleavage either vinylic oxidation to epoxides, aldehydes, ketones, or glycols, or allylic oxidation to α-β unsaturated alcohols, ketones, esters or acids occur [57]. Some of the well-known olefin oxidation catalysts are reviewed below.



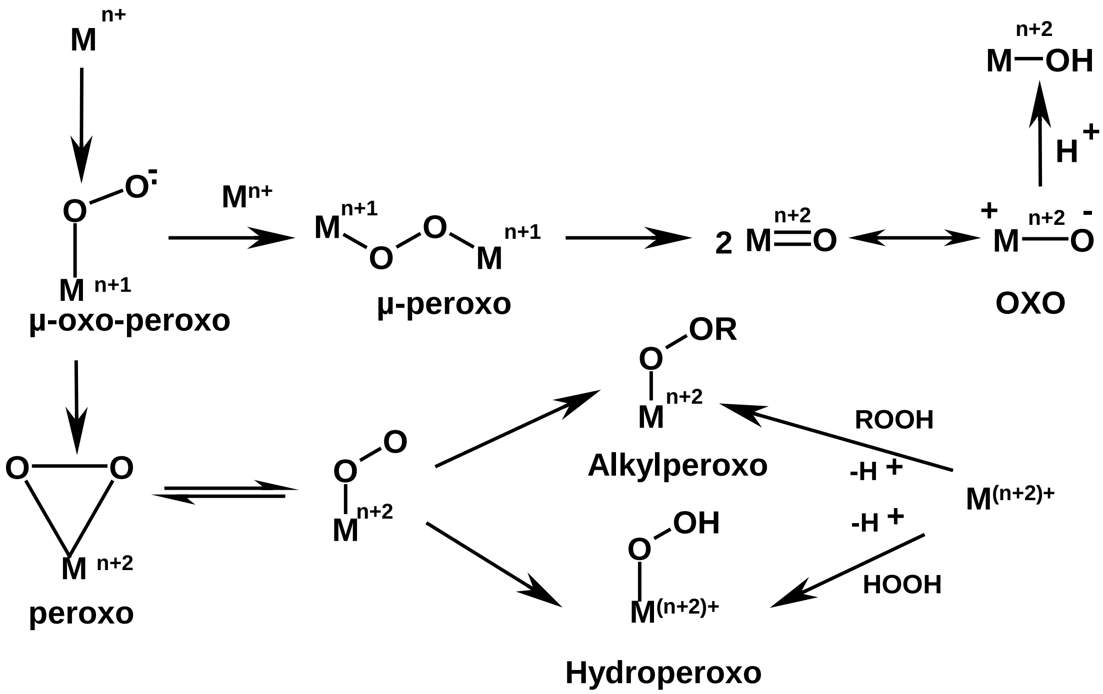
Scheme 1.3: Products obtained in metal catalyzed oxidation of terminal olefins

The industrially applied heterogeneous Ag catalyst for epoxidation of ethane [58] by O_2 (air) is important for the production of glycol (antifreeze). The enantioselective Sharpless *cis*-dihydroxylation of olefins by the terminal oxidants *t*-BuOOH, *N*-methylmorpholine *N*-oxide or $K_3Fe(CN)_6/OH^-$, catalyzed by homogeneous high valent Os-catalyst (e.g. OsO4) provide attractive alternative to obtain glycols directly from olefins [59]. Epoxidation of higher olefins can however not be carried out with Ag/O_2. Therefore we should certainly mention the industrially applied heterogeneous catalysts for epoxidation of propene by alkyl-hydroperoxides, from Halcon (Arco oxirane process, M= Mo) [60] and Shell (SM/PO process, M= Ti/SiO_2) [61]. The hydrophilicity of the silica in the latter prevents the use of H_2O_2 as oxidant. However, Ti-substituted silicalite (TS-1) has been introduced as an industrial catalyst for selective epoxidation with aqueous H_2O_2 (Enichem) [62]. Homogeneous chiral Sharpless Ti-catalysts are also well known for enantioselective epoxidation of allyl alcohols by *t*-BuOOH [63] and the homogeneous chiral (salen)Mn Kochi-Jacobsen-Katsuki-catalysts for enantioselective epoxidation of other olefins by PhIO, NaOCl or m-CPBA [64].

1.6.2 Mechanistic aspects of metal catalyzed olefin oxidation

The role of transition metal complexes in oxidation reactions is complicated due to many available different reaction pathways. Detailed mechanisms are generally not known. In those cases where kinetic studies have been carried out, complicated reaction mechanisms are often needed to account for the reactivity. In addition, mechanistic proposals are often controversial. Here, a brief schematic overview of some generally accepted reaction steps are given. The various species that invoked in activation of dioxygen and peroxides are summarized in Scheme 1.4.

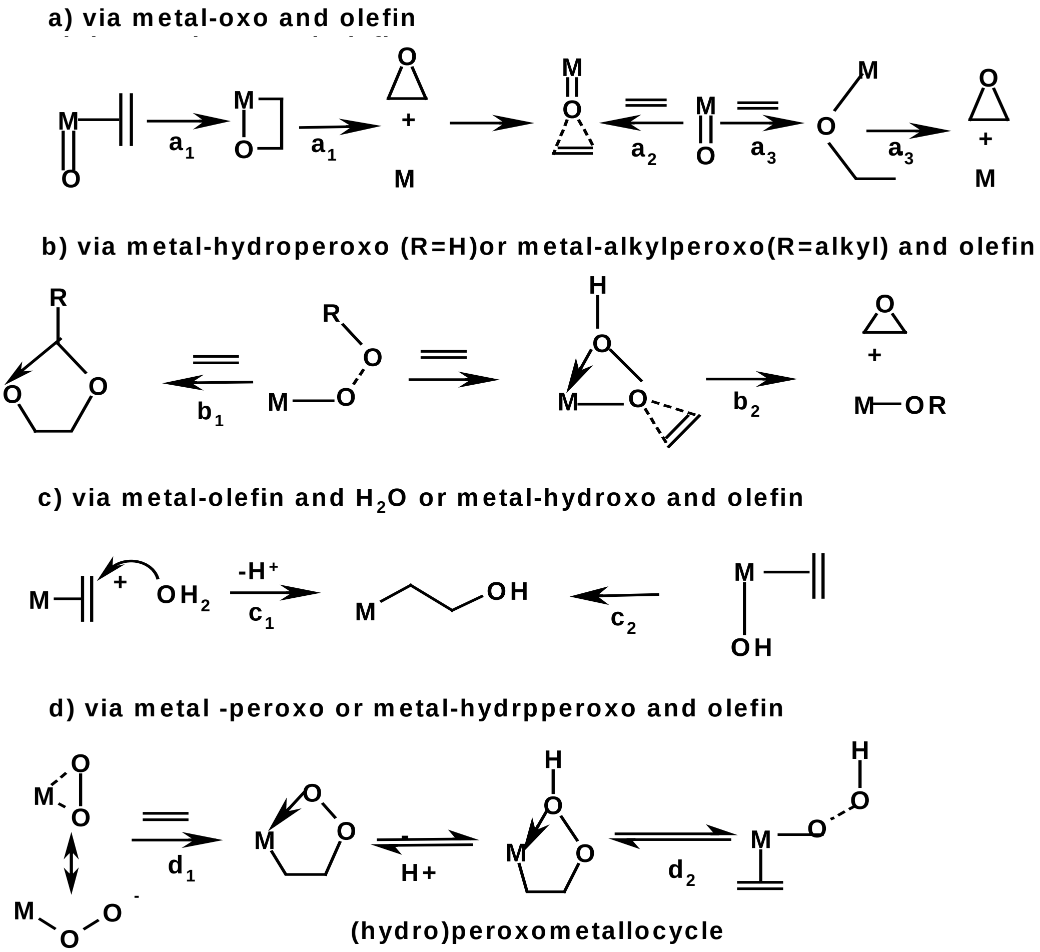
Metal catalyzed oxidation of olefins may be conveniently divided into reactions involving free radicals (homolytic oxidation) and oxidations proceeding via other pathways (heterolytic oxidation) [65]. Homolytic oxidations are generally not very selective and do not preserve the stereochemical configuration of the substrate. They are often catalyzed by first-row transition metals characterized by one-electron oxidation-reduction steps. Free radical pathways often lead to allylic oxidation or a combination of allylic and vinylic oxidation. Heterolytic oxidations are generally highly selective and stereospecific. In most cases vinylic oxidation is observed. This classification is not rigorous and there are a number of borderline examples and exceptions (especially for enzymatic oxidations).



Scheme 1.4: Species that involved in activation of dioxygen

When ligand is present on metal atom even in case of radical mechanism selective product can be obtained. Some transition metals are known to initiate homolytic autoxidation of olefins (free radical chain oxidation by O_2), and particular care is sometimes necessary to distinguish between a radical mechanism and other pathways.

Some important oxygen transfer mechanisms that have been proposed in metal catalyzed olefin oxidation are summarized in Scheme 1.5.



Scheme 1.5: Some important oxygen transfer mechanisms

Some representative examples supporting the above mechanism are given below:

- The mechanism by which the well-known Jacobsen epoxidation catalyst operates is controversial.

The direct oxygen transfer can take place by two ways from M-oxo species path a2) [66], and mechanisms involving 2-metallaoxetanes (path a1) [67] or radical species (path a3) [68].

- For early transition metal complex in high oxidation states (acidic metal centers), epoxidations have been proposed to proceed via olefin insertion into the metal-oxygen bond of the alkylperoxo or hydroperoxo-complex (route b1) and oxygen transfer via nucleophilic attack of the olefin on the electron poor peroxidic oxygen (route b2, analogous to epoxidation with organic peroxyacids). However theoretical calculations support the route b2 [69].

- In the Wacker oxidation coordination to palladium activates the olefin towards nucleophilic attack by H_2O/OH^- (path c1 and c2).
- The Pt-catalyzed epoxidation of olefins by hydrogen peroxide has been proposed to proceed via activation of both the olefin and the oxidant. Coordination increases the electrophilic character of the olefin on one hand, and the nucleophilic character of hydrogen peroxide on the other hand path d2) [70].
- Rhodium (and iridium) catalyzed reactions have mainly been proposed to proceed via the steps b1, c2, d1 and d2.

Hence above discussion indicates that nature of metal center, type of oxidant and olefin decides the route taken up for oxidation.

1.7 Scope and contents of thesis

One important hurdle in organometallic chemistry is air and moisture stable synthesis of metal complexes and their successful application in the catalysis. Current research efforts in this area, therefore include the synthesis of stable organometallic complexes. The most important drawbacks of the Mo based oxidation catalysts known at the starting point of this work were the difficulties to modify their reactivity by ligand modification, the lack of easy heterogenizability. A solution to these problems was also attempted in some other research groups, like of F. E. Kuehn and I. S. Gonçalves. While the former two research groups concentrated mainly on $Mo(O_2)_2O$ and $Mo(O_2)_2OL_{1-2}$ type catalyst systems, the latter group was working mostly on $MoO_2X_2L_2$ systems, L being a Lewis base and X usually a halide ligand. Tungstan acetylide complex $CpW(CO)_3(C{\equiv}CPh)$ is known to form corresponding oxo-peroxo complex after treatment with hydrogen peroxide in acidic medium hence these type of complexes are potential candidates for oxidation reactions. With this background we have synthesized various molybdenum acetylide complexes $CpMo(CO)_3(C{\equiv}CPh)$, characterized using various spectroscopic technique as well as single crystal X-ray diffraction analysis and used for various oxidation reactions using hydrogen peroxide and TBHP as oxidant. The attempt has also been made for easy synthesis of organometallic molybdenum oxide complex from simple precursor like MoO_3. The synthesis, characterization and catalytical oxidations using these complexes are reported in this thesis from chapters **2** to **6**.

Chapter 2 discusses the synthesis of various cyclopentadienyl molybdenum acetylide complexes $CpMo(CO)_3(C{\equiv}CR)$, R= Ph (**1**), C_6H_4-*p*-CF_3 (**2**), C_6H_4-*p*-CH_3 (**3**). All the complexes were characterized by various techniques including FTIR, UV-Vis and NMR spectroscopy and single crystal X-ray diffraction analysis. The homogeneous complex **1** was heterogenized by immobilizing it onto the silica (**4**). An alternative simple route for synthesis of cyclopentadienyl molybdenum acetylide dioxo complex $CpMo(O)_2(C{\equiv}CPh)$ (**5**) from MoO_3 as starting material was successfully achieved. This catalyst was characterized by various spectroscopic techniques.

The ***third chapter*** discusses the study of catalytic activity of complex **1** for oxidation of various olefins using aqueous hydrogen peroxide as oxidant. The catalyst was found to give selective *cis*-dihydroxylation of olefins with high olefin conversion. The products were confirmed by GC-MS, FTIR, and ^{1}H, ^{13}C NMR spectroscopy. The detailed characterization of the catalyst in different stages of the catalytic cycles was carried out using FTIR, UV, ESI-MS and cyclic voltametric studies. Based on the spectroscopic data mechanism of *cis*-dihydroxylation is proposed.

The ***fourth chapter*** discusses the oxidation of heteroatom such as aromatic amines, alcohol and sulfide using complex **1, 2, 3** and **4** and for all the reactions effect of different reaction parameters on conversion and selectivity was studied.

The ***fifth chapter*** discusses the catalytic activity of molybdenum acetylide dioxo complex **5** for oxidation of aromatic primary alkanes.

The major outcome of all the chapters from present study is summarized in the section ***Summary and future outlook***.

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9 Three researchers share the **2005** Nobel Prize in Chemistry: **Dr. Yves Chauvin** at the Institut Français du Pétrole, Rueil-Malmaison, France; Professor **Robert H. Grubbs,** California Institute of Technology, Pasadena, California, USA and Professor **Richard R. Schrock**, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA for the Development of the Metathesis Method in Organic Synthesis. For more information visit ***http://nobelprize.org/chemistry***

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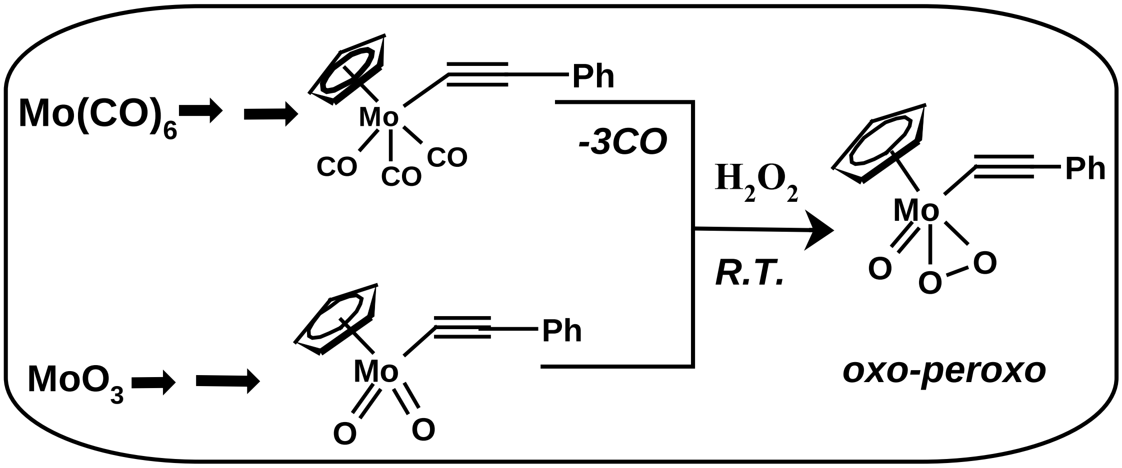
Chapter-2

Synthesis and characterization of cyclopentadienyl molybdenum acetylide complexes

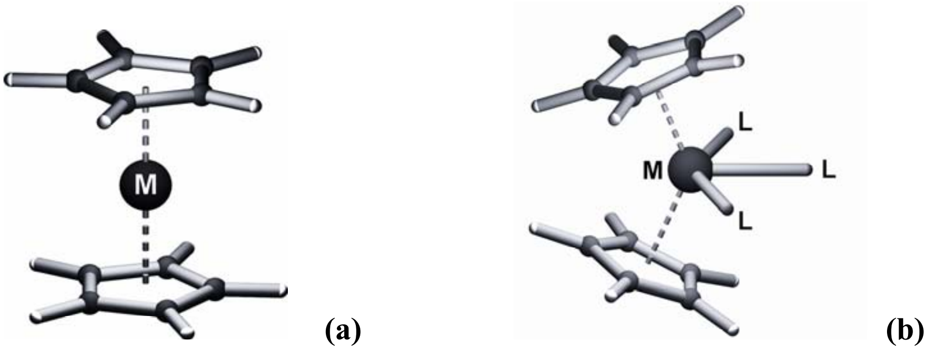
2. Synthesis and characterization of cyclopentadienyl molybdenum acetylide complexes

*Abstract: This chapter gives a detail synthesis and the characterization of cyclopentadienyl molybdenum acetylide complexes. η^5-cyclopentadienyl molybdenum acetylide complexes $CpMo(CO)_3(C\equiv CR)$, R= Ph (**1**), C_6H_4-p-CF_3 (**2**), C_6H_4-p-CH_3 (**3**), were prepared from $CpMo(CO)_3Cl$ via sonogashira coupling with excellent yields. Complexes **1** - **3** were characterized by UV-vis, FTIR, NMR spectroscopy, additionally structure of **1** and **2** were confirmed by single crystal X-ray diffraction analysis. The formation of oxo-peroxo species after addition of H_2O_2 to **1** was confirmed by FTIR and UV-vis spectroscopy. Complex **1** was immobilized on silica and characterized by UV-Vis, FTIR, and NMR spectroscopy. Cyclopentadienyl molybdenum dioxo acetylide complex $CpMo(O)_2(C\equiv CPh)$ was prepared from molybdenum oxychloride, which gave an excellent yield (76%) and the formation of complex was confirmed by FTIR.*



2.1 Introduction

Since the discovery of metallocene complex (metallocene: metallon = metal (Greek) + cene = cyclopentadiene) synthesized in 1951 by Kealy and Pauson [1], cyclopentadienyls have been among the most important ligands in organo-transition metal chemistry because they form a wide range of stable complexes. The σ-donor and π-acceptor abilities of the cyclopentadienyl ligand stabilize transition-metal complexes in low and high oxidation states. An enormous number of mono- and dicyclopentadienyl transition metal complexes have been reported [2]. There has been special and intense research interest in early transition metal cyclopentadienyl-type compounds usually containing one or two cyclopentadienyl (Cp), indenyl (Ind) or fluorenyl (Flu) moieties. The discovery of ferrocene (ferrocene: ferrum = iron (Latin)), which had been prepared unwittingly on previous occasions during the iron catalyzed cracking of dicyclopentadienyl [3], has led to a true run on other metallocene complexes of transition metals [4]. In case of complexes of the type $Cp_2M(II)$ ($Cp = \eta^5\text{-}C_5H_5$), the geometry is generally as depicted in Figure 2.1 [5]. A bent structure will results when additional ligands are bound to the metal center, along with cyclopentadienyl ligands (Figure 2.1 b).



(a) **(b)**

Figure 2.1: (a) Ball-stick representation of the structure of a metallocene, (b) Ball-stick representation of the bent metallocene geometry (M = metal center; L = ligand).

In metallocene complexes, the cyclopentadienyl ligand is mostly η^5-coordinated to the metal center, donating 5 electrons, but there are numerous examples, especially in case of main group metals, of η^1, η^2 or η^3 coordination and also of σ-bound cyclopentadienyl ligands (Figure 2.2) [6].

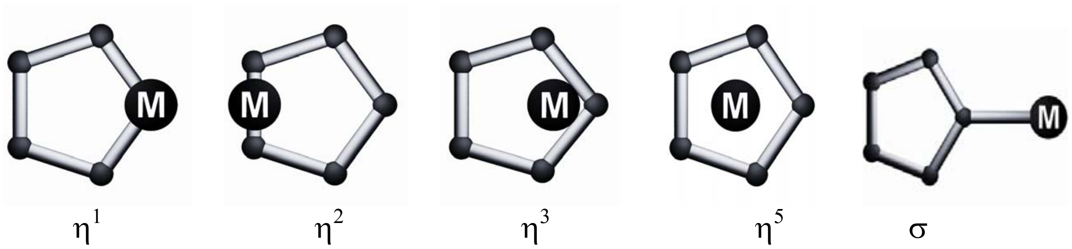


Figure 2.2: Different bonding modes of cyclopentadienyl ligand

2.1.2 Dioxomolybdenum (VI) complexes with cyclopentadienyl ligands

In 1963 Cousins and Green reported the first example of an organometallic molybdenum (VI) cyclopentadienyl dioxo complex, $CpMoO_2Cl$ [7], being one of the first monomeric high oxidation state organometallic oxides ever obtained. This complex was synthesized in very low yields and adventitiously as the only isolable product from air oxidation of $CpMo(CO)_3(\eta^3\text{-}C_3H_5)$ in presence of HCl. Two mononuclear dioxo complexes were obtained, namely $CpMoO_2Cl$ [8] and $CpMoO_2Br$ [9], which were stable only under nitrogen atmosphere and decomposed slowly in air. Green and co-workers later rationalized several synthetic methods of obtaining $CpMoO_2Cl$. The synthesis of organometallic oxides has improved substantially [10]. Concerning the $[Cp'Mo(O)_2Cl]$-type compounds, very mild synthetic routes have been recently found, after varying the substituents on Cp’ from H to very bulky groups, e.g., *i*Pr, CH_3, CH_2Ph. Whereas the $[(\eta^5\text{-}C_5H\textit{i}Pr_4)Mo(O)_2Cl]$ complex was obtained in 87% yield by hydrolysis of $[(\eta^5\text{-}C_5H\textit{i}Pr_4)MoCl_4]$ in the presence of either three or two equivalents of NaOH [11], other $[Cp'Mo(O)_2Cl]$ compounds (Cp’ = Cp, Cp*) were readily prepared by Romão and co-workers from the parent carbonyls $[Cp'Mo(CO)_3Cl]$ upon reaction with *t*-BuOOH in *n*-decane [12]. The latter method follows the oxidative decarbonylation strategy that was successfully used for the synthesis of Cp^*ReO_3 [13] and $TpMoO_3$, [14] starting from $Cp^*Re(CO)_3$ and $TpMo(CO)_3$ (Tp = $HB(pz)_3$) respectively, several years ago. The obtained yields were generally quite low and the synthetic pathways were unspecific for the dioxo complex. Although not depicted, for simplicity reasons, the oxidation of the carbonyl complexes leads to several different types of oxo complexes (monomeric and dimeric complexes). These synthetic difficulties have probably hindered the development of this chemistry, postponing its further development.

Motivated by the developments in the chemistry of diverse high oxidation state organometallic complexes and by the discovery that the introduction of Cp* instead of Cp results in high oxidation state compounds, which are more tractable, Faller and Ma were able to synthesize the Cp^*MoO_2Cl complex by oxidation of the carbonyl complex $[Cp^*Mo(CO)_2]_2$ with O_2 in chloroform to a μ-oxo bridged dimer and subsequent treatment of this dimer with PCl_5 [15]. X-ray crystallography showed that the complex presents the expected mononuclear piano-stool structure. The complex is thermally stable and can be handled easily in dry air. The bromide derivative was also obtained but was much more unstable than the chloride derivative.

In the same year Legzdins and collaborators proposed a more general synthetic route for compounds of the type $Cp'MoO_2R$ (Cp' = Cp, Cp*, R = Me, CH_2SiMe_3) by exposure of the dialkyl nitrosyl complexes $Cp'M(NO)_2R_2$ to water and molecular oxygen [16]. The compound Cp^*MoO_2Cl was also obtained by hydrolysis of Cp^*MoCl_4 under basic conditions in the presence of air and a reaction time of 30 minutes. According to the authors, shorter reaction times leads to a mixture of Cp^*MoO_2Cl and Cp^*MoOCl_2, and longer reaction times or excess base leads to a μ-oxo bridged dimer [17]. Using the same reaction type the compound $[\eta^5\text{-}C_5(i\text{-}Pr)_4H]MoO_2Cl$ was also obtained [18]. Inspired by the work of Cousins and Green [8], Trost and Bergman synthesized the complex Cp^*MoO_2Cl by light-induced oxidation of $Cp^*Mo(CO)_3Cl$ with O_2 in toluene. The authors confirmed the air stability of the compounds but referred its decomposition in solution upon exposure to the atmosphere [19]. The same method also afforded the compound $[\eta^5\text{-}C_5Ph_4Ph(OMe)_2]MoO_2OR$ (R = Me, Et, Pr, *t*-Bu) [20].

As an alternative to the synthesis presented by Faller and Ma, which was less suitable for large scale synthesis, Bottomley and co-workers synthesized Cp^*MoO_2Cl by oxidation of $[CpMo(CO)_2]_2$ with the powerful oxidant H_2O_2/HCl in chloroform [21]. It was reported that the decomposition of Cp^*MoO_2Cl is accelerated by light and inhibited in dry oxygen. A simple entry to $(\eta^5\text{-}C_5R_5)MoO_2Cl$ (R = H, CH_3), $CH_2C_5H_5$) was developed [22]. By reaction of the parent carbonyls $(\eta^5\text{-}C_5R_5)Mo(CO)_3Cl$ with TBHP in CH_2Cl_2 at room temperature. Colbran et. al. [23] studied the cyclooctene epoxidation with cyclopentadienyl molybdenum (VI) complexes and observed that the cyclopentadienyl ligand was lost from molybdenum center as the catalysis proceeds, leading to the *in situ* generation of a much more active catalyst. The latter the loss of the cyclopentadienyl ligand from a cyclopentadienyl molybdenum (VI) dioxo 'catalyst', should always be considered in catalyses of alkene epoxidation, because thus-formed molybdenum species may be the most active catalyst. Certainly, Poli has revealed a varied and rich aqueous chemistry for Cp*Mo(VI) oxo species, including remarkable stability under forcing conditions such as extremes of pH [24]. However, Poli and co-workers have also shown that loss of the Cp* ligand may occur under certain conditions [25], so the presumption of complete stability for an alkylcyclopentadienyl molybdenum (VI) oxo catalyst during epoxidation catalysis may be not be valid. Hence there is a need for more stabilization of organometallic compounds by putting more electron delocalisation sites.

2.1.3 Organometallic compounds containing metal carbon σ bonds

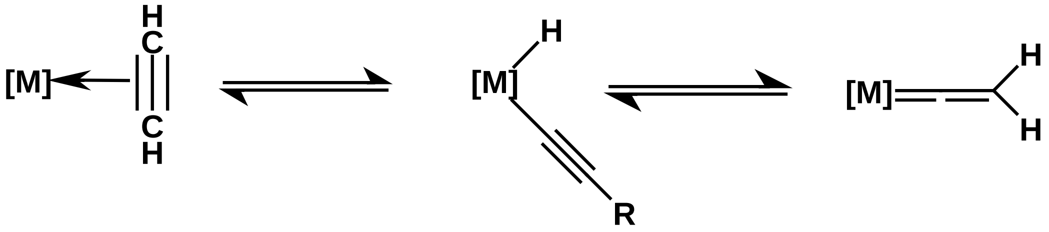
The study of compounds containing metal carbon σ bonds is of fundamental importance because these species play key roles in homogeneous (e.g. in Ziegler- Natta process and hydroformylation of olefins) and bio-organic (e.g. Vitamin B_{12} and CO dehydrogenase) catalysis. The beginning of the chemistry of metal σ-alkyl traced back to the isolation of zinc alkyl by Frankland in 1849 and the isolation of zinc alkyls let to the subsequent synthesis of mercury, lead [26] and later magnesium alkyls [27] that laid the foundation of modern organometallic chemistry. Within the broader area of organometallic chemistry the emergence of compounds containing transition metals and carbon is much more recent. The failure to isolate stable transition metal alkyls in the earlier years generated a serious misconception that hampered the development of the field, namely that transition metal carbon bonds are weak and such compounds are intrinsically unstable. However, the available thermodynamic data shows that metal to carbon bonds for transition metals are not exceptionally weak and the bond energies are comparable to the main group analogues. It was later realized that kinetic instability of transition metal alkyls, lead to the decomposition. The kinetic stability of transition metal alkyls can be enhanced by careful choice of the alkyl group (e.g. alkyls lacking β hydrogen such as neopentyl and trimethylsilylmethyl), metal oxidation state, other ligands or coordination number and geometry.

2.1.4 Transition metal alkynyl complexes

The study of transition metal alkynyl complexes ($L_nM-C\equiv CR$) has been intense area of research from last few decades. Transition metal alkynyl complexes are fascinating for synthetic chemists, structural chemists as well as material chemists. The linear geometry of the alkynyl unit and its π-unsaturated character have led to metal alkynyl becoming attractive building blocks for molecular wires and polymeric organometallic materials which posses interesting properties such as optical non linearity, luminescence, liquid crystallinity and electrical conductivity [28]. Also due to the multifunctional bonding behavior of acetylide anions and the ability of the coordinated ligands to react with both nucleophilic and electrophilic agents, there has been considerable interest in the preparation, chemical and physical properties of molybdenum and tungsten complexes in high oxidation states [29]. The $M-C\equiv C-$ unit allows the existence of a strong mesomery within the complexes and improves the intramolecular charge transfer between the organometallic group donor and the organic conjugated part that lies in the same plane as this unit. Theorotical and experimental studies on these complexes showed that the strong hyperpolarisability of the second order (β) characterizing the nonlinear optical efficiency of the molecule depends on the length of the π-conjugation and the force on the groups donor (metal) and acceptor. Moreover, it was observed that the nonlinear response of the second-order increases due to the multiple metal-carbon bonds present in this type of complexes [30]. Though they have been extensively studied for their applications in non-linear optics and liquid crystallinity, their applications for catalysis have not been fully explored. Considering their geometric structure it is expected that they may impose certain diffusional constrains leading to regioselective catalysis. Hence it will be interesting to explore the catalytic applications of transition metal alkynyl, especially acetylide complexes.

2.1.5 Syntheses and molecular structures of mono cyclopentadienyl molybdenum alkynyl complexes

The synthesis of mono and bis alkynyl complexes of mono cyclopentadienyl molybdenum (VI) might lead to interesting starting materials for further reactivity studies. For the mono alkynyl complexes the possibility of equilibria between metal-alkyne, metal-hydride alkynyl and metal vinylidene which have been shown to exist for several late transition-metal complexes (Scheme 2.1) [31], would be feasible and could provide synthetic pathways to molybdenum (VI) vinylidene complexes. Bis(alkynyl) titanocene (IV) derivatives have been used as organometallic bidentate chelate ligands in the preparation of homo- and heterobinuclear complexes containing bridging σ-π-alkynyl groups between the metal centers. Depending on the arrangement of the alkynyl ligands bis(alkynyl) complexes of molybdenum (VI) might display similar behavior.



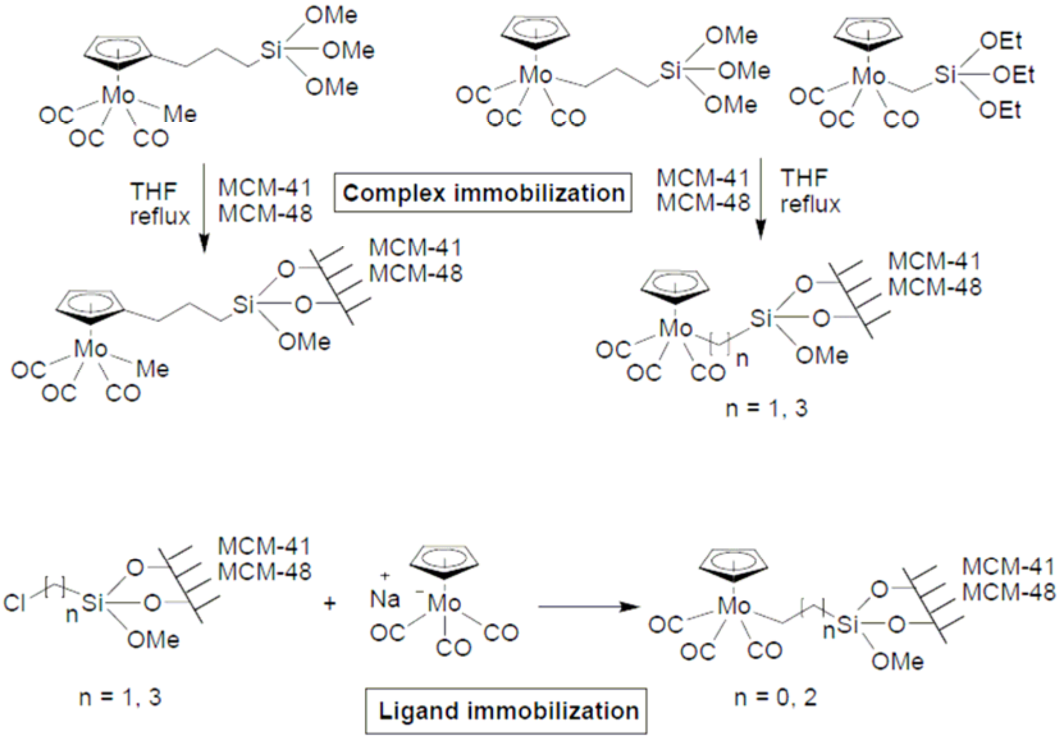
Scheme 2.1: Equilibria between metal-alkyne, metal-hydride alkynyl and metal vinylidene

There is an emerging and considerable interest in Cr-acetylides as models and precursors for polyalkyne polymers containing transition metals in the main chain backbone, a feature of great importance in the advanced materials field [32]. Tin acetylides have received increasing attention in the preparation of transition metal acetylides. A number of efficient methods that use such derivatives as intermediates [33] or partners [34] to attach an acetylene group to a metal have been reported.

2.1.6 The heterogenization of homogeneous transition metal catalysts

The heterogenization of homogeneous transition metal catalysts has received considerable attention in recent years, since such heterogenized homogeneous catalysts (surface organometallic catalysts) may combine the most advantageous properties of both homogeneous and heterogeneous systems like easier product/catalyst separation and high activity and selectivity. Many attempts have been made to enhance the activities of heterogenized complexes, which are usually lower than those of homogeneous systems due to low loadings and problems concerning the accessibility of catalytic sites. The latter point may, however, be an advantage, as the selectivity observed is often better supported catalysts than homogeneous catalysts. Since leaching may occur in some cases, some of the activity in fact may results from a homogeneous catalyst. It is therefore important to check the true nature of the process. In particular, recyclability is important for the industrial applications but is often not easy to obtain. Heterogenization of organorhenium (VII) and organomolybdenum (VI) complexes is an important example as these are very important catalysts for many reactions in the homogeneous phase.

Hermann *et. al.* have immobilized organometallic molybdenum complexes on structured silica using both the complex immobilization and the ligand immobilization approach (Scheme 2.2) [35]. η^5-CpMo(CO)$_3$R complexes with a triethoxysilane coupling group were synthesized and immobilized on the surface of mesoporous silica.



Scheme 2.2: Immobilization of η^5-CpMo(CO)$_3$R complexes using various approaches

The linker was connected to the complex through either the cyclopentadiene ring or directly to the metal. In second approach, the ligand itself was first immobilized and the modified silica was subsequently reacted with Na[CpMo(CO)$_3$] as a metal precursor.

Considering this background we have prepared molybdenum carbonyl acetylide complexes and characterized using various spectroscopic techniques. Heterogenization of the Mo-acetylide complex on mesoporous silica has been carried out. Additionally characterization of catalytically active species in presence of hydrogen peroxide as oxidizing agent has been studied and the results are presented in this chapter.

2.2 Experimental

2.2.1 Chemicals

All preparations and manipulations were performed using standard Schlenk techniques under an atmosphere of argon. Solvents were dried by standard procedures THF, over Na/benzophenone, distilled under argon and used immediately. Phenyl acetylene, dicyclopentadiene and diethyl amine (Aldrich), hydrochloric acid (SD fine India LTD), copper powder, dichloromethane, iodine, hydroidodic acid, silica gel mesh size 60 to 120 Merck India LTD were used as received unless stated otherwise. CuI was freshly prepared by addition of Cu power to hydroiodic acid and refluxing for 4 h fallowed by filteraton and washing with water and ether. MoO_3 was prepared by calcination of ammonium heptamolybdedate at 550°C for 8 h in muffle furnace. Cyclopentadiene was obtained by freshly cracking dicyclopentadiene by distillation prior to use.

