



Review

Oxido-peroxido molybdenum(VI) complexes in catalytic and stoichiometric oxidations

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ABSTRACT

This review mainly discusses the application of oxido-peroxido Molybdenum(VI) complexes as catalysts or mediators in homogeneous or heterogeneous catalytic systems for oxidations of olefins, sulfides, alcohols, alkanes, and amines toward the synthesis of a variety of organic compounds, such as epoxides, sulfoxides, aldehydes and ketones, carboxylic acids, alcohols and nitroso compounds.

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Abbreviations: 2-pybmz, 2-(2-pyridyl)benzimidazole; 3-pybmz, 2-(3-pyridyl)benzimidazole; AAPS, N-(2-aminoethyl)-3-aminopropyltriethoxysilane; AcPro, (S)-N-acetylprolinol; AIBN, azobisisobutyronitrile; βCD, β-cyclodextrin; BMTHAH, N-benzoyl N-meta- tolyl hydroxamic acids; BOTHAH, N-benzoyl N-ortho- tolyl hydroxamic acids; BPHAH, N-benzoyl N-phenyl hydroxamic acid; BPTHAH, N-benzoyl N-peta- tolyl hydroxamic acids; BzPro, (S)-N-benzoylprolinol; CCD, Central Composite Design; CMP, tris(cetylpyridinium) 12-molybdophosphate; CPHAH, N-cinnamoyl N-phenyl hydroxamic acid; CTAB, cetyltrimethylammonium bromide; DCE, dichloroethane; DMF, dimethylformamide; DMLA, (S)-N,N-dimethyl-lactamide; DMPLA, (S)-N,N-dimethyl-3-phenyllactamide; dmpz, 3,5-dimethylpyrazole; HBPA, (S)-3-hydroxybutanoic acid piperidineamide; HMBPA, (S)-2-hydroxy-3-methylbutanoic acid piperidineamide; HMPT, hexamethylphosphor triamide; HMPPA, (2S,3S)-2-hydroxy-3-methylpentanoic acid piperidineamide; HPEOH, 1-(2'-hydroxyphenyl) ethanone oxime; PyO, pyridine-N-oxide; PCMP, peroxido tris(cetylpyridinium) 12-molybdophosphate; Phox, 2-(2'-hydroxyphenyl)oxazoline; Pic, pyridin-2-carboxylate; PLA, (S)-piperidine lactamide; PyCOH, pyridine-2-carboxylic acid; PyCOXH, pyridine-2-carboxaldoxime; QOH, 8-quinolinol; Quin, 8-hydroxyquinolate; saloxH₂, salicylaldoxime; TEOS, tetraethyl orthosilicate; TBHP, tert-butylhydroperoxide; TPPA, {(3-triethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]acetamide}; UHP, urea hydrogen peroxide.

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1. Introduction

Catalytic oxidation is an area of key technologies for converting organic compounds to useful chemicals such as diols, epoxides, alcohols, and carbonyl compounds [1–6]. Oxido and peroxido transition metal compounds have played for some time an important role in the oxidation of organic substrates and a variety of peroxido complexes of various metals catalyze the oxidation of olefins, arenes, phenols, alcohols, phosphines and sulfides [7–9]. The catalytic activity of peroxido metal complexes is influenced by the type of metal atom, the number of peroxido ligands attached to the catalyst and the nature of the remaining ligands in the coordination sphere [9–12]. In this regard six- and seven-coordinate molybdenum oxido-peroxido complexes of the type $[\text{MoO}(\text{O}_2)_m(\text{L})_n]$ ($n, m = 1, 2$; L = monodentate or bidentate ligand) are an important class of catalyst for this type of reaction. Interestingly, these complexes are one of the very few stable transition metal complexes that can be used both as an oxidation catalyst and as a stoichiometric reactant. Therefore, very efficient and selective, including chemo- and enantioselective synthetic procedures employing either H_2O_2 or $t\text{BuOOH}$ combined with a molybdenum(VI) oxido-peroxido, have been reported in recent years. Oxido-peroxido chemistry of molybdenum involves two important, well-known structural motifs – one or two peroxido groups and a doubly bonded oxido ligand can create respectively the cationic core $\text{MoO}(\text{O}_2)_2^+$ or neutral core $\text{MoO}(\text{O}_2)_2$. Addition of an appropriate anionic or neutral ligand L to these structural cores gives the familiar oxido-peroxido molybdenum(VI) complexes.

The purpose of this review is to discuss the scope and limitations of oxido-peroxido Mo(VI) complexes as a stoichiometric reagent or as a catalyst for the oxidation of olefins, alcohols, alkanes, sulfides, and amines (Scheme 1). The mechanisms suggested for the oxidation reactions are surveyed and attempts to present a more coherent picture of oxygen transfer mechanism are made. Applications of these complexes to catalytic oxidation when grafted or supported on materials and their advantages or disadvantages over homogeneous catalytic systems are also discussed. Wherever applicable, we will attempt to compare the various results for

oxidation catalysis with an effort to identify and summarize some of the structural factors which may be important for future development. The application of Mo(VI) complexes as a stoichiometric reagent in the epoxidation of olefins until 1990 has been already reviewed [13]. Consequently, this review mainly covers the recent literature published during the past 20 years, although, for a more comprehensive discussion, some earlier works are also included. The review is divided into four main sections based on the reaction types. In each section, the articles are chronologically arranged according to publication date.

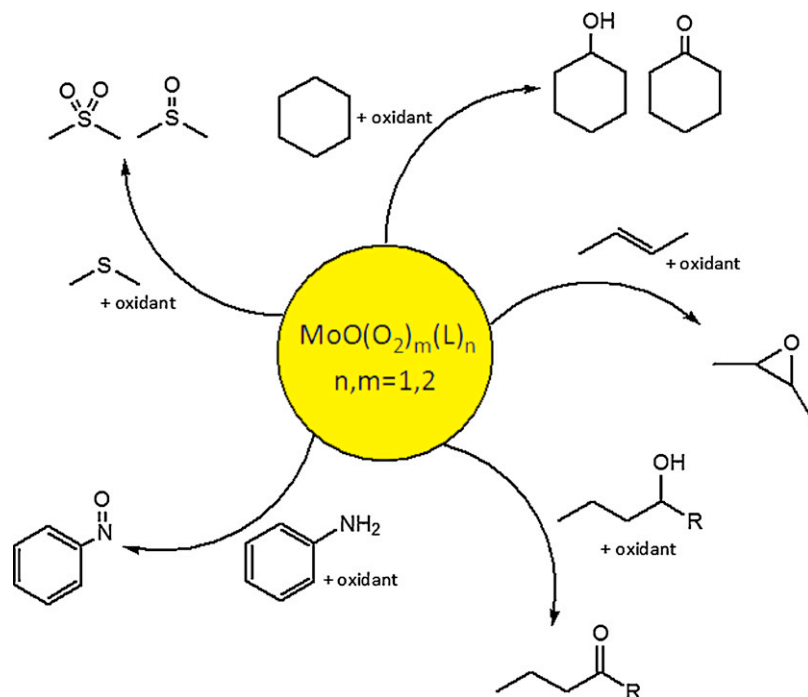
2. Epoxidation of olefins

2.1. Homogeneous epoxidation

The selective epoxidation of olefins to the corresponding epoxides is a fundamental transformation both in laboratory synthesis and industrial production. High valent metal oxido-peroxido species have demonstrated the ability to catalyse the epoxidation of a variety of alkenes, via homogeneous as well as heterogeneous routes. In particular, the Mo-catalysed alkene to epoxides conversion has received most attention, due to its industrial interest. Due to the strained three-membered ring structure of these compounds, epoxides react readily with a number of nucleophiles and therefore epoxides are utilized in a variety of the laboratory and industrial processes as intermediates in organic synthesis.

In 1969, Mimoun et al. reported for the first time, the preparation and use of oxido-bisperoxido molybdenum(VI) complexes of the general formula $[\text{MoO}(\text{O}_2)_2\text{L}_n]$ ($n = 1–2$; $\text{L} = \text{H}_2\text{O}$ **1a**, DMF **1b**, HMPT **1c**, Pyridine **1d**) (Fig. 1) as an oxidizing reagent for the epoxidation of olefins [14,15].

These workers also studied the dependence of factors such as substrate and complex concentration, temperature and choice of solvents on epoxidation rates of cyclohexene by $[\text{MoO}(\text{O}_2)_2(\text{HMPT})]$ **1c** [16]. In the presence of high concentration of water, $[\text{MoO}(\text{O}_2)_2(\text{HMPT})]$ converts to aqua complex $[\text{MoO}(\text{O}_2)_2(\text{HMPT})(\text{H}_2\text{O})]$ **1c.H₂O** in which the seventh



Scheme 1. Selected oxidations of organic compounds by oxido-peroxido Mo(VI) complexes.

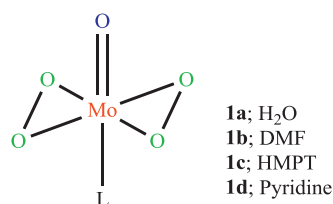


Fig. 1. The Mo(VI) oxido-bis(oxido) complexes developed by Mimoun [16].

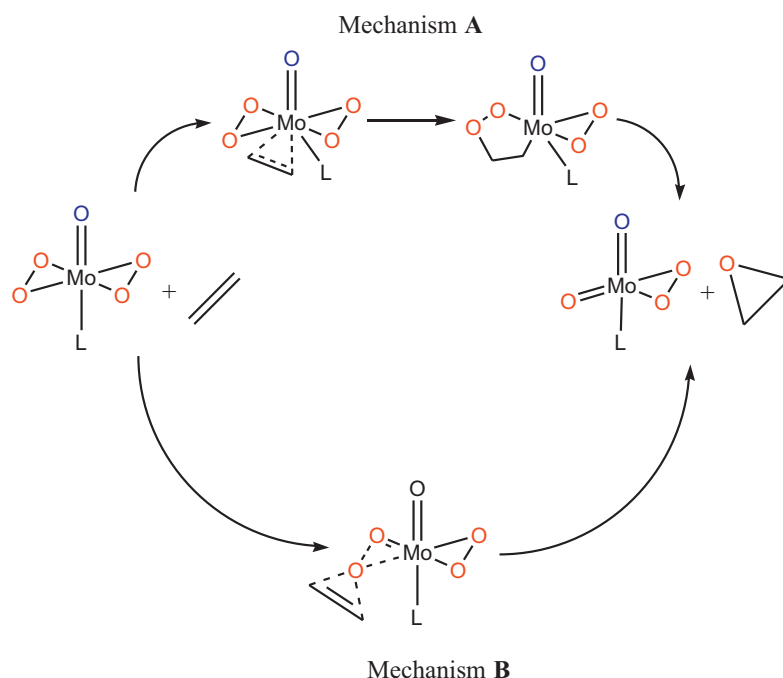
coordination site is occupied by the water molecule [17]. In 1985, Sakamoto and coworkers reported stereospecific epoxidation of *cis*-2-butene-1,4-diones with 2 equiv. of compound **1c**.H₂O, to give *cis* epoxide in 92% yield (CH₂Cl₂ solvent, rt) [18]. Interestingly, epoxidation was specific to *cis*-olefin and the *trans* isomer did not react with compound **1c**.H₂O. The replacement of HMPT with trialkylphosphine oxides with alkyl chain lengths of 2–4 carbons leads to an increase in epoxidation activity of **1** [19]. Oxidant **1c** utilizing HMPT ligand required 48 h to complete epoxidation of cyclooctene in CH₂Cl₂, but when triethylphosphine oxide was used, the complete conversion was achieved within 40 min.

To explain the epoxidation activity of **1a**–**1d**, Mimoun suggested that the olefin coordinates to the metal before subsequent insertion into the π^2 -Mo–O₂ bond to form a five-membered alkyl peroxide metallacycle [15,20]. At the final stage the epoxide molecule is released from the metallacycle (Scheme 2, Mechanism A). However, today this mechanism can be ruled out for two reasons: (1) such metallocyclic intermediates were not found in reactions involving transition metal peroxides with a *d*⁰ configuration [21]; (2) the decomposition reaction of the five-membered metallacycle would lead to aldehyde and not to the epoxide [22]. In an alternative mechanism proposed by Sharpless et al., it was assumed that olefin incorporation in the coordination sphere is not essential and epoxidation occurs by a direct attack at the double bond of the olefin at one of the oxygen centers of the peroxido group (Scheme 2, Mechanism B) [23,24]. The mechanism proposed by Sharpless, was proved with the help of modern quantum chemistry [25]. The B3LYP hybrid density functional calculations revealed that the epoxidation of

olefins by peroxido complexes of Cr(VI) and W(VI) also proceeds via the same pathway [26].