2.2.2 Synthesis of cyclopentadienyl molybdenum acetylide complexes

Synthesis of cyclopentadienyl molybdenum acetylide complexes $CpMo(CO)_3(C{\equiv}CR)$, R= Ph (**1**), C_6H_4-*p*-CF_3 (**2**), C_6H_4-*p*-CH_3 (**3**), cyclopentadienyl molybdenum acetylide complex anchored on silica (**4**), as well as dioxo cyclopentadienyl molybdenum acetylide (**5**) from molybdenum oxide have been discussed in the following sections.

2.2.2.1 Preparation of cyclopentadienyl molybdenum acetylide complex ($CpMo(CO)_3(C{\equiv}CR)$)

In a typical synthesis of $CpMo(CO)_3Cl$, dry freshly distilled THF (10 mL), freshly cracked cyclopentadiene (2.3 g, 0.035 mol) and sodium (0.9 g, 0.039 mol) were 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 (5 g, 0.0189 mol) and additional 50 mL dry THF was added. Reaction mixture was refluxed at 80 ºC for 4 h and then cooled to room temperature. To the reaction mixture 15 mL acetic acid was added and stirred for 15 min followed by addition of 30 mL carbon tetrachloride. Stirring was continued at room temperature for 30 min. The reaction mixture was extracted with ether (25 mL X 3). The combined organic extract was concentrated in vacuum and separated by column chromatography on silica gel with hexane/CH_2Cl_2 (80:20 v/v) mixture as solvent system. Yield of $CpMo(CO)_3Cl$ = 3.8 g, 55 % based on $Mo(CO)_6$.

$CpMo(CO)_3(-C{\equiv}CPh)$ complex was prepared by slight modification of the method described by Bruce et. al. [36]. A mixture of $CpMo(CO)_3Cl$ (2.0 g, 0.0071 mol), ($H-C{\equiv}CPh$) (1.05 g, 0.010 mol) and catalytic amount of CuI (5 mg) was stirred at room temperature in diethyl amine (50 mL) for 15 min. The progress of the reaction was monitored by TLC using hexane/dichloromethane (80/20) as solvent system. After the reaction was complete, diethyl amine was removed in vacuum. The residue was dissolved in minimum amount of dichloromethane (5 mL) and loaded on silica gel column and eluted using hexane/dichloromethane 80/20 v/v as solvent system. Yield of $CpMo(CO)_3(-C{\equiv}CPh)$ = 1.5 g, 68 % based on $CpMo(CO)_3Cl$.

2.2.2.2 Preparation of $CpMo(CO)_3(-C{\equiv}C-C_6H_4-p-CF_3)$ (2) and $CpMo(CO)_3(-C{\equiv}C-C_6H_4-p-CH_3)$ (3)

The above procedure was followed except addition of ($H-C{\equiv}C-C_6H_4-p-CF_3$) (0.010 mol) for preparation of **2** and ($H-C{\equiv}C-C_6H_4-p-CH_3$) (0.010 mol) for preparation of **3** instead of $HC{\equiv}CPh$ for **1**. Yield of **2** $CpMo(CO)_3(-C{\equiv}C-C_6H_4-p-CF_3)$ = 2.15 g, 65.8 % based on $CpMo(CO)_3Cl$. Yield of **3** $CpMo(CO)_3(-C{\equiv}C-C_6H_4-p-CH_3)$ = 1.82 g, 71.2 % based on $CpMo(CO)_3Cl$.

2.2.2.3 Heterogenization of cyclopentadienyl molybdenum acetylide complex on silica (4)

The complex **1** was heterogenized by immobilizing it onto the silica surface. Main focus was to form covalent bond between support and complex. Mesoporous silica was prepared by sol-gel method in our laboratory (surface area ~ 600 m^2/g) by following the reported procedure [37]. Pure silica was prepared by adding 52 g of ethyl silicate-40 to 30 g dry isopropyl alcohol; to this mixture 0.02 g ammonia solution (25%) was added with constant stirring. The transparent white gel thus obtained was air dried and calcined in a muffle furnace at 500 ºC for 8 h.

This dried silica (6 g) was dispersed in anhydrous toluene in a distillation apparatus. To this mixture, 3-chloro propyltriethoxysilane (3.23 g) was added and stirred at reflux temperature for 16 h. The toluene and ethanol formed during grafting step were distilled out; solid catalyst was dried under high vacuum. Solid material was then subjected to soxhlet extraction in boiling dichloromethane so as to remove unreacted 3-chloro propyl triethoxysilane. Using this heterogenized cyclopentadiene, the acetylide complex was prepared via chloride complex following the procedure in section 2.2.2.1. Heterogenized cyclopentadiene on silica (7.3 g) sodium (0.9 g, 0.039 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 (5 g, 0.0189 mol) and additional 50 mL dry THF was added. Reaction mixture was refluxed at 80 ºC for 4 h and then cooled to room temperature. To the reaction mixture 15 mL acetic acid was added and stirred for 15 min followed by addition of 30 mL carbon tetrachloride. Stirring was continued at room temperature for 30 min. washed with water followed by ether several times.

To a 100 ml round bottom flask was added 25 mL diethyl amine, cuprous iodide (10 mg), heterogenised Mo-chloride complex (7.3) and 0.8 mL pheylacetylene. The reaction mixture was stirred for 30 min at room temperature. The reaction mixture was filtered and washed with water, toluene and ether successively. The final compound was dried at room temperature. Weight of the final product named as **4** was 7.2 gm.

2.2.2.4 Preparation of the cyclopentadienyl molybdenum dioxo phenyl acetylide complex (5)

In a typical synthesis of $Mo(O_2)Cl_2(DMSO)_2$, to a solution of 20 g (20 mmol) powdered MoO_3, 80 ml concentrated hydrochloric acid was added. The mixture was stirred at room temperature for 30 min to obtain a colorless solution. DMSO (5 ml, 17.55 mmol) was added to the above solution with constant stirring. The resulting mixture was stirred for 5 min and the white microcrystalline precipitate was filtered, washed with 3 X 5 mL portions of diethyl ether and dried under vacuum and recrystallized from acetonitrile. $MoO_2Cl_2(Me_2SO)_2$: yield 45.22 g, 94 %.

For the preparation of $CpMo(O_2)Cl$ from $MoO_2Cl_2(DMSO)_2$, a 100 ml two necked flask was charged with 40 mL dry THF, 1.23 g cyclopentadiene and 0.23 g sodium. The reaction mixture was stirred for 2 h at room temperature and after that 5 g $MoO_2Cl_2(DMSO)_2$ was added and stirred at room temperature till completion of the reaction (8 h).

For the preparation of $CpMoO_2(C{\equiv}CPh)$ from $CpMoO_2Cl$, round bottom flask (100 mL) was charged with 25 mL diethyl amine, 5 mg cuprous iodide and 0.8 mL phenylacetylene. The reaction mixture was stirred for 30 min at room temperature. This reaction mixture was added to the above reaction mixture and reaction was continued till completion (4 h). Solvent was removed under vacuum and washed with water, toluene and ether successively and compound was dried at room temperature.

2.2.3 Single Crystal X-ray diffraction analysis of 1 and 2

Single crystals of the complex **1** and **2** were grown by slow evaporation of the solution a mixture of acetonitrile layered with hexane. The X-ray data of **1** to **2** were collected on a SMART APEX CCD single crystal X-ray diffractometer with omega and phi scan mode and different number of scans and exposure times for both the crystals using λ MoK_{α} = 0.71073 Å radiation, at room temperature. All the data was corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs. The crystal structures were solved by direct method using SHELXS-97 and the refinement was performed by full matrix least squares of F^2 using SHELXL-97 [38].

Crystal data.

Compound 1: Pale yellow rectangular crystal of approximate size 0.32 x 0.24 x 0.18 mm was used for data collection. Crystal to detector distance 6.05 cm, 512 x 512 pixels / frame. Total scans = 3, total frames = 1818, exposure / frame = 10.0 sec / frame, θ range = 2.09 to 25.0 °, completeness to θ of 25.0 ° is 95.0 %. SADABS correction applied, $C_{16}H_{10}MoO_3$, M = 346.18. Crystals belong to monoclinic, space group $P2_1/c$, a = 6.7308(4), b = 11.6071(6), c = 17.949(1) Å, β= 93.046(1) °, V = 1400.3 (14) $Å^3$, Z = 4, D_c = 1.642 g /cc, μ (Mo–K_{α}) = 0.939 mm^{-1}, 9068 reflections measured, 2324 unique [I>2σ(I)], R value 0.0342, wR2 = 0.1075.

Compound 2:

Brown plate of approximate size 0.44 x 0.36 x 0.12 mm was used for data collection. Crystal to detector distance 6.05 cm, 512 x 512 pixels / frame. Total scans = 3, total frames = 1271, θ range = 2.52 to 24.99 °, completeness to θ of 24.99 ° is 99.6 % SADABS correction applied, $C_{17}H_9F_3MoO_3$, M = 414.18.

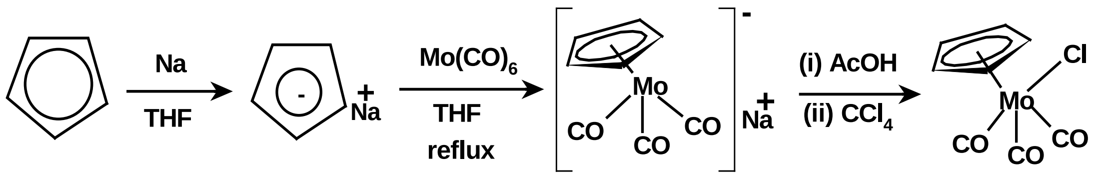
Crystals belong to Monoclinic, space group $P2_1/c$, a = 11.9333(7), b = 12.8247(8) , c = 21.023(1) Å, β= 90.413(1) °, V = 3217.3(3) $Å^3$, Z = 8, D_c = 1.710 g/cc, μ (Mo–K_{α}) = 0.859 mm^{-1}, 15543 reflections measured, 5636 unique [I>2σ(I)], R value 0.0504, wR2 = 0.1398.

2.2.4 Preparation of catalytically active species of 1a

In a dry 50 mL round bottom flask 100 mg of complex **1** was dissolved in 5 mL *t*-butanol. To this solution and 0.05g 30% H_2O_2 was added slowly. The reaction proceeds with eliminating of carbon monoxide gas. The reaction mixture was stirred at room temperature for 10 min. The resultant mixture was concentrated to 1 mL and named as **1a.**

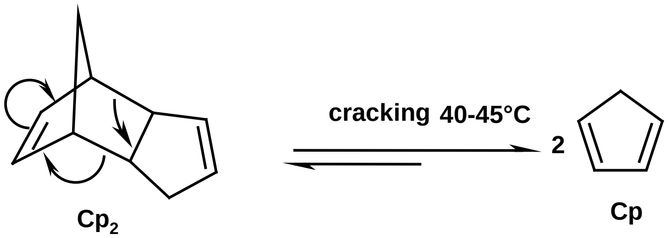
2.3 Results and discussions

Cyclopentadienyl molybdenum chloride was prepared according to the literature procedure [36]. A stepwise formation of $CpMo(CO)_3Cl$ from $Mo(CO)_6$ is shown in Scheme 2.3.



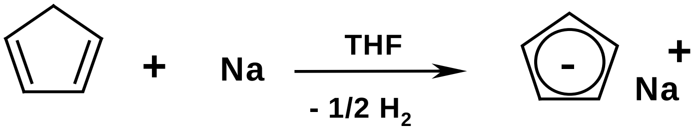
Scheme 2.3: Synthesis of cyclopentadienyl molybdenum chloride

Cyclopentadiene [39] (Cp) is a very useful ligand, which reinforces activity of metal center. Cyclopentadienyl ligand is 5 electron donor; it cannot be removed easily after coordination with metal in η^5 coordination compared to η^1 coordination. In the first step the dicyclopentadienyl dimer ($C_{10}H_{12}$) is cracked to the monomer C_5H_6 (Cp) by a retro Diels Alder reaction as shown in eq^n. 2.1 [40].



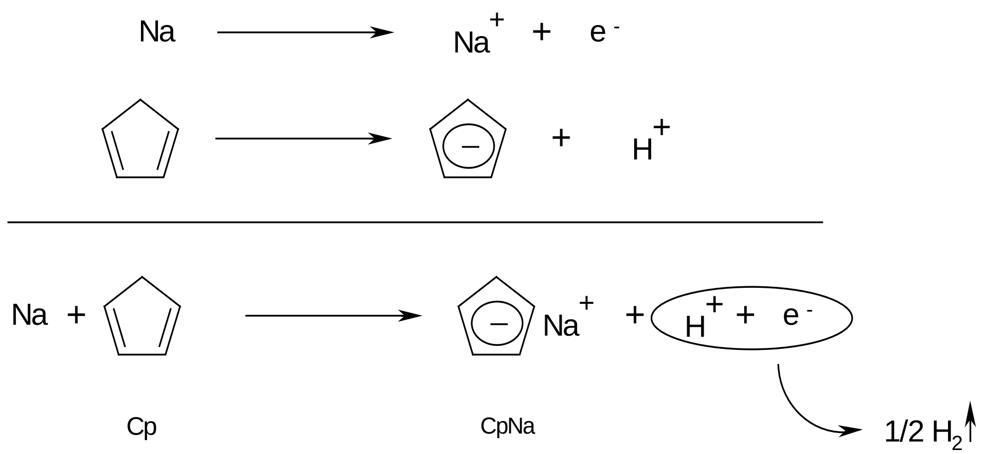
.........2.1

Diels-Alder reaction is an exothermic reaction; 2 π-bonds are replaced by 2 σ-bonds. By increasing temperature above the equilibrium temperature, reaction can be inversed leading to cyclopentadiene. Cyclopentadiene is usually acidic due to loss of a proton and it is converted from the nonaromatic diene to the aromatic cyclopentadienyl anion. This anion is very stable as it is a conjugated system. After deprotonation of the sp^3 carbon of Cp, electrons are delocalized over all five-carbon atoms (eq^n 2.2)



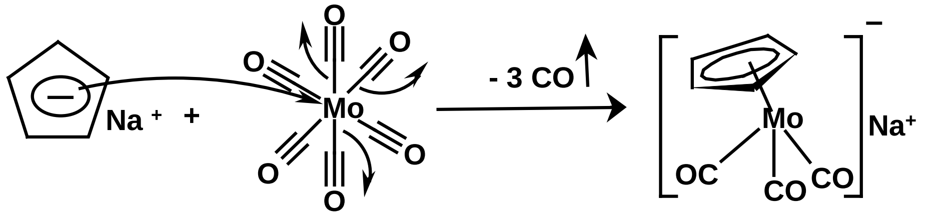
....2.2

This deprotonation is due to sodium metal by an oxido-reduction reaction; a release of dihydrogen is observed as shown above.

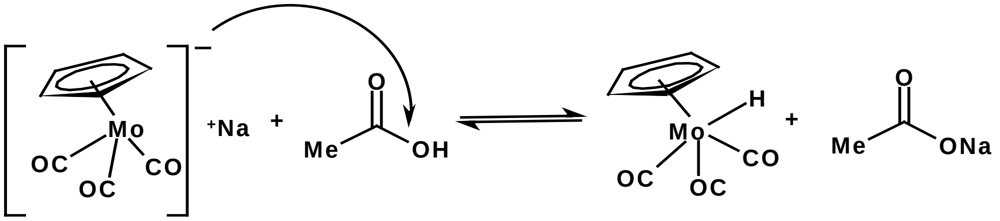


...2.3

In this step molybdenum hexacarbonyl, $Mo(CO)_6$ reacts with the corresponding cyclopentadienyl anion to produce the molybdenum Na intermediate $CpMo(CO)_3Na$, which after acidification with acetic acid forms corresponding hydride complex $CpMo(CO)_3H$ (eq^n 2.5). This hydride complex without isolation and purification is reacted with carbon tetrachloride (CCl_4) to form molybdenum chloride complex $CpMo(CO)_3Cl$ (Eq^n. 2.6).

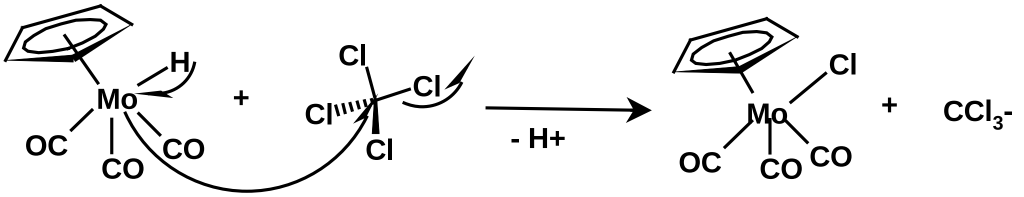


...2.4



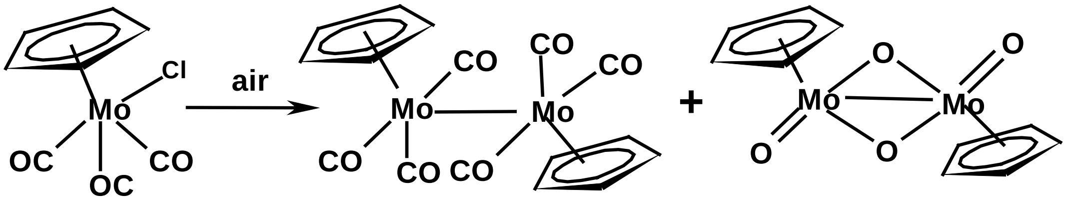
...2.5

$CpMo(CO)_3H$ is very unstable and cannot be isolated [41], hence carbon tetrachloride is directly added to drive equilibrium reaction to the right in favor of molybdenum hydride intermediate formation. This reaction is a nucleophilic substitution (SN^2) of hydride by chloride, which is more electronegative than hydride (eq^n 2.6).



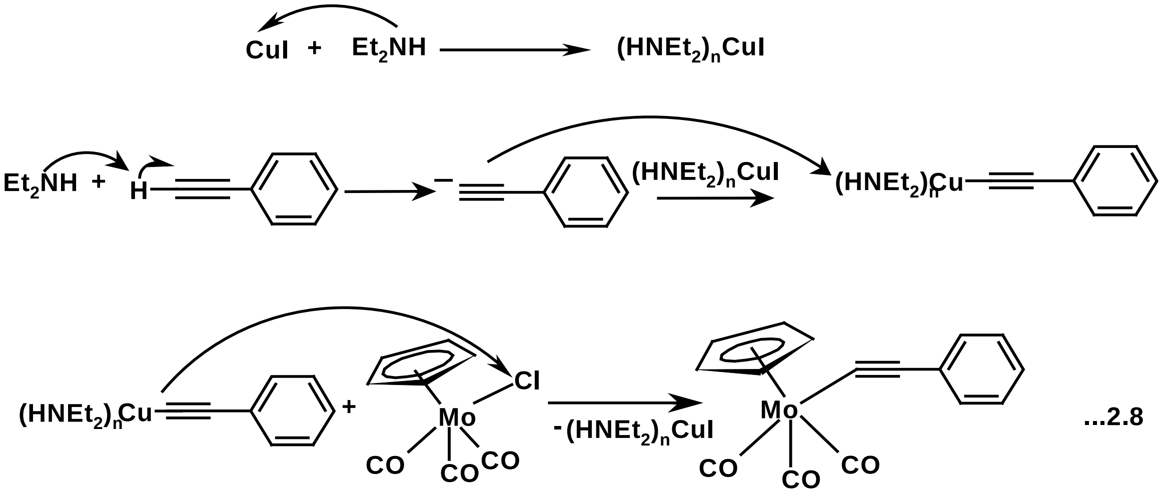
...2.6

CpMo(CO)$_3$Cl is very unstable in atmospheric conditions. It either gets decomposed or dimerizes to give carbonyl dimer or oxo-dimer.



...2.7

The transition metal alkynyl complex has been prepared from corresponding chloride complex under mild conditions by the direct reaction of acetylenes with metal halides in the presence of catalytic amounts of copper (I) iodide in diethyl amine.



...2.8

Initially copper iodide coordinates with diethyl amine to form Cu amine complex which facilates the abstraction of proton from acetylene using base by SN^2 mechanism thus generating Cu-acetylene. There exists coordination between copper iodine and the base diethyl amine to obtain a complex. This insitu generated ylide complex act as a catalyst for Sonogashira coupling. This Cu-acetylide complex reacts with Mo chloride complex liberating CuCl with formation of Mo-C bond of Mo-acetylide complex by Sonogashira coupling (eq^n 2.8).

2.3.1 Characterization of CpMo(CO)$_3$(-C≡CPh) 1

Complexes **1, 2** and **3** were characterized by various spectroscopic techniques. The FT-IR spectrum of CpMo(CO$_3$)(C≡CPh) shows strong CO vibration bands at 1940, 1980 and 2038 cm^{-1} and C-C stretching vibration band of Cp ring at 2958 cm^{-1}. IR band at 2109 cm^{-1} is due to C≡C stretching. In the ^{1}HNMR spectrum peak at 5.5 ppm (singlet) is due to aromatic protons of cyclopentadiene and multiplate at 7.15-7.38 ppm is due to aromatic phenyl ring protons. In ^{13}C NMR peak at 87.85 ppm is due to the Cp carbon. Peaks at 126.01, 127.0, 129.39, 130.8, 130.87 ppm are due to the aromatic phenyl ring carbons and peaks at 222.0, 238.8 ppm are due to metal carbonyl.

Single crystal X-ray diffraction analysis of 1

Crystals of compound **1** were grown from acetonitrile layered with hexane at 298 K. The structure of Mo acetylide complex 1 was ellucited by the single crystal X-ray diffraction analysis. ORTEP diagram of **1** is shown in Fig 2.3.

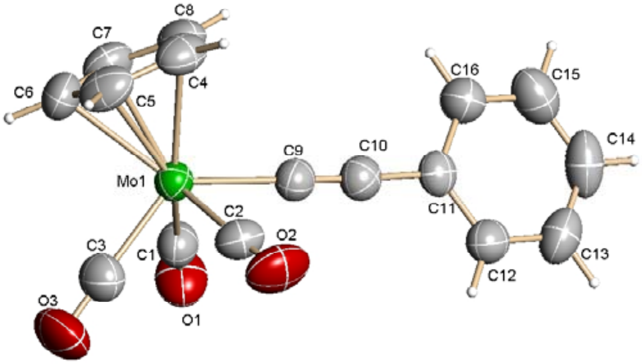


Figure 2.3: ORTEP diagram of the complex **1**. Ellipsoids are drawn at 40% probability.

Packing of the molecules in unit cell is shown in Fig 2.4b. The two molecules came close and packed in a zig-zag manner when viewed down “a”-axis. Compound a initially forms a dimer by intramolecular C-H….H hydrogen bonding and intramolecular C-H….H hydrogen bonding in the packing of the molecules when viewed down “a”-axis (Figure 2.4 b).

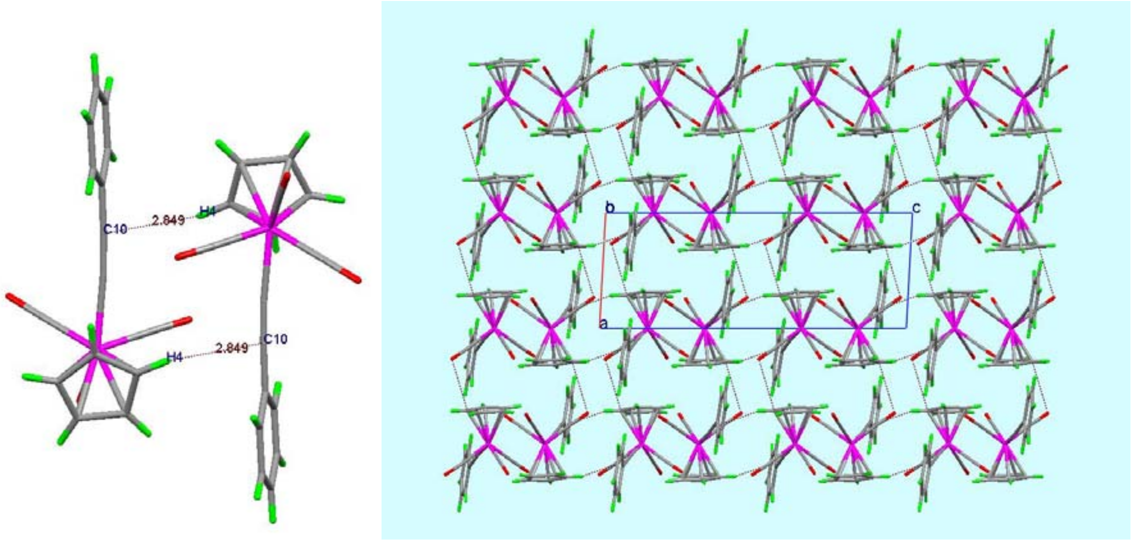


Figure 2.4: (a) Intra and intermolecular hydrogen bonding in a, (b) packing of a, in a zig-zag manner when viewed down “a”-axis.

2.3.2 Characterization of CpMo(CO)$_3$(-C≡C(C$_6$H$_4$)CF$_3$) 2

For complex **2**, the FT-IR spectrum of CpMo(CO$_3$) (C≡CC$_6$H$_4$CF$_3$) shows strong CO vibration bands at 1942, 1980 and 2036 cm^{-1} and C-C stretching vibration band of Cp ring at 2958 cm^{-1}. IR band at 2101 cm^{-1} is due to C≡C stretching.

In the ^{1}HNMR spectrum peak at 5.58 ppm (singlet) is due to aromatic protons of cyclopentadiene and multiplate at 7.35-7.49 ppm is due to aromatic phenyl protons. In ^{13}CNMR peak at 93.3 ppm is due to the Cp carbon. Peaks at 125.22, 128.12, 131.23 ppm are due to the phenyl carbons and peaks at 222.4, 238.78 ppm are due to metal carbonyl.

Single crystal X-ray diffraction analysis of 2

The structure of complex **2** was solved by the single crystal X-ray diffraction analysis. The ORTEP diagram of **2** is shown in Fig. 2.5. Crystal belongs to monoclinic with two symmetric in asymmetric unit and CF$_3$ group of one of the molecule is disordered and hence this group is refined isotropically and rest of the molecule is refind anisotropically (Fig. 2.6).

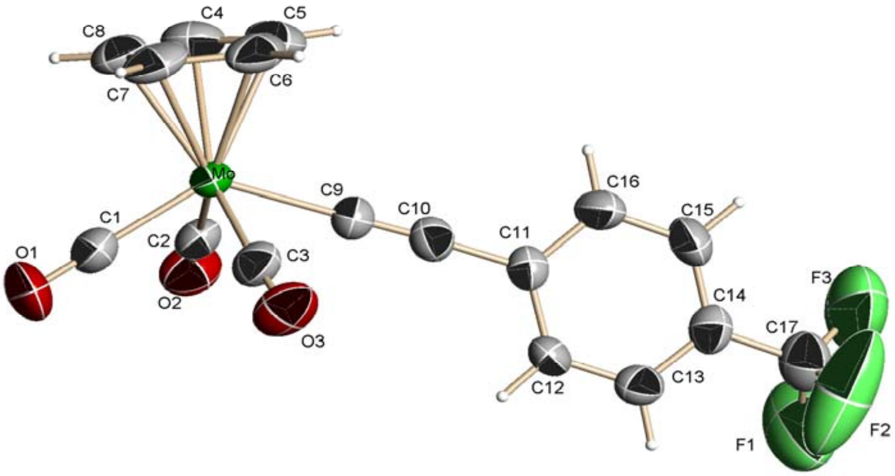


Figure 2.5: ORTEP diagram of the compound 2. Ellipsoids are drawn at 40% probability.

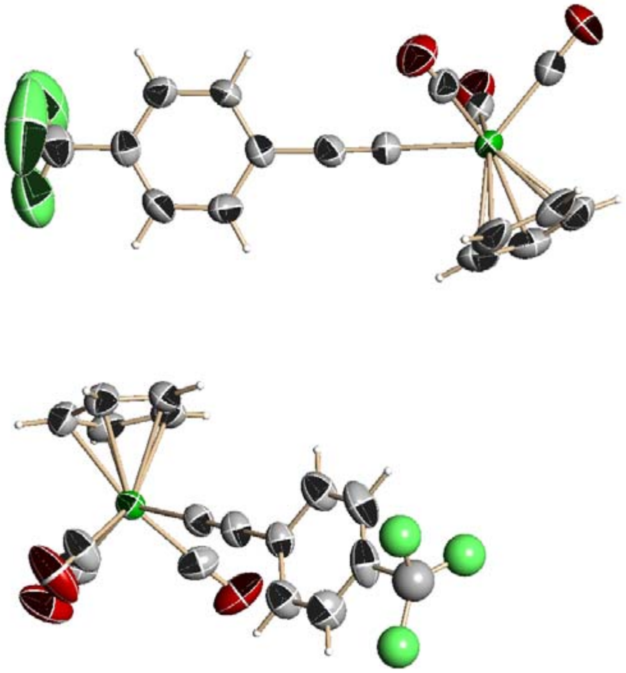


Figure 2.6: ORTEP diagram of the compound **2**. Ellipsoids are drawn at 40% probability.

Packing of the molecule in unit cell is shown in Fig 2.7. The cyclopentadienyl moiety of two symmetry related molecules face opposite to each other when viewed along a-axis. The two symmetry related molecules are packed alternatively in a zigzag manner when viewed down b axis.

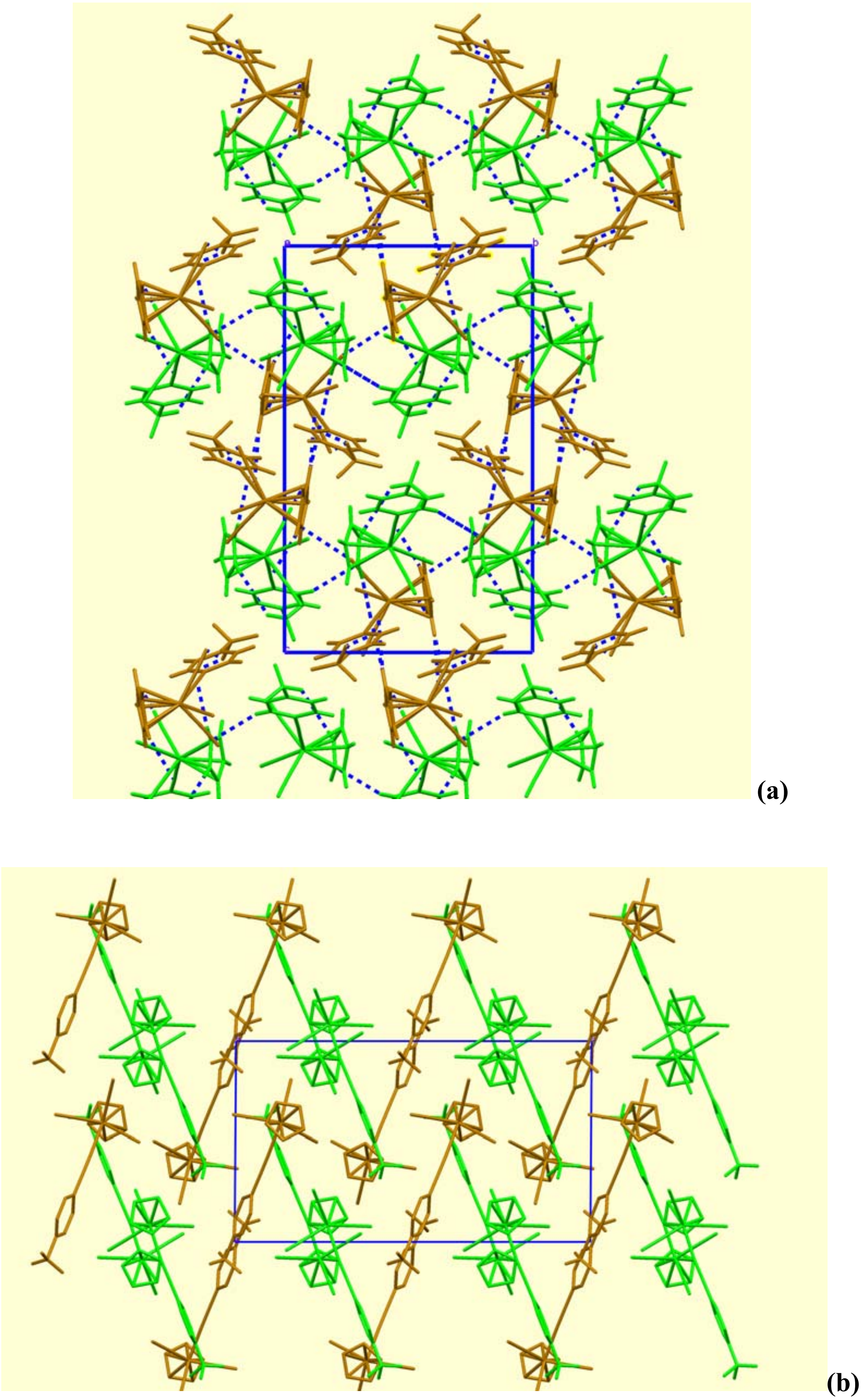


Figure 2.7: (a) Complex 2 down A, (b) Complex 2 down B

Table 2.1. Selected bond lengths [Å] for **1** and **2**

Bond lengths	Complex **1**	Complex **2**	Complex **2**a*
Mo(1)-C(3)	1.980(6)	2.007(6)	1.990(6)
Mo(1)-C(4)	2.292(5)	2.344(7)	2.302(5)
O(2)-C(2)	1.127(6)	1.129(7)	1.137(7)
C(4)-C(5)	1.387(7)	1.376(11	1.387(8)
C(4)-C(8)	1.393(7)	1.385(10)	1.413(8)
C(5)-C(6)	1.401(7)	1.386(11)	1.391(8)

* Second molecule in asymmetric unit of **2**

Table 2.2. Selected bond angles [°] for **1** and **2**

Bond lengths	Complex **1**	Complex **2**	Complex **2a***
C(3)-Mo(1)-C(1)	77.3(2)	78.9(3)	78.5(3)
C(3)-Mo(1)-C(9)	129.1(2)	72.2(2)	74.0(2)
C(3)-Mo(1)-C(5)	96.4(2)	122.5(3)	154.2(3)
C(9)-Mo(1)-C(5)	130.9(2)	82.3(3)	105.2(2)
C(9)-Mo(1)-C(4)	95.78(19)	104.6(3)	139.0(2)
C(5)-Mo(1)-C(6)	35.58(19)	34.7(3)	34.6(2)
C(4)-C(5)-C(6)	107.9(5)	109.5(8)	107.9(5)
C(7)-C(6)-Mo(1)	74.3(3)	71.9(3)	72.2(3)
C(9)-C(10)-C(11)	176.9(5)	177.7(6)	179.5(6)
C(12)-C(11)-C(16)	117.6(4)	117.9(5)	117.1(5)

* Second molecule in asymmetric unit of **2**

The overlap of Mo-C-C in two symmetric related molecules of complex **2** shows that the phenyl rings are oriented at 45 ^{o} Fig. 2.8.

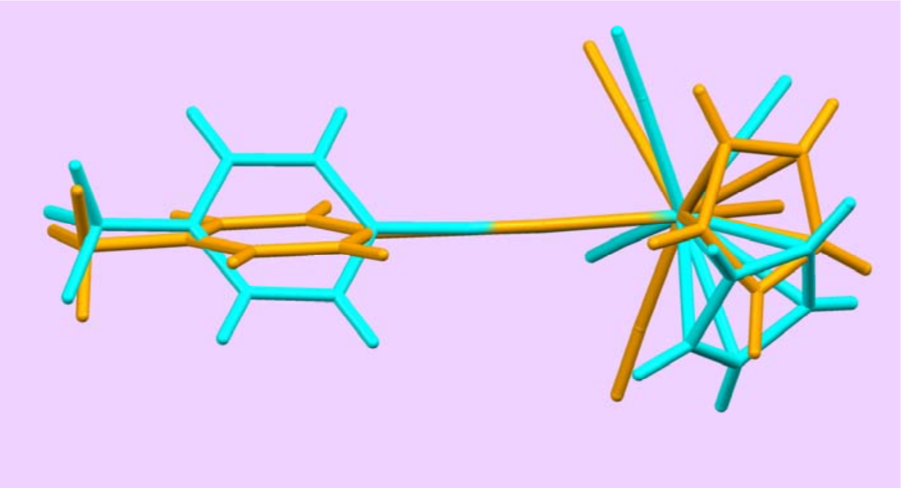


Figure 2.8: Two molecules of complex **2**

Wlile the simililar overlap of molecule complex **1** and **2** are overlaped with each other (Fig. 2.9) there is complete inversion of cyclopentadiene orientation. This could be due to the electron withdrawing nature of fluorine.