It was recently shown that the oxidation of olefins with some Mo(VI) peroxide species in alkaline medium does not follow the Sharpless mechanism. In 1997, Nardello et al. [27,28] reported that the oxidation of tiglic acid (CH₃CH=C(CH₃)CO₂H) with MoO₄²⁻/H₂O₂ system in H₂O at pH 5–6 leads to the formation of 2-epoxy-2-methylbutanoic acid. By contrast, under similar reaction condition in aqueous alkaline medium (pH 9–10) tiglic acid was converted into 3-hydroperoxy-2-methylenebutanoic acid. In fact, in this system there is a competition between epoxidation and peroxidation. In acidic medium, the in situ formed [MoO(O₂)₂(OOH)]⁻ complex behaves as a reactive epoxidation agent, reacting according to the Sharpless concerted mechanism. In alkaline medium, the hydroperoxide ligand of the [MoO(O₂)₂(OOH)]⁻ complex starts to deprotonate and peroxidation of the tiglic acid is performed by molybdenum(VI) oxido-tris(oxido) complex [Mo(O)(O₂)₃]²⁻, producing ¹O₂, which is inserted into the CH group of the reagent. At the same year, Aubry also reported the oxidations of hydrophobic substrates such as aromatic hydrocarbons in reverse microemulsions (water in oil) with chemically generated singlet oxygen, produced by MoO₄²⁻/H₂O₂ system [29]. Among all molybdenum(VI) complexes reported so far only [Mo(O)(O₂)₃]²⁻ complex has the potential to generate singlet oxygen [30,31]. Therefore, the ¹O₂ oxidation mechanism is only limited to the tris(oxido) Mo(VI) species.

Schurig and coworkers reported the synthesis and X-ray structure of an optically active oxido-bis(oxido) Mo(VI) complex [MoO(O₂)₂(DMLA)] **2** (Fig. 2) and its application as a reagent in the enantioselective epoxidation of olefins [32]. X-ray crystallographic studies have shown that complex **2** has a slightly distorted pentagonal-bipyramidal structure with two peroxide groups in equatorial positions. The chiral bidentate lactamide ligand is coordinated through the carbonyl oxygen at the fifth equatorial position and through the hydroxylic oxygen on the axial position opposite to the doubly bonded oxido group [32]. The prochiral olefin *trans*-but-2-ene could be transformed to the *trans*-(1*R*,2*R*)-but-2-ene oxide with a yield of 70% and an ee of



Scheme 2. Suggested mechanisms for oxidation of olefins by [MoO(O₂)₂(HMPT)] **1c** oxidant.

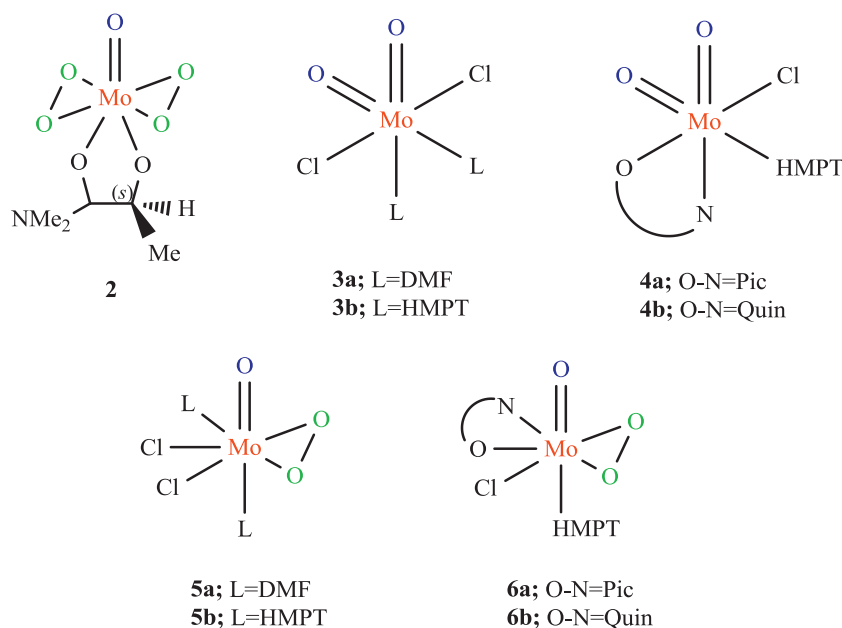


Fig. 2. The Mo(VI) oxido-peroxido complexes developed by Schurig and Mimoun [32–34].

up to 34% in nitromethane solvent at room temperature. The rate of epoxidation increased by about two orders of magnitude along the series ethene < 1-butene < trans-2-butene < 2-methyl-2-butene. Reducing the reaction rate by lowering the temperature and decreasing steric hindrance of the alkyl group in olefin led to an increase in the enantiomeric yield of products. A minimum enantiomeric excess was obtained in the case of the 2-Methyl-2-butene substrate (5.1% of (*R*)-epoxide) [33].

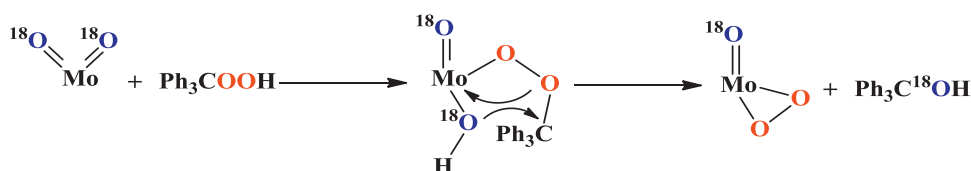
In 1983, Mimoun et al. synthesized monoperoxido complexes of the general formula MoO(O₂)L₂Cl₂ **5** (L = DMF **5a**, HMPT **5b**) and MoO(O₂)Cl(O-N)(HMPT) **6** (O-N = Pic **6a**, Quin **6b**) (Fig. 2) [34] by treatment of *cis*-dioxido molybdenum(VI) complexes MoO₂Cl₂L₂ **3** (L = DMF **3a**, HMPT **3b**) and MoO₂Cl(O-N)(HMPT) **4** (O-N = Pic **4a**, Quin **4b**) with one equivalent of tritylhydroperoxide Ph₃COOH. Stoichiometry of this reaction was confirmed for MoO₂Cl₂(HMPT)₂ **3b** (Scheme 3). The reaction of one equivalent of Ph₃COOH with labeled dioxido complex **3b** gave the peroxido complex **5b**, unlabeled on the peroxido oxygen atoms (no displacement in infrared of the ν(O–O) peroxido vibration at 920 cm^{−1}) and 95% labeled Ph₃COH. These results showed that both oxygen atoms of the peroxido group come from the hydroperoxide, while one labeled oxido oxygen atom is incorporated into Ph₃COH. The treatment of complexes **3** and **4** with H₂O₂ also gave complexes **5** and **6** albeit in poorer yields than those obtained with tritylhydroperoxide, and addition of an excess of other alkylhydroperoxide oxidants such as *t*-BuOOH, PhMe₂COOH, Ph₃SnOOH resulted in a change of coloration but the resulting complexes could not be isolated.

Complexes **5a** and **5b** having an adjacent coplanar site occupied by a monodentate basic ligand were particularly effective as an oxidant for the epoxidation of various olefins at room temperature but complexes **6a** and **6b** were completely inactive even when the

reaction was carried out at 60 °C for 4 h. Stirring of compound **5a** and 2.5 mol% of 2,3-dimethyl-2-butene at 0 °C in CH₂Cl₂ afforded the 2,3-epoxy-2,3-dimethylbutane with 40% yield at the beginning of the reaction, but progressively resulted in oxidative cleavage of the double bond and formation of acetone.

The absence of reactivity of complexes **6a** and **6b** initially led scientists to think that the presence of an equatorial, adjacent and releasable coordination site on the metal is necessary for the oxygen transfer reaction to occur. This theory was reinforced by the fact that the epoxidation reaction with complexes **5a** and **5b** is strongly inhibited by basic ligands such as DMF and HMPT. In similar study, Zamaraev et al. compared reactivity of monoperoxido MoO(O₂)(acac)₂ **7** and bisperoxido MoO(O₂)₂(H₂O) **1a** towards alkenes [17]. The bisperoxido complex **1a** reacts with cyclohexene in dioxane but monoperoxido complex **7**, which does not contain easily replaceable ligand, is completely inert. However the effect of replacement ability of coordinated ligands on the epoxidation activity of peroxido Mo(VI) complexes was never proven. In 2000, DFT/B3LYP calculation on the olefin epoxidation by mono and bisperoxido complexes of molybdenum(VI) revealed that all monoperoxido complexes show higher barriers for stoichiometric oxygen transfer to ethylene than the bisperoxido complex with the same ligand [35]. In fact since the reaction occurs by the concerted mechanism (Scheme 2, mechanism B), which does not require olefin coordination to molybdenum center, the effect of the ligands is only adjustment of the electronic structure of the complex [21].

Further catalyst tuning by Schurig et al. led to the preparation of a number of other chiral oxido-bisperoxido Mo(VI) complexes **8** based on a series of enantiomerically pure hydroxyamides. Ligands such as DMPLA **8a**, HMPPA **8b**, AcPro **8c**, PLA **8d**, HMBPA **8e**, HBPA **8f**, and BzPro **8g** (Fig. 3) were employed to investigate the influence



Scheme 3. The stoichiometric study of the reaction MoO₂Cl₂(HMPT)₂ with Ph₃COOH [33].

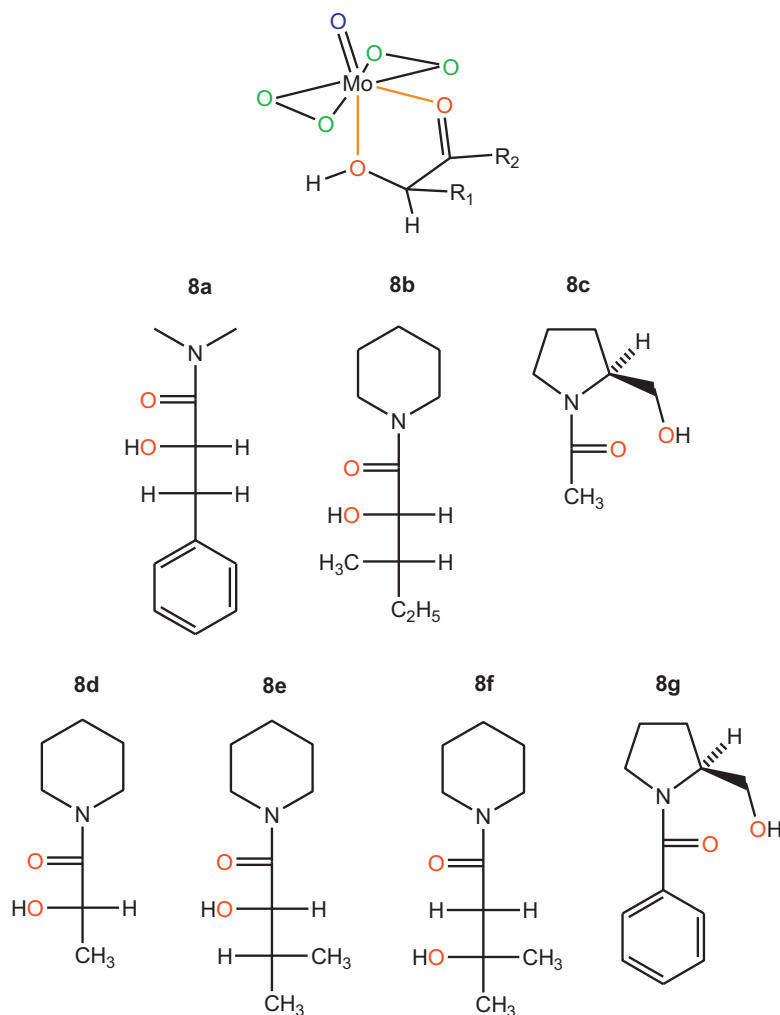


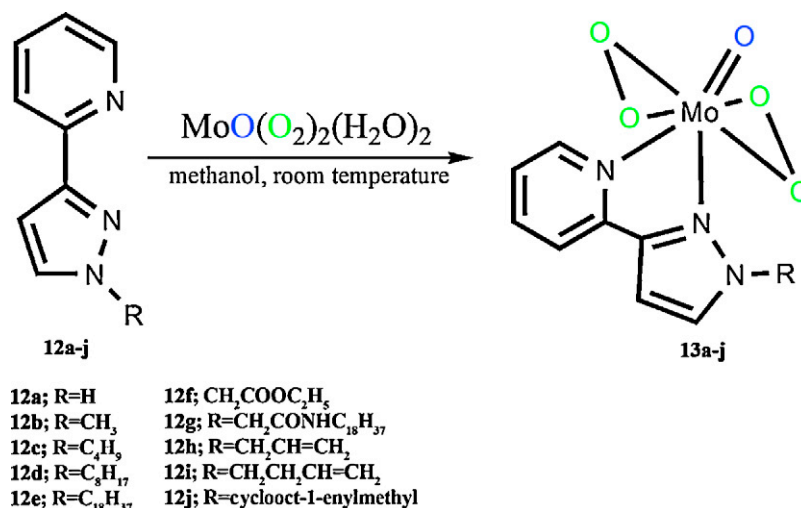
Fig. 3. The oxido-bis(oxido) Mo(VI) complexes **8a–g** obtained by Schurig and coworkers [36].

of (i) the size of the amide component, (ii) branching of alkyl substituents (**8d** vs. **8e**), (iii) an additional chiral center (**8b**), and (iv) the position of the hydroxy group (**8d** vs. **8f**) on enantioselective epoxide formation [36]. These oxido-bis(oxido) molybdenum(VI) complexes **8a–i** were obtained by stoichiometric reaction of the corresponding ligands with MoO_3 , and H_2O_2 . These complexes were effective reagents for the enantioselective epoxidation of trans-2-butene to (2*R*,2*R*)-trans-2,3-dimethyloxirane with distinct enantiomeric excesses. The highest ee is observed with the reagent **8d** at 23 °C (48.6% ee). In contrast with the previous study [33], the ee to (2*R*,2*R*)-trans-2,3-dimethyloxirane is reduced when the temperature is lowered. The position of the hydroxyl group in respect of the carbonyl group in the ligand has an influence on the enantioselective epoxide formation but an increase in the steric bulk of the ligand (HMBPA, HMPPA, and DMPLA vs. DMLA) results in a decrease in enantioselectivity.

In 1987, Ishii et al. reported synthesis of a peroxido molybdenum(VI) by treating the molybdophosphate $[(\text{C}_5\text{H}_5\text{N})(\text{CH}_2)_{15}\text{CH}_3]_3[\text{PMo}_{12}\text{O}_{40}]$ (CMP) **9** with aqueous hydrogen peroxide [37]. The peroxido specie obtained, PCMP **10**, was not characterized clearly but used as an efficient reagent for the oxidation of olefins to epoxides. The amount of active oxygen contained in PCMP, determined by iodometry, was 2.4 mmol g^{-1} . The selective oxygenation of 1-octene to 1,2-epoxyoctane using PCMP was carried out in CHCl_3 in 79% yield when the reaction time was prolonged to 24 h. Using PCMP, allylic alcohols were

oxidized more easily than olefins. The results showed that using this protocol, only the carbon double bond was oxidized, whereas terminal hydroxyl group remained intact. A precipitate which formed during the oxidation reaction was removed from the sample by filtration and could be reused after the treatment by hydrogen peroxide.

The literature on the stoichiometric epoxidation of olefins by peroxido molybdenum(VI) to 1990 has been reviewed [13]. In 1980, Westland briefly reported that $\text{MoO}(\text{O}_2)_2(\text{OP}(n\text{-C}_4\text{H}_9)_3)_3$ complex **11** can stoichiometrically oxidize styrene to its epoxide and also catalyze the epoxidation of cyclohexene by TBHP in benzene [38]. However, application of these complexes as a catalyst for the epoxidation of olefins mainly started to appear in literature in the 1990s decade. In order to study the solubility and the epoxidation catalytic activity of oxido-bis(oxido) molybdenum(VI) complexes in different organic solvents, Thiel et al. synthesized oxido-bis(oxido) molybdenum complexes **13a–g** of substituted 2-[3(5)-pyrazolyl]pyridines **12a–g** (Scheme 4) [39]. Alkyl side chain of ligands (butyl **12c**, octyl **12d**, octadecyl **12e**) increased the solubility of the complexes in organic solvents and offered two advantages: (1) with increasing the solubility of the complexes, spectroscopic investigations into the reaction mechanism could be done and (2) catalytic epoxidation was possible in hydrocarbon solvents such as isooctane. The most active complexes **12d–f** achieved a quantitative conversion of cyclooctene to the corresponding epoxide in presence of TBHP as an oxidant and CHCl_3 as a solvent in 65 °C for



Scheme 4. The oxido-bis(oxido) Mo(VI) complexes studied by Thiel and coworker [39,40].

3 h and no over oxidation to *trans*-1,2-diols were observed. Using complex **12f** as a catalyst, a total turnover number in the range of 1700 was possible, demonstrating efficient use of the catalyst in this highly selective reaction.

Thiel then reported the synthesis of the ligands **12h-j** and their oxido-peroxido molybdenum complexes **13h-j** (Scheme 4). NMR investigations showed that with compound **13j**, the cyclooctenyl ring is epoxidized only in the presence of *t*-BuOOH [40]. This indicates that direct transfer of oxygen atom from a peroxido ligand of complex to the olefin does not occur or is very slow. Thus, the Sharpless concerted mechanism for the stoichiometric epoxidation does not work for the catalytic epoxidation in the presence of oxido-peroxido molybdenum(VI). From these studies, Thiel proposed a mechanism [41,42] that in the first step the oxidizing agent coordinates to the Lewis acidic Mo(VI) center (A), followed by proton transfer from the hydroperoxide to a peroxido ligand (B). η^2 -coordination activates the alkyl hydroperoxide (C) for oxygen transfer (D). The resulting alcoholato ligand abstracts the proton from the hydroperoxido ligand, which regenerates the bis(oxido) complex (Scheme 5(a)). By ¹H NMR spectroscopic studies they reached to an important result that the ligand does not dissociate during the catalytic cycle. It was also previously reported that the HMPT ligand does not dissociate during the stoichiometric epoxidation of alkenes with complex **1c** [43]. However, in 2000, Thiel used NMR spectroscopy combine with quantum mechanics to show that, in contrast with his earlier reports [41,42], ligand fluxionality may play an important role in the activation of the hydroperoxide. Therefore, he developed his own mechanism and reported the mechanism of the epoxidation reaction based on ligand dissociation (Scheme 5(b)) [44].

The formation of inter- and intramolecular hydrogen bonding has proven to be a significant factor in Thiel's second mechanism. Evidence for such hydrogen bonds has been observed in the X-ray crystal structure and CHCl₃ solution of analogous complexes [45]. It was previously reported that the catalytic and the stoichiometric epoxidation of allylic alcohols with [MoO(O₂)₂(HMPT)] **1c**, is regiospecific and faster than that of simple olefins [46–48]. The accelerating effect of the hydroxo function also should be related to the intramolecular hydrogen bonding between OH group of olefin and peroxido groups of complex **1c** [24].

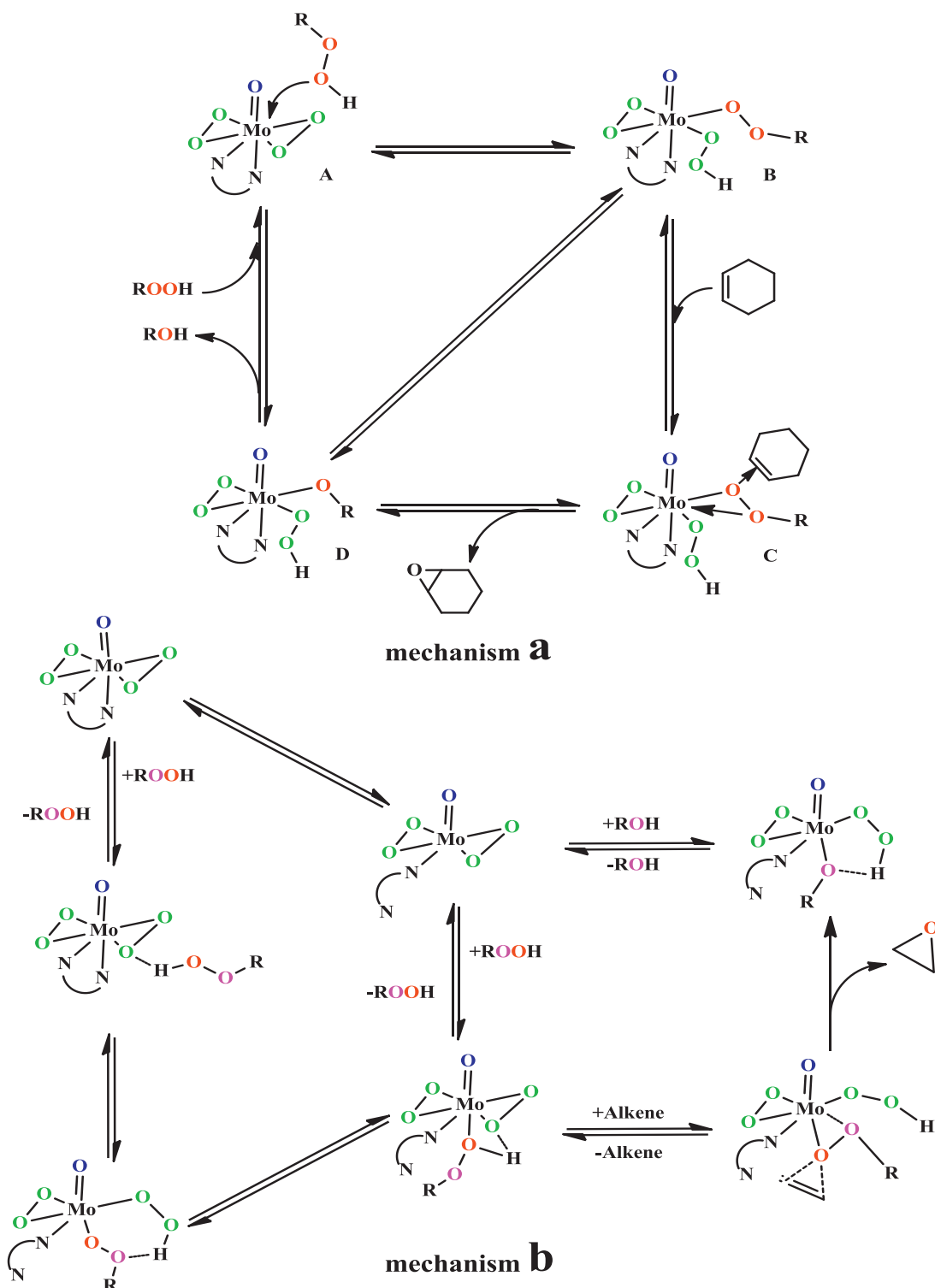
The MoOOR intermediate has competing reaction pathways that lead to formation of by-products. Very recently theoretical and experimental evidence is provided for a kinetically competing reaction of MoOOR species with additional ROOH reagent leading to MoOOOR species, which easily decompose into radicals [49].

Radicals appear to be formed in a homolytic reaction, causing the formation of undesired allylic byproducts during the epoxidation reaction. Although this competing mechanism is only reported for the molybdenum(VI) dioxido complex [MoO₂(OR)₂] at the high concentration of ROOH oxidant, it seems conceivable to imagine a similar mechanism for molybdenum(VI) oxido-peroxido complexes.

Thiel proved that the long chain derivatives of pyrazolyl pyridines are suitable ligands (e.g. **12d**) for catalysts of type (L-L)MoO(O₂)₂ for the epoxidation of olefins in apolar solvents [50]. Due to good solubility of the complex **13d** in toluene as well as in alkanes (isooctane) the epoxidation of a number of olefins in these solvents with particular regard to the stability of sensitive epoxides by TBHP as an oxidant at 100 °C was investigated. Several olefins (cyclic, multiple substituted linear, terminal linear, functionalized olefins, polyolefins, and chiral olefins) underwent oxidation and produced the corresponding epoxides. Best results were obtained for more electron-rich cyclic (cyclooctene) and multiple substituted linear (2,4,4-trimethyl-2-pentene) olefins. The catalytic epoxidation of (1*R*)-(+)- α -pinene, (*R*)-(-)-carvone and (*R*)-(+)-Citronellal in toluene solvent led to a 1:1 mixture of two diastereomeric epoxides with 24, 67 and 71% yields, respectively. (*R*)-(+)-limonene was unspecifically oxidized and a mixture of different diastereomeric mono- and diepoxides was formed.

Thiel also surveyed the effect of electron-withdrawing or -donating substitutions on the catalytic activities of compound **13d** [42]. Derivatives of **13d**, complexes **14a–14h** (Fig. 4) were obtained by reaction of a methanolic solution of the ligands with an excess of MoO₃ dissolved in hydrogen peroxide or by a ligand exchange with [MoO(O₂)₂(DMF)₂]. Lewis acidity of the metal center is a major factor for the reactivity of these catalysts in the epoxidation of alkenes. Electron withdrawing substituents such as CF₃ **14d** and NO₂ **14h** on the pyrazolyl moiety (X,Y) raise the Lewis acidity of the catalyst, markedly accelerating the catalytic oxidation reaction. Thus, using TBHP as an oxidant, maximum turnover frequency of more than 6400 h⁻¹ was reported for the epoxidation of cyclooctene with compound **14h**. Moreover, in contrast, the methyl substituent in compound **14b** had significantly decreased catalytic reactivity compared with unsubstituted complex **14a**.