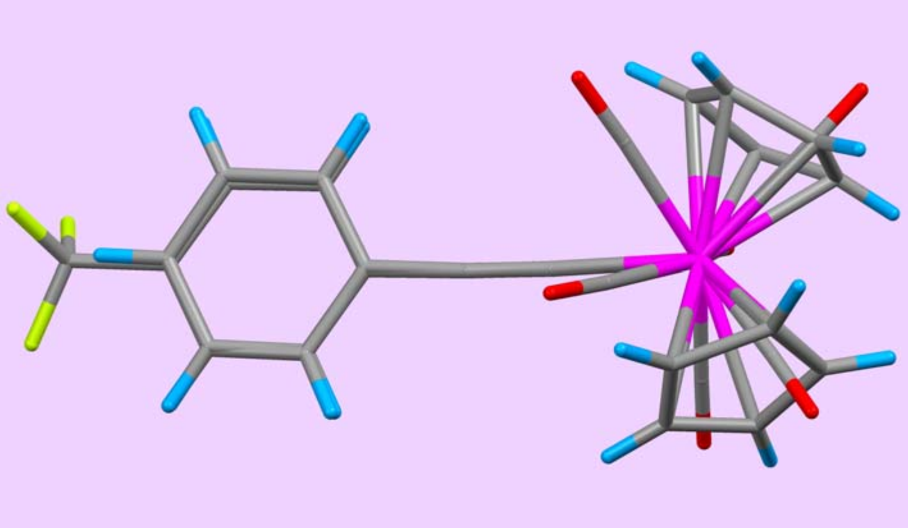


Figure 2.9: Complex **1** and **2** overlap

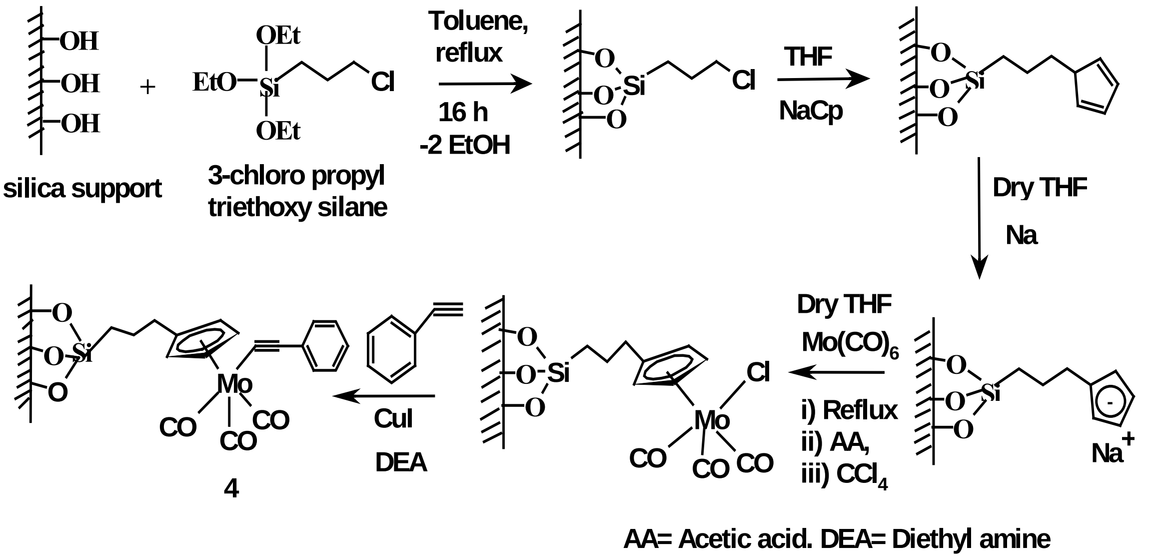
2.3.3 Characterization of CpMo(CO)$_3$(-C≡C-C$_6$H$_4$-CH$_3$) 3

FT-IR spectrum of complex **3**, CpMoCO$_3$C≡C(C$_6$H$_4$CH$_3$) shows strong CO vibrations band at 1942, 1980 and 2036 cm^{-1} and C-C stretching vibration band of Cp ring at 2958 cm^{-1}. IR band at 2106 cm^{-1} is due to C≡C stretching. In the ^{1}HNMR spectrum peak at 2.23 ppm (singlet) is for methyl proton, peak at 5.56 ppm (singlet) is due to aromatic protons of cyclopentadiene and multiplate at 7.0-7.23 ppm is for phenyl proton . In ^{13}C NMR peak at 90.4 ppm is due to the Cp carbon. Peaks at 127.8, 129.1, 128.5, 129.9, 131.2 ppm are due to the aromatic phenyl ring carbons and peaks at 222.0, 238.8 ppm is due to metal carbonyl.

Attempts were made to grow single crystal of complex **3** by varying the conditions. However the crystal of X-rays quality were not obtained.

2.3.4 Heterogenization of cyclopentadienyl molybdenum acetylide complexes 1 on silica

The cyclopentadienyl molybdenum acetylide complex was immobilized on mesoporous silica using ligand immobilization approaches. The ligand immobilization was carried out by literature procedure for η^5-CpMo(CO)$_3$R complexes with a triethoxysilane coupling group. (Scheme 2.4) [35].



Scheme 2.4: Heterogenization of cyclopentadienyl molybdenum acetylide complexes on silica (**4**)

The immobilized complex **4** was confirmed by FTIR and NMR. The Fig 2.10a depicts the IR spectrum of heterogenized Mo chloride complex and Fig 2.10b Mo-acetylide complex. The IR bands at 1206, 1060, and 794 cm^{-1} in Fig. 2.10a are attributed to stretching vibrations of the mesoporous framework Si-O-Si. The band around 960 cm^{-1} is assigned to a vibration mode of the silanol (*Si-O*H) groups in the mesoporous channels

[42]. The IR spectrum (2.10a) shows bands around 1580 (aryl) and two bands around 2929 and 2867 cm^{-1} due to C-H stretching vibrations, of CH_2 groups. Bands around 2016 and 1956 cm^{-1} can be assigned to terminal carbonyl (CO) vibrations of the grafted compound. Further bonds in the range of 2949 and 2853 cm^{-1} are due to C-H stretching vibrations of Cp ligand. In the Fig.2.9b the C≡C stretching vibration was observed at 2106 cm^{-1}, which confirms the presence of acetylide group.

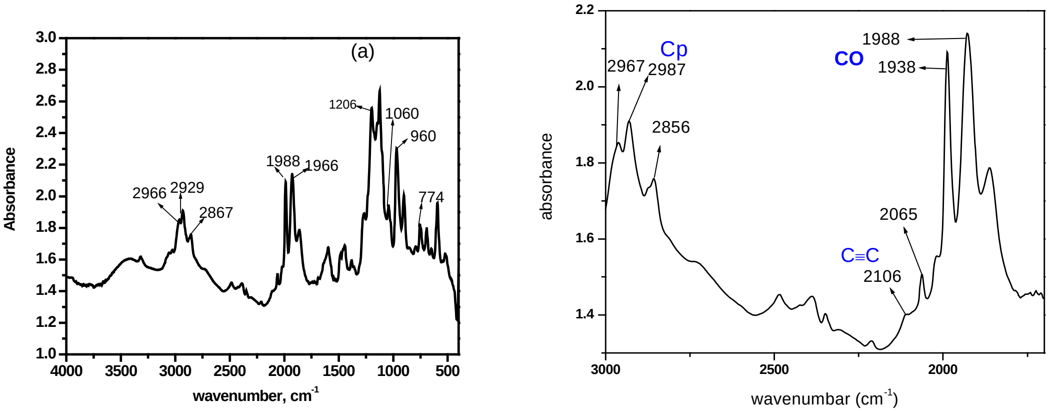


Figure 2.10: FTIR spectrum of (a) cyclopentadienyl molybdenum chloride on silica (b) cyclopentadienyl molybdenum acetylide on silica

The heterogenized complex **4** was analyzed by ^{29}Si MAS NMR. The parent SiO_2 exhibits two broad elaborate resonances in the ^{29}Si CP MAS NMR spectrum at δ = -112.8 and -102.8 ppm, assigned to Q^4 and Q^3 species of the silica framework, respectively [Qn = $Si(OSi)_n(OH)_{4-n}$] [43]. A weak shoulder is also observed at δ = -94.5 ppm for the Q^2 species. As expected, the silyated and grafted samples show nearly identical ^{29}Si CP MAS NMR signals (Fig. 2.11), since the chemical environment of the Si atoms has not changed drastically during the grafting process. The ^{29}Si CPMAS NMR spectrum also exhibit three signals at δ= -49.8, -57.9 and -68.0 ppm assigned to T_1, T_2 and T_3 organosilica species, respectively [Tm = $RSi(OSi)m(OR)_{3-m}$]. A possible reason for the lower Q^3/Q^4 values might be the decrease in population of the free silanol groups of the Q^3 species due to the linkage arising from anchoring the silanol groups (of the Q^3 species) present in the materials.

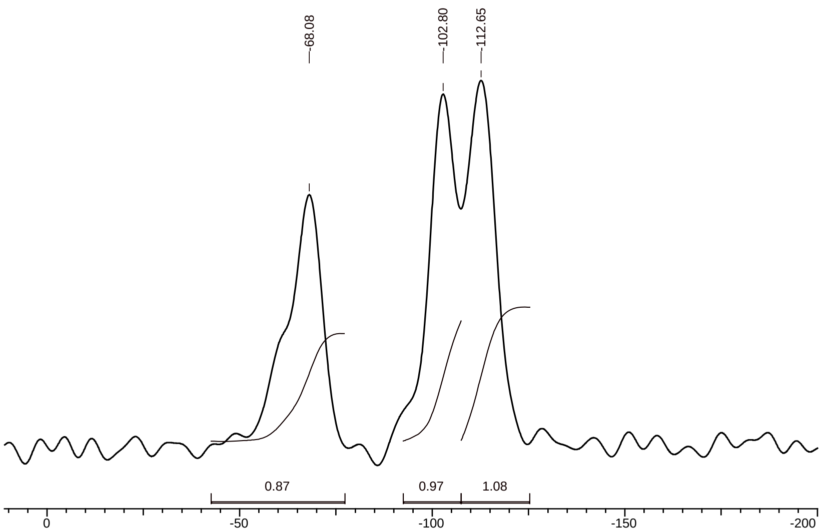


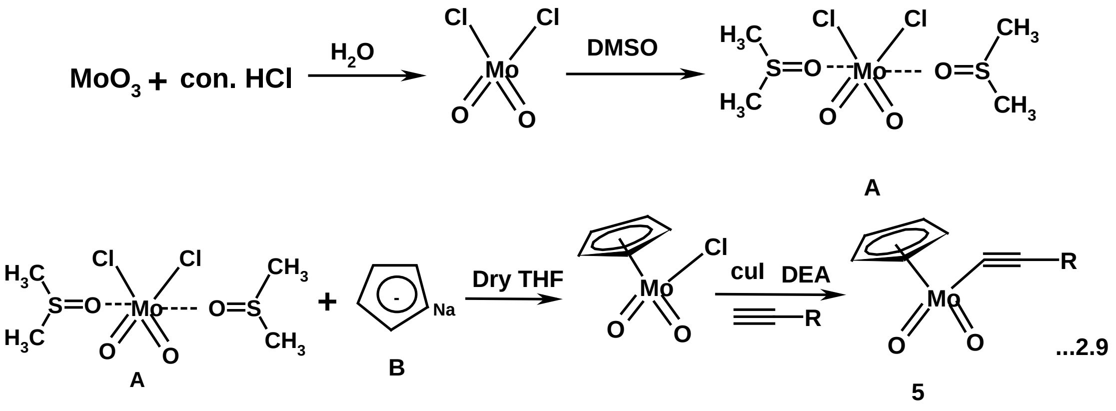
Figure 2.11: ^{29}Si NMR of heterogenized catalyst **4**

2.3.5 Preparation of the cyclopentadienyl molybdenum dioxo phenyl acetylide complex 5

Generally organometallic complexes are prepared from corresponding carbonyl precursor. Molybdenum acetylide complex (**1**) was also prepared from $Mo(CO)_6$ which after multistep synthesis gave complex **1**. As it is multistep synthesis to be carried out under inert atmosphere the yield are relatively poor. The overall yield of the final product is less as well as tedious workup procedure is involved. Secondly the cost of $Mo(CO)_6$ is very high. Hence the objective of this work is to develop a very simple procedure for preparation of Mo acetylide dioxo complex from a cheaply available precursor MoO_3. This new procedure will reduce the number of steps in the synthesis of final complex.

2.3.6 Preparation of the $MoO_2Cl_2(DMSO)_2$

MoO_2Cl_2 complex was prepared from molybdenum oxide by literature method by treating MoO_3 with conc. hydrochloric acid [44]. As MoO_2Cl_2 is not very stable, it is crystallized as its DMSO adduct (eq^n. 2.9) by addition of DMSO to MoO_2Cl_2, which can easily be obtained in pure form. $MoO_2Cl_2(DMSO)_2$ reacts with freshly prepared NaCp giving $CpMoO_2Cl$ which was further treated with phenyl acetylene without isolation for further Sonogashira coupling. Using this simple method very high yield of $CpMo(O)_2(C{\equiv}CPh)$ (5) was obtained.



...2.9

Fig. 2.12 shows the FTIR spectrum of dioxo cyclopendinyl molybdenum acetylide complex **5**. The IR band at 950-900 cm^{-1} is assigned to M=O. Molybdenum (VI) complexes with the *cis*-dioxo unit typically show two very strong IR bands in this range indicating the presence of a Mo=O terminal bond [45]. The symmetric and asymmetric stretching vibrations of MoO_2 are observed at 950 and 900 cm^{-1} respectively. Broad low intensity band centered at 2109 cm^{-1} is assigned to M(C≡C). The bands due to C–H stretching vibrations of the Cp ring were observed in the range 2975, 2910, 2836 cm^{-1} and the C–C stretching vibrations of the phenyl ring were observed at 1458 and 1385 cm^{-1}.

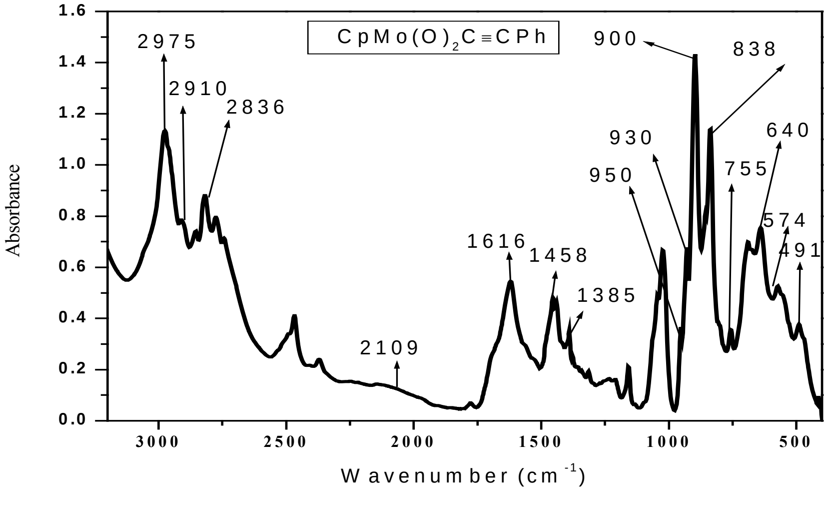
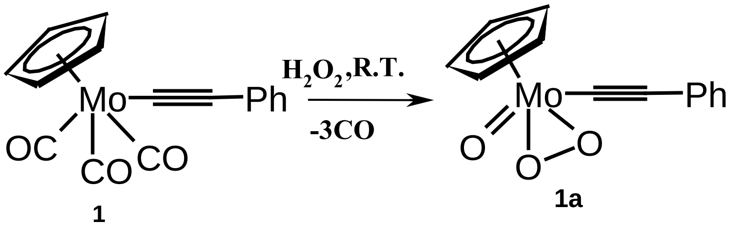


Figure 2.12: FTIR spectrum of dioxo cyclopendinyl molybdenum acetylide complex **5**

2.3.7 Characterization of catalytically active species of 1

To determine the structure of catalytically active species, H_2O_2 was added to alcoholic solution of **1**. Liberation of carbon monoxide gas was observed as effervesces [46] and resultant species (**1a**) was extensively characterized using different spectroscopic techniques.



1 **1a**

Scheme 2.5: Cyclopentadienyl molybdenum acetylide oxo-peroxo species

The FTIR spectrum of the concentrated solution of **1a** is shown in Fig. 2.13. The IR band at 953 cm^{-1} indicates the presence of a Mo=O terminal bond. The band at 858 cm^{-1} corresponds to the O–O stretching vibration of the peroxo species. The weak bands at 664 and 577 cm^{-1} are assigned to the Mo–O_2 (peroxo) asymmetric and symmetric stretching vibrations, respectively.

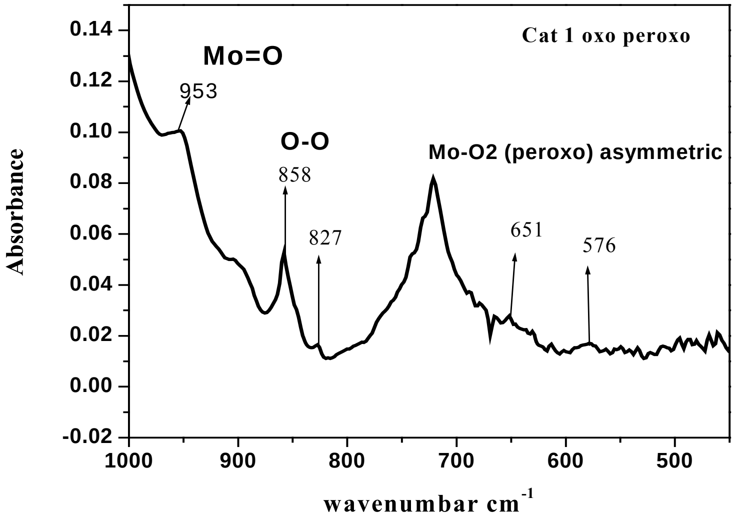


Figure 2.13: FTIR spectrum of cyclopentadienyl molybdenum acetylide oxo-peroxo species

The IR positions for the Mo oxo and peroxo moieties are in good agreement with the literature reports for various Mo oxo peroxo complexes. The acetylide moiety remained intact even after the addition of H_2O_2, as confirmed by broad low intensity band centered at 2100 cm^{-1} assigned to M(C≡C). The bands due to C–H stretching vibrations of the phenyl ring were observed in the range 2854–2955 cm^{-1} and the C≡C stretching vibrations of the ring were observed at 1464 and 1377 cm^{-1}. The bands due to the carbonyl stretching vibrations (1940, 2031 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 acetylide moiety attached to the Mo center.

UV-Vis measurements were carried out with *t*-butanol as reference. The Fig. 2.14 shows the spectrum of catalyst **1** after addition of hydrogen peroxide where two intense absorption peaks at λ_{max} 233 and 315 nm are observed, which confirms the formation of molybdenum peroxo species.

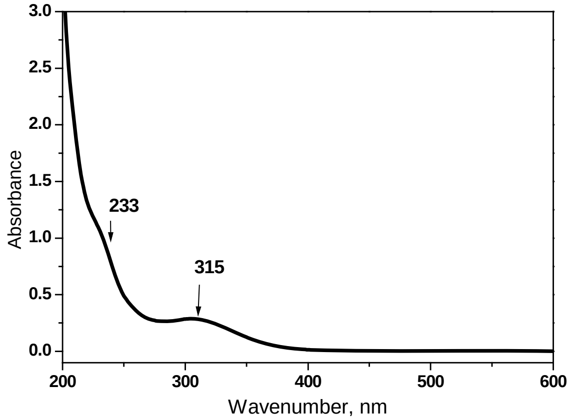


Figure 2.14: UV-vis the spectrum of catalyst **1** after addition of hydrogen peroxide

2.4 Confirmation of formation of oxo-peroxo species of 5

The formation of oxo peroxo of complex **5** was confirmed by UV-vis and FTIR spectroscopy. The FTIR spectrum of the concentrated solution of **5a** (after addition of H_2O_2 to **5**) is shown in Fig. 2.15a. The IR band at 951cm^{-1} indicates the presence of a Mo=O terminal bond. The band at 848 cm^{-1} corresponds to the O–O stretching vibration of the peroxo species. The weak bands at 748 cm^{-1} can be assigned to the Mo–O_2 (peroxo) asymmetric and symmetric stretching vibrations, respectively.

The UV spectrum of catalyst **5** after addition of hydrogen peroxide (Fig. 2.15b) shows two broad absorptions at 219 and 326 nm, which confirms the formation of molybdenum oxo-peroxo species.

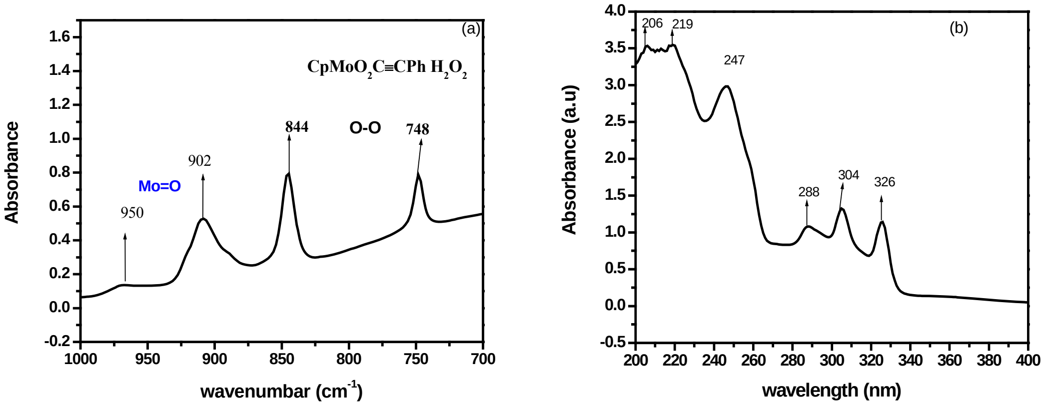


Figure 2.15: (a) FTIR and (b) UV-Vis of **5a** of H_2O_2

2.5 Summary and conclusions

Different cyclopentadienyl molybdenum acetylide complexes were successfully prepared and characterized by various spectroscopic techniques as well as single crystal X-ray diffraction analysis. These complexes are very stable and can be stored in air for longer period without decomposition unlike corresponding chloride complex. The catalytically active species formed after addition of H_2O_2 was extensively characterized and shown to be Mo oxo-peroxo acetylide complex. Complex **1** was heterogenized on mesoporous silica and well characterized by various spectroscopic techniques. A very simple and efficient route for preparation of cyclopentadienyl molybdenum dioxo acetylide complex from MoO_3 has been successfully developed.

2.6 Reference

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Chapter-3

Selective cis- dihydroxylation of alkenes using a molybdenum acetylide catalyst

3. Selective *cis*- dihydroxylation of alkenes using a molybdenum acetylide catalyst

Abstract: This chapter discuss about the cis-dihydroxylation of alkenes using molybdenum acetylide complex $CpMo(CO)_3(C\equiv CPh)$ *(**1**) and hydrogen peroxide as an efficient and environmentally benign oxidant. In case of cyclohexene, very high conversion (95%) and selectivity (86%) for cis-dihydroxylated product has been achieved using* H_2O_2 *as an oxidant and t-butanol as a solvent. cis-Dihydroxylation of other substrates like styrene, α-methyl styrene, limonene and cyclopentene has also been carried out with very high selectivity for diol. The catalyst and intermediate species have been characterized using FT-IR, UV–Vis spectral analysis and XPS studies as well as cyclic voltametric studies. These studies suggest that molybdenum oxo–peroxo complex is the catalytically active species. The intermediate blue complex when characterized by ESI MS suggested the formation of dimeric molybdenum complex and XPS as well as cyclic voltametric studies confirm the presence of mixed valence Mo (V) and Mo (VI) in the intermediate blue complex. Based on the characterization results possible mechanism for dihydroxylation is proposed. Interestingly, even though the catalyst is homogeneous, it could be recovered quantitatively by extraction in aqueous phase and recycled five times without any appreciable loss in cyclohexene conversion and selectivity for cis-1, 2-cyclohexanediol.*

3.1 Introduction:

Oxidation reactions play an important role in organic synthesis and currently there is a demand for more selective and efficient oxidation methods [1]. Pressure from society has placed restrictions on industrial oxidation technology, with emphasis on the need for sustainable and environmentally friendly processes. Reasons for interest in oxidation are the necessity for functionalization of alkenes; understanding reactions of biological importance and the need for selective oxidation for the preparation of compounds with a specific spatial structure. The transition metal complexes seem to fulfill some of these requirements. Today there is an increasing demand for use of oxidants such as molecular oxygen and hydrogen peroxide, which are environmental friendly and do not generate any hydrocarbon waste. Both these oxidants fulfill the requirement of "green chemistry" [2]. Many different systems are available that can utilize a variety of oxygen sources for these oxidation reactions. The oxidation of alkenes to epoxides, aldehydes, ketones and glycols is a growing part of homogeneous catalysis with direct industrial applications [3].

1,2-Dihydroxy compounds are important intermediates in the synthesis of different pharmaceuticals such as antagonists of central and peripheral dopamine receptors [4], fragrance, [5], cosmetics [6], photographic plates [7], lubricants [8], and as additives [9], in various synthetic reactions.

Several homogeneous transition-metal-catalyzed oxidation reactions have been reported to display high selectivity for epoxidation of alkenes. Generally 1, 2-diols are prepared either by acid [10] catalyzed hydrolysis of epoxides in the presence of metal oxides, transition metal complexes [11], epoxides hydrolase enzymes [12], or dihydroxylation of olefins with potassium permanganate [13]. However, considering atom efficiency, the performance of these reagents is very poor. Furthermore, over-oxidation with consequent cleavage of C=C bonds in certain cases, poor selectivity, long reaction times [14] and use of toxic solvents are some of the limitations of above mentioned processes. Therefore, the use of hydrogen peroxide for 1, 2-dihydroxylation of olefins would provides a better solution [15].

Osmium tetroxide is the only efficient catalyst known till date for dihydroxylation, especially Sharpless asymmetric dihydroxylation of enantiomerically pure product. Sharpless has achieved highest enantioselectivity by employing cinchona alkoloid ligands. OsO_4 catalyzed dihydroxylation needs co-oxidants like *N*-methyl morpholine *N*-oxide (NMO) [16] or $K_3Fe(CN)_6$ [17] so as to facilitate use of OsO_4 in catalytic amounts as against stoichiometric amounts in traditional dihydroxylation reactions. High cost, toxicity and possible contamination of the osmium catalyst in the products prohibit its use in industry. To overcome these drawbacks, complexation of osmium with ligands, which are heterogenized on soluble and insoluble polymers, silica gel, ion exchange or dendrimer support has been attempted by several groups [18]. Another disadvantage of osmium system is the need of various co-oxidants to oxidize Os (VI) Os back to Os(VIII). Hydrogen peroxide has also been used as terminal oxidant for recycle of Os (VI) to Os(VIII) along with NMO and biomimetic flavin [19] zeolite catalysts [20]. Beller et. al. has used molecular oxygen or air as stoichiometric oxidants for osmium catalyzed dihydroxylation with good to excellent chemo selectivity under optimized pH conditions. For α-methyl styrene as model substrate, under slightly elevated oxygen pressure very high yields of diols are obtained even at very low catalyst concentrations [21]. In order to overcome the problem of toxicity, cost and also to have environmentally benign process for dihydroxylation of olefins, there is a need to search for an alternative metal catalyst system for the production of vicinal diols. There are few reports on Os/Re [22], Os/Pd and Os/W [23] catalytic systems for dihydroxylation, however addition of co-oxidant and/or addition of various carboxylic acids for maintaining acidic medium is essential for dihydroxylation. Feringa et. al. [24] has used manganese complexes as catalysts for dihydroxylation using hydrogen peroxide as oxidant. However, the use of various carboxylic acids as co-catalysts is essential in this case and epoxide was obtained as a major product along with *cis*-diol in many cases. Warwel et. al. [25] have reported oxidation of higher olefins with hydrogen peroxide in dioxane solvent forming vicinal diols using Re_2O_7 as catalyst. However selectively *trans*-diol was obtained only in the case of cyclohexene. Bhaumik et. al. [26] has used Co (III) containing mesoporous silica as catalyst and H_2O_2, TBHP or oxygen as oxidant for dihydroxylation of cyclohexene. However, the selectivity for *trans*-diol is much higher than *cis*-diol. Noyori et. al. [27] have reported oxidation of various olefins including cyclohexene to dicarboxylic acids with H_2O_2 using sodium tungstate as catalyst and quaternary ammonium hydrogensulphate as phase transfer catalyst. This provides very efficient route for adipic acid synthesis. Oldenburg and Que Jr. [28] have used nonheme iron complexes for *cis*-dihydroxylation of olefins using ten equivalents hydrogen peroxide with respect to catalyst, due to which turnover numbers are extremely low. Beller et. al. [29] has shown the efficient use of $FeCl_3$ with 2, 6-pyridine dicarboxylic acid and various *N*-containing ligands for epoxidation of olefins using hydrogen peroxide as an oxidant. They have also extended this to asymmetric epoxidation using chiral *N*-containing ligands with excellent yields and *ee* up to 97% [30] or by reduction of α-hydroxy ketones and diketones [31].

Molybdenum has proved to be versatile for homogeneous as well as heterogeneous catalyst for variety of reactions such as oxidation/epoxidation reactions. MoO_3 on different solid supports is used for oxidation [32], nitration [33] and transesterification [34] reactions. Molybdenum is found in variety of biological enzymes. All molybdenum containing enzymes catalyze redox processes by involving one or two electron transfer per enzyme molecule and this electron transfer depends on the oxidation states of the molybdenum atoms present in the neighboring enzymes [35]. Similar kind of behavior of molybdenum is expected in complexes containing mixed valent molybdenum centers. Bhattacharya et. al. have prepared different Mo (VI) oxo–peroxo or oxo–diperoxo complexes with various ligands and successfully used these complexes for epoxidation of various olefins and oxidation of alcohols to carbonyl compounds [36]. Molybdenum carbonyl complexes with different ligands like halides [37], *N*-containing [38] and cyclopentadienyl; η^5-C_5R_5; R=H, Me, Ph [39] are mainly used for epoxidation of variety of olefins. Kuehn et. al. [40] as well as Goncalves et. al. [41] has reported use of $CpMo(CO)_3Cl$ as catalyst for olefin oxidation with very high selectivity for epoxides [42]. Tungsten acetylide complexes are reported to form oxo–peroxo complexes on treatment with H_2O_2 in acidic medium [43]. Hence similar molybdenum complexes are expected to be good oxidation catalysts. Molybdenum acetylide complexes have been extensively used for preparation of higher nuclearity mixed metal cluster [44]. However the applications of Mo-acetylide complexes for catalytic oxidation have not been explored so far. To the best of our knowledge there are no reports in the literature on use of molybdenum acetylide complex as catalyst for oxidation reaction. In the current chapter oxidation of various olefins using molybdenum acetylide complex,

$CpMo(CO)_3(C{\equiv}CPh)$; Cp = η^5-C_5H_5 (1) as a catalyst and H_2O_2 as a green oxidant has been discussed in detail.

3.2. Experimental

Cyclohexene, styrene, methyl styrene and limonene were purchased from Aldrich and used as received unless stated otherwise. Hydrogen peroxide used was 35% w/w in water. All solvents (SD Fine) were freshly distilled prior to use.

3.2.1 General procedure for *cis*-dihydroxylation using $CpMo(CO)_3(C{\equiv}CPh)$ complex 1

In a typical catalytic reaction, 50 mL two necked round bottom flask was charged with olefin (0.02 mol), 35% hydrogen peroxide (0.04 mol), 10 g solvent and catalyst **1** (0.04 mmol). The reaction mixture was heated to desired temperature and stirred till completion of the reaction. All samples were analyzed on an Agilent 6890 Gas Chromatograph. The reaction products were confirmed by GC-MS (Model GC Agilent 6890N) and GCIR Perkin Elmer Spectrum 2001. The FT-IR was recorded as nujol mull using Shimadzu 8300. The electro spray mass spectra were recorded on a MICROMASS QUATTRO II triple quadrupole mass spectrometer. The sample dissolved in water was introduced into ESI source through syringe pump at the rate of 5 µL per min. The ESI capillary was set at 3.5 kV. The spectrum was collected in 6 s scans. For each sample the spectra were recorded at a cone voltage of 30 and 80V.

3.2.2 Product isolation

Cis-1, 2 cyclohexandiol was isolated by following procedure. After completion of the reaction, the reaction mixture was cooled to room temperature and solvent was removed in vacuum. To the residue ethyl acetate and water was added and crude diol extracted in organic layer was obtained after removal of the solvent in vacuum. Diol was purified by column chromatography on silica gel using petroleum ether and ethyl acetate (90/10, v/v) as solvent system.

3.2.3 Cyclic voltametric studies

The cyclic voltametric measurements were performed using a three-electrode system comprised of platinum wires as counter and working electrodes in dichloromethane containing 0.1 M tetra butyl ammonium hexaflorophosphate as supporting electrolyte. A Pt quasi reference electrode was used to report all potentials values. Cyclic voltammograms were recorded using a CH instrument model no 400B, after purging the electrolyte with pure argon. For calibrating the quasi reference electrode, ferrocene was added to the electrolyte to make a 0.1 M solution with respect to supporting electrolyte (tetra butyl ammonium hexaflorophosphate) and cyclic voltammogram was recorded. The $E_{1/2}$ for the ferrocene/ ferrocinium redox couple was found to be 0.235 V.

3.2.4 UV–VIS spectral analysis

UV-VIS spectrum was recorded using Perkin Elmer Lambda 650 UV-VIS spectrometer. The spectra were recorded at 20°C as a *t*-BuOH solution with *t*-BuOH as reference in the range 200 to 800 nm (at the concentration of 10^{-5} M).

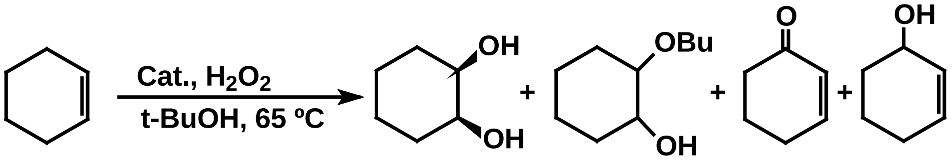
3.2.5 XPS experiments

XPS experiments were performed in a vacuum generator Escalab 220 XL spectrometer using a non-monochromatic Al-Kα (hv=1486.6 eV) operated at 15kV and 20 mA. The pressure in the sample chamber was maintained at 10^{-9} mbar or lower during the analysis. All the binding energies were with reference to carbon (C1s) at 285 eV. Curve fitting of the Mo (3d) peaks was done using VG Eclipse Software.

3.3 Results and discussion

3.3.1 Screening of various molybdenum complexes for cyclohexene oxidation

The oxidation of cyclohexene was carried out using various molybdenum complexes and hydrogen peroxide as oxidant. The possible oxidation products of cyclohexene are shown in Scheme 3.1 and results are summarized in Table 3.1.



Scheme 3.1: Oxidation product of cyclohexene

Table 3.1. Oxidation of cyclohexene with various molybdenum complexes

The results depict that, in absence of catalyst reaction proceeds very slow with very low conversion of cyclohexene (~5 %) in 48 h (Table 3.1 entry 1) with 100 % selectivity for cyclohexenol, which is an auto oxidation via radical mechanism in presence of oxidant. When oxidation property of $Mo(CO)_6$ was tested for this reaction, it showed high cyclohexene conversion (Table 3.1, entry 2) but with 100% selectivity for allylic oxidation product, cyclohexenone. Further cyclopentadienyl molybdenum chloride complex, $CpMo(CO)_3Cl$ gave very high conversion of cyclohexene with high selectivity for allylic oxidation products, cyclohexenone cyclohexenol, however this complex is unstable in nature and it decomposes as the reaction progresses [45]. When cyclohexene was treated with H_2O_2 in *t*-BuOH solvent in presence of catalytic amount of Mo–acetylide complex **1** (1/substrate ratio 1/500), *cis*-1, 2-cyclohexane diol was obtained as the major product along with 2-alkoxy cyclohexanol, cyclohexenol and cyclohexenone as minor products. Monoetherification of diol due to excess of alcohol used as solvent led to the formation of 2-alkoxy cyclohexanol. Cyclohexenol and cyclohexenone are obtained as a result of allylic oxidation (Table 3.1 entry 5). Further substitutions on phenyl ring of acetylide ligand with electron withdrawing CF_3 (**2**) or electron donating CH_3 (**3**) group in complex **1** showed marginally less conversion as well as marginally less selectivity for diol. Among all the Mo complexes studied for oxidation of cyclohexene the catalytic activity of **1** is superior to the others in terms of conversion as well as diol selectivity, hence it was used for further studies for *cis*-dihydroxylation.