In 1999, Stirling and coworker reported the synthesis and characterization of chiral oxido-bis(oxido) molybdenum(VI) complexes of the type [MoO(O₂)₂(L)(ROH)] where L=chiral β -phosphinoyl alcohols **15a–g** (Fig. 5) is bound through the phosphinoyl oxygen as a monodentate ligand [51]. The large down field shift of about 20 ppm for ³¹P NMR of complexes compared with



Scheme 5. The mechanism of the epoxidation reaction proposed by Thiel et al. (a) bidentate ligand does not dissociate [41,42], (b) bidentate ligand demonstrates fluxional behavior during catalytic cycle [44].

the free ligands was consistent with the monodentate nature of the ligands. All the complexes were investigated as stoichiometric oxidants for the epoxidation of various alkenes. In the case of non-cyclic alkenes, the highest conversion observed was 91% epoxide of 3,3-dimethylbut-1-ene using oxido-peroxido molybdenum complex of ligand **15c** as an oxidant in nitromethane solvent. However, the enantioselectivity was small, only 6% ee of (*S*)-epoxide was obtained. With the same substrate and under identical reaction

conditions, highest enantioselectivity (39%) was obtained by use of binaphthyl ligand **15e**. Comparison of these results with those published by Schurig [36], revealed that bidentate chiral ligands give the product in moderate enantiomeric excesses (up to 50% ee), whereas monodentate ligands produce small enantioselectivities. $\text{MoO}(\text{O}_2)_2$ of ligand **15g** also was employed as a catalyst in the TBHP oxidations of hept-1-ene and 3,3-dimethylbut-1-ene in dichloromethane. Selective oxidation of alkenes occurred to afford

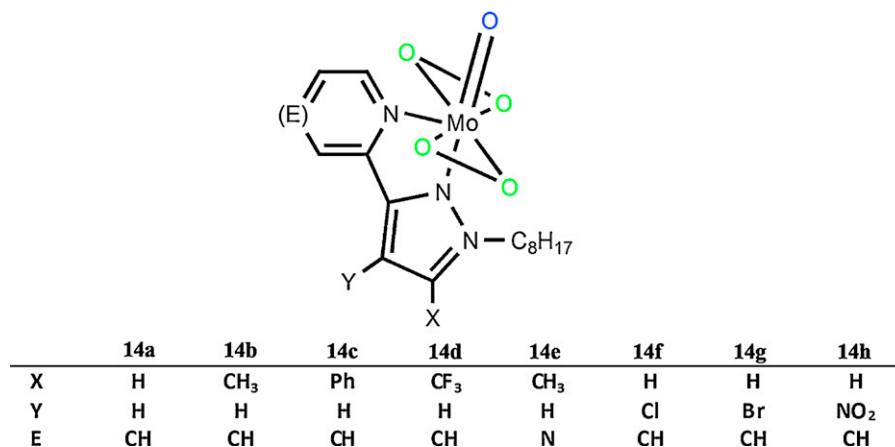


Fig. 4. The oxido-bis(oxazoline) Mo(VI) complexes **14a–h** studied by Thiel and coworkers [42].

corresponding epoxides in 70% yield, but with the same small enantiomeric excesses values produced in the stoichiometric reactions.

The modest enantioselectivities were explained on the basis of the mode of coordination of the chiral ligand and there are inherent limits in the use of these systems in asymmetric oxidations. Efforts that have been made to 2007 on the application of oxido-peroxido Mo(VI) chiral complexes for the epoxidation of alkenes at either the stoichiometric or catalytic level have already been reviewed by Burke [52], so we do not need to focus on this aspect.

Mimoun-type peroxido complexes $[\text{MoO}(\text{O}_2)_2\text{L}_x]$ (L =monodentate ligand, $x=1, 2$) are effective stoichiometric oxidants for the epoxidation of olefins but have poor ability in hydrogen peroxide activation. The ligand L in complexes

$[\text{MoO}(\text{O}_2)_2\text{L}(\text{H}_2\text{O})]$ has a critical impact on their catalytic activity in hydrogen peroxide activation. When L is pyridines, pyridine N -oxides, pyrazoles, OPPh_3 , DMF, HMPA, or derivatives thereof, the complexes show low catalytic activity in the epoxidation of olefins using hydrogen peroxide as a terminal oxidant. However, some enhanced catalytic reactivity was possible through ligand modification. Sundermeyer and coworkers showed that although $[\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})(\text{OEn-Bu}_3)]$ ($\text{E}=\text{N}$ **16a**, **P** **16b**, **As** **16c**) (Fig. 6) complexes are catalytically inactive, but $[\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})(\text{OEnDodec}_3)]$ ($\text{E}=\text{N}$ **17a**, **P** **17b**, **As** **17c**) (Fig. 6) complexes, which contain long-chain group 5 element oxides ligand, are highly active catalyst in hydrogen peroxide activation [53]. The catalytic epoxidation of 1-octene carried out with H_2O_2 and compounds **17a–c** as catalyst

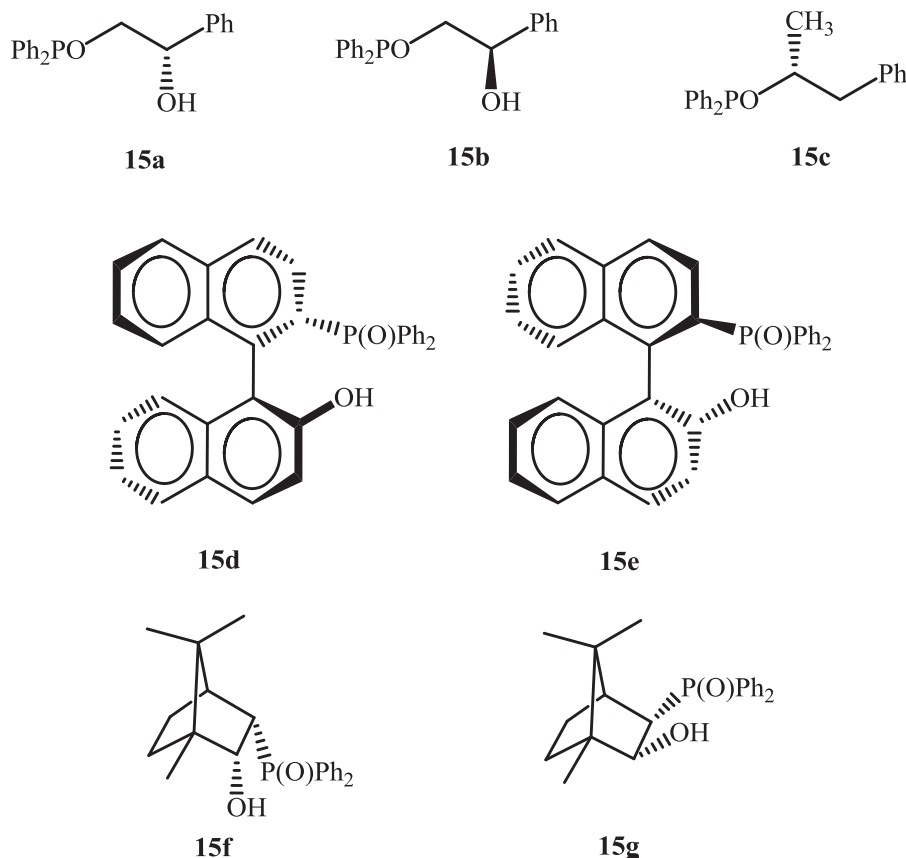


Fig. 5. The phosphinoyl alcohol ligands used by Stirling and coworkers [51].

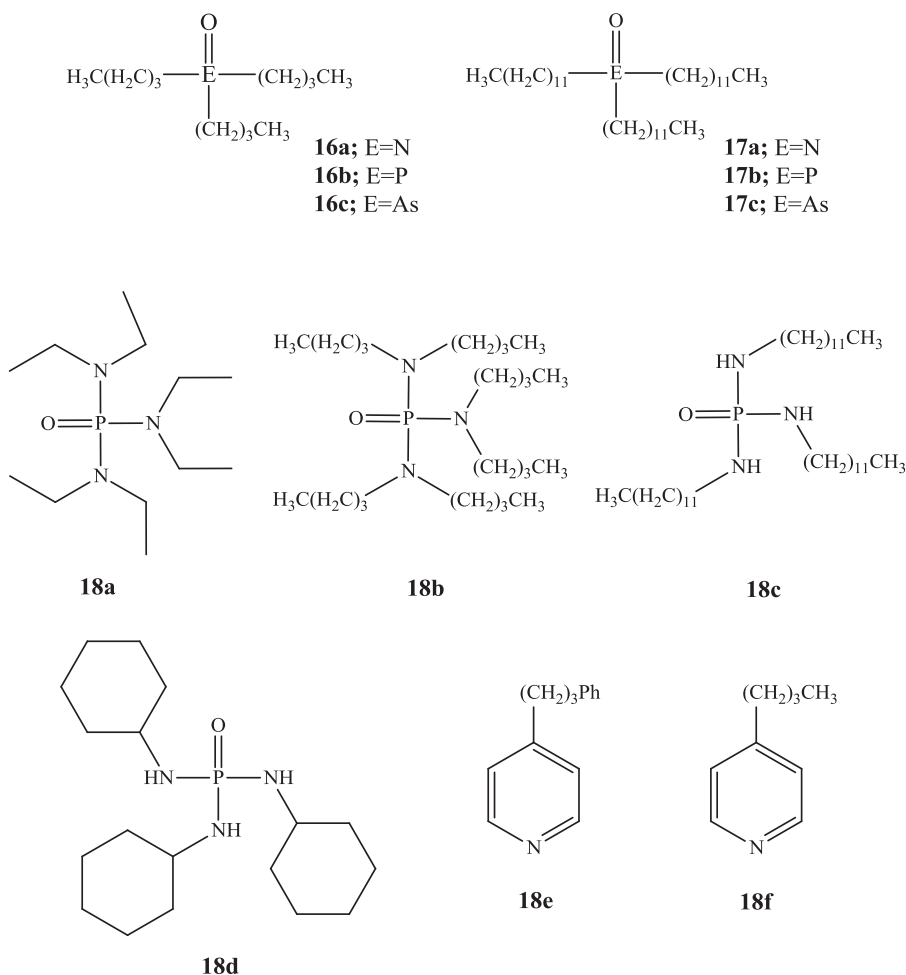


Fig. 6. The ligands used by Sundermeyer and Di Furia [53,54].

under biphasic conditions $\text{CHCl}_3/\text{H}_2\text{O}_2$ (30%) at 60°C . Among all the catalysts investigated, complex **17c** showed the best catalytic performance for the epoxidation of 1-octene in the presence of H_2O_2 (83% conversion, 24 h).

Before Sundermeyer and coworkers reported their results, Di Furia and Modena reported their work on the use of $\text{MoO}(\text{O}_2)_2\text{L}$ complexes **18a–f** (Fig. 6) as a catalyst for the epoxidation of olefins in biphasic conditions [54]. In such a system, the neutral $\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O})$ complexes formed in aqueous solution are extracted by a lipophilic monodentate ligand in an DCE organic phase, where the oxidation of the substrate takes place. The efficiency of the catalysts and product yields depend on the lipophilicity of the ligand, increase in the order **18b** > **18a** > **18c** for hexaalkylphosphoric triamides and **18c** > **18d** for trialkylphosphoric triamides. The pyridine *N*-oxides ligands **18e** and **18f** appear to be more effective than phosphoric amides. Catalyst screening showed that the best cyclohexene conversions were obtained with compounds **18e** and **18f** as a ligand, H_2O_2 as the oxidant, and in the presence of 0.8 M H^+ (64% conversion, 98% selectivity to epoxide). An increase of the H^+ ion concentration from 0.8 M to 2.5 M results in increase of the olefin conversion (80%), likely as a result of neutralization of anionic peroxido complexes in the aqueous phase making the extraction by the ligand more effective. However, the epoxide selectivities tend to drop (24% selectivity to epoxide), owing to the acid-catalyzed hydrolysis of the epoxide, giving cyclohexene-1,2-diol.

In 2004, Gómez and coworkers reported the preparation of the new seven-coordinate Mo(VI)-oxidoperoxido **19** and

Mo(VI)-oxidobisperoxido **20** complexes with bidentate anionic and neutral chiral oxazolines and the first report of the catalytic epoxidation using this type of complex (Fig. 7) [55]. The oxidation of cyclooctene with TBHP in the presence of complexes **19** and **20**, in toluene, was carried out and produced only the corresponding *cis* epoxide in 95% and 15% yields, respectively. The Mo(VI) oxido-monoperoxido was the most active catalyst. The catalytic activity of complex **19** was higher than that of the corresponding oxido-bisperoxido and dioxido complexes [55,56].

According to information derived from NMR experiments and catalytic reactivity patterns, a mechanism of the epoxidation was suggested [55] similar to the mechanism proposed by Thiel involving hemilabile ligands (Scheme 6) [44]. Due to the hemilabile nature of the oxazolinyphenolate ligand, complex **19** can easily form a vacant site (A) which is offered to TBHP for the coordination. The low catalytic activity observed for complex **20** can be attributed to the nonlability of the oxazoliny pyridine ligand and can be explained by this mechanism. Further coordination of TBHP (B) leads to the formation of a transition state (TS), in which the olefin approaches towards the *tert*-butyl peroxide fragment, yielding the epoxide and concomitant elimination of *tert*-butyl alcohol, the active catalytic specie **19** being regenerated.

New oxido-peroxido Mo(VI) complexes $[\text{MoO}(\text{O}_2)(\text{BPHA})_2]$ **21a**, $[\text{MoO}(\text{O}_2)(\text{BOTH})_2]$ **21b**, $[\text{MoO}(\text{O}_2)(\text{BMTH})_2]$ **21c**, $[\text{MoO}(\text{O}_2)(\text{BPTH})_2]$ **21d**, $[\text{MoO}(\text{O}_2)(\text{CPHA})_2]$ **21e** respectively were synthesized with a high yield by first dissolving MoO_3 in H_2O_2 and treating the resulting solution with the appropriate hydroxamic acids (BPHAH **22a**, BOTHAH **22b**, BMTHAH **22c**,

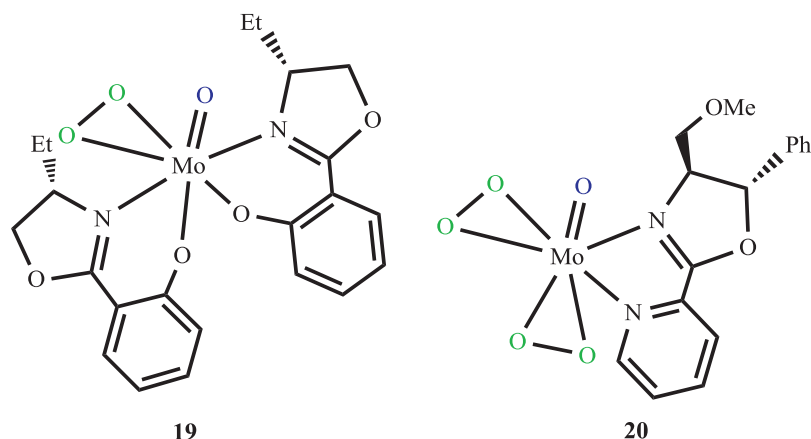


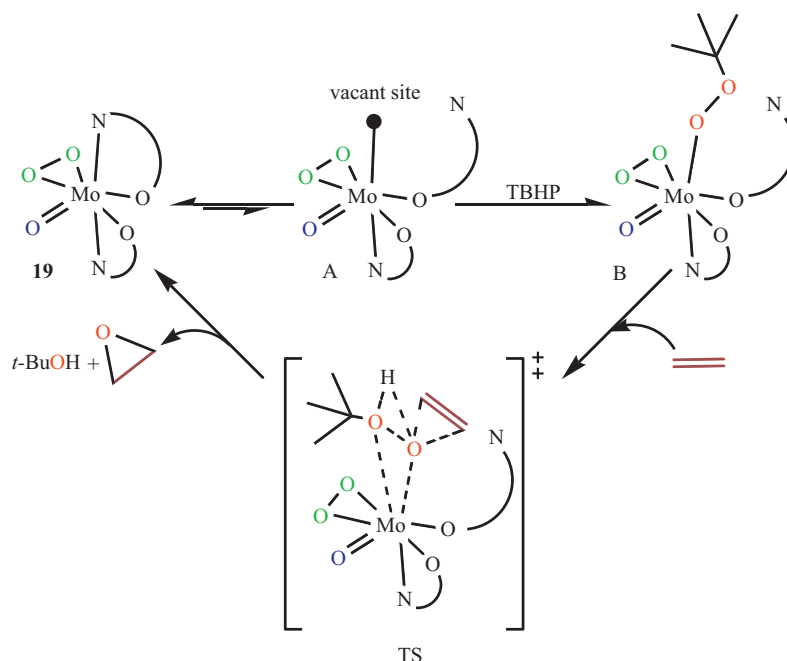
Fig. 7. The Mo(VI) oxido-bis(oxazoline)peroxido complex **19** and Mo(VI) oxido-monoperoxido complex **20** [55].

BPTAH **22d**, and CPHAH **22e**) (Fig. 8) [57]. All complexes **21a–e** showed high activity and selectivity both as a catalyst and a stoichiometric reagent for the epoxidation of olefins. The comparative catalytic activities of the structurally characterized complexes **21a–e** were studied on the epoxidation of cyclohexene and styrene and on that basis, they can be arranged in order of their increasing activities as **21a** < **21d** < **21b** < **21c** < **21e**. Using **21e** as a catalyst, H_2O_2 as a terminal oxidant, and in the presence of NaHCO_3 as a promoter, complete conversion of cyclohexene to its corresponding epoxide was achieved within 1 h (TON = 4500). The superior catalytic activity of complex **21e** may be the result of an extended conjugation of the aromatic ring with the planar aliphatic residue which implies that the low-lying and delocalized empty antibonding orbital in the catalyst makes the oxidation reactions more facile. Similar to Gómez results [55,56], the dioxido complexes have lower catalytic activity compared with their corresponding oxido-peroxido complexes. An attempt to the synthesis of bis(oxazoline)peroxido $[\text{MoO}(\text{O}_2)_2(\text{BMTA})_2]$ complex was unsuccessful but resulted in isolation of the catalytically active species, $[\text{MoO}(\text{O}_2)_2(\text{C}_6\text{H}_5\text{COO})]^-$ **23** (Fig. 8). This anionic oxido-peroxido

complex shows the highest catalytic efficiency among the all isolated complexes, due to the presence of two highly reactive peroxido groups and lability of the carboxylate ligand. Before this study, the same research group reported synthesis of another anionic molybdenum peroxido complex, $[\text{MoO}(\text{O}_2)_2(\text{saloxH})]^-$ **24** (Fig. 8). The catalytic activity of complex **24** in the epoxidation reaction is comparable to complex **23** in the same conditions [58].

There is a significant reduction in the catalytic activity of complex **23** in absence of NaHCO_3 additive. The peroxymonocarbonate (HCO_4^-) oxidant which is formed from bicarbonate and hydrogen peroxide speeds up the epoxidation reaction very probably due to the higher nucleophilicity of the HCO_4^- . In the absence of NaHCO_3 cocatalyst, similar to Mimoun-type peroxido complexes $[\text{MoO}(\text{O}_2)_2\text{L}_x]$ [53], neutral $[\text{MoO}(\text{O}_2)(\text{L-L})_2]$ complexes could scarcely activate hydrogen peroxide.

In 1980, 26 years before Bhattacharyya reported their results, the $[\text{MoO}(\text{O}_2)(\text{BPHA})_2]$ **21a** was used as a stoichiometric reagent for the oxidation of allylic alcohols to epoxides in fair yields (60–70%). Reactions were done in DCE at 70°C [59].



Scheme 6. The mechanism of the epoxidation reaction in the presence of oxido-peroxido Mo(VI) complex **19** reported by Gómez and Teruel et al. [55].

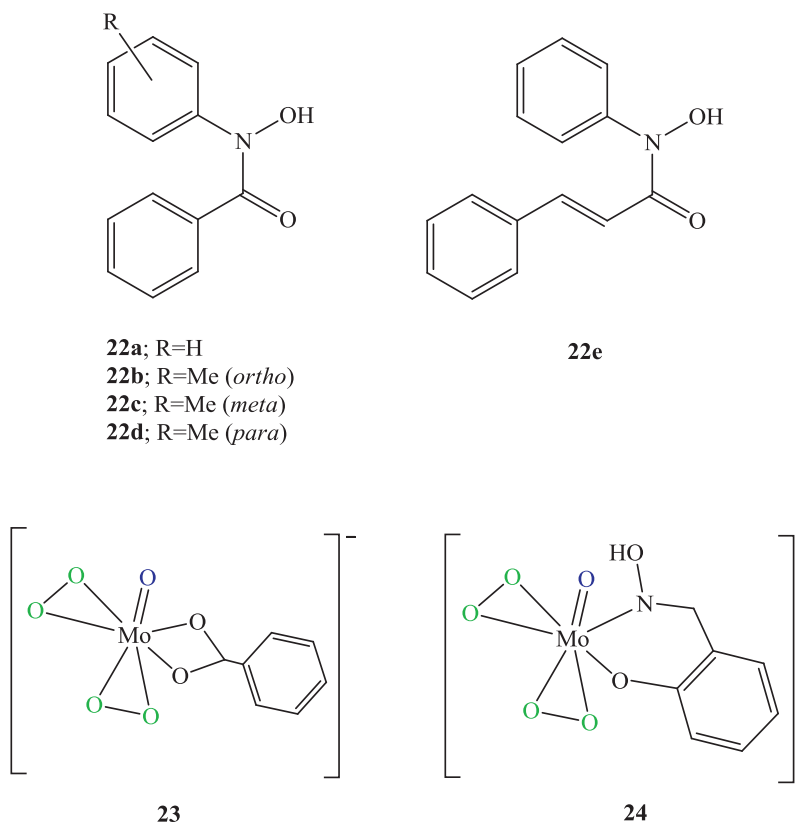


Fig. 8. The hydroxamic acid ligands 22a-e and Mo(VI) oxido-bis(oxido)peroxido complexes **23** and **24** [57,58].

Multinuclear molybdenum(VI) peroxido complexes were also tested as catalysts for the epoxidation of olefins. Griffith and coworkers reported trinuclear peroxido Mo(VI) complex $[\text{NMe}_4][(\text{RPO}_3)\{\text{Mo}(\text{O}_2)_2\}_2\{\text{Mo}(\text{O}_2)_2(\text{H}_2\text{O})\}]$ **25** for the catalytic epoxidation of alkenes in the presence of the phase-transfer cation in biphasic 15% H_2O_2 -benzene [60]. However, complex **25** catalyzed the epoxidation reaction far less efficiently than its tungsten analogue. This result was in line with the previously reported higher activity of W species compared with Mo [61,62]. Shortly before, Griffith et al. also reported their work on the use of two novel tetrameric $[\text{N}(\text{C}_6\text{H}_{13})_4]_3[\text{XO}_4\{\text{Mo}(\text{O}_2)_2\}_4]$ ($\text{X}=\text{P}$ **26a**, As **26b**) complexes as a catalyst for the oxidation of a number of cyclic and linear olefins by H_2O_2 [63]. In a typical catalytic experiment a biphasic mixture of compounds **26a** or **26b** dissolved in benzene, cyclooctene and 15% aqueous H_2O_2 was stirred vigorously at 70°C for 3 h, but the production of epoxide was not achieved in good yields (33% and 40%, respectively). Griffith observed similar low conversion with another multinuclear molybdenum(VI) peroxido complexes [64]. Spectroscopic evidence revealed that the catalysts framework did not completely break down during the course of the oxidation reaction and was restored on addition of hydrogen peroxide.

A great variety of olefins are selectively oxidized with molybdenum(VI) peroxido complexes, namely $[\text{MoO}(\text{O}_2)_2 \cdot 2\text{QOH}]$ **27**, $[\text{MoO}(\text{O}_2)(\text{QO})_2]$ **28**, $[\text{PPh}_4][\text{MoO}(\text{O}_2)_2(\text{QO})]$ **29**, $[\text{PPh}_4][\text{Mo}(\text{O})_2(\text{O}_2)(\text{QO})]$ **30** and as a catalyst, NaHCO_3 as a co-catalyst and H_2O_2 as the terminal oxidant, at room temperature [65]. Yield and TOF follow the catalyst order **27** > **29** > **28** > **30**. At room temperature, using complex **29** as a catalyst, the epoxidation of cyclopentene, in the presence of $\text{H}_2\text{O}_2/\text{NaHCO}_3$, produced cyclopentene oxide with TOF as high as $89,100\text{ h}^{-1}$, which exceeded all previously published data at that time. The efficiency of the epoxidation is a result of the compactness of the ligand

QOH (Fig. 9). Besides compactness, the enhancement of catalytic potentiality of QOH ligand lies on the fact that the ring nitrogen can act as an electron source or electron sink required for the catalytic reactions. The oxido-bis(oxido)peroxido complexes **27** and **29** can be also act as a stoichiometric epoxidation reagent.