Table 3.1. Oxidation of cyclohexene with various molybdenum complexes[a]

Entry	Catalyst	Time h	Conv. %	% Selectivity			
				Diol *	Ene-ol	Ene-none	-ether
1	Blank	48	5	00	100	0	0
2	$Mo(CO)_6$	48	97	21	2	67	10
3	$CpMo(CO)_3Cl$	48	96	3	67	21	9
4	$CpMo(CO)_3$ (C≡CPh) - **1**	48	95	86	00	5	9
5	$CpMo(CO)_3$ ($C{\equiv}CC_6H_4CF_3$) **-2**	48	85	80	7	5	8
6	$CpMo(CO)_3(C{\equiv}CC_6H_4CH_3)$ **-3**	48	92	83	5	6	9

[a]**Reaction conditions:** Cyclohexene-0.02 mol; H_2O_2 (35%)- 0.04 mol; Catalyst-0.04 mmol; TOS- 48 h; Temp-65 ºC, **cis*-1, 2-cyclohexanediol was confirmed by its melting point (98 ºC). NMR ($CDCl_3$) ppm: 2.63 (2H, CHO***H***), 3.35 (2H, C*H*O**H**), 1.97 (2H, HC$\boldsymbol{H}_e$ CHO**H**), 1.71 (2H, HC$\boldsymbol{H}_a$ CHO**H**), 1.27 (4H, C$H_2$$CH_2$CHO**H**).

3.3.2 The role of the solvents in oxidation of cyclohexene

The effect of solvent on cyclohexene conversion and diol selectivity was studied using different solvents and the results are presented in Table 3.2. In case of lower alcohols like methanol, etherification was prominent leading to decrease in diol selectivity (entry 2). When bulky alcohol like *t*-BuOH was used (entry 3), selectivity for ether decreased drastically leading to very high selectivity for vicinal diol. In case of other solvents (entries 1 and 5-7) conversion as well as selectivity was less compared to alcohol. In all the cases the turn over number (TON= moles of product formed / moles of **1**) in one cycle for *cis*-diol was high. Especially with *t*-BuOH as solvent (entry 3) very high TON (**409**) was obtained showing very high efficiency of the catalyst. This shows that alcohols are preferred solvents for this system, as it forms single phase with organic substrate and aqueous hydrogen peroxide.

Table 3.2. Effect of solvent on conversion and selectivity[a]

Entry	Solvent	Conv. %	Selectivity, %				TON
			Cis-Diol	Ene-ol	Ene-one	Other	*cis*-diol
1	CH_3CN	67	60	17	23	0	201
2	MeOH	91	42	4	6	48*	191
3	***t*-BuOH**	**95**	**86**	**0**	**5**	**9#**	**409**
4	CH_2Cl_2	69	68	4	19	9	235
5	$CHCl_3$	72	62	23	15	0	223
6	CCl_4	68	60	21	19	0	204

[a]**Reaction conditions:** Cyclohexene-0.02 mol; H_2O_2 (35%)-0.04 mol; **1**- 0.04 mmol; TOS- 48 h; Temp-65 ºC; * 2-methoxy cyclohexanol, # 2-butoxy cyclohexanol.

3.3.3 The effect of catalyst loading

The catalyst concentration was varied gradually from 1 mol% to 0.2 mol%.

Table 3.3. Effect of catalyst loading[a]

Entry	**1,** mol %	TOS, h	Conv. %	Selectivity, %				TON	TOF, h^{-1}
				Diol	Eneol	Enenone	Ether		
1	0.2	48	95	86	00	5	9	**409**	**8.5**
2	0.4	24	93	85	00	4	11	320	**8.5**
3	0.6	18	94	86	00	5	9	250	**8.5**
4	0.8	13	94	86	00	5.1	8.9	180	**8.6**
5	1	9	91	86	00	5.8	8.2	78	**8.6**

[a]**Reaction conditions:** Cyclohexene-0.020 mol; 35 % H_2O_2-0.04 mol; *t*-butanol-10 g; Temperature- 65 ºC.

With decrease in catalyst concentration the reaction rate decreased and hence the time for completion of the reaction increased from 9 h to 48 h, however there was no decrease in the selectivity for *cis*-diol. The results are summarized in Table 3.3.

3.3.4 Influence of temperature

The influence of temperature on cyclohexene conversion and product selectivity was examined (Table 3.4). When the reaction temperature was increased gradually from room temperature to 65 °C, the rate of the reaction increased however the product distribution changed significantly. At room temperature there was no reaction even after 48 h (entry 1). At 40 °C, only 20 % cyclohexene was converted giving up to 65 % *cis*-diol along with 35 % allylic oxidation products. On further increasing the temperature up to 65 °C, nearly complete conversion of cyclohexene occurred giving high selectivity for diol (Table 3.4 entry 3). When the temperature was further increased to 80 °C and 100 °C, the reaction was complete in less time (30 and 22 h respectively) however the selectivity for diol decreased with increase in ether formation. Hence 65 °C was used as the optimum temperature for further reactions.

Table 3.4. Temperature effect[a]

Entry	Temp °C	Conv, %	Selectivity, %			
			Diol	Ene-ol	Ene-none	Ether
1	RT	00	00	00	00	00
2	40	20	65	4	29	2
3	65	95	86	00	5	9
4	80#	100	80	00	6	14
5	100*	100	72	00	6	22

[a] **Reaction conditions:** Cyclohexene- 0.02 mol; Catalyst **1**- 0.04 mol; *t*-butanol-10 g; TOS 48 h, # 30 h, * 22 h.

3.3.5 Progress of the reaction

To study the product distribution as a function of time, the reaction was monitored as a function of time (Fig. 3.1). The results show that initial rate of the reaction is slow and the allylic oxidation product dominates. However in the later stage diol formation predominates giving overall high selectivity for *cis*-diol. Hence it can be concluded that initially there is time lag till catalytically active species is formed and this time lag is responsible for auto oxidation products i.e. allylic oxidation products.

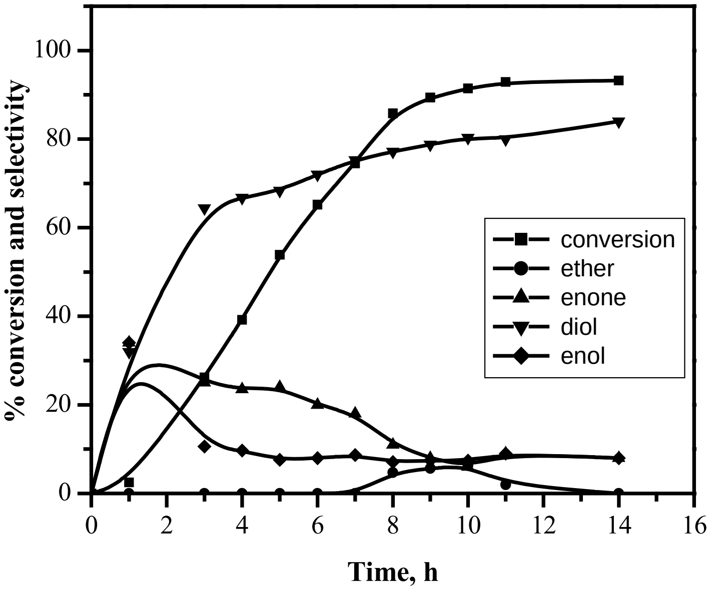


Figure 3.1: Conversion and product selectivity profile with time

3.3.6 Catalyst recycle study

In order to check the stability of the catalyst under reaction condition, fresh cyclohexene and H_2O_2 was added to the reaction mixture after completion of the reaction with 1 mol% catalyst loading. The reaction was further continued and the turn over frequency (TOF) was determined. There was no change in TOF even after five such additions of reactants (Table 3.5). After testing the stability of the catalytically active species under reaction condition, the catalyst was recycled by isolating the product in organic phase and recovering the catalyst in aqueous phase for use in the next run.

Table 3.5. Batch wise additions of substrate and oxidant without catalyst separation[a]

Cycle,[b]	TOS [c] h	Conv, %	Selectivity, %				TON	TOF
			Diol	Ene-ol	Ene-one	Ether		
0	9	91	86	00	5.6	8.4	78	**8.6**
1	18	86	85.5	00	6	7.5	147	**8.2**
2	27	83	86	00	7	7	214	**7.9**
3	36	84	84	3	6	7	282	**7.8**
4	45	92	83.3	5.1	5.6	5.8	343	**7.6**
5	54	82	84	3.5	6.5	6	413	**7.6**

[a]**Reaction conditions: 1** -0.2 mmol; Temperature-65 °C; *t*-BuOH-10 g. [b] Charge added before each cycle: Cyclohexene-0.020 mol; 35% H_2O_2-0.04 mmol; [c] Time up to each cycle.

Table 3.6. Catalyst recycles study by isolating the catalyst[a]

Recycle [a]	TOS,[b] h	Conversion, %	Diol selectivity, %	TOF, h^{-1}
0	9	92	86	**8.8**
1	9	89	85	**8.4**
2	9	86	86	**8.3**
3	9	85	85	**8.2**
4	9	83	84	**7.9**
5	9	82	83	**7.8**

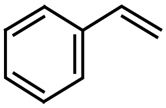
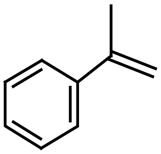
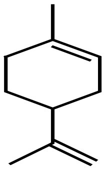
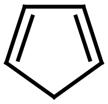
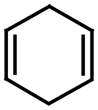
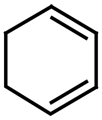
[a]**Reaction conditions: 1**-0.2 mmol, [a] Charge added before each cycle: Cyclohexene-0.02 mol; 35 % H_2O_2-0.04 mmol; t-butanol-10 g; [b] Time for each cycle separately.

The catalyst was recycled by removing the solvent in vaccum. To the residue ethyl acetate and water was added. The catalyst extracted in the aqueous phase was isolated using separating funnel. Further, the aqueous phase was concentrated to remove maximum water before next recycle. The selectivity for *cis*-diol did not decrease considerably even after five recycles (Table 3.6). The marginal decrease in the conversion can be attributed to the losses during handling of the small amount of catalyst during recycle. These results clearly show the stability of the molybdenum acetylide catalyst in the reaction media as well as its recovery and recycle without any appreciable decrease in catalytic activity and selectivity, which is rare in case of homogeneous catalysis.

3.4 Oxidation of different alkenes

In order to check the wider applicability of this catalyst to other olefins, various other olefins like styrene, α-methyl styrene, limonene and cyclopentene were tested for oxidation and the results are summarized in Table 3.7. The results for styrene show very high conversion (>90%) using hydrogen peroxide (entry 1) as well as TBHP (entry 2) with no formation of epoxide. Very high selectivity for diol is obtained with formation of benzaldehyde as minor product. Etherification of styrene diol was observed to very less extent (H_2O_2 8% and TBHP 10.8%). In case of α-methyl styrene (entry 3 and 4) though the conversion was slightly lower compared to styrene, no formation of epoxide was observed. Although, formation of diol is prominent, it is observed that with longer reaction time, the diol gets further converted to 2-phenyl propionaldehyde. The diol selectivity decreased from 73% at 5 h to 53% at 9 h with corresponding increase in the 2-phenyl propionaldehyde selectivity when H_2O_2 was used as an oxidant. Similarly, when TBHP was used as an oxidant the selectivity for diol decreased from 63 (5 h) to 45% (12 h) with corresponding increase in 2-phenyl propionaldehyde selectivity. In case of cyclopentene (entry 8) high conversion (85%) with very high selectivity (82%) for diol was obtained with low selectivity (18%) for allylic oxidation products (cyclopentenone and cyclopentenol). In this case also no epoxide formation was observed. Though in case of limonene also very high conversion was obtained with H_2O_2 (92%) as well as TBHP (86%) the number of products obtained are more. The products obtained are limonene 1, 2-diol, limonene 8, 9- diol, limonene diepoxide and limonene 1, 2-diol 8, 9-oxide. Very high selectivity for limonene 1, 2-diol (92%) was obtained when TBHP was used compared to H_2O_2 (35 %).

Table 3.7. Oxidation of olefins using catalyst **1**^{a}

Entry	Substrate	Oxidant	Time, h	Conv %	Selectivity %	
					Diol	Others
1		H_2O_2	10	95	82	8^{b}, 10^{c}
2		TBHP	14	92	73	11^{b},16^{c}
3		H_2O_2	9	90	58	42^{d}
4		TBHP	12	80	45	55^{d}
5		H_2O_2	48	92	30^{e,} 15^{f,} 17^{g}	29h 9^{i}
6		TBHP	48	86	92^{e}, 6^{g}	2^{i}
7		H_2O_2	48	65	82	18^{j}
8		H_2O_2	48	78	63	27^{k}, 10^{l}
9		H_2O_2	48	80	70	20,^{m} 10^{n}

^{a}**Reaction conditions:** Catalyst **1**-0.04 mmol; Substrate-0.02 mol; Oxidant-0.04 mol; *t*-BuOH-10 g; Temp-65 ºC; ^{b}diolether; ^{c}benzaldehyde; ^{d}2-phenyl propionaldehyde; ^{e}limonene 1, 2-diol; ^{f}limonene 8,9-diol; ^{g}limonene 1, 2-diol 8-9 oxide; ^{i}limonene diepoxide; ^{k}unidentified product; ^{j}allylic oxidation products (cyclopentenone 13 % + cyclopentenol 5%); $^{k\ m}$diether ; $^{l\ n}$ monoether.

Though in case of TBHP no epoxide was obtained, in case of H_2O_2, 29 % diepoxide was obtained. In both the cases small amount of limonene 1, 2- diol 8, 9-oxide was obtained. Above results show that in all the cases very high selectivity for diol was obtained though in some cases further etherification of diol was observed. 1, 3-Cyclohexadiene (entry 8) and 1, 5-cyclohexadiene (entry 9) oxidation also gave high conversion and about 80 % selectivity to diol. In all the cases either no or very less quantity of epoxide was formed which shows very high efficiency of the catalyst for dihydroxylation. It is also observed that with TBHP the reaction is slow compared to H_2O_2, though no considerable change in the product distribution is observed.

3.5 Reaction mechanism

To study the mechanism of *cis*-dihydroxylation of olefins using Mo-acetylide complex **1**, catalytically active species as well as one of intermediate was characterized using various spectroscopic techniques in case of cyclohexene oxidation**.**

3.5.1 FTIR analysis

To study the nature of catalytically active species, H_2O_2 was added to **1** and the resultant species was characterized by FTIR, UV-Vis and XPS. The Figure 3.2 shows the FTIR spectrum of complex **1** after addition of H_2O_2. The IR band at 953 cm^{-1} indicates the presence of a Mo=O terminal bond. The band at 858 cm^{-1} corresponds to the O–O stretching vibration of the peroxo species. The weak bands at 664 and 577 cm^{-1} can be assigned to the Mo–O_2 (peroxo) asymmetric and symmetric stretching vibrations, respectively. The IR positions for the Mo oxo and peroxo moieties are in good agreement with the literature reports for various Mo oxo peroxo complexes [46]. The acetylide moiety remained intact even after the addition of H_2O_2, as confirmed by broad low intensity band centered at 2100 cm^{-1} assigned to (C≡C). The bands due to C–H stretching vibrations of the phenyl ring were observed in the range 2854–2955 cm^{-1} and the C=C stretching vibrations of the ring were observed at 1464 and 1377 cm^{-1}. The bands due to the carbonyl stretching vibrations (1940, 2031 cm^{-1}) disappeared after the 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 acetylide moiety attached to the Mo center.

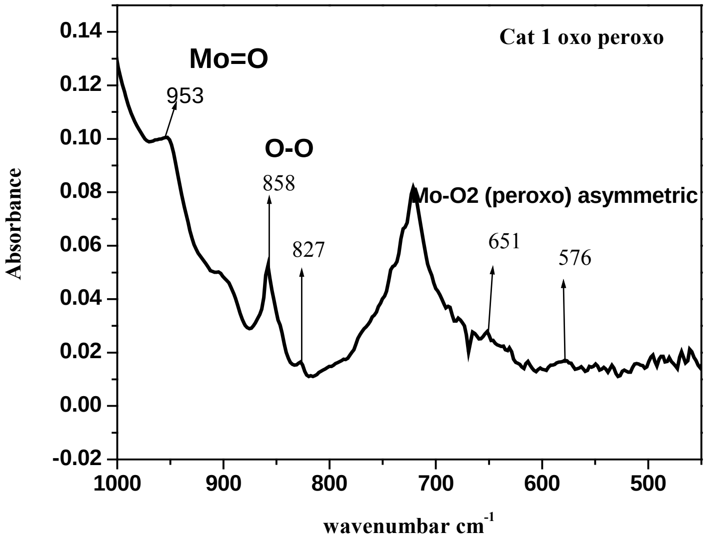


Figure 3.2: FTIR spectrum of oxo peroxo cyclopentadienyl molybdenum acetylide complex

3.5.2 UV-Vis analysis

The UV spectrum of catalyst **1** after addition of hydrogen peroxide (Fig. 3.3) shows two broad absorptions at 233 and 315 nm, which confirms the formation of molybdenum peroxo species. The UV spectrum of catalyst **1** shows absorption at λ_{max} 270 nm, with a shoulder at 285 nm and a broad band centered at 386 nm.

When the reaction of cyclohexene dihydroxylation was carried out using less than stoichiometric amount of hydrogen peroxide, the reaction stopped with formation of blue complex. The original color of the reaction mixture was faint yellow. It was observed that when further H_2O_2 was added to the same reaction mixture, the reaction continued with disappearance of the blue color. The color change of the catalyst from faint yellow to blue to again faint yellow indicates the redox behavior of molybdenum center. The blue color is characteristics of mixed valence molybdenum (Mo^{VI} and Mo^{V}), well known as molybdenum blue. Color of pure Mo (VI) species is faint yellow or brown where as the color of pure Mo (V) species is red [47]. Molybdenum blue species are referred to as compounds coming from redox process resulting in a mixture of Mo (VI) and Mo in lower oxidation state Mo(V) [48]. Further, presence of mixed valence molybdenum species was confirmed by cyclic voltammetric studies of blue complex, which showed presence of two reversible redox couples, one for Mo (V) to Mo (VI) and back to Mo (V) and other for Mo (VI) to Mo (V) and back to Mo (VI).

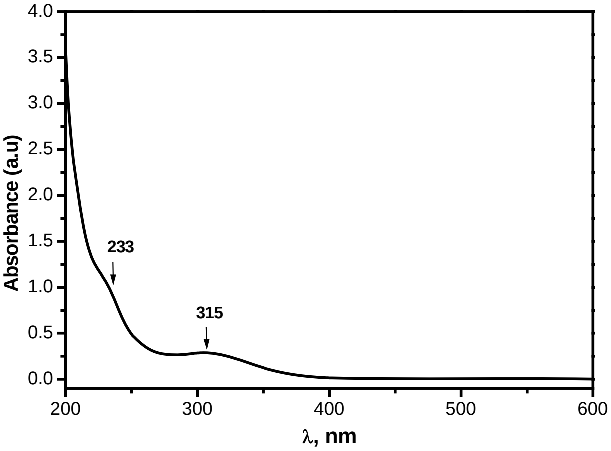


Figure 3.3: UV-Vis spectrum of catalyst **1** after addition of hydrogen peroxide

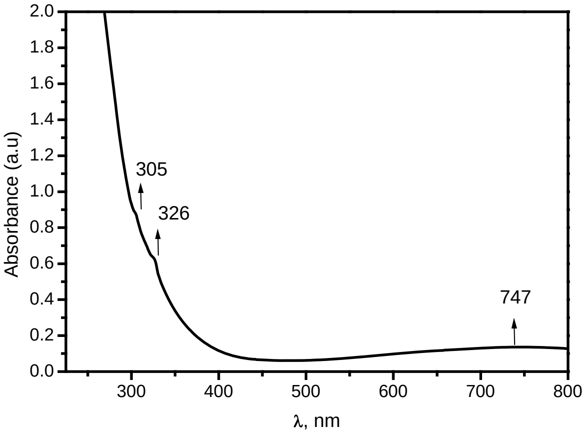


Figure 3.4: UV spectrum of blue complex

UV spectral analysis of the blue complex (Fig. 3.4) shows absorbance in the UV region at λ_{max} 221 nm and shoulder at 305 and 326 nm. This can be attributed to charge transfer associated with organic group to MoO_3 moiety. Broad absorption in visible region ~ 747 nm is responsible for the blue color of the complex. It can be due to d-d transitions involving Mo(V) and inter valence charge transfer transition (IVCT) between Mo (V) and Mo(VI) via an oxo bridge. The shoulder peaks at 305 and 326 nm can be attributed to peroxo ligand to metal charge transfer (LMCT), which is in good agreement with the literature values reported for peroxo Mo-nicotinic acid complexes (304 and 310 nm) [49]. Attempts were made to record the ^{1}H and ^{95}Mo NMR spectrum of blue complex, however no signal was obtained due to presence of paramagnetic Mo (V) center.

3.5.3 XPS analysis

Fig. 3.5 shows the XPS spectrum of the Mo 3d levels of blue complex. The experimental data represented by solid circles clearly shows the characteristic Mo (3d) doublet composed of the $3d_{5/2}$ and $3d_{3/2}$ levels produced by spin-orbit coupling. Good fitting of the data points is made using two pairs of Gaussian functions, corresponding to two possible 3d doublets of Mo in different oxidation states viz Mo (VI) and Mo (V).

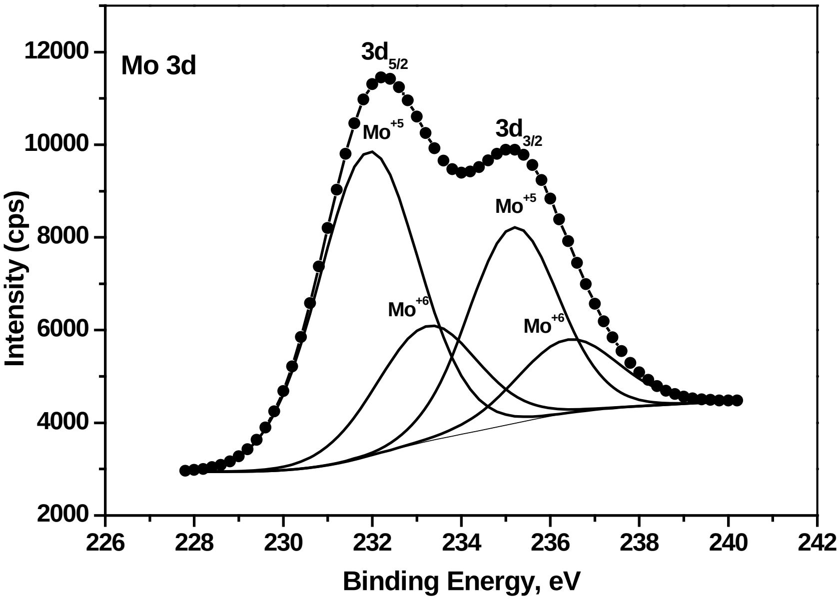


Figure 3.5: XPS spectrum of the Mo(3d) levels of blue complex

The contribution from the Gaussian peaks centered at 232.0 and 235.2 eV is major and is assigned to Mo (V). However, the minor peaks centered at 233.4 and 236.4 eV are assigned to Mo (VI). From the ratio of the areas of the two Gaussian pairs, the ratio of Mo(V) to Mo(VI) is 0.72/0.28, which clearly shows that Mo(V) is predominantly present in the blue complex. The binding energies are in agreement with the literature values [50]. Moraes et al have prepared molybdenum oxide thin films by hot filament metal oxide deposition technique and characterized using XPS which indicates that Mo atoms are in mixed valence state, Mo (VI) (232.7 and 235.8 eV) and Mo (V) (231.6 and 234.6 eV) with high predominance of Mo(VI) and formation of oxygen deficient MoO_3 film [51]. Thus XPS results of blue complex support the FTIR as well as UV-Vis data for presence of molybdenum centers in mixed oxidation state, Mo(V) and Mo(VI).

3.5.4 Cyclic Voltametric studies (CV)

The electrochemical behavior of Mo acetylide complex was investigated at various steps. The voltammetric response of 0.1 M catalyst **1** in dichloromethane shows no peak corresponding to the redox behavior of catalyst (Fig. 3.6 A). The cyclic voltammetric response of the same catalyst after addition of hydrogen peroxide (Fig. 3.6 B) shows the time dependent increment in the irreversible oxidation peak at potential –0.080 V (whereas a slightly time dependent shift towards negative potential –0.370 V), which indicates the direct conversion of electro inactive species Mo (0) to stable higher oxidation state species Mo (VI) [52].

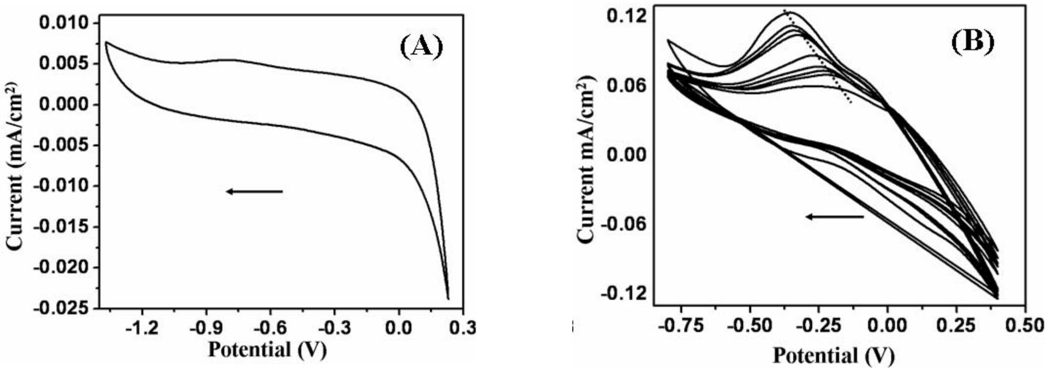


Figure 3.6: (A) Cyclic voltammogram of catalyst **1** in CH_2Cl_2 at 50mV/s scan rate (B) Time dependent (after each five minutes) cyclic voltammograms of catalyst **1** after addition of H_2O_2 at 50 mV/s scan rate.

The slight oxidation peak could be observed in the voltammograms after the addition of the H_2O_2 to the catalytic solution, due to the oxygen adsorption on the platinum wire in a potential window between -0.5 V to –0.2 V v/s Fc/Fc^+ redox couple. Due to this reason the shift of nearly 290 mV in potential towards negative potential is seen.

The voltammograms for blue intermediate complex is shown in Fig 3.7, which illustrates at a point of cathodic potential cycle (-0.65 V and -0.96 V v/s Fc/Fc$^+$) indicates one electron per molybdenum reduction and the same occurs in the case of anodic potential cycle giving the second pair of peaks at -0.3 V and -0.89 V v/s Fc/Fc$^+$ respectively. A cyclic voltammogram of the freshly prepared complex recorded immediately indicates that the peaks at -0.96 V and –0.89 V dominates initially and with time the -0.65 V and -0.3 V peaks increase in height, these voltammetric results confirm that the -0.96 V species is coupled with -0.89 V species and the -0.3 V peak is coupled with the -0.89 V peak. The first two peaks are for two forms of Mo (VI) and the second two peaks are for Mo (V). The results summarize the redox behavior of a blue complex containing molybdenum in two different oxidation states viz. Mo (V) and Mo (VI).

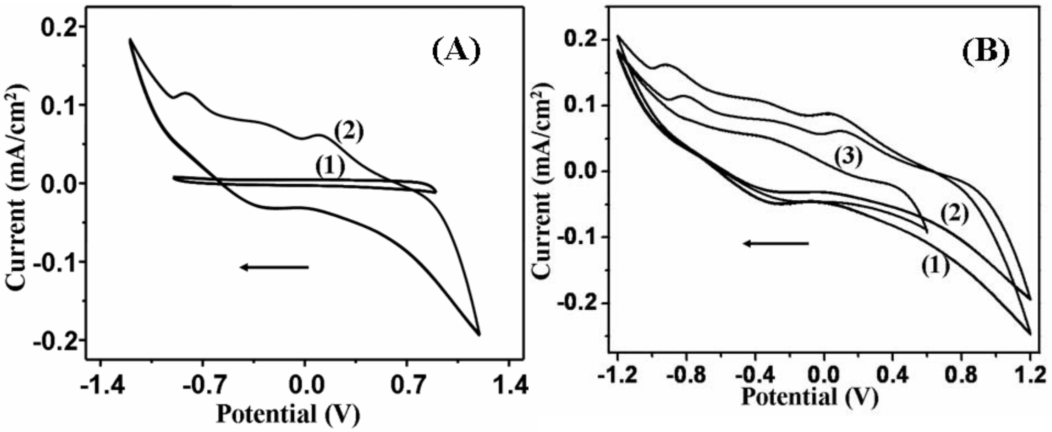
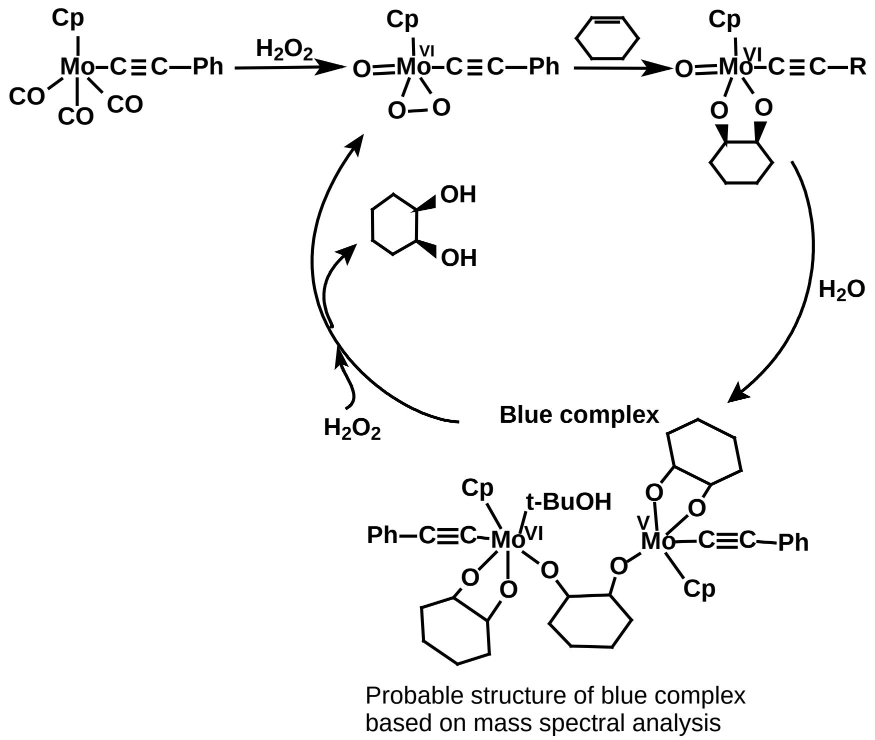


Figure 3.7: (A) Superimposed cyclic voltammograms of blank (1) and of blue complex (2) in CH$_2$Cl$_2$ using 0.1M tetrabutyl ammoniumhexaflorophosphate as a supporting electrolyte. (B) Cycle dependence redox peaks of blue complex.

Figure 3.7 B shows an increment in peak currents of Mo (VI) and Mo (V) accompanied by a shift to more positive values in the first two cycles indicating increased difficulty in oxidation. This can be attributed to some structural changes accompanying oxidation of the Mo centers, decreasing the thermodynamic feasibility (known from the formal potentials) of the anodic processes [53]. Interestingly, both the anodic peaks are found to merge in the third cycle giving rise to one broad peak at an intermediate potential, which could be due to the formation of mixed valence [Mo (VI) and Mo (V)] species.

Based on the evidence from spectroscopic techniques the mechanism of *cis* dihydroxylation of alkene is postulated. In the well known traditional OsO_4 catalyzed dihydroxylation, C=C double bond undergoes either 3+2 addition to O=Os=O to form 5 membered metallacycle or 2+2 addition to Os=O to give 4 membered metallacycle followed by rearrangement [54]. During the five membered ring formation Os(VIII) gets reduced to Os(VI), which is reoxidized using co-oxidant. Che et al [55] have reported stoichiometric *cis*-dihydroxylation of alkenes using $[(Me_3tanc)(CF_3CO_2)Ru^{VI}O_2]^+$ complex where dioxo ligands are in *cis* configuration.

In this reaction the 3+2 cyclo addition of alkene to *cis*-dioxo moiety has been proved by isolating and characterizing the adduct by single crystal X-ray diffraction analysis. This gives an evidence for five membered metallacycle as intermediate for *cis*-dihydroxylation using MnO_2 systems. Geoffroy [56] has reported 2+2 cyclo addition of ketene to $Cp^*WO_3^-$ anion where C=C bond of ketene adds to W=O to give four membered ring. Many organic and inorganic moieties add across one of the W=O bond of Cp^*WO_3 to give cyclic or acyclic addition products. Based on the literature mechanism for *cis*-dihydroxylation using OsO_4 as well as characterization result of catalytically active species and blue intermediate in case of **1**, the mechanism for *cis*-dihydroxylation has been proposed in Scheme 3.2. In the first step Mo oxo-peroxo complex is formed in presence of H_2O_2. The formation of Mo oxo peroxo complex has been confirmed by FTIR and UV-Vis spectral analysis. In the second step 3+2 addition of C=C of cyclohexene to Mo-peroxo moiety takes place to give five membered metallacycle intermediate. In this case, 2+2 addition followed by rearrangement to give five member ring does not look probable as initial presence of 2 rings (3 membered M-peroxo and 4 membered ring) on one metal center would be sterically hindered, hence 3+2 addition seems more probable. Dimerisation of the intermediate after probable reaction with water to give blue complex formation before the diol is liberated followed by reaction of Mo (V) species thus formed with H_2O_2 to give again Mo-oxo-peroxo complex completes the catalytic cycle. The probable structure of blue complex is suggested based on the ESI-MS studies of the reaction mixture.



Scheme 3.2: Proposed mechanism for cyclohexene dihydroxylation

In the case of cyclohexene initial epoxide formation followed by hydrolysis of epoxide ring to yield diol does not look probable, as no traces of epoxide was observed in GC analysis. Kholdeeva et. al [57] have reported epoxide ring opening to give selective *trans* diol formation using polyoxometalate. However in case of cyclohexene only *cis* isomer is obtained without formation of even trace amount of *trans* isomer.

3.6 Summary and conclusions

In summary molybdenum acetylide complex **1** has proved to be efficient catalyst for *cis*-dihydroxylation of various olefins with high conversion and selectivity for vicinal diols. This molybdenum acetylide complex is highly stable and can be recycled efficiently. Hydrogen peroxide acts as efficient and environmentally benign oxidizing agent. Very high TON is obtained when *t*-butanol is used as solvent.

Mo-acetylide oxo-peroxo complex is proved to be catalytically active species, where as dimeric molybdenum species with presence of mixed valent molybdenum center (Mo V and Mo VI) has been characterized as intermediate species. The structure of blue intermediate dimeric species has been proposed based on extensive characterizations by UV-Vis, XPS and cyclic voltametric studies.

The mechanism for *cis*-dihydroxylation of olefins is the 3+2 cycloaddition of C=C of olefin to Mo-peroxo moiety to give five member metallacycle intermediate. Dimerisation of the intermediate after probable reaction with water to give blue complex formation before the diol is liberated followed by reaction of Mo (IV) species thus formed with H_2O_2 to give again Mo oxo-peroxo complex completes the catalytic cycle. The ESI-MS gives the evidence of blue complex structure.