Bhattacharyya then reported the preparation of $[\text{MoO}(\text{O}_2)_2(\text{PyCOXH})(\text{H}_2\text{O})]$ **31** and $\text{PMePh}_3[\text{MoO}(\text{O}_2)_2(\text{PyCO})]$ **32** (Fig. 10) [66]. The X-ray crystallographic studies have shown that the structure of complex **32** contains discrete $[\text{PMePh}_3]^+$ cations and $[\text{MoO}(\text{O}_2)_2(\text{PyCO})]^-$ anions and the geometry of the metal coordination sphere can be best considered as pentagonal bipyramidal. The complexes were tested in the epoxidation of different olefin substrates, including benzylic, carbocyclic, aromatic, and aliphatic systems that include functionalized as well as non-functionalized olefins (solvent: acetonitrile, oxidant: $\text{H}_2\text{O}_2/\text{NaHCO}_3$, room temperature). Both the complexes behaved as good epoxidation catalysts with good conversion (40–99%). A comparative catalytic study revealed the superiority of anionic complex **32** over neutral complex **31** in the epoxidation of cyclohexene, cinnamyl alcohol, 1-hexene, and trans-5-decene. The distribution of electronic charge within the anion was thought to be the cause of the higher catalytic activity of complex **30**.

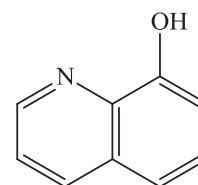


Fig. 9. The QOH ligand was used by Bhattacharyya and coworkers for the synthesis of Mo(VI) peroxide complexes **27–30** [65].

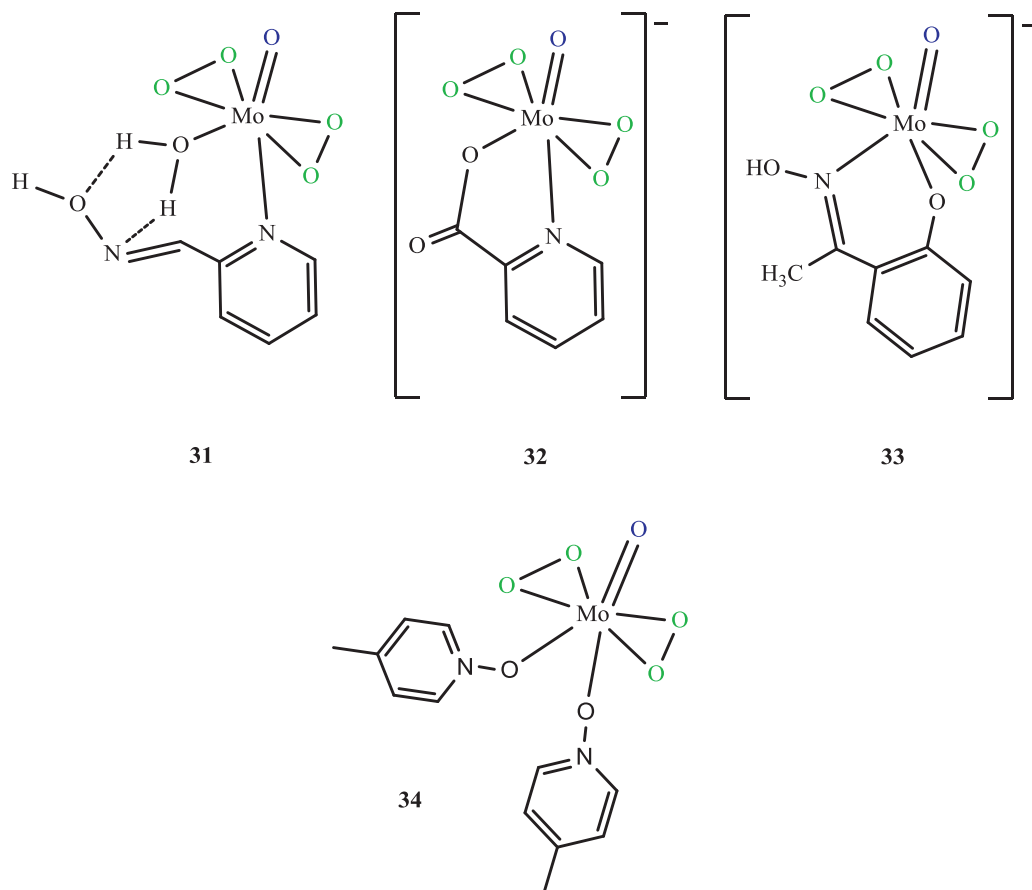


Fig. 10. The Mo(VI) oxido-bis(oxido)peroxido complexes **31–34** [66–68].

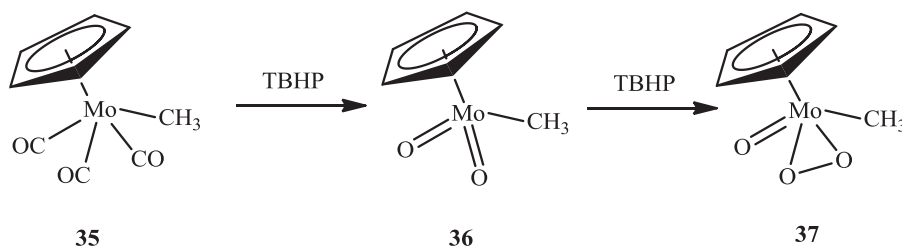
In the follow-up publication by this group, complex $\text{PPh}_4[\text{MoO}(\text{O}_2)_2(\text{HPEOH})]$ **33** (Fig. 10) was synthesized by dissolving MoO_3 (freshly precipitated) in H_2O_2 and treating the resulting solution with 1-(2'-hydroxyphenyl) ethanone dissolved in methanol, followed by addition of methanol solution of tetraphenylphosphonium chloride [67]. The catalytic activity of the complex **31** in the epoxidation of cyclooctene using NaHCO_3 as a co-catalyst and H_2O_2 as the terminal oxidant was high ($\text{TOF} = 3291 \text{ h}^{-1}$). Various cyclic and linear alkenes could be converted into the corresponding epoxides in high yields with this Mo(VI) oxido-bis(oxido)peroxido catalyst (conversion: 67–99%). The analogous tungsten complex showed higher reactivity toward the alcohol-functionalized olefins compared with the molybdenum compound. However, Mo and W catalysts showed similar catalytic activity in the epoxidation of proactive olefins such as cyclic olefins. When H_2O_2 was used as a sole oxidant the catalytic efficiency was rather poor.

Two molybdenum(VI) peroxido complexes, $[\text{Mo}(\text{O})(\text{O}_2)_2(\text{bipy})]$ and $[\text{MoO}(\text{O}_2)_2(4\text{-MePyO})_2]$ **34** (Fig. 10) were successfully employed as catalyst precursors in the epoxidation of olefins with UHP in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, $[\text{C}_4\text{mim}][\text{PF}_6]$ [68]. Cyclooctene was converted quantitatively into the corresponding epoxide at 60°C and $t = 18 \text{ h}$ in the presence of 0.025 mmol of catalyst. Using ionic liquid provided no advantage. High temperature and a rather long reaction time were required.

Montilla and Galindo reported the catalytic epoxidation of olefins in the ionic liquid, using in situ formed oxido-bis(oxido)peroxido Mo(VI) complexes by reaction of MoO_3 , UHP and pyrazol ligands [69]. They also investigated means of controlling the undesired hydrolytic side reaction, allowing the use of aqueous hydrogen

peroxide as an oxidant, and the influence of coordinating ligand on the catalysis. Complete conversion to epoxide was achieved for cyclooctene within 2 h in the presence of dmpz ligand in $[\text{C}_{12}\text{mim}][\text{PF}_6]$ media. In similar reaction condition, CHCl_3 solvent led to a lower conversion (23%). A similar oxidation in $[\text{C}_{12}\text{mim}][\text{PF}_6]$ using unsubstituted pyrazole as a ligand instead of dmpz reduced conversion from 99% to 84%. The stoichiometric oxidation experiment revealed that these oxido-bis(oxido)peroxido molybdenum complexes are capable of epoxidizing only one equivalent of olefin despite possessing two peroxido ligands. If the dmpz ligand was replenished between cycles, the system could be recycled up to a remarkable 10 times with consistent activity and selectivity. After each cycle, epoxide product was extracted thoroughly with ethyl ether.

Many organomolybdenum(VI) dioxido complexes are epoxidation catalysts, however the reactivity of their corresponding oxido-peroxido complexes is variable [70,71]. In some cases, in the presence of ROOH oxidant, either of the oxido-peroxido molybdenum(VI) and dioxido molybdenum(VI) species transfers an oxygen atom to an olefin. Kühn and coworkers oxidized $\text{CpMo}(\text{CO})_3\text{CH}_3$ **35** with a TBHP excess of at least 5 equiv. in dichloromethane, leading to the formation of the $\text{CpMoO}(\text{O}_2)\text{CH}_3$ **37** complex [72]. The ^1H and ^{95}Mo NMR studies showed that the formation of complex **37** from the reaction of the complex **35** with TBHP proceeds via $\text{CpMoO}_2\text{CH}_3$ **36** (Scheme 7). Both complexes **36** and **37** are active catalysts in the epoxidation of olefins in the presence of TBHP. For cyclooctene, the rate constant for reactions catalyzed by dioxido molybdenum(VI) are 3–5 times higher than those catalyzed by parent oxido-peroxido species under the same conditions probably due to the slight difference in the intermediates structure. On the other hand there are numbers of reports describing that a dioxido molybdenum(VI)



Scheme 7. The formation of the $\text{CpMoO}(\text{O}_2)\text{CH}_3$ complex by oxidation of $\text{CpMo}(\text{CO})_3\text{CH}_3$ with TBHP [72].

complex is effective catalyst precursors in the olefin epoxidation with TBHP but its corresponding oxido-peroxido complex is totally inactive under the same condition [73]. $\text{Cp}^*\text{MoO}_2\text{Cl}$ **38** complex acts as a catalyst for the reaction of alkyl hydroperoxides and olefins to yield the corresponding epoxides in toluene solvent [73]. In contrast with the $\text{Cp}^*\text{MoO}_2\text{Cl}$, its related oxido-peroxido complex $\text{Cp}^*\text{Mo}(\text{O})(\text{O}_2)\text{Cl}$ **39** cannot be considered as catalysts for the olefin epoxidation [73,74], thus ruling out oxido-peroxido complex as the intermediate responsible for the olefin epoxidation in the dioxido molybdenum(VI)/ROOH catalytic system. In fact, in such a system formation of oxido-peroxido complex even poisons the active catalyst. Very recently, Calhadró et al. performed DFT study to investigate the exact mechanism for the catalytic epoxidation by compounds **36** and **37** [75]. However, calculations did not provide a clear-cut answer to the reaction mechanism, suggesting that a series of competitive pathways are available, several of them with comparable activation barriers.

Some similarities can be found when comparing the reactivity of molybdenum oxido-peroxido complexes, which are discussed in this review, and the reactivity of isoelectronic organometallic η^5 -cyclopentadienyl molybdenum(VI) complexes. Both types of complexes are efficient olefins epoxidation catalysts when TBHP is the oxidant but they do not yield significant amounts of epoxidation product when TBHP is replaced by H_2O_2 . As mentioned before, molybdenum(VI) oxido-peroxido complexes are not active catalysts in hydrogen peroxide activation and this drawback can be overcome by using NaHCO_3 as a co-catalyst. In addition to this problem [76], organometallic counterparts are faced with another serious difficulty. Some complexes of this type underwent slow decomposition in the presence of a relatively high amount of water [71,77]. Consequently, using H_2O_2 as an oxidant is ineffectual in the olefin epoxidation by this type of complex. However, there are exceptions. For example, some recent reports discuss successful use of H_2O_2 with water-stable half sandwich molybdenum(VI) catalysts under a certain set of experimental conditions for various oxidative transformations such as the epoxidation [78] and *cis*-dihydroxylation of olefins [79], and the oxidation of sulfides [80].

In order to obtain catalysts with enhanced solubility in the apolar solvents, Galindo and coworkers prepared a series of oxido-bis(oxido) molybdenum(VI) complexes of several pyridine, 2,2'-bipyridine and pyrazole ligands **40a-j** (Fig. 11) with apolar functions (alkyl chains, alkyl-trimethylsilyl groups and polydimethylsiloxanyl polymer) [81]. Both the isolated complexes and in situ preparations were catalytically active in the epoxidation of olefins. The in situ epoxidation carried out in a catalytic system wherein the catalyst and olefin substrate were dissolved in the organic solvent with the aqueous hydrogen peroxide oxidant forming a separate phase. In the case of the epoxidation of cyclooctene in CHCl_3 , the epoxide yields with bidentate ligands **40e-h** (12–17% conversion) were markedly lower than those obtained with their monodentate counterparts (72–99% conversion). The steric hindrance of 2,6-bis(trimethylsilylmethyl)pyridine ligand **40d** resulted in reductions in catalyst activity (38% conversion).

Under similar reaction conditions, **40a** and **40b** showed poor catalytic activity in the oxidation of linear alkenes such as 1-octene, *trans*-2-octene, *trans*-4-octene and *cis*-2-heptene (less than 29% conversion). The epoxidation reactions, catalyzed by oxido-bis(oxido) molybdenum(VI) complexes of ligands **40a-j**, can also be carried out in solventless conditions. In solventless system, functionalized pyrazole ligands produced more activated oxido-peroxido molybdenum catalysts for the epoxidation. **40i** and **40j** promoted the complete oxidation of cyclooctene to cyclooctene oxide in solventless conditions at 60 °C in 4 h. Only 16% cyclooctene conversion was observed under identical conditions with unfunctionalized pyrazole ligand even after 18 h. The enhanced catalytic activity of the oxido-bis(oxido) molybdenum(VI) complexes of **40i** and **40j** was attributed to the enhanced solubility of the metal complexes in organic substrate.

Complex **41** (Fig. 12) was used, in 2012, as a catalyst using salicylidene benzoyl hydrazine as a tridentate ONO donor Schiff base ligand [82]. This complex **41** catalyzes the epoxidation of several linear and cyclic olefins, under air at room temperature, with H_2O_2 as an oxidant and NaHCO_3 as a co-catalyst. Full optimization of the parameters affecting the epoxidation of olefins such as solvent volume, the amount of substrate, catalyst, co-catalyst and oxidant and the reaction time was screened by half-fraction factorial design (2^{6-1}) and optimized by CCD. The optimized conditions were as follows: The molar ratios for catalyst:substrate: NaHCO_3 : H_2O_2 were 1:298:117:1170 and the reactions were performed in the (70:30) mixture of $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ (1.2 mL) under air at room temperature. Generally, excellent epoxide yields (89–100%) and selectivities (100%) were observed after optimization for all aliphatic and aromatic substrates.

2.2. Heterogeneous epoxidation

The immobilization of transition metal complexes on solid supports can provide catalysts that are easier to handle and possibly exhibit improved activities and selectivities in reactions. In an attempt to develop a novel heterogeneous procedure for the epoxidation of olefins, Thiel et al. prepared heterogeneous olefin epoxidation catalyst **42** by immobilization of oxido-peroxido molybdenum(VI) complexes in mesoporous Si-MCM-41 and Al-MCM-41 functionalized with a bidentate 2-[3(5)-pyrazolyl]pyridines ligand (Fig. 13) [83,84].

To obtain a catalyst with higher surface hydrophobicity, catalyst **43** was synthesized by modification of catalyst **42** through silylation with Me_3SiCl . Cyclooctene was completely oxidized to cyclooctene epoxide with TBHP in the presence of catalysts **42** or **43** in refluxing chloroform. These results were consistent with the homogeneous system **13a-j** previously reported by Thiel et al. [41,42]. Under similar reaction conditions, catalyst **43** showed higher reaction rates and better stability against leaching than catalyst **42**, probably due to the higher hydrophobicity of catalyst **43**. Immobilized molybdenum complex on Al-MCM-41 also showed better activity than the corresponding siliceous materials Si-MCM-41, which might be due to the higher Lewis acidity of Al-MCM-41

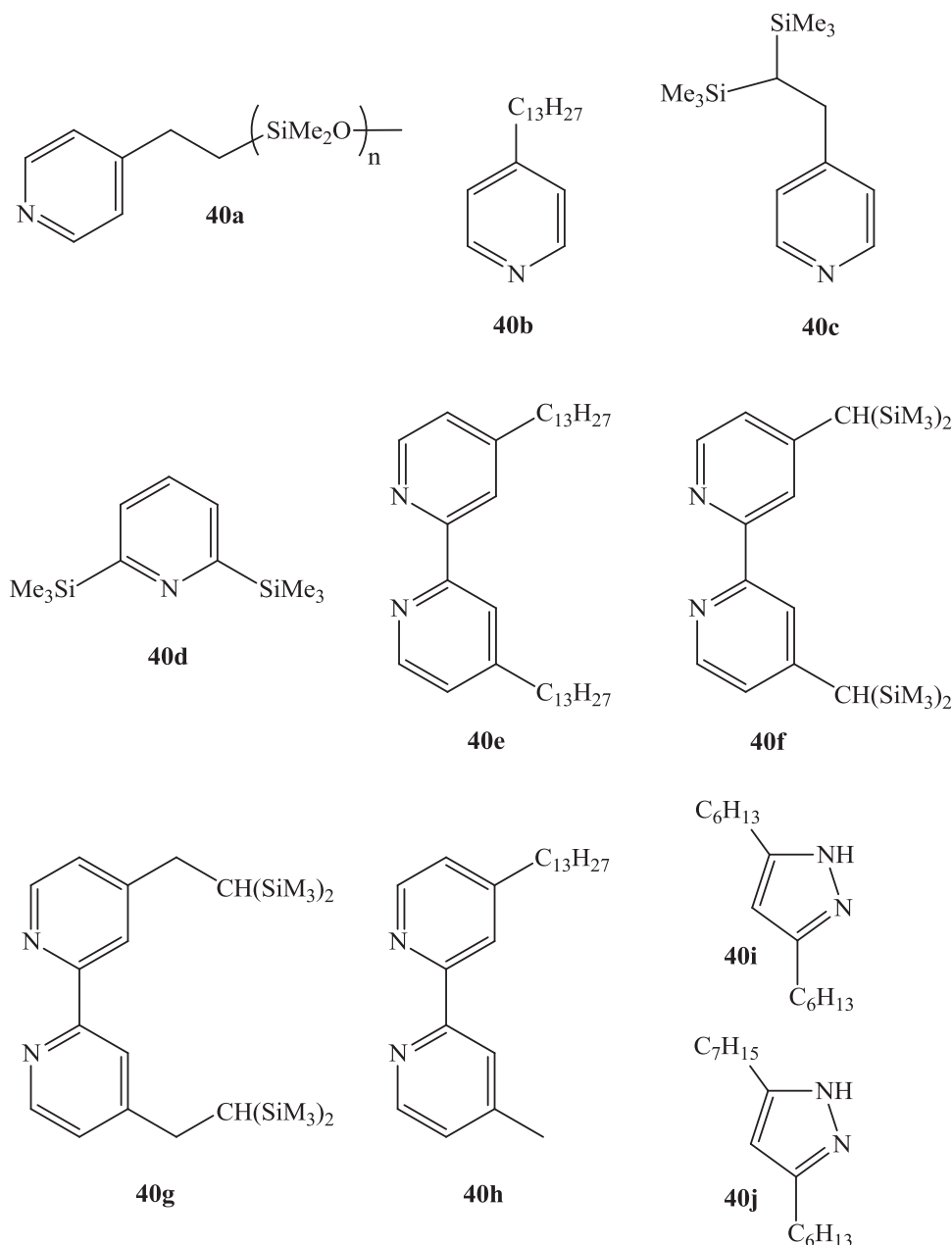


Fig. 11. The pyridine, 2,2'-bipyridine and pyrazole ligands used by Galindo et al. [81].

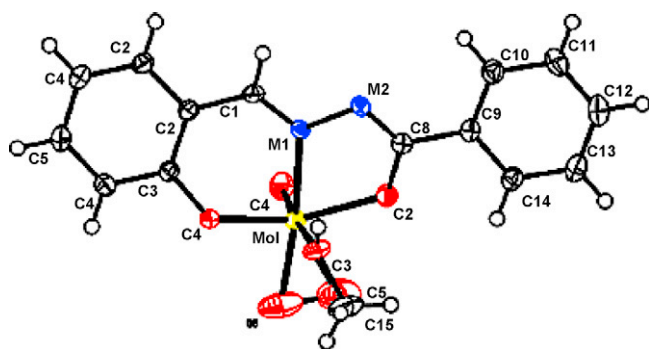


Fig. 12. Molecular structure of complex 41. Figure was reproduced from ref. [82], with permission of the copyright holders.

[84]. Heterogeneous catalysts **44a–c** (Fig. 13) was also synthesized by condensation of TEOS and the chelate ligand in the presence of CTAB as template and introducing oxido-bis(oxido) molybdenum species $\text{MoO}(\text{O}_2)_2$ into hybrid mesoporous material obtained [85]. Three Mo-containing catalysts **44a–c** were active catalyst for the oxidation of cyclooctene using TBHP as an oxidant in refluxing chloroform with a selectivity to epoxycyclooctane of 100%. Hybrid mesoporous material containing the highest loading of peroxido molybdenum complex **44c**, showed the highest activity but comparing the specific activity, catalyst **44a** was the most active system (highest TOF). The peroxido molybdenum(VI) catalysts can be immobilized on silica by interaction with the surface silanol groups, even in the absence of a chelate ligand [86]. However, the binding is unstable under the epoxidation reaction condition or in the presence of the polar solvents [85]. To investigate leaching of the active species into the liquid phase under operating conditions, the solid catalysts **42–44** were filtered at the reaction temperature

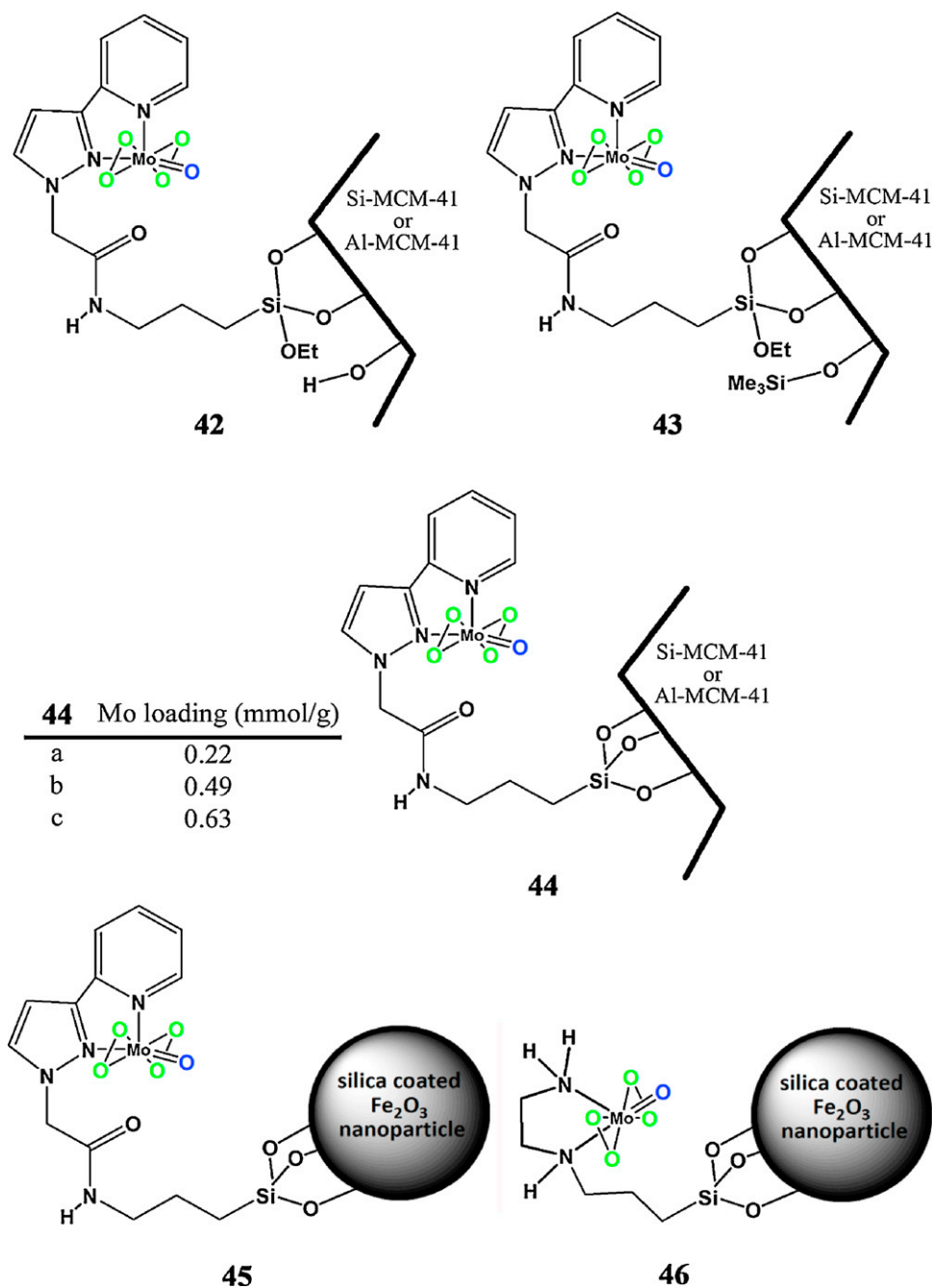


Fig. 13. The heterogeneous Mo(VI) oxido-bis(oxido) catalysts used by Thiel et al. [83–87].

of 61 °C at ~50% conversion of cyclooctene. The reaction then continued in the absence of solid catalyst, no further conversion was observed in the supernatant [83–86]. These results showed that these catalysts have the very high stability against leaching. The excellent stability of these catalysts was attributed to the covalent grafting between the organic ligand system and the inorganic mesoporous material, the mild reaction conditions which were used to produce catalysts, and the strong binding between the $\text{MoO}(\text{O}_2)_2$ unit and the chelating ligand.