This system overcomes some drawbacks of osmium systems as well as no co-catalyst or co-oxidant is needed. This catalyst has the potential to be used for asymmetric dihydroxylation (AD) with use of chiral cyclopentadiene as ligand instead of simple cyclopentadiene.

3.7 References

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Chapter- 4

Oxidation of amines, alcohols and sulfide using cyclopentadienyl molybdenum (VI) oxo-peroxo complex

4. Oxidation of Amines, Alcohols and sulfide using cyclopentadienyl molybdenum (VI) Oxo peroxo complex

Abstract: The molybdenum acetylide oxo-peroxo complex obtained in situ by the treatment of the cyclopentadienyl molybdenum acetylide carbonyl complex, $CpMo(CO)_3(C\equiv CPh)$*; with* H_2O_2 *has been used as an efficient catalyst for selective oxidation of primary amines to nitroso derivatives, alcohols to carbonyl compounds and sulphides to either sulfoxides or sulfones. In case of amine oxidation excellent conversion (up to 100%) and very high selectivity for nitroso compound (99%) has been obtained using 30% hydrogen peroxide as an oxidant. The oxo peroxo Mo (VI) complex has also been found to be very active for the oxidation of various substituted primary aromatic amines with electron donating as well as electron withdrawing substituents on the aromatic ring. Even p-nitro aniline was successfully oxidized to corresponding nitroso derivative with equally high conversion and selectivity.*

The catalytic oxidation of alcohols to carbonyl compounds carried out under solvent free conditions gave excellent alcohol conversion (upto 90%) and very high selectivity for aldehydes (90%). The in situ formed oxo peroxo Mo(VI) complex is stable under reaction conditions and has been used for oxidation of various substituted primary aromatic alcohol.

The selectivity for oxidation of sulfides to either sulfoxides or sulfones was tuned by controlling various reaction parameters like oxidant, temperature, reaction time and catalyst concentration. Various lower as well as higher sulfides with different functionalities were successfully oxidized. Importantly even refractory sulfides like dibenzothiophene and 4,6 dimethyl dibenzothiophene could be efficiently oxidized to corresponding sulfones. Electron withdrawing as well as electron donating substituents on phenyl ring of acetylide moiety has led to the higher reaction rates as well as higher selectivity for sulfones. Interestingly even though complexes ***1 - 3*** *are homogeneous catalysts; they were successfully recycled for five cycles without appreciable loss in the conversion and selectivity.*

4.1. Introduction

The chemo-, regio and stereoselective oxyfunctionalization of heteroatoms is an important area of oxidation chemistry. Thus, to date, a number of oxidants have been developed to achieve the selective oxidative transformation of N and S heteroatoms [1]. However, for various reasons like selectivity, cost, efficiency, environmental constraints, etc. the use of many reagents is restricted to specially favorable cases. Thus, the demand for suitable, cost-effective, and ecofriendly selective oxidants with a wide range of application continues to increase to cope up with the ever-growing complexity of chemical oxidations [1g]. This chapter deals with selective oxidation of amines to nitroso compounds, alcohols to aldehydes and sulfides (thiother) to sulfoxide or sulfones using molybdenum acetylide complexes.

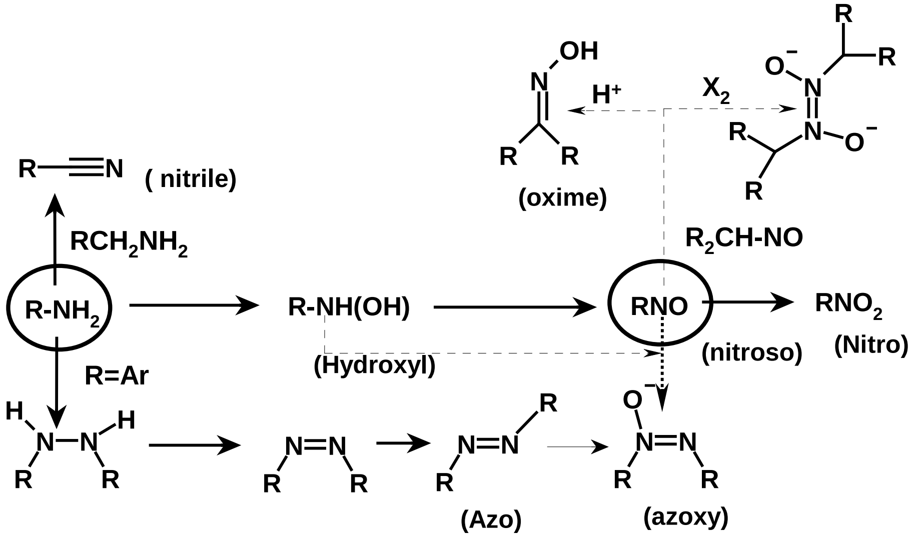
4.2 Part A: Selective *N*-oxidation of aromatic amines to nitroso derivatives

4.2.1 Introduction

Transition metal mediated oxidations and reductions are of general relevance to synthetic organic chemistry. Such transformations are mainly carried out at carbon atoms but are also known for nitrogen, silicon, phosphorus and sulfur [2]. Purely inorganic nitrogen compounds form stable compounds with variable oxidation states from -3 in (NH_3) to +5 in (NO_3^-). The catalytic reduction of N_2 to NH_3 (Haber-Bosch Process) and the catalytic oxidation of NH_3 to NO (Ostwald Process), the precursor for HNO_3 and nitrates have become milestones for the development of industrialized societies. In organic chemistry, a broad range of different oxidation state nitrogen centers are well known, with amines and nitro derivatives found at the top and the bottom of the scale. Since amino and nitro groups can be introduced into organic fragments by simple procedures such as nucleophilic aliphatic/aromatic substitution or electrophilic aromatic substitution, there is a demand for selective pathways to compounds bearing nitrogen moieties in intermediate oxidation states. Beside classical oxygen transfer reactions, organic nitrogen compounds undergo a series of other oxidations like diazotisation, radical type reactions, dehydrogenations, oxidative aminations, nitrations, halogenation, etc.

4.2.2 The oxidation of primary amines

The oxidation of primary amines leads to a variety of different products such as hydroxyl, nitroso, nitro, azo and azoxy compounds. Aromatic nitroso compounds are utilized extensively as chemical feed stocks for a wide range of useful materials such as dyes, pharmaceuticals, perfumes and plastics [3]. The main oxidation pathways of primary amines are summarized in Scheme 4.1. Hydroxylamines and nitroso derivatives are the intermediates for the direct oxidation to nitro compounds. Depending on the nature of the substituents different pathways and side reactions are possible: aromatic primary amines can be converted by a radical mechanism via 1, 2-diarylhydrazines to azo compounds, which can be oxidized subsequently to the corresponding azoxy derivatives. These systems are alternatively accessible via condensation (dashed lines) of hydroxylamines and nitroso compounds. Aliphatic primary amines of the type $R_2CH–NH_2$ gives the corresponding nitroso compounds $R_2CH–NO$ which can dimerize before undergoing further oxidation or rearrange to oximes in the presence of an acid. Aliphatic primary amines of the type $RCH_2–NH_2$ can also be oxidized to yield the nitriles RCN.



Scheme 4.1: Oxidation pathways of primary amines

For many of the reactions described above, peroxidic compounds like peracids or hydrogen peroxide are the oxygen transfer agents of choice. This opens up the door to transition metal catalysis, since a multitude of homogeneous and heterogeneous transition metal complexes have found to activate peroxidic compounds in the past. Other *N*-oxidations involve electron transfer reactions, which also include transition metal complexes as catalysts or stoichiometric reagents.

Transition metal based oxidations of primary amines to hydroxylamines have not been reported so far, probably due to over oxidation of the sensitive hydroxylamine moiety giving nitroso or nitro compounds. For the synthesis of nitroso derivatives from primary amines, dimethyl dioxirane, percarboxylic acids, oxaziridinium salts or DDQ – (dichloro dicyano quinone) have been used as organic reagents [4]. Sodium perborate and percarbonate oxidize primary aliphatic amines to aliphatic nitroso compounds in good to excellent yields [5]. However, compared to hydroxylamines, nitroso compounds have a reduced reactivity towards oxidizing compounds. This allows transition metal complexes to be introduced in the synthesis of these interesting systems. Therefore some catalytic routes to aromatic nitroso derivatives have been worked out during the last few years. Most of the work on the oxidation of primary aromatic amines to the corresponding nitroso derivatives has been done with group VI metal complexes like $Na_2MoO_4{\cdot}(H_2O)_2$, $(n\mathrm{Bu}_4\mathrm{N})_4\mathrm{Mo}_8\mathrm{O}_{26}$, and *cis*-$MoO_2(acac)_2$ which were found to activate hydrogen peroxide for this reaction [6]. Due to the mild conditions, the desired aromatic nitroso compounds are obtained in high yields.

The selective oxidation of amines to nitro compounds requires more drastic conditions than the oxidations discussed before and therefore highly reactive oxidizing agents are required for these transformations. During the last years dimethyl dioxirane, either isolated in acetone solution or generated in situ from $KHSO_5$ and acetone, and HOF-generated from fluorine and water in acetonitrile turned out to be the reagents of choice [7]. Before, sodium percarbonate, ozone and percarboxylic acids were used [8]. Transition metal complexes can fulfill the demands for this oxidation reaction by different mechanisms: a high oxidation potential which is closely related to a high oxidation state especially for vanadium, chromium and group VIb to VIII metals will give rise to radical type oxidations of the amine, which finally lead to the corresponding nitro compounds. There are some examples for this kind of reactivity, like chromium exchanged silicalites with *t*-BuOOH as the oxidizing agent or $RuCl_3$ with hydrogen peroxide [9]. Secondly, reacting Fe(III) or Mn(III) porphyrins with PhIO or *t*-BuOOH gives rise to the formation of high valent oxo species which are also capable of oxidizing nitroso compounds to the corresponding nitro compounds [10]. A third type of reactivity is based on the Lewis acidity of early transition metal centers in high but nevertheless stable oxidation states. These species are able to activate peroxidic agents like hydrogen peroxide or *t*-BuOOH for the oxygen transfer without changing their oxidation states. Therefore radical type side reactions are suppressed.

Classical examples are the methyltrioxorhenium/hydrogen peroxide system, which catalyzes the oxidation of organonitrogen compounds with the activity similar to dimethyl dioxirane, or Na_2WO_4/hydrogen peroxide, which has been applied for the oxidation of 3-nitro-1, 2, 4-triazoles [11]. Krohn et. al. has developed probably the best system for the oxidation of primary aromatic and aliphatic amines to nitro compounds. Depending on the organic substituent on nitrogen, the catalyst $Zr(O^tBu)_4$ gives yields of nitro compounds up to 98% with *t*-BuOOH as the oxygen source [12].

Oxidation of amines poses problems due to nonregioselective or over-oxidation of amines and competitive oxidation of substrates. General methods for the preparation of nitroso compounds have been addressed by Gowenlock et. al. [13]. Several organo catalysts [14] as well as metal catalysts [15] are reported for the oxidation of amines. However, mainly the nitro compounds are obtained in many cases. $FeCl_2$–Py_4 complex is reported to give selectively nitroso or nitro product depending on the oxidant used, however the oxidant used is a limiting agent leading to a very low TON for the product [16]. TS-1 is reported to give high selectivity (73%) for nitroso compound but at very low conversions (7.3%) [17].

Amongst the early transition-metal complexes, molybdenum (VI) complexes have functional as well as structural similarity with molybdo-enzymes and have the ability to catalyze a variety of oxidation reactions [18]. Various molybdenum organometallic complexes and oxides are known to be very good homogeneous and heterogeneous catalysts for the oxidation/epoxidation reactions [19]. Preyssler's catalysts (W and mixed W/Mo) have been reported to oxidize anilines with maximum selectivity (82%) for the azoxy compound [20]. Several Mo catalysts with acac [21] or hmpa [22] ligands as well as Mo- and W-based coordination polymers [23] have been used for aniline oxidation. In this part of the chapter results of the oxidation of primary aromatic amines using CpMo(CO)$_3$(C≡CPh) (**1**) and hydrogen peroxide as an oxidizing agent are described.

4.3. Experimental

Materials - All reagents of commercial grade (Aldrich, SD fine) were used as received unless stated otherwise. Hydrogen peroxide used was 30% w/w in water.

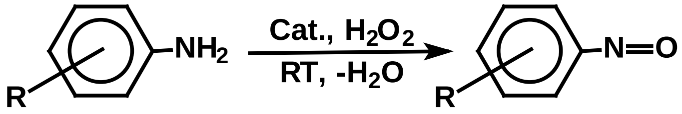
4.3.1 General reaction conditions

The liquid-phase catalytic oxidation of amines was carried out in a two necked 50 mL round bottom flask charged with amine (0.01 mol), 30% hydrogen peroxide (0.02 mol), 10 g solvent and catalyst **1** (0.02 mmol). The reaction mixture was stirred at room temperature till the completion of the reaction. All samples were analyzed on an Agilent 6890 Gas Chromatograph equipped with a HP-5 dimethyl polysiloxane (60 m length, 0.25 mm internal diameter, 0.25 μm film thickness) with flame ionization detector. Products were confirmed using GCMS, Model GC Agilent 6890N with HP5 MS 30 m capillary column, MS Agilent 5973 Network MSD.

4.4 Result and discussion

4.4.1 Effect of solvent on oxidation of amines

The preliminary experiments were carried out with aniline as a model substrate in order to establish the optimum reaction conditions (Scheme 4.2).



Scheme 4.2: Oxidation of primary aromatic amines

Based on our previous experience, the liquid-phase catalytic oxidation of aniline was carried out in *t*-butanol at room temperature to form single-phase system with aqueous oxidant and organic substrates and product. Table 4.1 shows the results of aniline oxidation using catalyst **1** and H_2O_2 as an oxidant. Very high aniline conversion (97%) and excellent selectivity for nitroso benzene (97%) was obtained with *t*-butanol. When other solvents were tested for the same reaction slightly lower conversion as well as selectivity for nitrosobenzene was obtained, hence alcohols were found to be better with high conversion and selectivity for the nitroso compound. In case of chlorinated solvents, the conversion was high, however, the selectivity for the nitroso product decreased to 80% and 84%, respectively (Table 4.1, entries 3 and 4). Comparatively lower conversions were obtained when toluene and acetonitrile were used as a solvent (entries 5 and 6). In all the cases, the turnover number (TON) for the nitroso compound was very high (up to 470).

Table 4.1. Aniline oxidation in various solvents[a]

Entry	Solvent	Conv, %	Selectivity, %			TON* for nitroso compound
			Nitroso	Azo	Azoxy	
1	***t*-Butanol**	**97**	**97**	**2**	**1**	**470**
2	Methanol	95	90	7	3	428
3	Dichloromethane	96	80	14	6	384
4	Carbon tetrachloride	97	84	11	5	407
5	Toluene	84	83	12	5	349
6	Acetonitrile	72	90	7	3	324

[a] **Reaction conditions:** $PhNH_2$-0.01 mol; 30% H_2O_2- 0.02 mol; Solvent- 10 g; Catalyst **1**-0.02 mmol; Time-12 h; Temp. RT; * TON for nitroso derivative = moles of nitroso product formed per mole of catalyst.

4.4.2 The effect of catalyst loading on aniline oxidation

The effect of substrate to catalyst ratio on aniline oxidation was studied. In the presence of 0.1 mol% catalyst **1**, the rate of reaction was very slow and 48 h were needed to achieve complete aniline conversion (Table 4.2 entry 1) however the selectivity for nitroso compound remained high. As the catalyst loading was increased to 0.2 mol% the rate enhanced by almost double (Table 4.2 entry 2). Further increase in catalyst loading to 0.4 mol% lead to complete aniline conversion in 12 h (Table 4.2 entry 3). When catalyst loading was further increased to 1 mole %, the complete aniline conversion was obtained in only 4 h with slight decrease in the selectivity for nitroso benzene. Hence it can be concluded that rate of aniline oxidation is proportional to catalyst concentration.

Table 4. 2. Effect of catalyst loading on aniline oxidation[a]

Entry	Catalyst **1** loading mol%	Reaction time, h	Conv, %	Selectivity, %			
				Nitroso	nitro	azo	azoxy
1	0.1	48	97	99	0	0	1
2	0.2	26	99	99	0	0	1
3	0.4	12	99	97	0	1	2
4	1	4	99	92	2	1	5

[a]**Reaction conditions:** Aniline-0.01 mol; 30 % H_2O_2- 0.02 mol; *t*-BuOH- 10 g;

4.4.3 Effect of the reaction time

In order to study the progress of the reaction with time, the product distribution was monitored as a function of time under optimum reaction condition. The progress of the reaction was monitored by withdrawing the samples at intervals of time. The results are shown in Fig. 4.1. Aniline conversion gradually increased with maximum selectivity for nitrosobenzene throughout the reaction. The reaction was complete after 12 h with 0.4 mol% catalyst loading. The optimum reaction time was 12 h at room temperature giving 97% selectivity for nitroso compound.

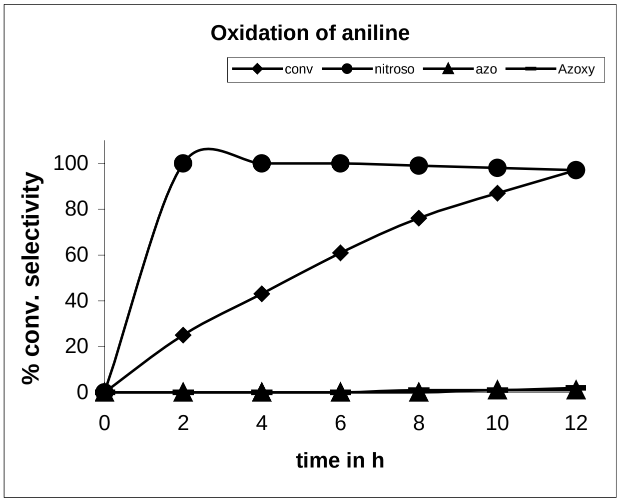
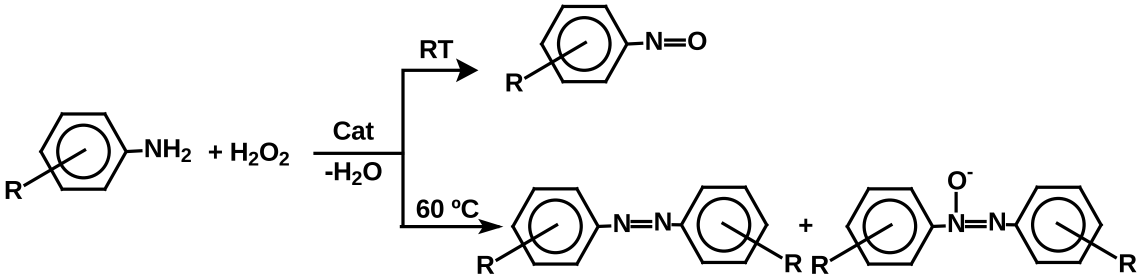


Figure 4.1: Conversion and selectivity vs. time

4.4.4 Influence of temperature on aniline oxidation

The influence of reaction temperature on aniline conversion and product selectivity was studied in the temperature range from room temperature to 100 °C (Table 4.3). When the reaction temperature was increased gradually from room temperature to 100 °C, the rate of the reaction increased however the product distribution changed significantly (Scheme 4.3).



Scheme 4.3: Temperature effect on oxidation of primary amines

At room temperature reaction was complete in 12 h (Table 4.3 entry 1), whereas at 100 °C, it was complete in only 4 h (Table 4.3 entry 5); however, the selectivity for the nitroso compound was maximum (97%) at r.t. which decreased to only 8% at 100 °C. At higher temperatures azo and azoxy compounds were formed as major products compared to nitroso derivative. Formation of the nitro product was also observed at high temperatures.

Table 4.3. Influence of temperature on aniline oxidation [a]

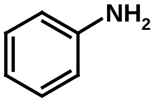
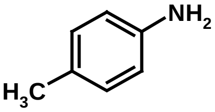
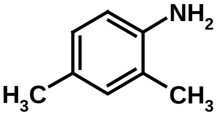
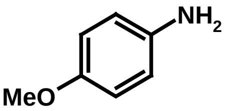
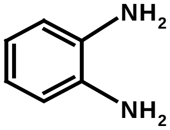
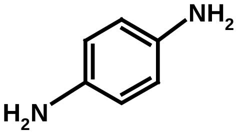
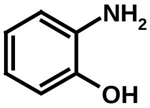
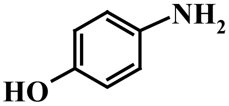
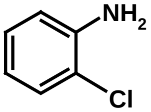
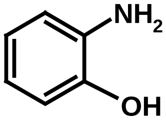
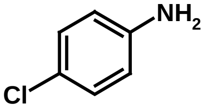
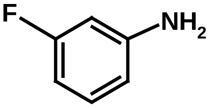
Entry	Temp, ºC	Time, h	Conv. %	Selectivity %			
				Nitroso	Azo	Azoxy	Nitro
1	**RT**	**12**	**97**	**97**	**2**	**1**	**0**
2	40	10	99	80	14	6	0
3	60	6	99	56	18	21	5
4	80	4	99	24	25	43	8
5	100	4	99	8	30	47	15

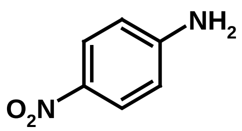
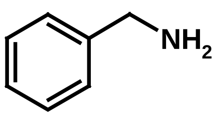
[a] **Reaction conditions**: Aniline-0.01 mol; 30 % H_2O_2- 0.02 mol; Solvent- 10 g; Catalyst **1**-0.02 mmol.

4.5 Oxidation of substituted anilines

After optimizing the reaction conditions (0.4 mol% catalyst loading, room temperature and *t*-butanol as solvent), further applicability of catalyst **1** was explored for the oxidation of a variety of substituted aromatic amines and the results are summarized in Table 4.4. Amongst the substrates tested, the best results were obtained for *p*-methyl aniline with 100% conversion and 99% selectivity for the nitroso compound. High conversions and selectivity for nitroso compounds were obtained for activated and electron rich anilines (Table 4.4 entries 2 and 4); however, the conversion decreased for sterically hindered 2, 6-dimethylaniline though with very high selectivity (99%) for the nitroso product. Halogenated anilines (Table 4.4 entries 9–12) were also oxidized successfully with high conversion and very high selectivity for the nitroso compounds. In case of hydroxyanilines conversion decreased slightly but the selectivity remained very high (98%) (Table 4.4 Entries 7 and 8). In case of all amines tested, very high selectivity for nitroso compound was obtained. The TON for nitroso compound in all the cases is high with the maximum TON of 495 for *p*-methyl aniline which is much higher than that reported previously with different molybdenum/tungsten-based catalysts (<10) [16–18]. It is interesting to note that *p*-nitro aniline was also oxidized successfully using catalyst **1**.

Table 4.4. Oxidation of various amines [a]

	Amines	Conv, %	Selectivity, %				TON* for nitroso
			Nitroso	Azo	Azoxy	Nitro	
1		97	97	2	1	0	**470**
2		100	99	1	0	0	**495**
3		75	99	1	0	0	**371**
4		83	97	2	1	0	**403**
5		77	98	1	1	0	**371**
6		84	99	1	0	0	**416**
7		73	98	1	1	0	**358**
8		75	98	1	1	0	**368**
9		60	96	2	2	0	**288**
10		72	99	0	1	0	**356**
11		79	79	8	11	2	**312**
12		70	74	10	14	2	**259**

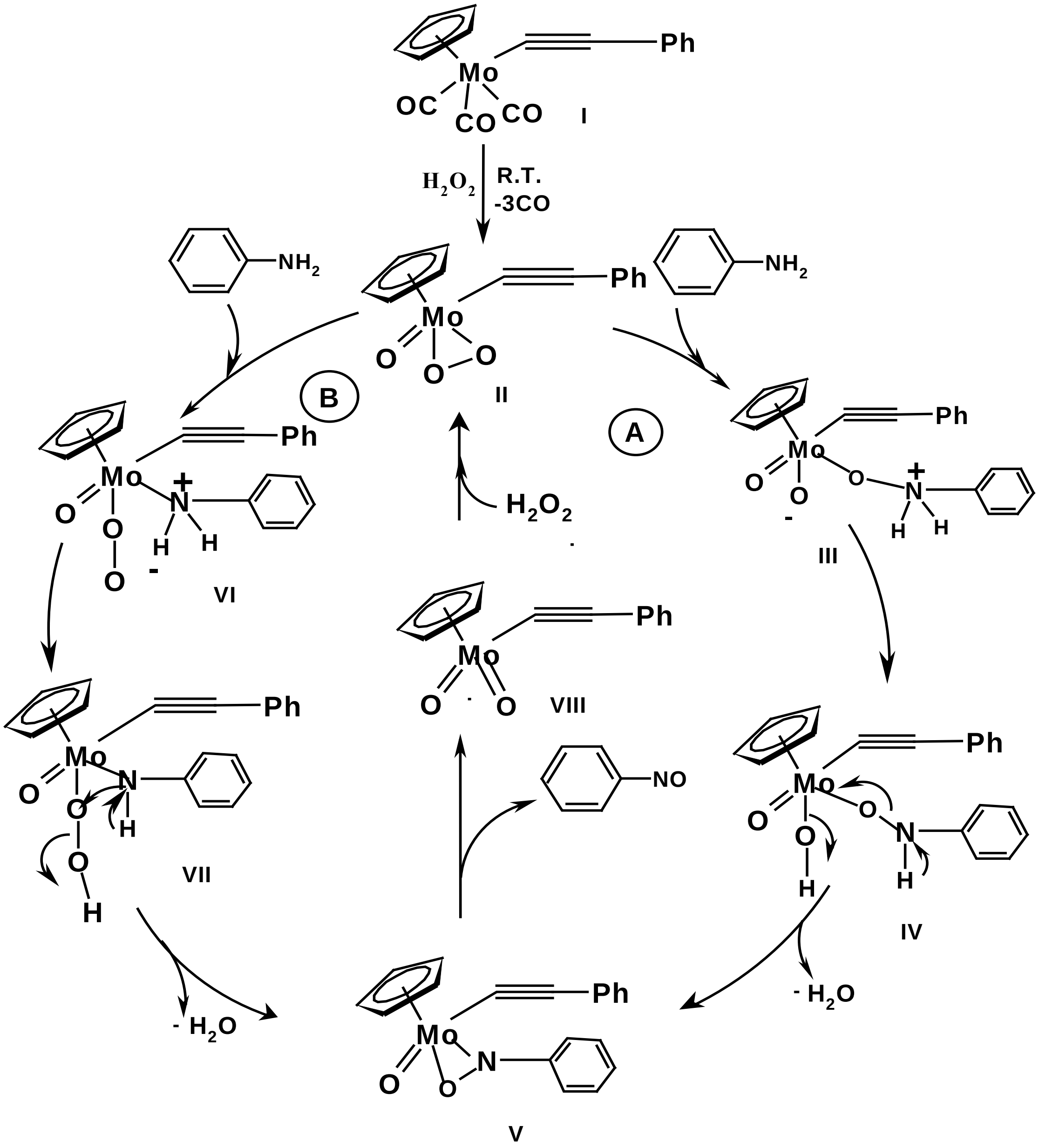
13		85	95	2	1	2	**404**
14		80	75	12	7	6	**300**

[a] **Reaction conditions:** Amine-0.01 mol; 30% H_2O_2- 0.02 mol; *t*-BuOH - 10 g; Catalyst **1**-0.02 mmol; Temperature-RT; Time-12 h; * TON for nitroso derivative = moles of nitroso product formed per mole of catalyst.

The conversion as well as selectivity for *p*-nitro aniline oxidation did not decrease significantly compared to aniline. In earlier reports, when Mo/W-based coordination polymers were used for *p*-nitro aniline oxidation, the yield dropped drastically from 82% for aniline to 20% for *p*-nitro aniline [18]. Similar drastic reduction in yield was reported for [Mo(O_2)(O)(- H_2O)(hmpa)] (77% for aniline and 10 % for *p*-nitro aniline) [17]. When Mo(O)$_2$(acac)$_2$ was used as a catalyst no catalytic activity was observed with anilines with electron withdrawing substituents on the aromatic ring compared to a 77% yield for aniline using the same catalyst [16]. In the present case, the conversion was marginally decreased from 97% for aniline to 85% for *p*-nitroaniline with almost similar selectivity for nitroso compound (97% for aniline and 95% for *p*-nitroaniline).

4.6 Mechanism

The probable mechanism for selective oxidation of anilines to nitroso compound using **1** is depicted in Scheme 4.4. After addition of H_2O_2 to **1** corresponding oxo-peroxo complex II is formed, which is catalytically active species [40a] The formation of oxazidines intermediate **V** from **II** can take place via two routes, based on the literature mechanism for oxidation of amines using molybdenum catalyst. The first step in mechanism A is a nucleophilic attack of the aniline nitrogen at one of the peroxygen atoms of oxo-peroxo **II**, which are known to be electrophilic [24], leading to breaking of the oxygen-oxygen bond in peroxide. Proton transfer, followed by a nucleophilic attack of the aniline nitrogen atom on the molybdenum atom and elimination of water, leads to the formation of **V**. In reaction mechanism **B** of Scheme 4.4, the aniline nitrogen atom attacks the molybdenum atom, leading to a cleavage of the molybdenum-peroxygen bond, followed by proton transfer. In the final step in path **B**, the aniline nitrogen atom attacks the α-oxygen atom of the hydroperoxide ligand, cleaving the oxygen-oxygen bond, and producing **V** and water. Intermediate **V** on successive decomposition gives nitroso compound and dioxo molybdenum complex **VIII**. On further treatment of **VIII** with hydrogen peroxide gives oxo-peroxo intermediate **II**.



Scheme 4.4: Possible mechanism of amine oxidation

4.7 Summary and conclusions

In this part of the chapter selective oxidation of anilines with H_2O_2 catalyzed by molybdenum acetylide complex $CpMo(CO)_3(C\equiv CPh)$ **1** has been demonstrated which is a simple and novel methodology for direct conversion of primary amines to the corresponding nitroso derivatives with very high conversion and selectivity for the nitroso compounds at room temperature. At higher temperature the selectivity totally shifted to azo and azoxy benzenes. In situ generated oxo-peroxo molybdenum acetylide complex is proved to be the catalytically active species. A variety of substituted anilines such as electron donating and withdrawing groups including *p*-nitroaniline were successfully oxidized to the corresponding nitroso compounds under very mild conditions with very high TON. This catalyst provides a simple, clean and general procedure for preparation of nitroso compounds as major product that are difficult to prepare by the conventional methods.

Part B: Solvent free Oxidation of Aromatic Primary Alcohols to Aldehydes

4.8 Introduction

Oxidation of alcohols to aldehydes and ketones is one of the most important transformations in organic synthesis [25]. In particular, the oxidation of primary alcohols to aldehydes is important due to importance of aldehydes as intermediates and as high value components for the perfume industry [26, 27]. Traditionally, the oxidation of alcohols has been achieved with stoichiometric inorganic oxidants, permanganate, bromate [28] or Cr (VI) based reagents [29]. Several transition metal-based homogeneous systems such as palladium [30], ruthenium [31], manganese [32], tungsten [33], rhenium [34] and iron [35] have been reported. However in many cases the resulting mixture of organic substrates, products, solvents and molecular oxygen can be quite dangerous. Also, some oxidation reactions have to be performed under severe conditions, such as high temperature and high oxygen pressure [36] and these oxidants are relatively expensive, and generate large amounts of noxious heavy-metal waste. Moreover, the reactions are often performed in environmentally hazardous solvents, such as chlorinated hydrocarbons. Due to these limitations there is substantial interest in the development of versatile catalyst. In search for greener technologies, there is a definite need for catalytic oxidations that use organometallic complexes with hydrogen peroxide. For development of environmentally benign and safe catalytic system for oxidation of alcohol, hydrogen peroxide is a preferred oxidant as it produces only water as byproduct. Moreover, when a water-soluble catalyst is used in a biphasic system, most products can be separated by simple decantation, and the catalyst solution can be recycled. Among the early transition-metal complexes, molybdenum (VI) complexes have functional as well as structural similarities with molybdo-enzymes and have the ability to catalyze a variety of oxidation reactions [37]. Various molybdenum organometallic complexes and oxides are known to be very good homogeneous and heterogeneous catalysts for the oxidation/epoxidation reactions. Molybdenum carbonyl complexes with different ligands like halides [18] *N*-containing and cyclopentadienyl; η^5-C_5R_5; R = H, Me, Ph [38] have been proved to be good oxidation catalyst. Molybdenum acetylide complex, $CpMo(CO)_3(C{\equiv}CPh)$; Cp = η^5-C_5H_5 complex, (**1**) is demonstrated to be good oxidation catalyst for *cis*-dihydroxylation of various olefins and *N*- oxidation of amines [39]. Oxo peroxo Mo (VI) acetylide species is proved to be involved in this oxygenation process and because of easy formation of oxo peroxo species, this catalyst is expected to be effective for the oxidation of alcohols. To our knowledge there are no reports in the literature on the use of above complex for oxidation of alcohols. In this part of the chapter, results of the selective oxidation of primary aromatic alcohols to aldehydes using catalyst **1** and hydrogen peroxide as an oxidizing agent is described.

4.9 Experimental

All the solvents procured from SD fine, Merck India of AR grads were distilled prior to use. All alcohols were purchased from Aldrich Chemicals and used as received.

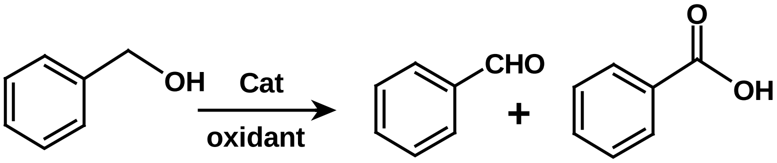
4.9.1 General procedure for oxidation of alcohols

Two necked round bottom flask was charged with benzyl alcohol (5.41 g, 0.05 mol), **1** (34.5 mg, 0.01 mmol), and 30 wt % H_2O_2 (10.02 gm, 0.1 mol). The reaction mixture was vigorously stirred at 80 ^oC for 8 h. After the reaction, a two-layered mixture was obtained, (organic phase containg product and/aqueous phase containing catalytically active species as well as unreacted alcohol). The reaction was monitored using GC (Agilent 6890 Gas Chromatograph equipped with a HP-5 dimethyl polysiloxane 60 m length, 0.25 mm internal diameter, 0.25 μm film thickness) with flame ionization detector. Products were confirmed using GCMS, Model GC Agilent 6890N with HP5 MS 30 m capillary column, MS Agilent 5973 Network MSD .

4.10 Results and discussion

4.10.1 The role of solvents in oxidation of benzyl alcohol

Benzyl alcohol was first examined as a model substrate with H_2O_2 (30%) as oxidant (Scheme 4.5).



Scheme 4.5: Oxidation of aromatic alcohol

The oxidation reaction was initially carried out without any solvent in the presence of catalytic amount of **1**, (Table 4.5). The reaction mixture was allowed to reflux at 80 ºC in the presence of 1 mol% catalyst for 8 h. The progress of the reaction was monitored by GC. A high alcohol conversion of 86% with very high selectivity (92%) for aldehyde was obtained (Table 4.5, Entry 1). Very high turn over number (TON = moles of benzaldehyde formed per mole of the catalyst) of 396 was obtained for benzaldehyde in one cycle. To improve the conversion and selectivity, various other solvents were tried and to our surprise the conversions and selectivities were considerably lower (entry 2-5) compared to solventless reaction. Since the catalyst is water soluble initially it forms single phase system with alcohol and as the reaction proceeds the product (aldehyde) formed forms separate layer because of which the concentration of reactant is constant in aqueous phase and this may be the reason for higher catalytic activity.

Table 4.5. Benzyl alcohol oxidation in various solvents [a]

Entry	Solvent	Conv, %	Selectivity, %		TON*
			Aldehyde	Acid	
1	Acetonitrile	45.2	85.2	14.8	38.5
2	*t*-butanol	22.6	80.5	19.5	18.1
3	Methanol	17.4	45.9	54.1	8
4	Chlorobenzene	23.8	86.9	13.1	20.7
5	No solvent[a,b]	**86**	**92**	**8**	**395.6**

[a]**Reaction conditions:** Benzyl alcohol-0.01 mole; 30% H_2O_2 - 0.02 mole; Solvent- 10 g; Catalyst **1**- 0.1 mmol; Time 8 h; Temp. 80 °C; * TON for aldehyde = moles of aldehyde formed per mole of catalyst, [b] Benzyl alcohol-0.05 mole; 30% H_2O_2- 0.1 mole; Catalyst **1**- 0.1 mmol.

4.10.2 The influence of temperature

The influence of temperature on benzyl alcohol conversion and product selectivity was examined (Table 4.6).

Table 4.6. Effect of temperature on benzyl alcohol oxidation[a]

Entry	Temperature °C	Conv, %	Selectivity, %	
			Aldehyde	Acid
1	RT	0	0	0
2	40	0	0	0
3	60	40	100	0
4	80	86	92	8
5	100	90	60	40

[a] **Reaction conditions:** Benzyl alcohol-0.05 mole; 30% H_2O_2- 0.1 mole; Catalyst **1**-0.1 mmol; Time 8 h.

When reaction temperature was increased gradually from RT to 100 °C, the rate of the reaction increased. Even upto 40 ºC, no reaction took place and at 60 ºC only 40% conversion was obtained (Table 4.6, entry 1-3). At 80 ºC highest conversion (86%) was obtained after 8 h with maximum selectivity for aldehyde (92%) (Table 4.6,entry 4). At 100 °C the conversion increased to 90% however the selectivity for aldehyde decreased considerably to 60% with 40% selectivity for acid (Table 4.6, entry 5).

4.10.3 Catalyst recycle study

One major advantage with catalyst **1** is the recyclability of the catalyst in spite of being homogeneous complex. After addition of hydrogen peroxide to complex **1**, the in situ formed oxo peroxo Mo acetylide complex is soluble in aqueous hydrogen peroxide and hence forms miscible phase with alcohol. As the reaction progresses and aldehyde are formed, it forms separate organic phase and hence the catalyst recycle becomes very easy for this system. After completion of the reaction the organic phase (aldehyde) was easily separated using separating funnel and the fresh charge of alcohol was added for the next recycle. The catalyst was recycled efficiently for five cycles (Table 4.7) without considerable loss in the conversion and aldehyde selectivity at the end of fifth recycles. Hence recycling of these homogeneous catalysts is the major achievement in this work.

Table 4.7. Catalyst recycles studies[a]

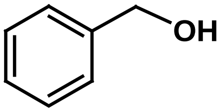
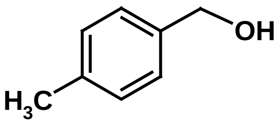
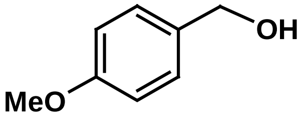
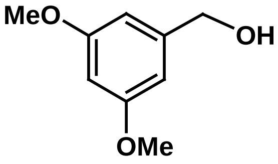
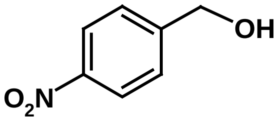
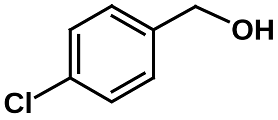
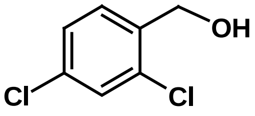
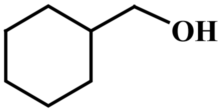
Entry	Run	Conv, %	Selectivity, %	
			Aldehyde	Acid
1	0	86	92	8
2	1	85	93	7
3	2	84	90	10
4	3	83	92	8
5	4	82	92	8
6	5	80	92	8

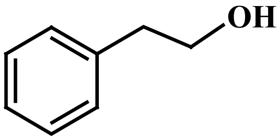
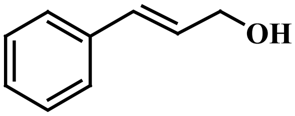
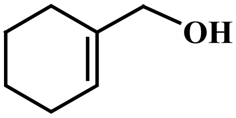
[a] **Reaction conditions**: Benzyl alcohol-0.05 mole; 30% H_2O_2- 0.1 mole; Catalyst **1**-0.1 mmol; Temperature- 80 ºC ; Time 8 h.

4.11 The scope of substrate

After optimization of the reaction parameters, wider applicability of catalyst **1** was tested for oxidation of variety of substituted aromatic primary alcohols and the results are summarized in Table 4.8.

Table 4.8. Oxidation of different alcohols[a]

Entry	Substrate	Conv. %	Selectivity %		TON
			Aldehyde	Acid	
1		86	92	8	395.6
2		90	87	13	391.5
3		90	90	10	391.5
4		83	85	15	352
5		60	88	12	264
6		65	91	9	296
7		78	90	10	343
8		82	88	12	361

9		72	82	18	295
10		70	75	25	262
11		82	85	15	348.5

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[a]**Reaction conditions:** Alcohol-0.05 mole; 30% H_2O_2- 0.1 mole; Catalyst **1**-0.01 mmol; (Substrate: Catalyst 1:500); Temperature- 80 ºC; Time -8 h.

In case of *p*-methyl benzyl alcohol best results were obtained with 90% conversion and 90% selectivity for aldehyde. Activated and electron rich alcohols like *p*-methyl (entry 2) and *p*-methoxy benzyl alcohol (entry 3) gave high conversion and selectivity for aldehydes. Lower conversion (60%) was obtained for benzyl alcohol with electron-withdrawing substituents such as *p*-nitro, *p*-chloro and 2, 4-dicholoro benzyl alcohols (entries 5-7). Catalyst **1** has been proved to catalyze oxidation of olefins also, hence to check whether oxidation takes place selectively at double bond or alcohol group in case of molecules containing both the functionalities, oxidation of cinnamyl alcohol was carried out. Alcohol group was selectively oxidized without oxidation of double bond with 70% conversion and 75% selectivity for aldehyde. Lower selectivity for aldehyde may be due to presence of double bond that makes further oxidation of aldehyde to acid more favorable. When non-aromatic alcohols like cyclohexanemethanol and cyclohexenemethanol (entry 8) were oxidized, 82% conversion with more than 85% selectivity for aldehyde was obtained.

4.12 Summary and conclusions

In conclusion, the use of molybdenum acetylide complex **1** as an efficient catalyst for alcohol oxidation has been demonstrated. The complex is an efficient catalyst for oxidation of variety of primary aromatic alcohols with maximum selectivity for aldehydes under solvent free condition. It can very well tolerate electron rich as well as electron withdrawing substituents on aromatic ring without drastic effect on selectivity demonstrating the wider applicability of this catalyst for selective oxidation of primary aromatic alcohols to aldehydes. Variety of substituted benzyl alcohols were successfully oxidized to corresponding aldehydes. In case of molecules containing alcohol and double bond, selective oxidation of alcohol is favored without oxidizing double bond.

Part C: Selective oxidation of sulfides to sulfoxide or sulfones

4.13 Introduction

The selective oxidation of sulfides to sulfoxides or sulfones is an important organic transformation, and the resulting sulfoxides are versatile intermediates for the preparation of biologically and medicinally important products [40] e.g. therapeutic agents such as anti-ulcer (proton pump inhibitors) [41], antibacterial, antifungal, anti-atherosclerotic [42] and cardiotonic agents [43] as well as psychotropic [44] and vasodilators [45]. Conventionally stoichiometric amounts of organic or inorganic reagents were used for these transformations [46]. In recent years several metal catalysts have been used for selective oxidation of sulfides to sulfoxides. Due to the large volume of toxic wastes associated with stoichiometric processes, there is a growing interest in scientific and industrial circles for a cheap and environmentally benign process for these transformations. A catalytic method associated with hydrogen peroxide as the oxidizing agent is a quite attractive system for large-scale processes from economic and environmental points of view [47]. Conventional oxidants include, $NaBO_3$ [48], NaClO [49], $Ca(ClO)_2$ [50], $H_5IO_6/[Mn\ IV\ \text{-}Mn\ IV\text{-}\ (\mu\text{-}O)_3L_2](PF_6)_2$ [51], $KHSO_5$ [52], HNO_3 [53], $(NH_4)_2Ce(NO_3)_6$ [54], $NaIO_4$ [55], MnO_2 [56], $KMnO_4$ [57], RuO_4 [58], CF_3CO_3H [59], dimethyldioxirane [60], $t\text{-}C_4H_9O_2H$ [61], 4-methylmorpholine oxide with OsO_4 [62], $3\text{-}ClC_6H_4CO_3H$ [63] and $[(n\text{-}C_4H_9)_4N]\text{-}HSO_5$ [64]. Oxidants like hydrogen peroxide, *t*-butyl hypochlorite, *N*-halosuccinimides, *m*-chloroperbenzoic acid, sodium metaperiodate, nitrogen tetroxide, CAN, tetrabutylammonium peroxydisulfate, 2, 6-dicarboxypyridinium chlorochromate [65] are used in liquid phase with soluble metal complexes of Ti, V, Re, Mn, Cr, and W [66] metal Schiff base complexes [67]. However the major shortcoming of all heme-dependent peroxidases and Schiff base-metal complexes is their low operation stability due to facile oxidative degradation of heterocyclic or porphyrine ring. Furthermore, enzymatic catalysis has also been reported [68].

Sheldon and Van Doorn [69] proposed that in oxidation reactions the main function of the metal catalyst is to form co-coordinated peroxide complex that acts as a Lewis acid and removes electron density from the peroxidic oxygen. Several molybdenum compounds are known as selective catalysts for the oxidation of various sulphides. Molybdenum salts such as molybdyldiacetylacetonate [$MoO_2(acac)_2$] [70] molybdenumhexacarbonyl [$Mo(CO)_6$] and molybdenum peroxide [$MoO(O_2)_2$] are widely used as catalysts for the oxidation of sulfides using H_2O_2 as oxidant [71]. Mimoun and coworkers have used stable oxo-diperoxo molybdenum (VI) complexes for epoxidation of olefins [72].

4.14 Oxidation of refractory sulfides

Sulfur contamination in transportation fuels represent a major source of atmospheric SOx, which contributes to air pollution and acid rain, as well as poisoning of auto exhaust catalysts. In order to minimize the sulfur oxide emissions, the desulfurization of crude oil has long been a topic of interest, deep desulfurization being even more critical for the production of fuel-cell-grade fuel. Currently, the majority of sulfur is removed by hydrodesulfurization (HDS) technology [73], which requires high temperatures and high H_2 pressures in the presence of a Mo-based catalyst. A few sulfur compounds, however, are highly resistant to this process and can only be desulfurized slowly under extreme conditions, which raises the cost of the process. Particularly challenging compounds are fused-ring thiophenes, such as benzothiophene (BT), dibenzothiophene (DBT), and their derivatives. 4, 6-Dimethyldibenzothiophene (DMDBT), in particular, is one of the most refractory compound due to the steric hindrance generated by the substituents at 4 and 6 positions limiting the access to the sulfur atom.

Although other techniques have been considered, including selective adsorption [74] and extraction with ionic liquids, [75] oxidative desulfurization (ODS) combined with extraction is considered as the most promising solution [76]. With regard to the choice of oxidant, H_2O_2 appears to be the best compromise, being more affordable and more environmentally compatible than O_3, NO_2, TBHP, or peracids and in general being more reactive than dioxygen.

Thiophenes are known to be inherently difficult to oxidize. For example the ease with which RSR and thiophenes are oxidized by H_2O_2 using $MeReO_3$ (MTO) can be compared by comparing the rate constants. The rate constants for oxidation of MeSPh and dibenzothiophene by $MeReO_3$ are 2.65×10^{-3} and 10.2 L mol^{-1} s^{-1} respectively, which clearly indicates difficulty in oxidizing thiophenes [77]. Dibenzothiophene (DBT) and 4, 6-dimethyldibenzothiphene (DMDBT) called as refractory dibenzothiophenes are very difficult to remove by current hydrodesulfurisation (HDS) process of petroleum feedstock. This may be due to steric hindrance of methyl groups of DMDBT, which does not allow close contact with the surface of Co-Mo HDS catalyst. The same reason makes bacterial bio-oxidation of DMDBT difficult though it works for other dimethylated DBT isomers [78].

In this section the selective oxidation of various sulphides to sulfoxides or sulfones including refractory sulphides using different molybdenum acetylide complexes $CpMo(CO)_3(C{\equiv}CR)$ (R = Ph, CH_4-*p*-CF_3 , CH_4-*p*-CH_3) and H_2O_2 or TBHP as oxidant has been reported.

4.15 Experimental

4.15.1 General

All reagents of commercial grade (Aldrich, SD fine) were used as received unless stated otherwise. Hydrogen peroxide used was 30% w/w in water.

4.15.2 Typical catalytic reaction procedure

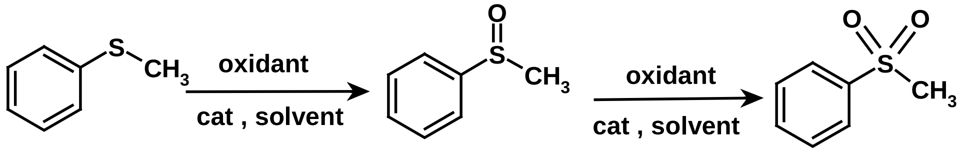
The oxidation of sulphides was performed under ambient atmosphere in a 50 ml round-bottom flask equipped with a magnetic stirrer. A solution of sulfide (0.2 mol) in CH_3CN (5 ml), 30% (w/w) H_2O_2 or 70% TBHP and Mo-acetylide complex (**1**, **2**,or**3**) (0.4 mmol) was magnetically stirred at desired temperature. Reaction was monitored by withdrawing the sample at regular time intervals and analyzing using a gas chromatograph (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). After completion of the reaction the products were confirmed by GC-MS (Model GC Agilent 6890N with HP5 MS 30 m capillary column, MS Agilent 5973 Network MSD) and ^{1}H NMR on 200.0 Bruker instrument. Chemical shifts were denoted relative to the solvent residual peak (^{1}H: $CDCl_3$-7.27 ppm, TMS 0.0 ppm).

4.15.3 Catalyst recycles studies

In a typical catalyst recycle experiment, a two necked 50 mL round bottom flask was charged with thioanisole (0.01 mol), 30% hydrogen peroxide (0.02 mol), 10 g solvent and catalyst (**1, 2, 3** or **4**) (0.007, 0.007, 0.007 and 0.230g). In case of homogeneous complexes, the reaction mixture was stirred at room temperature till the completion of the reaction. Catalyst was recycled by isolating the product in organic phase and recovering the catalyst in aqueous phase for use in the next run. In case of heterogeneous catalyst, after completion of the reaction, the catalyst was allowed to settle down and the clear supernatant liquid was decanted slowly. The residual solid catalyst was re-used with fresh charge of solvent and reactants for further recycle runs maintaining the same reaction conditions.

4.16 Result and discussion

To evaluate the catalytic activity of **1** for oxidation of sulphides, initially thioanisole was used as model substrate using hydrogen peroxide as oxidant and 0.2 mol% catalyst with respect to the substrate (Scheme 4.6).



Scheme 4.6: Oxidation of thioanisole

After 2 h, 54% conversion and 92% selectivity for Sulfoxide was obtained in presence of catalyst **1** at room temperature (Table 4.9, entry 1). When reaction was continued further the conversion increased to 96% however the selectivity for Sulfoxide decreased to 80% with corresponding increase in sulfone formation. This suggests the two-step oxidation of sulfides, initial oxidation to Sulfoxide and in second step further oxidation of sulfoxide to sulfone. Hydrogen peroxide being an electrophilic oxidant, the initial oxidation of the highly nucleophilic sulphide to Sulfoxide is an easier process than the second step where oxidation of much less nucleophilic sulfoxide to sulfone takes place [79]. When catalyst **2** was used for oxidation of thioanisole with H_2O_2 as oxidant, 73% conversion was obtained after 2 h with 79% selectivity for sulfone and the reaction was complete (100% conversion) in 6 h with 83% selectivity for sulfone (Table 4.9 entry 3). The reaction is the fastest when catalyst **3** was used with H_2O_2 as oxidant (Table 4.9 entry 5) and the reaction was complete (100% conversion) in just 2 h, however the selectivity for sulfoxide and sulfone was almost 50%. The results show that the rate of reaction for catalysts 1-3 is in the order **3** > **2** > **1** with exactly reverse order for sulfoxide selectivity **1** > **2** > **3**.

Table 4.9. Thioanisole oxidation using different catalysts[a]

Entry	Catalyst	Time, h	Conv, %	Selectivity, %	
				Sulfoxide	Sulfone
1	$CpMo(CO)_3(C{\equiv}CPh)$ (**1**)	2	54	91	9
		10	96	80	20
2	$CpMo(CO)_3(C{\equiv}C\text{-}C_6H_4\text{-}p\text{-}CF_3)$ (**2**)	2	73	21	79
		6	100	17	83
3	$CpMo(CO)_3(C{\equiv}C\text{-}C_6H_4\text{-}p\text{-}CH_3)$ (**3**)	2	100	51	49

[a]**Reaction conditions:** Thioanisole- 0.01 mol; 30% H_2O_2- 0.02 mol; Catalyst- 0.02 mmol; Acetonitrile- 10 g; Temperature-r.t.

4.16.1 Effect of solvent

The nature of the solvent play a very important role in the catalytic reactions carried out in liquid phase. To determine the appropriate solvent for the oxidation of sulfides, thioanisole was oxidized by changing the solvent at room temperature with 2 equivalents of H_2O_2 as terminal oxidant and 0.4 mol% of catalyst. The results are shown in Table 4.10. In aprotic solvents like acetonitrile and toluene the rate of reaction is maximum and

100% conversion is obtained after 2 h with 100% selectivity for sulfone (Table 4.10 entries 1 and 2). In case of protic solvent the rate of reaction decreased marginally giving sulfoxide as major product, this may be due to solvolysis of the substrate. Dichloromethane as a solvent showed excellent selectivity towards sulfoxide but the rate of reaction decreased to a greater extent (Table 4.10 entry 5). This may be due to the formation of a biphasic system with the oxidant that led to insufficient availability of oxygen for the oxidation of the sulfide. Thus acetonitrile was used as an ideal solvent for the reaction.

Table 4.10. Thioanisole oxidation in various solvents

Entry	Solvent	Conversion %	Selectivity %	
			Sulfoxide	Sulfone
1	Acetonitrile	100	0	100
2	Toluene	100	0	100
3	*ter*-Butanol	84	70.5	29.5
4	Methanol	83	86	14
5	Dichloromethane	60	97.5	2.5

Reaction conditions: Thioanisole- 0.01 mol; H_2O_2- 0.02 mol; Catalyst **1**- 0.02 mmol; Temp.- R.T.; Time-2 h.

4.16.2 Effect of catalyst concentration

Oxidation of thioanisole using H_2O_2 without catalyst gives 41% conversion with 66% selectivity for Sulfoxide. When catalyst loading was varied gradually from 1 mol% to 0.1 mol% the conversion in 2 h decreased gradually from 100% to 80% (Table 4.11). At high catalyst loading (1 and 0.4 mol%) the selectivity for sulfone was maximum (100%), however at lower catalyst loading the selectivity for sulfoxide was higher.

Table 4.11. Thioanisole oxidation with varying catalyst concentrations[a]

Entry	Catalyst loading, mol%	Conversion %	Selectivity %	
			Sulfoxide	Sulfone
1	Blank	41	67	33
2	1	100	0	100
3	0.4	100	0	100
4	0.2	80	79	21
5	0.1	54	91	9

[a]**Reaction conditions:** Thioanisole- 0.01 mol; H_2O_2- 0.02 mol; Acetonitrile- 10 g; Time-2 h; Temperature-r.t.

4.16.3 Product distribution as a function of time

The concentration time profile was followed for the oxidation of thioanisole to sulfoxide and sulfones and the results are summarized in Figure 4.2.

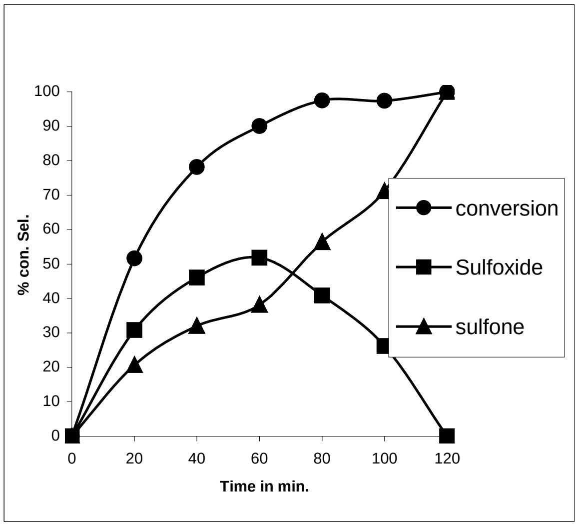


Figure 4.2: Progress of reaction of thioanisole oxidation

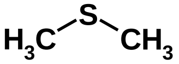
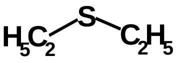
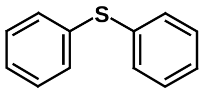
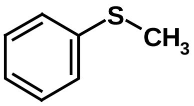
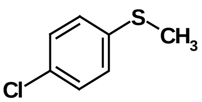
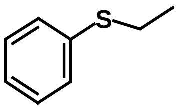
Figure 4.2 reveal that the rate of oxidation of thioanisole is very high initially, 51.7 % conversion is obtained in initial 20 min, and reaction goes to completion (100%)

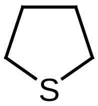
gradually in next 100 min. Initially formation of sulfoxide is higher and it reaches maxima after 60 min after which the selectivity for sulfoxide decreases with corresponding increase in sulfone formation this shows that sulfone formation takes place at the cost of sulfoxide.

4.17 Substrate scope

Wider applicability of the acetylide complex **1** was studied for the oxidation of a range of sulfides containing various functionalities. Very small quantity of catalyst has been used in all the reactions (0.2 mol%). The effect of oxidant was also studied using either H_2O_2 or TBHP as oxidant (Table 4.12). The results showed that the rate of the reaction is faster when H_2O_2 is used as an oxidant compared to TBHP. This change in the rate can be attributed to the electronegativity difference in both the oxidants and the strength of the H_2O_2, which is greater than TBHP that enhances the electrophilic character of the substrate increasing the rate of reaction and also leading to over oxidation of sulfoxide. The in situ formation of oxo peroxo molybdenum acetylide complex after addition of hydrogen peroxide to complex **1** is well characterized by FTIR and UV-Vis spectroscopy (Chapter 2 section 2.3.7). This in situ generated oxo peroxo Mo species is the catalytically active species for sulphides oxidation. For lower sulphides maximum conversion was achieved in less time at room temperature (entry 1-3). However for higher sulfides the temperature had to be increased to 60 ºC or higher to achieve maximum conversion (entry 5-10). In most of the cases very high selectivity for sulfoxide was obtained under very mild reaction conditions. In case of thioanisole, electron donating or withdrawing substituents on phenyl ring did not have any adverse effect on conversion as well as sulfoxide selectivity (entry 5 & 6 respectively). The selectivity could be switched to 100% sulfone by using higher catalyst concentration (0.1 or 0.4 mol%, Table 4.12). Tetrahydrothiphene could be oxidized with 100% conversion at 60 ºC in only 2 h (entry 8).

Table 4.12: Oxidation of various sulfides[a]

Entry.	Substrate	Oxidant	Temp. ºC	Time h	Conv. %	Selectivity %	
						Sulfoxide	Sulfone
1		H_2O_2	R.T.	2	100	92	8
		TBHP	R.T.	4	100	100	0
2		H_2O_2	R.T.	2	76	68	32
				6	89	70	30
		TBHP	R.T.	2	60	100	0
3		H_2O_2	R.T.	2	64	87	13
				4	86	87	13
		TBHP	R.T.	2	37	81	19
				12	83	78	22
4		H_2O_2	R.T.	2	54	91	9
				10	96	80	20
		TBHP	R.T.	2	32	100	0
				26	80	93	7
5		H_2O_2	60	2	62	79	21
				6	100	74	26
		TBHP	60	2	57.6	100	00
				6	84	70	30
6		H_2O_2	60	2	54.6	100	00
				8	100	80	20
		TBHP	60	2	54.5	93	7
				13	100	73	27
7		H_2O_2	60	8	100	75	26
		TBHP	60	2	52	100	00
				11	86	75	25

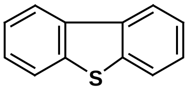
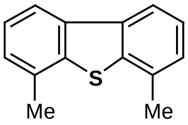
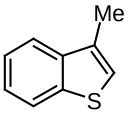
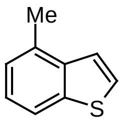
8		H_2O_2	60	2	93.7	6	94
		TBHP	60	5	100	43	57

[a]**Reaction conditions:** Substrate-0.01 mol; Oxidant- 0.02 mol; Catalyst **1**- 0.02 mmol; Acetonitrile- 10 g.

4.17.1 Oxidation of refractory sulfide

Interestingly refractory sulphides, which are difficult to oxidize like dibenzothiophene (DBT) and 4, 6-dimethylbenzothiophene (DMDBT) (Table 4.13 entry 1 and 2) also could be oxidized efficiently using catalyst **1** and hydrogen peroxide as oxidant.

Table 4.13. Oxidation of refractory sulfide[a]

Entry	Substrate	Time h	Conv, %	Selectivity, %	
				Sulfoxide	Sulfone
1		18	100	0	100
2		20	75	0	100
3		4	84	0	100
4		18	70	0	100

[a]**Reaction conditions:** Substrate- 0.01 mol; H_2O_2-0.02 mol; Catalyst **1**- 0.02 mmol; Toluene-10 g; Temp. - 100 ºC.

At 100 ºC, 100 % DBT conversion was achieved with 100% selectivity for sulfone where as 75% conversion with 100% selectivity for sulfone was achieved for DMDBT. In case of 3- methyl thiophene 84% conversion with 100% selectivity for sulfone was obtained. In case of 5-methyl thiophenes 70% conversion with 100% selectivity to sulfone obtained. In case of DMDBT, formation of sulfone is desired as the solubility of sulfone is very less in petroleum feedstock and hence removal from petroleum feedstock becomes easier.

4.18 Catalyst recycle study

One important aspect of catalysts **1-3** is that even though the catalysts are homogeneous in nature, they could be recycled very efficiently by isolating the product in organic phase and recycling the catalytically active species in aqueous phase.

Table 4.14. Catalysts recycle studies for catalyst **1-3**[a]

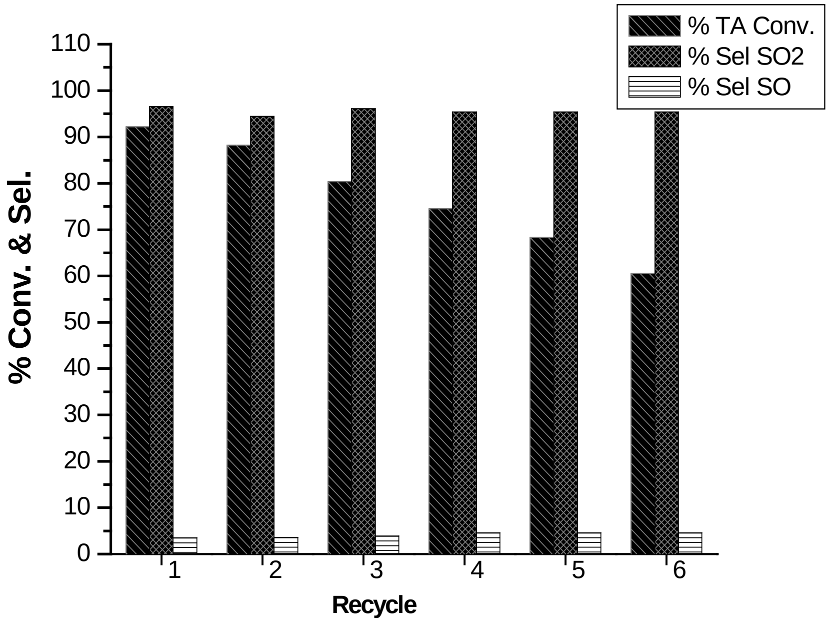
Cycle	Catalyst **1**[b]			Catalyst **2**[c]			Catalyst **3**[d]		
	Conv,	Selectivity		Conv,	Selectivity		Conv,	Selectivity, %	
	%	SO	SO_2	%	SO	SO_2	%	SO	SO_2
0	100	0	100	100	0	100	100	0	100
1	99.5	0	100	99.3	0	100	98.9	0	100
2	99.3	0	100	99	0	100	98.6	0	100
3	98.7	0	100	98.6	0	100	98.1	0	100
4	98.5	0	100	98.2	0	100	97.8	0	100
5	98.3	0	100	98	0	100	97.5	0	100

[a]**Reaction conditions:** Thioanisole-0.01 mol; H_2O_2-0.02 mol; Catalyst-0.01 mmol; Acetonitrile- 10 g; Temperature-R.T.; Reaction time for each cycle [b] 2h; [c] 1h; [d] 0.5 h; SO = Sulfoxide; SO_2 = Sulfone.

The recyclability of the catalysts **1-3** was tested for 5 cycles after extracting the catalytically active species in aqueous phase (Table 4.14), which proves the stability of these catalysts under reaction conditions. As the catalyst used is very small in all above reactions (0.2 mol%), handling of such small quantities of catalyst is difficult during extraction and concentration, hence slightly higher catalyst concentration (1 mol%) was used for recycle studies in case of all three acetylide complexes. In case of all the catalysts the conversion and the product selectivity does not decrease significantly even after five recycles. Hence recycling of these homogeneous catalysts is the major achievement in this work.

4.19 Oxidation of thioanisole with heterogenized catalyst 4

When thioanisole was oxidized using heterogeneous catalyst **4**, 99% conversion was obtained with more then 95% selectivity for sulfone in 30 min (Fig.4.3). This catalyst was recycled after decanting the reaction mixture.



PhSMe-0.01 mol, H_2O_2 0.02 mol, catalyst 210 mg; Acetonitrile 10 gm, Temperature R.T.; Time 0.5 h; SO = sulphoxide; SO2 = sulphone

Figure 4.3: Recycle study of **4** for thioanisole oxidation

The results shows that there is a gradual decrease in thioanisole conversion from 99% in the first run to 60% in 5th recycle. During all the recycle run the selectivity for sulfone remained constant. The catalysts recovered after 1st, 3rd and 5th run during recycle study was analyzed by EDAX analysis for Mo content in the catalyst to confirm the leaching of the catalyst (Table 4.15). The EDAX result shows that after 5th recycle only 50% Mo remained in the catalyst that means 50% of the initial complex used has leached out during the reaction. The results show that heterogenization of the catalyst **1** on silica support **4** is not completely successful and the heterogenized complex is not stable under reaction condition.

Table 4.15. EDAX analysis of recycled catalyst **4**

Catalyst after	Mo Wt. %	Si Wt. %	O Wt %.
Fresh	10.96	63.89	25.16
1st run	8.93	65.89	25.18
3rd run	6.27	66.61	27.11
5th run	5.06	66.75	28.19

4.20 Summary and conclusions

Molybdenum acetylide complexes have been proved to be very efficient catalysts for selective oxidation of various sulphides to sulfoxide or sulfone using H_2O_2 or TBHP as an oxidant under very mild reaction conditions. The selectivity could be tuned to either sulfoxide or sulfone effectively. Sulfides with various functional groups could be oxidized with equal efficiency. The hard refractory sulphides like dibenzothiophene and 4, 6 dimethyldibenzothiophene could also be oxidized efficiently to corresponding sulfone. Even though complexes **1 - 3** are homogeneous catalysts; they were successfully recycled for five cycles without appreciable loss in the conversion and selectivity. The heterogenized molybdenum acetylide complex was also used for oxidation of thioanisole and recycle studied showed the leaching of the complex under reaction condition.

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Chapter-5

Dioxo cyclopentadiene molybdenum acetylide catalyzed oxyfunctionazation of hydrocarbons

5. Dioxo cyclopentadiene molybdenum acetylide catalyzed oxyfunctionazation of hydrocarbons

Abstract: The design of efficient method for the selective oxyfunctionalization of unactivated carbon-hydrogen bonds continue to represent a major challenge for the community of chemists, despite the fact that the oxidation of alkanes is a major feature of the chemical economy. Alkanes like various ethyl benzenes, cumene and n-hexane were efficiently oxidized with ter-butyl hydrogen peroxide (TBHP) in acetonitrile using dioxo cyclopentadienyl molybdenum acetylide complex $[CpMo(O)_2(C{\equiv}CPh)]$ **5** *as a catalyst. This new complex* **5** *has been synthesized from* MoO_3*, which forms oxo-perxo complex on treatment with oxidant. The oxo-peroxo Mo(VI) complex is found to be very active for the oxidation of alkanes to the corresponding ketones (or aldehydes) and alcohols. The oxidation of ethyl benzene at 80 °C in acetonitrile gave 81 % conversion with 85 % selectivity for acetophenone after 20 h with overall yield of 68 % based on the alkane.*

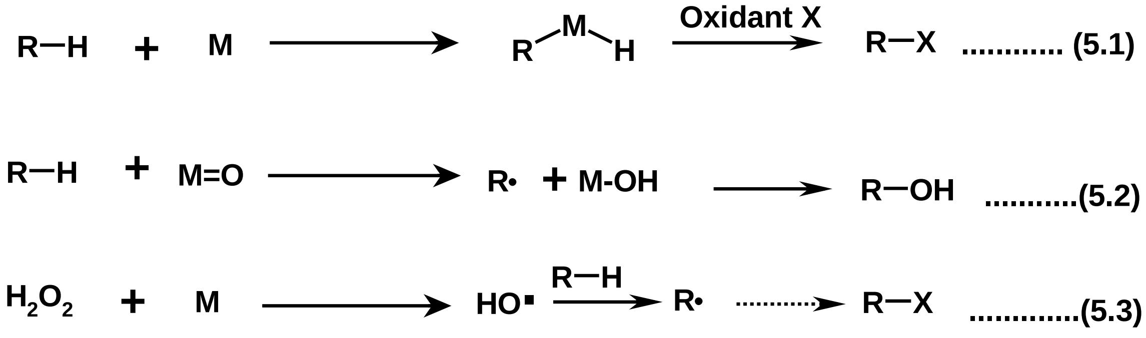
5.1 Introduction

Catalytic activation of C–H bonds of alkanes and arenes, leading to direct transformations into various functionalized chemicals, is of considerable interest to chemical industries and remain a challenge to chemists, especially of the least reactive alkanes. The success of such processes would provide simple, economic and clean methods for making many chemicals directly from hydrocarbons, such as alcohols, alkanes and carbonyl compounds, ranging from agrochemicals to large scale commodities [1]. Some of the large scale industrial catalytic alkane oxidation processes [2] include: oxidation of

- *p*-Xylene to terephthalic acid (oxidant – oxygen, liquid phase process),
- Methanol to formaldehyde (oxygen, gas phase),
- Ethylene to ethylene oxide (oxygen, gas phase),
- Propene to propene oxide (organic hydroperoxide, liquid phase),
- Ethene to vinyl acetate (oxygen, liquid & gas phase),
- Toluene to benzoic acid (oxygen, liquid phase),
- Benzene to adipic acid (oxygen, liquid phase),
- *n*-Butane to maleic anhydride (oxygen, gas phase) etc.

These processes are conducted at high temperatures and pressures. Nature performs the task of biological oxidations at ambient conditions, employing metalloenzyme and protein catalysts, which are remarkably more efficient, specific and particularly selective for producing a specific oxygenated compound [3]. Functionalisation of alkanes and cycloalkanes is rare and challenging [4]. Alkanes have neither lone pairs nor low-lying empty orbitals but only the C-H and C-C σ- and σ*- levels. It is therefore relatively hard to attack either the former with an oxidizing agent or the latter with a reducing agent or base. This means that harsh conditions and reactive reagents must be used. It is almost always is the case that the product of an alkane functionalisation reaction is more reactive than the starting material and therefore reacts faster with the fuctionalizing reagent. As a consequence, over-oxidation can be a severe problem and many of the oxidation reactions have to be run at low or very low conversion level in order to obtain a satisfactory selectivity. This aspect can be tolerable for substrates such as methane, but becomes a problem with more valuable starting materials.

A second important selectivity issue arises when there are different types of C-H bonds in the molecule. Since tertiary radicals and carbonium ions are more stable than their secondary or primary analogues, many oxidation processes display the expected selectivity pattern: tertiary > secondary > primary. From the mechanistic point of view, C−H activation processes can be divided into three types [5]. The first group includes reactions where organometallic derivatives (*i.e.*, compounds containing a metal-carbon σ-bond) are formed as an intermediate or as the final product (Scheme 5.1, eq^n. 5.1). The second group involves in reactions in which the contact between the complex and the C−H bond is achieved via a ligand, leading to C−H bond cleavage and an σ-C−M bond not being generated at any stage (eq^n. 5.2). In these reactions, the function of the metal complex usually is abstraction of an electron or a hydrogen atom from the hydrocarbon. Finally, in the processes that belong to the third type, a complex initially activates the oxidant and not the hydrocarbon (*e.g.* hydrogen peroxide, eq^n. 5.3 or molecular oxygen). The reactive species formed (*e.g.* hydroxyl radical) then attacks the hydrocarbon without any participation of the metal complex in the latter process. The metal catalyst does not take part in the direct "activation" of the C−H bond by the radical.

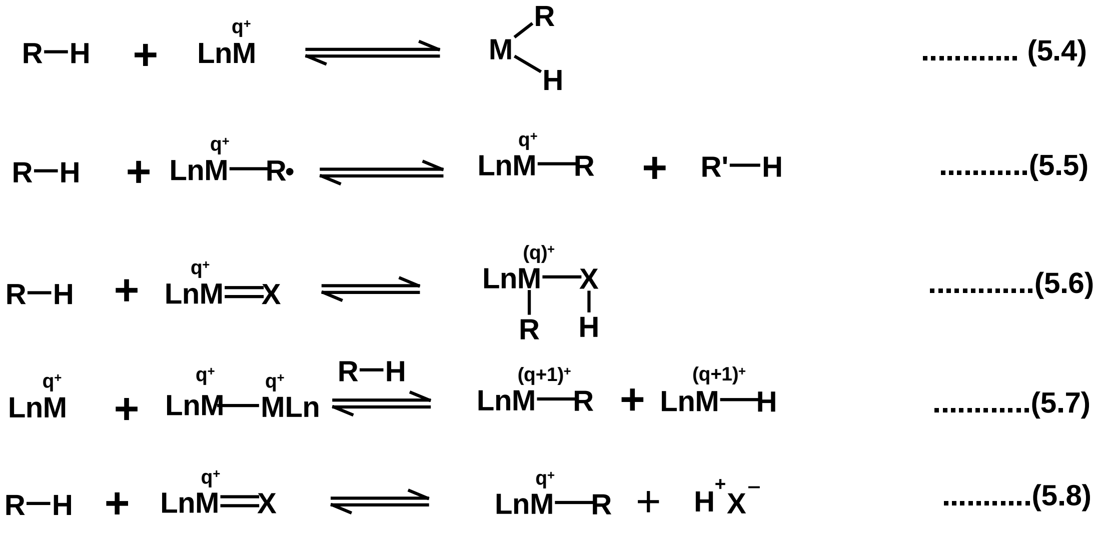


Scheme 5.1. Types of oxidative activation of C−H bonds

About one quarter of all the organic compounds produced worldwide is synthesized via selective oxidation of the hydrocarbons [6]. While molecular oxygen and hydrogen peroxide are preferred in industrial applications, other oxidants including organic peroxides, iodosylbenzene, persulphates, meta-chloroperbenzoic acid, hypochlorites etc., are also used in producing oxygenated compounds [7].

5.1.1 Transition-metal catalyzed oxidation of C−H bonds

Although alkanes are generally unreactive toward soluble transition-metal complexes, chemists have identified several classes of compounds that react readily with the C−H bonds of hydrocarbons, including alkanes, under mild conditions (first type of activation). Five general mechanisms for alkane oxidation have been proposed (Scheme 5.2) [8] (i) A oxidative addition of the C−H bond to a low-valent, electron-rich transition-metal center, yielding an alkyl hydride intermediate complex (eq^{n}. 5.4); (ii) σ-bond metathesis of the C−H bond with high valent electrophilic metal hydrides to exchange the alkyl fragments between metal and hydrogen (eq^{n}. 5.5: R, R' = H, alkyl, alkenyl, alkynyl); (iii) 1, 2-addition of the C−H bond across the metal double bond for metal heteroatom, imido or oxo complexes, yielding the corresponding metal amido (hydroxo) alkyl intermediate (eq^{n}. 5.6: X = NR, O) [9] (iv) homolytic cleavage of the C−H bond (especially for methane) by two metal-centered radicals to afford a metal alkyl and a metal hydride intermediate (eq^{n}. 5.7) [10] (v) electrophilic activation (eq^{n}. 5.8: X = halide, hydroxide, *etc*.).



Scheme 5.2: Mechanisms for C−H bond activation with organometallic compounds (q = oxidation state of the metal center)

Although the first four processes represent highly significant developments in contemporary chemistry, the applications of these reaction types for the catalytic oxidative functionalization of hydrocarbons are still rare [11]. Electrophilic activation, according to eq. 5.8, by late transition-metal ions such as Pt(II) [12], Pd(II) [13], Rh [14] Au(I)/Au(III) [15] and Hg(II) [16] stands in marked contrast to the first four processes. Indeed, frontier orbital considerations indicate, that "soft" electrophiles with low lying, polarizable LUMOs of σ^*-symmetry would be effective for this mode of C−H bond activation [17].

Transition metal salts are often used in catalytic low-temperature hydrocarbon oxidations with air. Catalytic systems consisting of cobalt or manganese acetate and sodium bromide efficiently catalyzes the oxidation of methylarenes to corresponding arenecarboxylic acids in acetic acid solution [18]. The catalytic oxidation of cyclohexane in the presence of manganese or cobalt naphthenate to give a mixture of cyclohexanone and cyclohexanol is an important industrial process [19]. Ishii and co-workers described the oxidation of hydrocarbons by molecular oxygen catalyzed by *N*-hydroxyphthalimide (NHPI) combined with manganese acetylacetonate or transition metal (mainly cobalt) salts [20]. Although air is the cheapest source of oxygen, it provides the lowest selectivity in many reactions [21]. Over the past decades, new catalysts have been developed for the use of oxidants called "oxygen atom donors", such as hydrogen peroxide, alkylhydroperoxides, peracids, hypochlorite, iodosobenzene, nitrous oxide.

The oxidation of hydrocarbons with oxygen donors is an important field of research, since some industrial processes are based on these reactions [22], e.g. textile and paper bleaching [23]. In many cases the key step includes the interaction of an oxygen atom donor, such as hydrogen peroxide, with a low-valent form of the metal affording free oxygen centered radicals [24] and/or high-valent metal-oxo species [25]. In the classical Fenton system, a stoichiometric mixture of Fe(II) with H_2O_2, is transformed gradually into the catalytic Fe(III)-Fe(II)-H_2O_2 system in the course of the hydrogen peroxide decomposition, generating hydroxyl radicals. Other catalytic systems for the selective oxyfunctionalization of hydrocarbons with oxygen atom donors have been described by Barton (Gif systems, i.e. iron complexes in pyridine/acetic acid) [26] (nonheme transition metal catalysts containing polydentate nitrogen ligands), Mansuy

[27] (manganese and iron porphyrinates with imidazole), E. N. Jacobsen [28], (manganese Schiff-base complexes,) and Herrmann [29] (methyltrioxorhenium/H_2O_2).

Recent studies have shown that transition metals in combination with various oxidizing agents convert a wide range of hydrocarbons to the corresponding oxidized products. These oxidations are modeled on certain enzymes that perform the oxidation of hydrocarbons in natural systems [30]. In spite of many studies, there are very few which use TBHP as a source of oxygen in the C-H oxidation of alkanes [31].

Various molybdenum complexes and oxides are known to be very good homogeneous as well as heterogeneous catalysts for oxidation/epoxidation reactions. MoO_3 on different solid supports is used for oxidation [32]. Bhattacharyya et al have prepared and characterized different Mo(VI) oxo-peroxo and oxodiperoxo complexes with various ligands and have successfully used these complexes for epoxidation of various olefins and oxidation of alcohols to carbonyl compounds [33]. Molybdenum carbonyl complexes with different ligands like halides [34] and cyclopentadienyl; η^5-C_5R_5; R = H, Me, Ph [35] are mainly used for epoxidation of variety of olefins. Tungsten acetylide complexes are reported to form oxo-peroxo complexes on treatment with H_2O_2 in acidic medium [36]. Molybdenum being in the same group in the periodic table as that of tungsten it is expected to behave in the similar manner. Hence these complexes are expected to be good oxidation catalysts. There are no reports in the literature on the use of molybdenum catalyst, homogeneous or heterogeneous, for oxidation of alkanes.

Here the use of molybdenum acetylide dioxo complex has been explored for first time for efficient and selective oxidation of aromatic alkanes to corresponding carbonyl compound or alcohol using TBHP as oxidant. The details of all the results are reported in this chapter.

5.2 Experimental

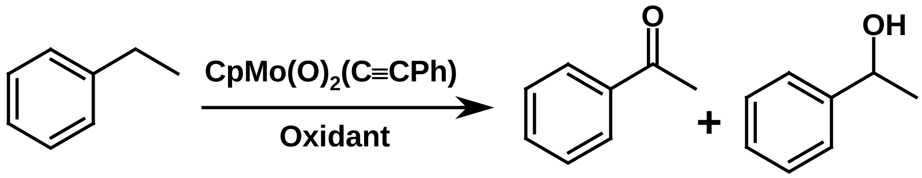
Ethyl benzene, diethylbenzene, cumene, cyclohexene, n-hexane were purchased from Aldrich and used as received. TBHP used was 70 % w/w in water. All solvents SD Fine were freshly distilled priors to use.

General procedure for oxidation of ethyl benzene

In a typical catalytic reaction, 50 mL two necked round bottom flask was charged with ethyl benzene (0.01 mol), 70 % TBHP (0.02 mol), 10 g solvent and catalyst **5** (0.02 mmol). The reaction mixture was heated to desired temperature and stirred till completion of the reaction. Reaction was monitored by GC. All samples were analyzed on an Agilent 6890 Gas Chromatograph. The reaction products were confirmed by GC-MS (Model GC Agilent 6890N).

5.3 Results and Discussion

Initially ethyl benzene was oxidized as model substrate using catalytic amount of complex **5** and an excess of 70% aqueous TBHP in acetonitrile at 80°C (Scheme 5.1).



Scheme 5.1: Oxidation of ethyl benzene

The oxidation of ethyl benzene was carried using various molybdenum complexes. The results are summarized in Table 5.1.

The results depict that, in absence of catalyst the reaction does not proceed. In presence of $Mo(CO)_6$ as well as $CpMo(CO)_3Cl$ the ethyl benzene oxidation did not takes place. Cyclopentadienyl molybdenum pheylacetylene, **1** gave high conversion of ethyl benzene (70%) and selectivity for acetophenone (81%) and phenylethanol 19% (Table 5.1 entry 4). Whereas dioxo cyclopentadienyl molybdenum phenylacetylide complex (**5**) showed still higher conversion (85%) of ethyl benzene with higher selectivity for acetophenone (85%). Among all of the complexes studied for oxidation of ethyl benzene the catalytic activity of **5** is superior to those of the others. Hence complex **5** was chosen as catalyst for further parametric study for oxidation of ethyl benzene.

Table 5.1. Oxidation of ethyl benzene with various molybdenum complexes

Entry	Catalyst	Conv. %	Selectivity %	
			Acetophenone	Phenylethanol
1	Blank	0	0	0
2	Mo(CO)$_6$	0	0	0
3	CpMo(CO)$_3$Cl	0	0	0
4	CpMo(CO)$_3$(C≡CPh) **1**	70	81	19
5	CpMo(O)$_2$(C≡CPh) **5**	81	85	15

Reaction conditions: Ethyl benzene- 0.01 mol; TBHP-0.02 mol; Catalyst- 0.02 mmol; Acetonitrile- 10 g; Time-20 h; Temp- 80 °C.

5.3.1 Effect of oxidant

Oxidation of ethyl benzene was studied with hydrogen peroxide and *t*-butylhydroperoxide. TBHP is found to be very efficient compared to H_2O_2 with very high conversion though selectivity for acetophenone and phenyl ethanol did not alter much after changing the oxidant.

Table 5.2. Oxidation of ethyl benzene with various oxidants

Entry	Catalyst	Oxidant	Conv. %	Selectivity %	
				Acetophenone	Phenylethanol
1	CpMo(CO)$_3$(C≡CPh) **1**	H_2O_2	7	83	17
		TBHP	70	81	19
2	CpMo(O$_2$) (C≡CPh)	H_2O_2	30	90	10
		TBHP	81	85	15

Reaction conditions: Ethyl benzene- 0.01 mol; Oxidant- 0.02 mol; Catalyst: 0.02 mmol, Acetonitrile- 10 g; Time-20 h.; Temp: 80 °C.

5.3.2 The role of the solvents in oxidation of ethyl benzene

Considering the previous experience [37] alcohol was selected as solvent. As shown in Table 5.3 the co-solvent has indeed a dramatic influence on the outcome of the oxidation of ethyl benzene. The reactions were carried out at 80 ºC for 20 h. In case of lower alcohols like methanol, low conversion of ethyl benzene occurred leading to decrease in acetophenone selectivity (Table 5.3, entry 1). When bulky alcohol like *t*-BuOH was used (Table 5.3, entry 2), further decrease in activity and selectivity was observed. In case of chlorinated solvents (entries 3- 5) no conversion was observed, this might be due to low boiling point of the corresponding solvent. However when acetonitrile was used very high conversion (81%) with high selectivity for acetophenone was obtained. This shows that acetonitrile is preferred solvent for this system.

Table 5.3. Effect of solvent on conversion and selectivity

Entry	Solvent	Conv. %	Selectivity %	
			Acetophenone	Phenylethanol
1	MeOH	68	74	26
2	*t*-BuOH	60	76	24
3	$CH_2Cl_2^{\#}$	00	0	0
4	$CHCl_3^{\#}$	00	0	0
5	$CCl_4^{\#}$	0	0	0
6	CH_3CN	81	85	15

Reaction conditions: Ethyl benzene- 0.01 mol; TBHP- 0.02 mol; Catalyst **5**-0.02 mmol; Solvent-10 g; Time-20 h; Temp- 80 °C. # at 40 °C.

5.3.3 The influence of catalyst loading on reaction

To study the effect of catalyst loading on conversion and selectivity, catalyst concentration was varied gradually from 0.2 mol% to 1 mol%. With increase in catalyst concentration the reaction rate increased and hence the time for completion of the reaction decreased from 20 h to 4 h with no change in the product selectivity. The results are summarized in Table 5.4.

Table 5. 4. Catalyst loading effect

Entry	**5**, mol %	TOS h	Conv. %	Selectivity %	
				Acetophenone	Phenylethanol
1	0.2	20	81	85	15
2	0.4	12	83	84	16
3	0.6	6	80	86	14
4	0.8	5	85	85	15
5	1	4	90	84	16

Reaction conditions: Ethyl benzene- 0.01 mol; TBHP-0.02 mol; Acetonitrile-10 g; Time- 20 h; Temp: 80 °C

5.3.4 The effect of temperature

The influence of temperature on ethyl benzene conversion and product selectivity was examined (Table 5.5). When the reaction temperature was increased gradually from room temperature to 100 °C, the rate of the reaction increased with significant change in product distribution. At room temperature as well as at 40 °C there was no reaction even after 20 h (entry 1 and 2). On further increasing the temperature to 60 °C, only 37 % ethyl benzene was converted giving up to 84% selectivity for acetophenone and 16% selectivity for phenylethanol. When temperature was further increased to 80 °C, the conversion increased to 81% with 85% selectivity for acetophenone. However with further increases in the temperature to 100 °C, no further increase in conversion or selectivity was observed. Hence 80 °C was used as optimum temperature for further reactions.

Table 5.5: Temperature effect

Entry	Temp. °C	Conv. %	Selectivity %	
			Acetophenone	Phenylethanol
1	RT	0	0	0
2	40	00	0	0
3	60	37	84	16
4	80	81	85	15
5	100	82	86	14

Reaction conditions: Ethyl benzene- 0.01 mol; TBHP- 0.02 mol; Catalyst **5**- 0.02 mmol, Acetonitrile- 10 g; Time-20 h.

5.3.5 Progress of the reaction

To study the product distribution as a function of time, the reaction was monitored as a function of time.

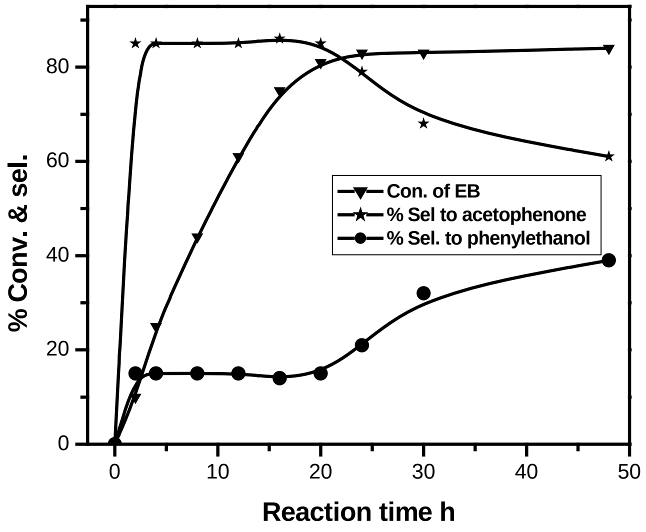


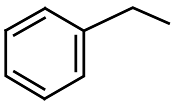
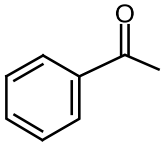
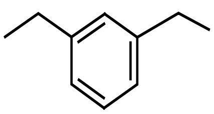
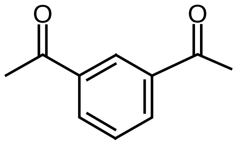
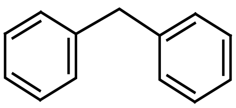
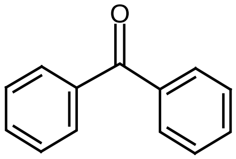
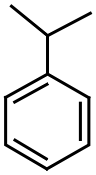
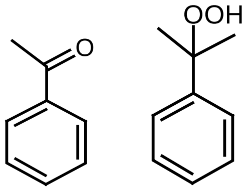
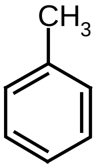
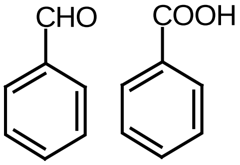
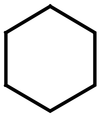
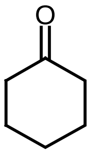
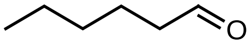
Figure 5.1: Conversion and product selectivity profile with time

The result shows that the maximum conversion of 86% is obtained in 20 h with 81% selectivity for acetophenone and 19 % selectivity for phenylethanol. However after 20 h there is no considerable change in the conversion even up to 48 h (82 %) with decrease in the acetophenone selectivity to 60% with corresponding increase in the alcohol selectivity (40%).

5.3.6 Substrate Scope

Various alkylarenes, cycloalkanes and alkanes were oxidized using **5** and the results are reported in Table 5.6. Diethyl benzene gave 80% selectivity for diacetophenone with 72% conversion where as diphenylmethane gave benzophenone with a rather remarkable selectivity 100%, (Table 5.6, entry 2) with 71% conversion. Cumene was also converted with excellent conversion (100%) and 56% selectivity for acetophenone and 44% for cumene hydroperoxide (Table 5.6, entry 4). However toluene gave very poor conversion with moderate selectivity for benzaldehyde (Table 5.6, entry 5). More challenging oxidations of fully saturated cycloalkanes were also attempted. The less reactive cyclohexane was oxidized with 70% conversion with an equimolar mixture of cyclohexanol and cyclohexanone with overall cyclohexanone yield of 39%. The oxidation of cyclohexane under mild conditions is of great industrial interest for the production of adipic acid and ε-caprolactam [38]. The conversion in case of linear alkane was poor, when n-hexane was oxidized; only 15% conversion was obtained with 59% selectivity for hexaldehyde with overall 9 % yield of hexaldehyde (Table 5.6, entry 8).

Table 5.6. Oxidation of hydrocarbons

Entry	Substrate	Major products	Conv. %	Selectivity %		Ketone Yield %
				Carbonyl	Other	
1			80	85	15	68
2			72	80	20	57.6
3			81	100	0	81
4			100	56	44	56
5			8	84	16	7
6			70	56	44	39
8			15	59	41	9

Reaction conditions: Substrate- 0.01 mol; TBHP- 0.02 mol; Catalyst **5**-0.02 mmol, Acetonitrile: 10 g; Time: 20 h; Temp: 80 °C.

5.4 Summary and conclusions

Dioxo cyclopentadienyl molybdenum acetylide catalyzed oxidation system for saturated hydrocarbons has been developed. TBHP was found to be better oxidant than H_2O_2 in this case. This catalyst system does not require any additives like carboxylic acid. Various activated alkanes like ethyl benzene, diethyl benzene and cumene as well as non-activated alkanes like cyclohexane were successfully oxidized to corresponding ketones with high conversion and high selectivity, though conversion in case of n-hexane was lower.

5.5 References

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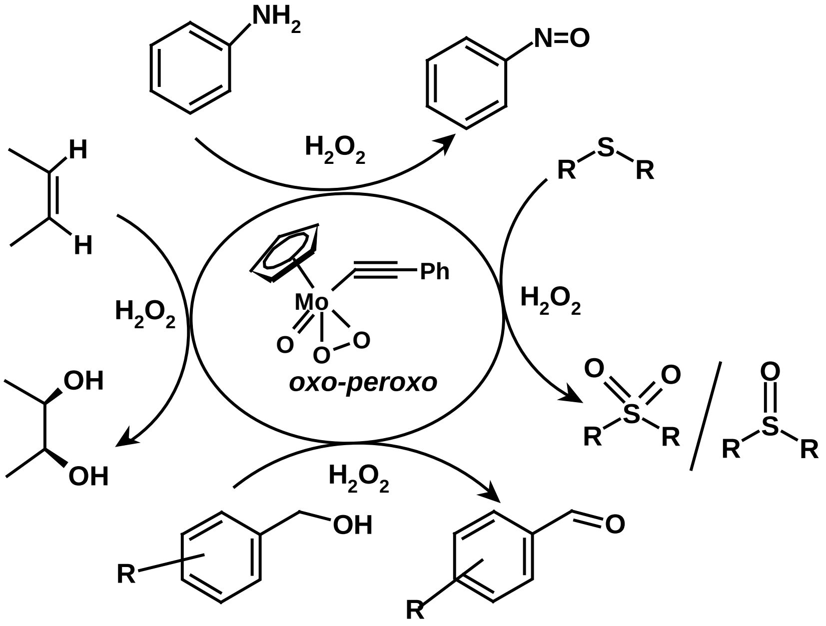
Summary, Conclusions and Future Prospects

Abstract: In this part the most important results of the previous chapters are summarized



Selective oxidation of olefins and alcohols to produce epoxides, aldehydes, and ketones is of great importance in the fine chemical and pharmaceutical industries. Traditionally, these catalytic procedures produce a great deal of environmentally undesirable wastes because inorganic oxidants and organic solvents are used. Replacing the conventional process by an environmentally benign procedure along with the use of environment friendly oxidants like molecular oxygen or hydrogen peroxide is highly desirable. However, it is known that both these eco friendly oxidants generally do not show any direct activity towards the organic substrates. There are various transition metal based catalyst systems that are known to activate molecular oxygen and hydrogen peroxide.

Molybdenum complexes have already shown the value as potentially efficient oxidation catalysts. We have tuned the ligand environment to get highly stable and reusable catalytic system. This thesis describes synthesis of various cyclopentadienyl molybdenum acetylide complexes. It also describes catalytic application of these synthesized complexes in various important organic transformations. This chapter presents a brief summary of the work described in previous chapters and general conclusions arrived from the work.

In the first chapter given general introduction about importance of oxidation reaction as well as the conventional procedures used for different oxidation reaction and its merits and demerits. This chapter also given the introduction about homogeneous catalysis, importance of transition metal complexes in homogeneous catalysis as well as some of the industrial problems, which use homogeneous catalyst. Brief overview of different Mo complexes used in different catalytic and biological process is given.

Second chapter describes the detailed synthesis and characterization of cyclopentadienyl molybdenum acetylide complexes. η^5-Cyclopentadienyl molybdenum acetylide complexes $CpMo(CO)_3(C{\equiv}CR)$, R= Ph (**1**), C_6H_4-p-CF_3 (**2**), C_6H_4-*p*-CH_3 (**3**), were prepared from $CpMo(CO)_3Cl$ via sonogashira coupling with excellent yields. Complexes are characterized by various spectroscopy techniques. These complexes on treatment with oxidant form the oxo-peroxo species which was confirmed by FTIR and UV-Vis spectroscopy. The complex **1** was immobilized on silica and characterized. The alternative route for synthesis of dioxo cyclopentadienyl molybdenum acetylide $CpMo(O)_2C{\equiv}CPh$) from MoO_3 was developed via molybdenum oxychloride, which gave excellent yield (76 %) and this synthesis follows greener route as the number of steps in the synthesis are much less and hence separation and purification at each step is saved avoiding use of expensive starting material like $Mo(CO)_6$ and liberation of CO on treatment with oxidant.

In the chapter **3** we have discussed the *cis*-dihydroxylation of alkenes using molybdenum acetylide complex $CpMo(CO)_3(C{\equiv}CPh)$ (**1**) and hydrogen peroxide as an efficient and environmentally benign oxidant. This catalyst gave high TON (409) in case of dihydroxylation of cyclohexene with H_2O_2 (9). Another major outcome was the extensive characterization of the intermediate species using FTIR, UV spectral analysis, XPS studies as well as cyclic voltametric studies. Based on spectral analysis, probable mechanism for dihydroxylation was proposed. Interestingly, even though the catalyst is homogeneous; it could be recovered quantitatively by extraction in aqueous phase and recycled five times without appreciable loss in cyclohexene conversion and selectivity for *cis*-1, 2-cyclohexanediol. This catalyst was applied for *cis*–dihydroxylation of other substrates like styrene, α-methyl styrene, limonene and cyclopentene with very high selectivity for *cis* diol.

In the fourth chapter the application of complex 1 for heteroatom oxidation has been discussed. The molybdenum acetylide oxo-peroxo complex obtained insitu by the treatment of the cyclopentadienyl molybdenum acetylide carbonyl complex, $CpMo(CO)_3(C{\equiv}CPh)$; Cp = η^5-C_5H_5 with H_2O_2, has been used as an efficient catalyst for selective oxidation of primary amines to nitroso derivatives, alcohols to carbonyl compounds and of sulphides to either sulfoxide or sulfone. In case of amine oxidation excellent conversion (up to 100%) and very high selectivity for nitroso compounds (99%) have been obtained using 30% hydrogen peroxide as an oxidant. The oxo peroxo Mo (VI) complex has also been found to be very active for the oxidation of various substituted primary aromatic amines with electron donating as well as electron withdrawing substituents on the aromatic ring. The catalytic oxidation of alcohols to carbonyl compounds was carried out under solvent free conditions. Excellent alcohol conversion (up to 90%) and very high selectivity for aldehyde compounds (90%) was obtained. The formed oxo peroxo Mo (VI) complex is stable under reaction conditions and has been used for oxidation of various substituted primary aromatic alcohol.

The selectivity for oxidation of sulphides to either sulfoxide or sulfone was tuned by controlling various reaction parameters like oxidant, temperature, reaction time and catalyst concentration. Various lower as well as higher sulphides with different functionalities were also successfully oxidized. Electron withdrawing as well as electron donating substituents on phenyl ring of acetylide moiety has led to the higher reaction rates as well as higher selectivity for sulfone. Interestingly even though complexes **1 - 3** are homogeneous catalysts; they were successfully recycled for five cycles without appreciable loss in the conversion and selectivity.

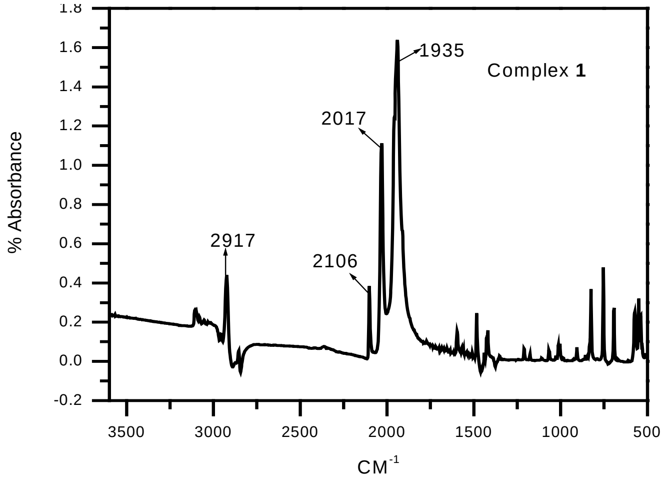
In the fifth chapter we have demonstrated the efficient methods for the selective Oxyfunctionilization of unactivated alkanes like ethyl benzene, cumene, n-hexane etc. Cyclopentadiene molybdenum acetylide dioxo complex $CpMo(O)_2(C{\equiv}CPh)$ (**5**) was efficient alkane oxidation catalyst using TBHP in acetonitrile. This complex has been found to be very active for oxidation of alkanes to the corresponding ketones (aldehydes) and alcohols. The oxidation of ethyl benzene at 80 °C in acetonitrile gave 81% conversion and 85 % selectivity for acetophenone in 20 h the overall yield is 68 % based on the alkane.

Final conclusions and future prospects

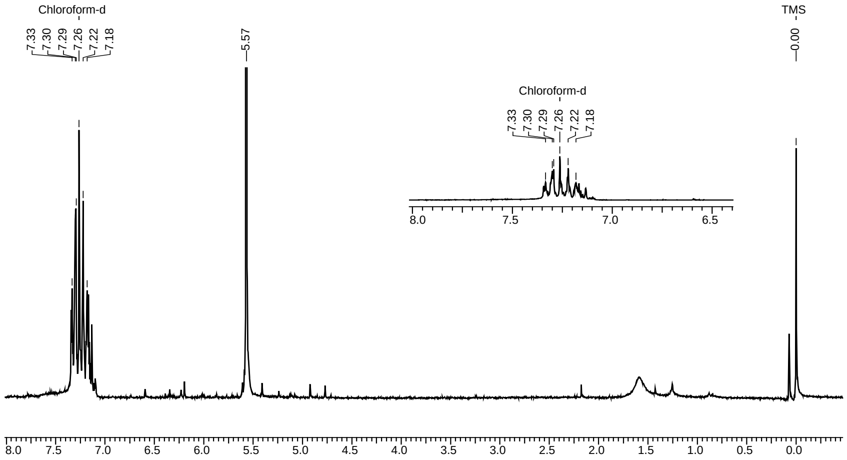
In conclusion, this work describes a new catalytic system based on Mo-acetylide complex for variety of oxidation reactions using environmental friendly oxidant like H_2O_2 and TBHP. The conversion and selectivities for desired products in olefin dihydroxylation, amine, alcohol and sulfide oxidation are very encouraging, showing improved performance compared to literature reports. Considering versatile nature of cyclopentadienyl ligand, there is a scope of using chiral cyclopentadienyl ligand for preparation of chiral molybdenum acetylide complex and use for asymmetric dihydroxylation as well as oxidation of prochiral sulfide to chiral sulfoxides.

Selected analytical data

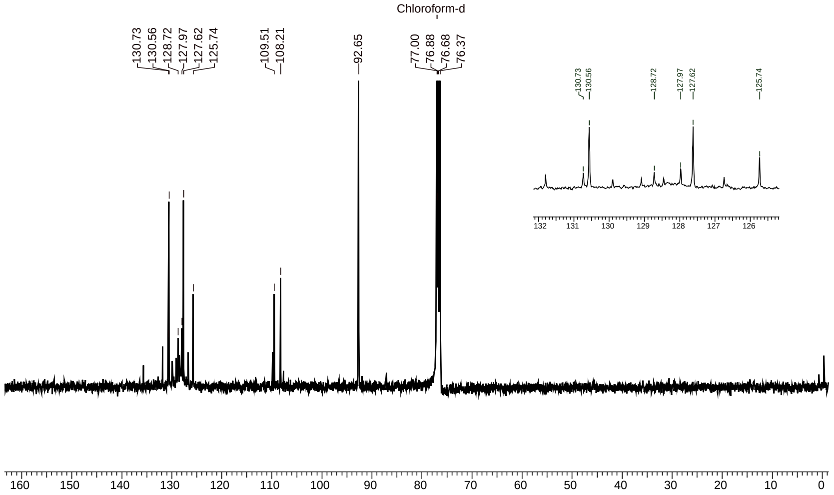
Spectra 1: FTIR of $\mathrm{CpMo(CO)3C{\equiv}CPh}$



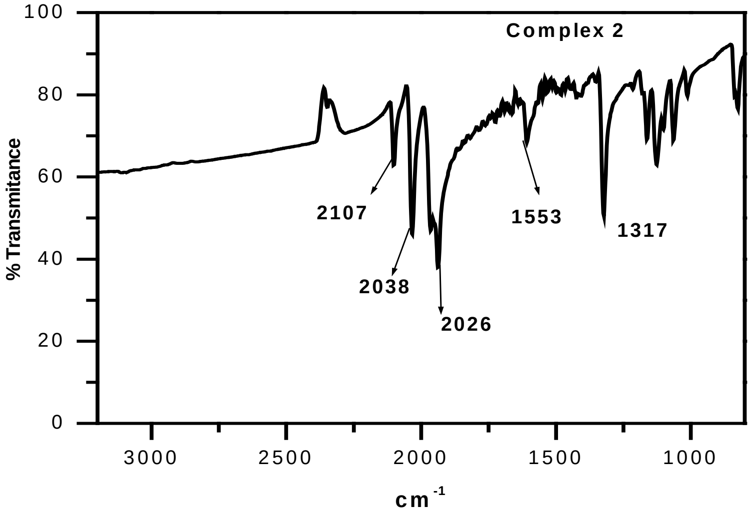
Spectra 2: NMR of $\mathrm{CpMo(CO)3C{\equiv}CPh}$



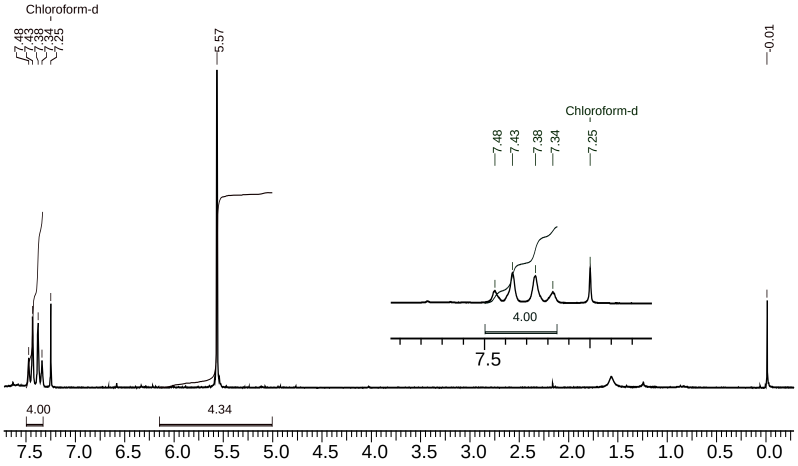
Spectra 3: ^{13}C NMR of $\mathrm{CpMo(CO)3C{\equiv}CPh}$



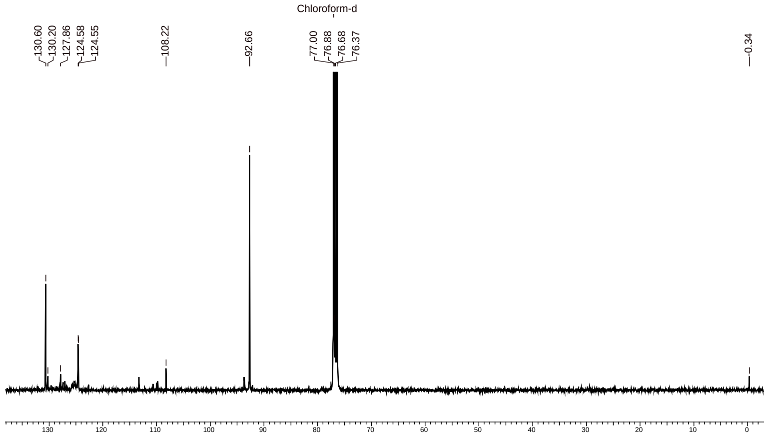
Spectra 4: FTIR of $CpMo(CO)3C{\equiv}C(C_6H_4)CF_3$



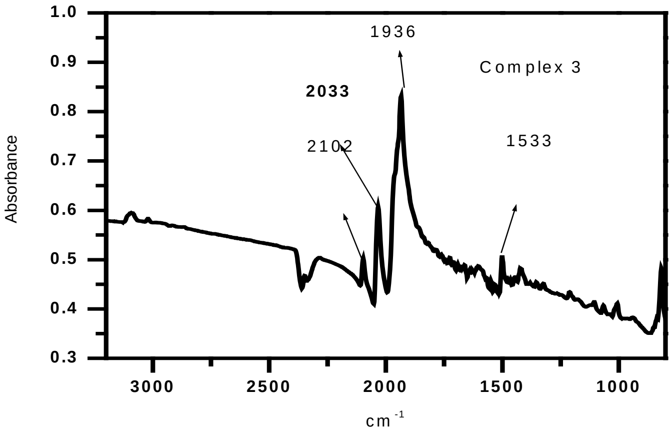
Spectra 5: NMR of $CpMo(CO)3C{\equiv}C(C_6H_4)CF_3$



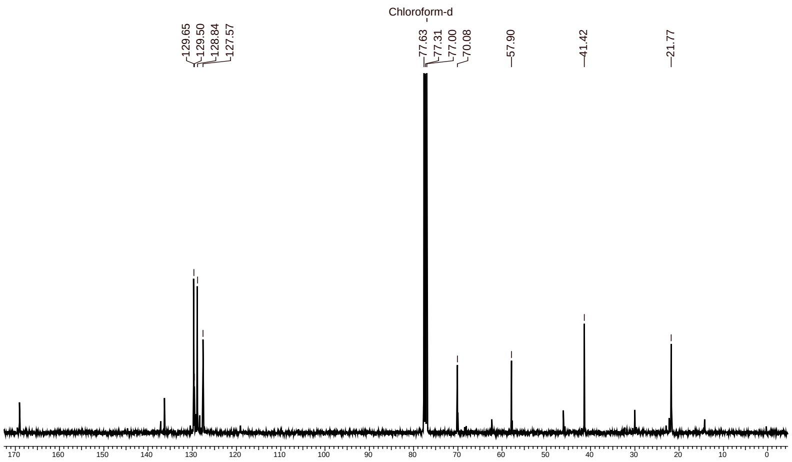
Spectra 6: ^{13}CNMR of $CpMo(CO)3C{\equiv}C(C_6H_4)CF_3$



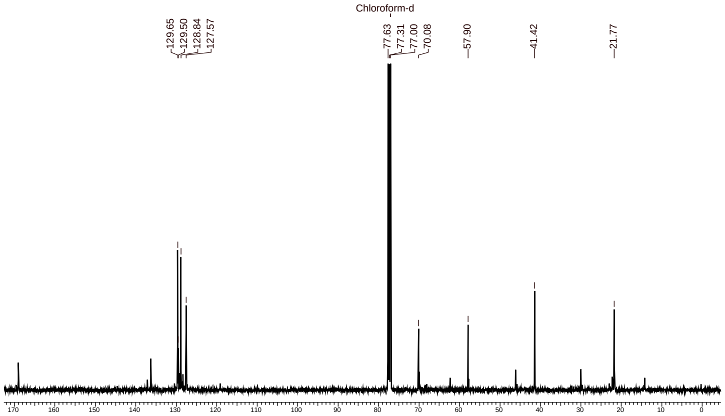
Spectra 7: FTIR of CpMo(CO)3C≡C(C_6H_4)CF_3



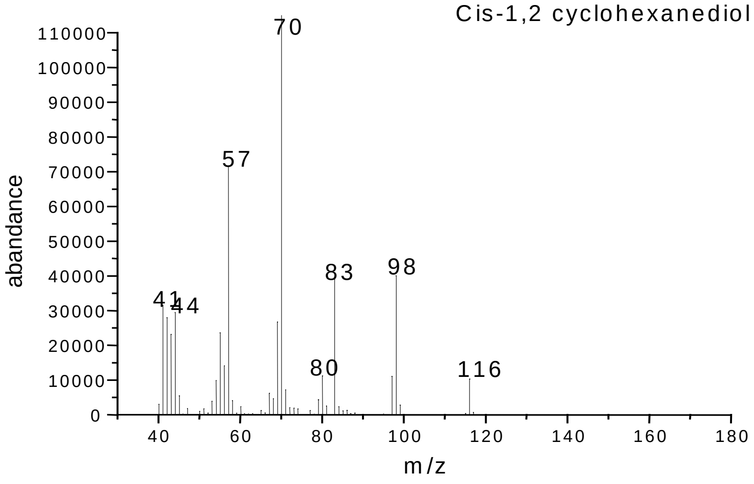
Spectra 8: NMR of CpMo(CO)3C≡C(C_6H_4)CH_3



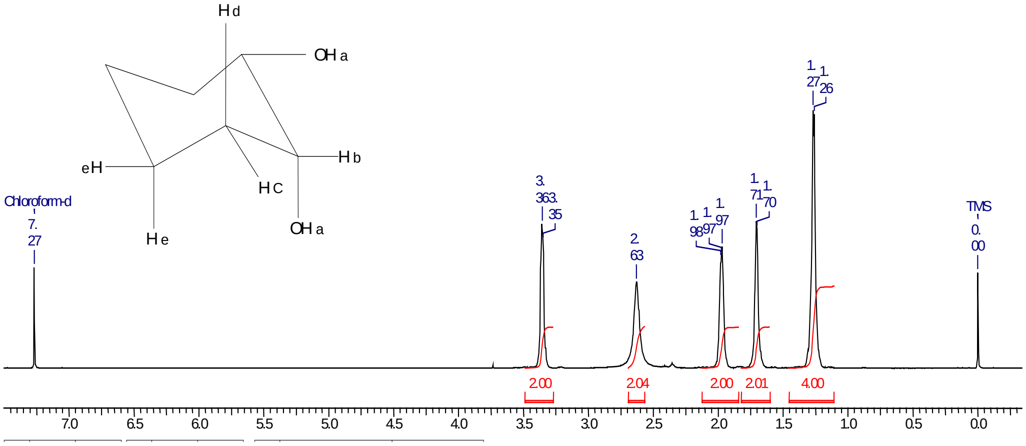
Spectra 9: ^{13}CNMR of CpMo(CO)3C≡C(C_6H_4)CH_3



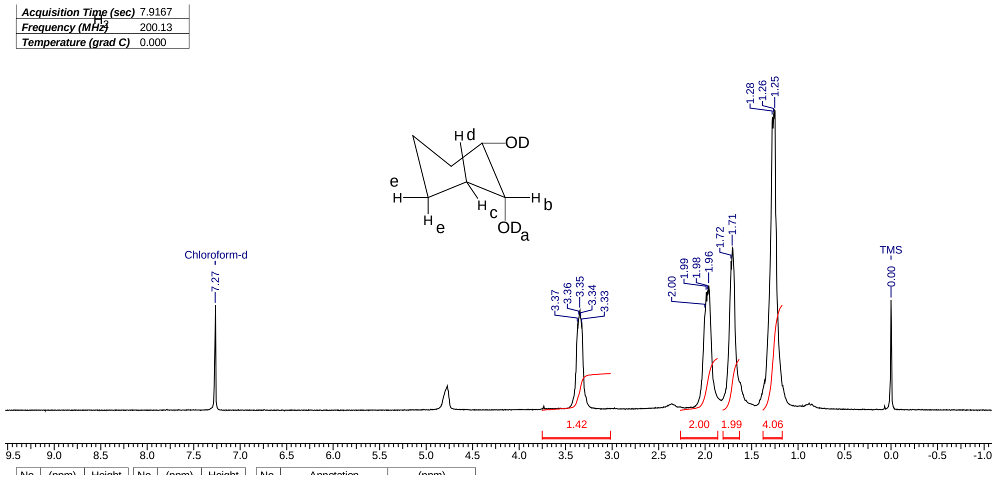
Spectrum 10: Mass spectrum of *cis*-1, 2-cyclohexanediol



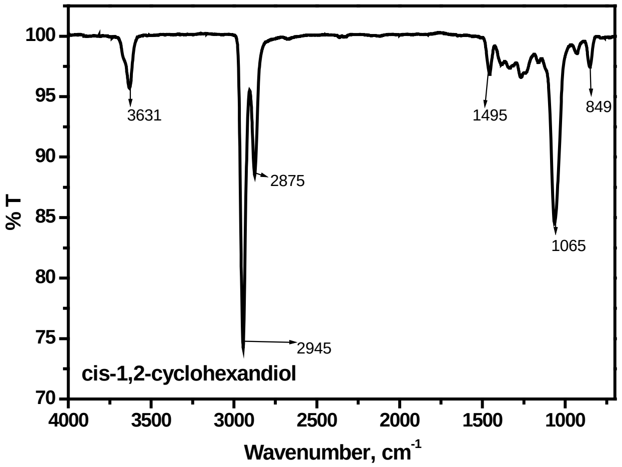
Spectrum11: ^{1}H NMR spectrum of *cis*-1,2-cyclohexanediol



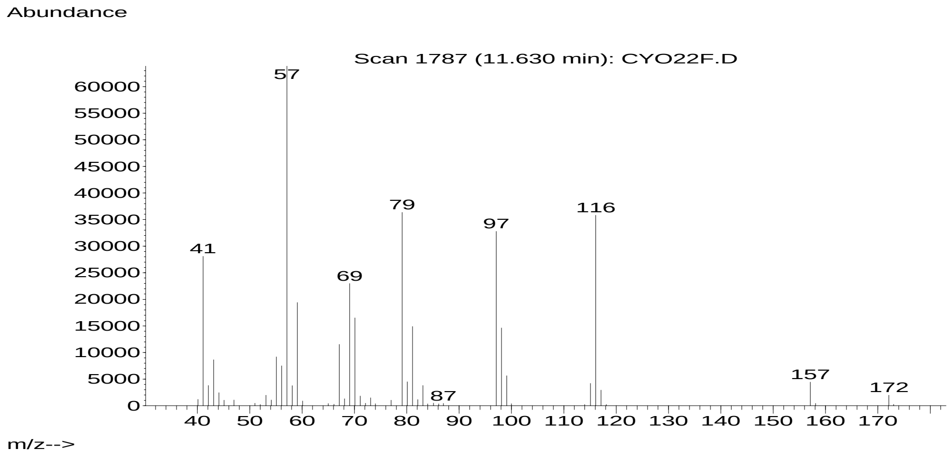
Spectrum 12: ^{1}H NMR spectrum of D_2O exchanged *cis*-1, 2-cyclohexanediol



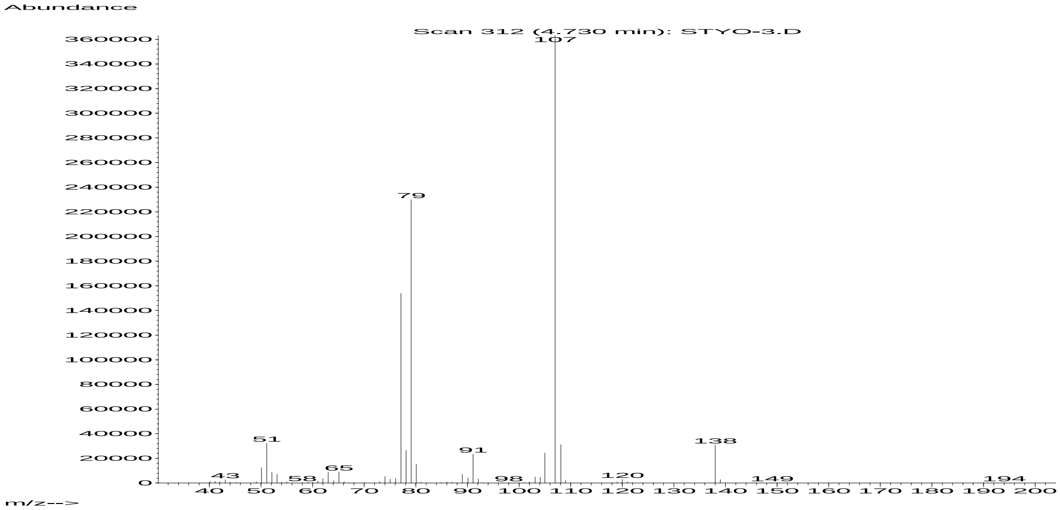
Spectrum 13: IR spectrum of cis-1, 2-cyclohexenol



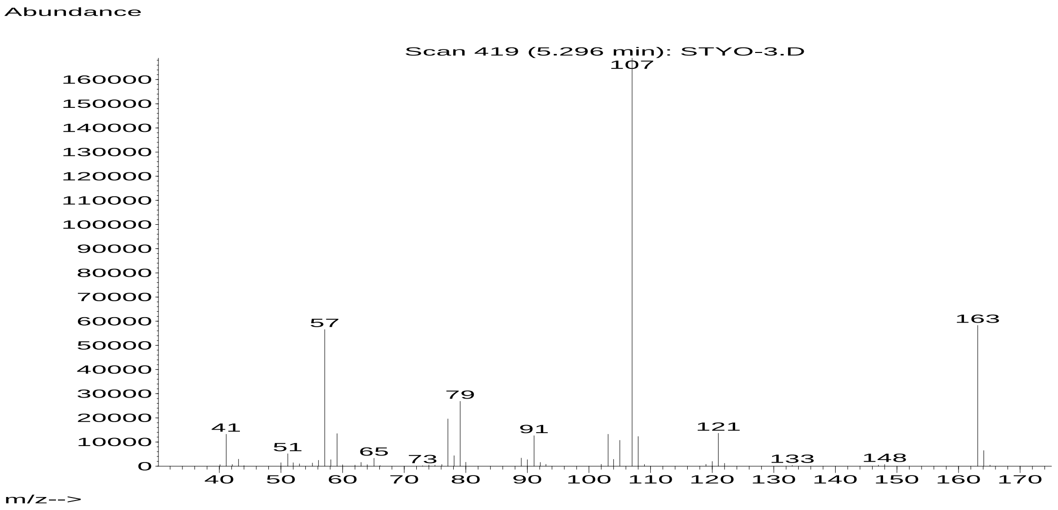
Spectrum 14: Mass spectrum of cyclohexendiol monoacetate



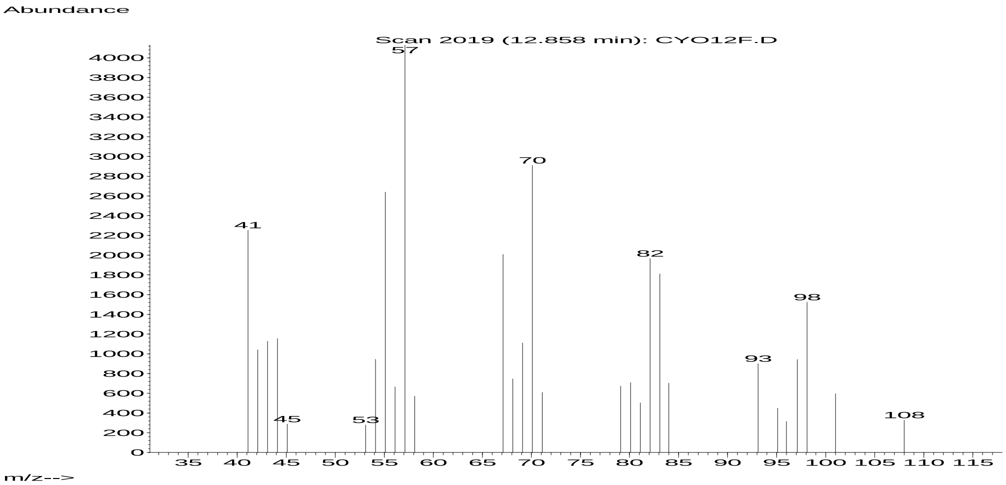
Spectrum 15: Mass spectrum of benzene ethandiol



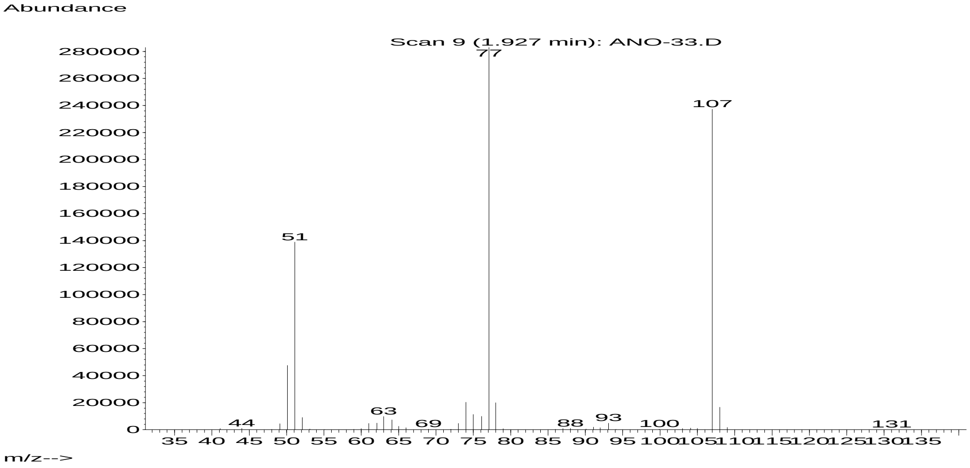
Spectrum 16: Mass spectrum of benzene ethandiol monoether



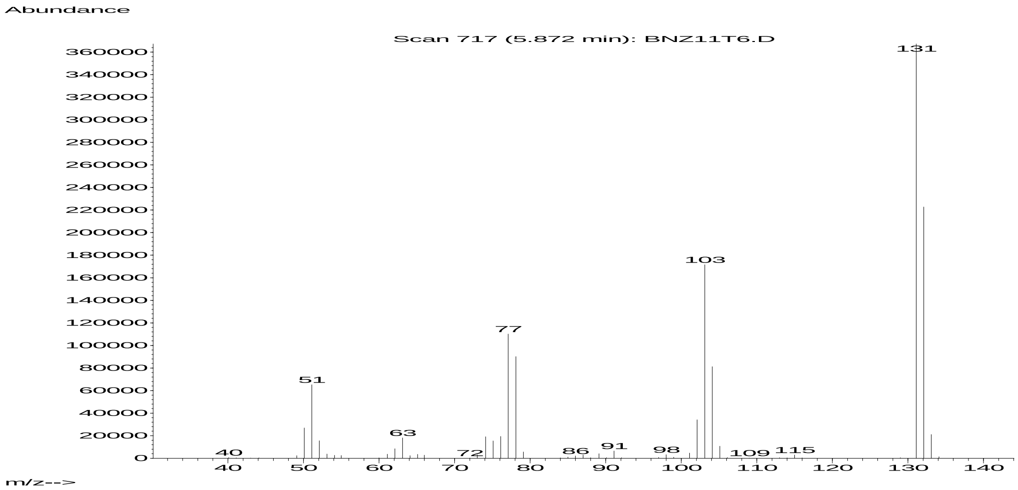
Spectrum 17: Mass spectrum of octanediol



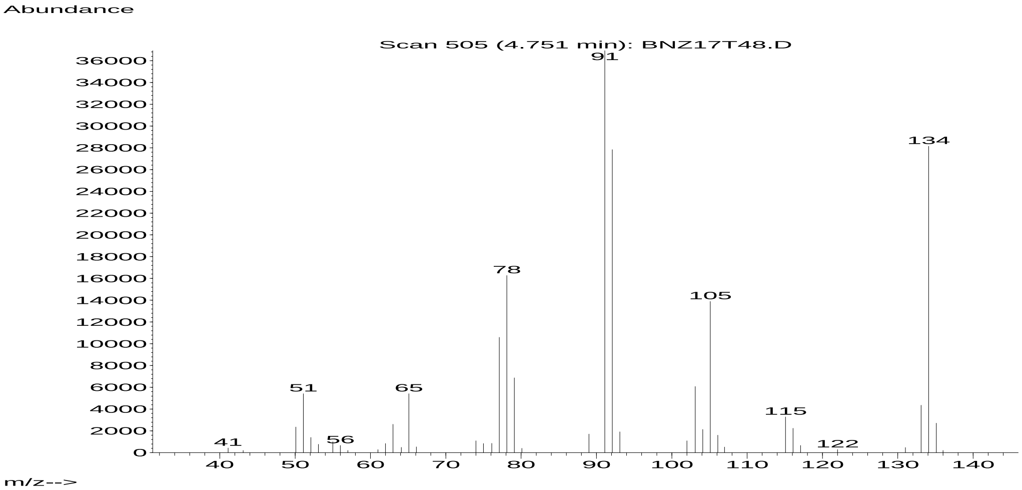
Spectrum 18: Mass spectrum of nitrosobenzene



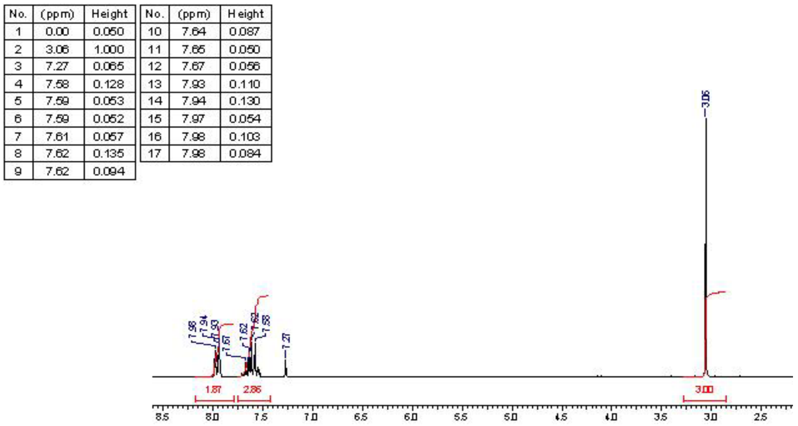
Spectrum 19: Mass spectrum of benzaldehyde



Spectrum 20: Mass spectrum of benzenepropanaol

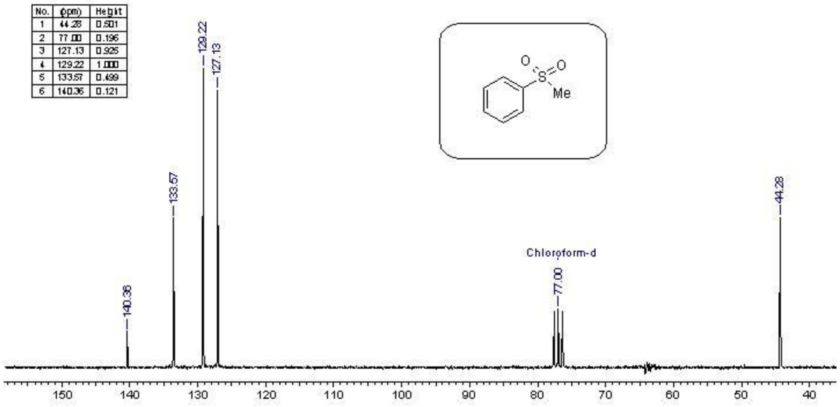


Spectrum21: ^{1}H NMR spectra of methylphenylsulfone

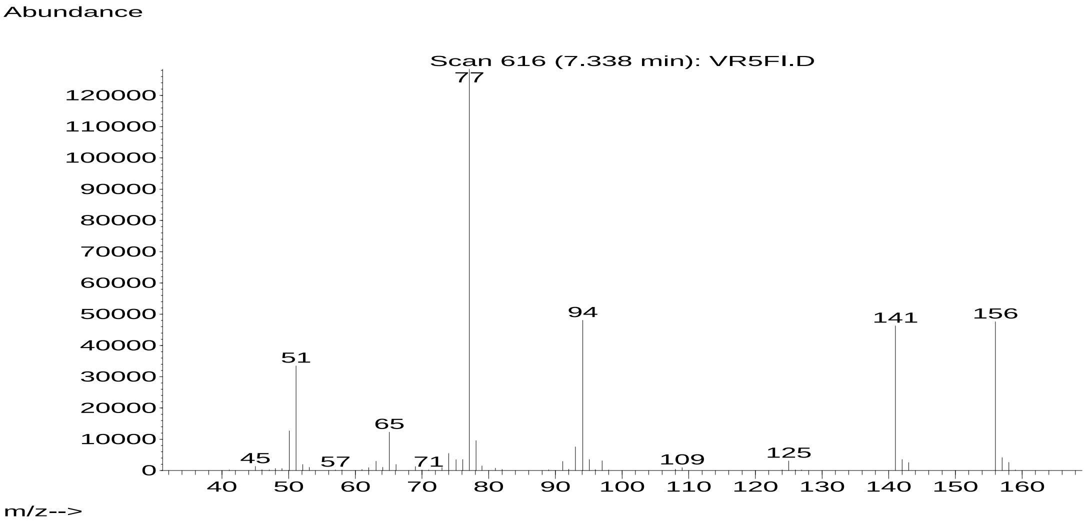


No.	(ppm)	Height	No.	(ppm)	Height
1	0.00	0.050	10	7.64	0.087
2	3.06	1.000	11	7.65	0.050
3	7.27	0.065	12	7.67	0.056
4	7.58	0.128	13	7.93	0.110
5	7.59	0.053	14	7.94	0.130
6	7.59	0.052	15	7.97	0.054
7	7.61	0.057	16	7.98	0.103
8	7.62	0.135	17	7.98	0.084
9	7.62	0.094			

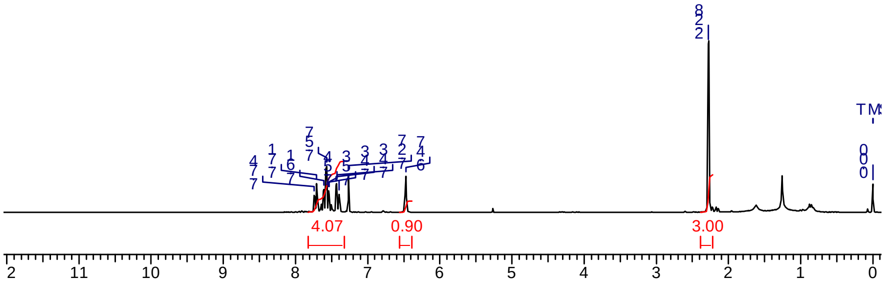
Spectrum 22: ^{13}C NMR spectra of 3 Methylphenylsulfone



Spectrum 23: Mass spectra of methylphenylsulfone

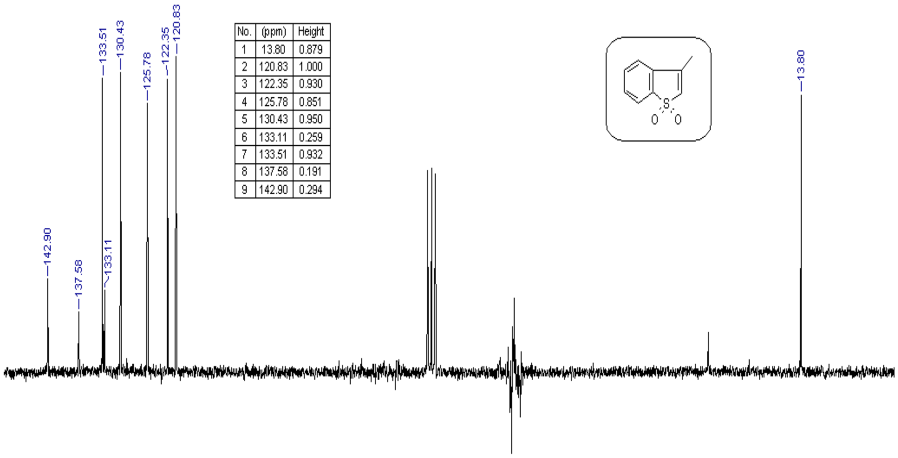


Spectrum 24: ^{1}H NMR spectra of 3-methylbenzothiophene sulfone



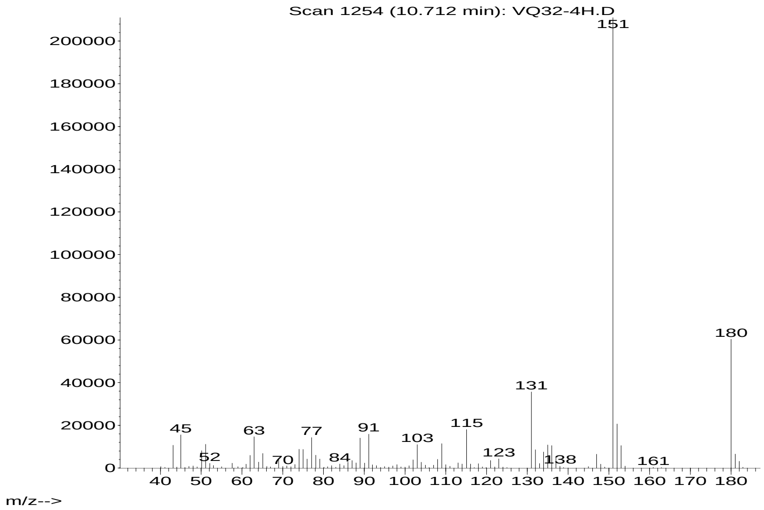
No.	Annotation	(ppm)
1	TMS	0.00

Spectrum 25: ^{13}C NMR spectra of 3-methylbenzothiophenedioxo

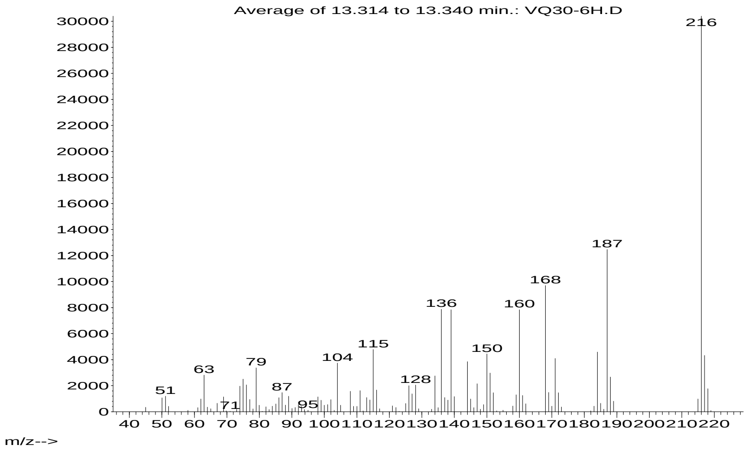


No.	(ppm)	Height
1	13.80	0.879
2	120.83	1.000
3	122.35	0.930
4	125.78	0.851
5	130.43	0.950
6	133.11	0.259
7	133.51	0.932
8	137.58	0.191
9	142.90	0.294

Spectrum 26: Mass spectra of 3-methylbenzothiophene-dioxoxo



Spectrum 27: Mass spectra of dibenzothiophene-dioxo



Publications from thesis

1 Selective *N*-oxidation of aromatic amines to nitroso derivatives using a molybdenum acetylide oxo-peroxo complex as catalyst

Ankush V. Biradar, Trupti V. Kotbagi, Mohan K. Dongare, Shubhangi B. Umbarkar, *Tetrahedron Letters* **2008**, 49, 3616 (***Highlighted in Catalysts & Catalyzed Reactions RSC Publications July 2008,*** **15961**)

2 Selective *cis*-Dihydroxylation of Olefins using Recyclable Homogeneous Molybdenum Acetylide Catalyst

Ankush V. Biradar, Bhaskar R. Sathe, Shubhangi B. Umbarkar, and Mohan K. Dongare, *Journal of Molecular Catalysis A: Chemical,* **2008**, *285*, 111.

3 Selective oxidation of sulphides to sulfoxide or sulfone using η^5-cyclopentadienyl molybdenum (VI) acetylide complexes as catalyst

Ankush V. Biradar, Trupti V. Kotbagi, Vincent QUATGLAS, Vedavati Puranik Mohan K. Dongare, Shubhangi B. Umbarkar ***submitted for publication***

4 Solvent free oxidation of primary aromatic alcohol using Cyclopentadienyl Molybdenum acetylide catalyst

Ankush V. Biradar, Mohan K. Dongare, Shubhangi B. Umbarkar ***submitted for publication***

5 Novel synthesis of Cyclopentadienyl Molybdenum acetylide from molybdenum oxide for alkanes functionazation

Ankush V. Biradar, Mohan K. Dongare, Shubhangi B. Umbarkar ***manuscript under preparation***

Publications other than thesis

1 Vapor phase nitration of benzene using mesoporous MoO_3/SiO_2 solid acid catalyst

S. B. Umbarkar, **A. V. Biradar**, S. M. Mathew, S. B. Shelke, K. M. Malshe, P. T. Patil, S. P. Dagde, S. P. Niphadkar and M. K. Dongare; *Green Chemistry*, **2006**, 8, 488 (***Highlighted in Catalysts & Catalyzed Reactions RSC Publications 2006*** 11210)

2 Regioselective nitration of cumene to 4-nitro cumene using nitric acid over solid acid catalyst

Sanyo M. Mathew, **Ankush V. Biradar**, Shubhangi B. Umbarkar, Mohan K. Dongare; *Catalysis Communications,* **2006**, 7, 394

3 Transesterification of diethyl oxalate with phenol using MoO_3/SiO_2 catalyst

A. V. Biradar, S. B. Umbarkar, M.K. Dongare; *Applied Catalysis A: General,* **2005**, 285 190 (***Highlighted in Catalysts & Catalyzed Reactions RSC Publications July 2006*** **8877**)

4 Magnesium Perchlorate: An Efficient Catalyst for One-Pot Synthesis of Pyrano- and Furanoquinolines

Vinod T. Kamble, Vijaymala R. Ekhe, Neeta S. Joshi, **Ankush V. Biradar**; *Synlett*, **2007**, 9, 1379

5 An efficient method for the synthesis of acylals from aldehydes using silica-supported perchloric acid ($HClO_4$–SiO_2)

Vinod T. Kamble, Vasant S. Jamode Neeta S. Joshi, **Ankush V. Biradar** and Rameshchandra Y. Deshmukh*; Tetrahedron Letters,* **2006**, *47 (31),* 5573

6 Practical and General Method for Direct Synthesis of Alkyl Fluorides from Alcohols under Mild Conditions

Babasaheb P. Bandgar, Vinod T. Kamble, and **Ankush V. Biradar**, *Monatshefte fur Chemie,* **2005**, 136, 1579

7 Acetalization of glycerol using mesoporous MoO_3/SiO_2 solid acid catalyst

Shubhangi B Umbarkar, Trupti V Kotbagi, **Ankush V Biradar**, Jyoti Chanale, Renu Pasricha, Mohan K. Dongare, Anne-Sophie Mamede, Christine Lancelot, Edmond Payen. ***Submitted for publication***

Poster presentations

1 Cyclopentadienyl Molybdenum Acetylide Catalyzed Oxyfunctionilization of Alkane, Alkenes and heteroatom

Ankush V. Biradar, Vaibhav R. Acham, Shubhangi B. Umbarkar, Mohan K. Dongare

11th CRSI National Symposium in Chemistry Feb 2009 Pune India

2 Selective oxidation of sulphides to Sulfoxide or Sulfone using η^5-cyclopentadienyl molybdenum (VI) acetylide complexes as catalyst

Trupti V. Kotbagi, **Ankush V. Biradar**, Vincent Quetglas, Vedavati G. Puranik, Mohan K. Dongare, Shubhangi B. Umbarkar

Catsymp-19 at NCL January 18-21st 2009 Pune India

3 Influence of operating method on reforming of glycerol in aqueous phase

Udo Armbruster, Shubhangi Umbarkar, **Ankush Biradar**, Mohan Dongare, Arunabha Datta, Smita Darmora, Andreas Martin

Future Feedstocks for Fuels and Chemicals DGMK Conference September 29 – October 1, 2008, Berlin, Germany

4 *Cis*-Dihydroxylation of Olefins using Recyclable Homogeneous Molybdenum Acetylide Catalyst

Ankush V. Biradar, Shubhangi B. Umbarkar, Mohan K. Dongare

National Science Day Celebrations, National Chemical Laboratory, Pune, India, February 27, 2008

5 MoO_3/SiO_2 as a versatile catalyst for organic reaction

Ankush V. Biradar, Sanyo T. Mathew, Shubhangi B. Umbarkar, Mohan K. Dongare

National Science Day Celebrations, National Chemical Laboratory, Pune, India, February 27, 2007.

6 Mesoporous Silica Supported Molybdenum Oxide Nano Particles for Catalysis

Mohan K. Dongare, Shubhangi B. Umbarkar, **Ankush V. Biradar**, Sanyo Mathews

Novel Porous Materials for Emerging Applications July 2005, Singapore