Two magnetically recoverable heterogeneous epoxidation catalysts $\text{MoO}(\text{O}_2)_2\text{L}$ (L = bidentate TPPA **45**, AAPS **46**) (Fig. 13) were synthesized by covalent anchoring of complexes on silica coated Fe_2O_3 nanoparticles [87]. The heterogeneous catalyst **46** showed considerably lower conversion than the pyrazolpyridine-based system **45**. The catalytic properties of catalyst **45** were evaluated in the

epoxidation of cyclooctene by TBHP: epoxide was formed in 96% yield after 6 h in refluxing CHCl_3 , and the activity remained almost constant over six successive cycles. This catalyst showed a significantly enhanced catalytic activity and recyclability compared with compounds **42–44**.

The oxido-peroxido molybdenum(VI) moiety was also immobilized on polystyrene cross-linked with 5% divinylbenzene through the chelating ligands 2-pybmz and 3-pybmz, to give the $\text{PS}[\text{MoO}(\text{O}_2)_2(\text{L})]$ (L = 2-pybmz **47a**, 3-pybmz **47b**) [88]. When compounds **47a** and **47b** applied as catalysts in the oxidation of styrene using H_2O_2 as an oxidant in refluxing acetonitrile, only poor to moderate catalytic activity (14–17% conversion, TOF 5.9 h^{-1} for **47a** and 7.2 h^{-1} for **47b**) was observed. Selectivity to the epoxide was also poor, and the major product was identified to be benzoic acid (70% selectivity). In fact, these catalysts showed poorer

Table 1
Summary of the results of the stoichiometric oxidation of alkenes by Mo(VI) oxido-peroxido complexes.

Ent.	Mo complex	Substrate	Reaction conditions	Epoxide yield	Ref.	Remarks
1	[MoO(O ₂) ₂ (HMPT)(H ₂ O)] (1c.H ₂ O)	<i>cis</i> -2-butene-1,4-diones	CH ₂ Cl ₂ /rt/24 h	92%	[18]	No epoxide was obtained in the case of <i>trans</i> isomer.
2	[MoO(O ₂) ₂ (Et ₃ PO)]	cyclooctene	CH ₂ Cl ₂ /rt/40 min	50%	[19]	Substrate conversion was quantitative. The oxidation proceeds via an external nucleophilic attack of substrates to the peroxido ligands, so the oxidation rates increase with increasing nucleophilicity of the substrate.
3	[MoO(O ₂) ₂ (DMLA)] (2)	<i>trans</i> -2-butene	C ₆ H ₅ NO ₂ /20 °C	70%	[33]	Oxidation reactions are strongly inhibited in the presence of basic ligands.
4	[MoO(O ₂)(DMF) ₂ Cl ₂] (5a)	2,3-dimethyl-2-butene	CH ₂ Cl ₂ /20 °C/20 min	38%	[34]	
5	[MoO(O ₂)(HMPT) ₂ Cl ₂] (5b)	<i>trans</i> -2-butene	CH ₂ Cl ₂ /20 °C/4 h	15%	[34]	
6	PCMP (10)	1-octene	CHCl ₃ /rt/24 h	79%	[37]	Because of intramolecular hydrogen bonding between OH group of allylic alcohols and peroxido groups, allylic alcohols were epoxidized more easily than simple olefins.
7	MoO(O ₂) ₂ .15a	3,3-dimethylbut-1-ene	CH ₃ NO ₂ /rt/2 h	92%	[51]	The highest enantioselectivities obtained by use of binaphthyl ligand 15e. Bidentate chiral ligands give the moderate enantiomeric excesses in the epoxide products, whereas monodentate ligands produce small enantioselectivities.
8	MoO(O ₂) ₂ .15b	3,3-dimethylbut-1-ene	CH ₃ NO ₂ /rt/2 h	63%	[51]	
9	MoO(O ₂) ₂ .15c	3,3-dimethylbut-1-ene	CH ₃ NO ₂ /rt/2 h	91%	[51]	
10	MoO(O ₂) ₂ .15d	3,3-dimethylbut-1-ene	CH ₃ NO ₂ /rt/2 h	64%	[51]	
11	MoO(O ₂) ₂ .15e	3,3-dimethylbut-1-ene	CH ₃ NO ₂ /rt/2 h	58%	[51]	
12	MoO(O ₂) ₂ .15f	3,3-dimethylbut-1-ene	CH ₃ NO ₂ /rt/2 h	89%	[51]	
13	MoO(O ₂) ₂ .15g	3,3-dimethylbut-1-ene	CH ₃ NO ₂ /rt/2 h	55%	[51]	

selectivity and activity compared with their homogeneous counterparts **13a–j** [41,42]. However, when NaHCO₃ was used as a co-catalyst the catalytic activity would be improved.

When taking TBHP as an oxidant, both catalysts gave conversion between 4% and 7% only. However, selectivity of the products differed for these two oxidants. When TBHP was employed, styrene oxide was obtained as the major product with 50% selectivity. The catalysts can be recycled without any loss of the activity [88].

In 2007, Mahjoub and coworker reported the synthesis of polymeric compound of oxido-peroxido molybdenum (VI), [MoO(O₂)₂.4,4'-bipy]_n **48** by a simple and inexpensive route [89]. This polymeric complex was used as a catalyst for the epoxidation of cyclohexene and cyclooctene in a heterogeneous system in the presence of H₂O₂ as an oxidant at room temperature. In order to find the optimum conditions for the epoxidation reactions, the effects of reaction conditions such as the reaction time, the amount of the catalyst and oxidant and effect of solvent were investigated. The highest conversion and selectivity in the epoxidation of cyclohexene and cyclooctene occur in the system performed at 40 °C under air in CH₂Cl₂ (1.5 mL) containing the catalyst (0.11 mmol), selected substrate (3.65 mmol) and H₂O₂ (1 mL). The stability of the catalyst was also determined by recycling experiments and only a slight decrease in cyclohexene conversion during five recycling experiments was observed (from 95% in the first to 65% in the fifth run).

Here at the end of this section, we summarize the results of the stoichiometric (Table 1) and the catalytic (Table 2) oxidation of alkenes by oxido-peroxido complexes of the type [MoO(O₂)_m(L)_n] (*n*, *m* = 1,2). For further details about the reaction conditions, the reader is referred to the original publication.

3. Oxidation of alcohols

Many molybdenum species are known that catalyze the oxidation of alcohols to aldehydes/ketones, and in all cases, the active species is believed to be a Mo(VI) compound [90–103].

In 1979 Jacobson and Mares reported [90,91] the synthesis of complex H⁺[MoO(O₂)₂(C₅H₄NCO₂)][−] **49** (Fig. 14) by the reaction of MoO₃, 30% H₂O₂ and the N,O-bidentate picolinate ligand. They also reported the use of this complex as a stoichiometric oxidant of secondary alcohols. Complex **49** is an efficient reagent for the selective stoichiometric oxidation of 2-octanol to 2-octanone at 50 °C in deuterated methanol. One mol of complex **49** oxidizes up to 1.7 mol of 2-octanol suggesting that both peroxido ligands in the complex are active, although the second one may react more slowly than the first one. Interestingly, no ketone or low yields of ketone was obtained using [MoO(O₂)₂(HMPA)(H₂O)] **1c.H₂O** which contain a monodentate ligand, and [Mo(O)(O₂)(C₅H₃N(CO₂)₂)] complex **50** (Fig. 14), which contain tridentate pyridine-2,6-dicarboxylato ligand. Similar to reactivity trend observed in the epoxidation reactions [60–62], the tungsten complex H⁺[WO(O₂)₂(C₅H₄NCO₂)][−] reacted much faster than the corresponding molybdenum complex. In the case of the catalytic oxidation of secondary alcohols by hydrogen peroxide, the tungsten complex was an active catalyst but molybdenum analogous **49** was inactive.

In 1987, Di Furia and coworker reported [92] the synthesis of complexes **51** and **52** (Fig. 14) belonging to the family of oxido-bis(oxido) complexes containing bidentate ligands studied by Mares et al. [90,91]. Complex **51** contains *bidentate picolinate* ligand with pyridine nitrogen coordination and complex **52** contains *picolinate-N-oxide* ligand with pyridine oxide oxygen

Table 2
Summary of the results of the catalytic oxidation of alkenes by Mo(VI) oxido-peroxido complexes.

Ent.	Mo complex	Substrate	Reaction conditions	Epoxide yield	Ref.	Remarks
1	MoO(O ₂) ₂ . 13d	Cyclooctene	TBHP/toluene/100 °C/1 h	100%	[50]	Alkyl side chain of ligands increased the solubility of the complexes in organic solvents and enhanced catalytic activity.
2	MoO(O ₂) ₂ . 13f	Cyclooctene	TBHP/CHCl ₃ /65 °C/3 h	100%	[39]	
3	MoO(O ₂) ₂ . 15g	3,3-dimethylbut-1-ene	TBHP/CH ₂ Cl ₂ /r.t./overnight	□70%	[51]	
4	[MoO(O ₂) ₂ (H ₂ O)(ONnDodec ₃)] (17a)	1-octene	H ₂ O ₂ /CH ₃ CN/65 °C/24 h	75%	[53]	Analogues of 17a-c with <i>n</i> -Bu instead of <i>n</i> -Dodec (16a-c) are catalytically inactive.
5	[MoO(O ₂) ₂ (H ₂ O)(OPnDodec ₃)] (17b)	1-octene	H ₂ O ₂ /CH ₃ CN/65 °C/24 h	14%	[53]	
6	[MoO(O ₂) ₂ (H ₂ O)(OAsnDodec ₃)] (17c)	1-octene	H ₂ O ₂ /CH ₃ CN/65 °C/24 h	83%	[53]	
7	[MoO(O ₂) ₂ (HMPT)] (1c)	Cyclohexene	H ₂ O ₂ /DCE/50 °C/5 h/[H ⁺] = 0.6 M	14%	[54]	Low-efficient catalyst.
8	MoO(O ₂) ₂ . 18a	Cyclohexene	H ₂ O ₂ /DCE/50 °C/5 h/[H ⁺] = 0.6 M	21%	[54]	
9	MoO(O ₂) ₂ . 18b	Cyclohexene	H ₂ O ₂ /DCE/50 °C/5 h/[H ⁺] = 0.6 M	21%	[54]	
10	MoO(O ₂) ₂ . 18c	Cyclohexene	H ₂ O ₂ /DCE/50 °C/5 h/[H ⁺] = 0.6 M	51%	[54]	Efficiency of the catalysts and product yields depend on the lipophilicity of the ligand. An increase of the H ⁺ ion concentration results in increase of the olefin conversion and decrease of the selectivities to epoxide.
11	MoO(O ₂) ₂ . 18d	Cyclohexene	H ₂ O ₂ /DCE/50 °C/5 h/[H ⁺] = 0.8 M	33%	[54]	
12	MoO(O ₂) ₂ . 18e	Cyclohexene	H ₂ O ₂ /DCE/50 °C/5 h/[H ⁺] = 0.8 M	64%	[54]	
13	MoO(O ₂) ₂ . 18f	Cyclohexene	H ₂ O ₂ /DCE/50 °C/5 h/[H ⁺] = 0.8 M	65%	[54]	Efficient catalyst in regard to epoxide yield, but a very long reaction time is necessary to obtain high yields.
14	19	Cyclooctene	TBHP/toluene/rt/22 h	95%	[55]	
15	20	Cyclooctene	TBHP/toluene/rt/22 h	15%	[55]	
16	[MoO(O ₂)(BPHA) ₂] (21a)	Cyclohexene	H ₂ O ₂ /NaHCO ₃ /CH ₃ CN/rt/1 h	80%	[57]	Significant reduction in the catalytic activity in absence of NaHCO ₃ additive. The anionic complexes (23,24) show the highest catalytic efficiency.
17	[MoO(O ₂)(BOTH ₂) ₂] (21b)	Cyclohexene	H ₂ O ₂ /NaHCO ₃ /CH ₃ CN/rt/1 h	83%	[57]	
18	[MoO(O ₂)(BMTH ₂) ₂] (21c)	Cyclohexene	H ₂ O ₂ /NaHCO ₃ /CH ₃ CN/rt/1 h	85%	[57]	
19	[MoO(O ₂)(BPTh ₂) ₂] (21d)	Cyclohexene	H ₂ O ₂ /NaHCO ₃ /CH ₃ CN/rt/1 h	82%	[57]	
20	[MoO(O ₂)(CPHA) ₂] (21e)	Cyclohexene	H ₂ O ₂ /NaHCO ₃ /CH ₃ CN/rt/1 h	90%	[57]	
21	[MoO(O ₂) ₂ (C ₆ H ₅ COO)] [−] (23)	Cyclohexene	H ₂ O ₂ /NaHCO ₃ /CH ₃ CN/rt/1 h	93%	[57]	
22	[MoO(O ₂) ₂ (saloxH)] [−] (24)	Cyclohexene	H ₂ O ₂ /NaHCO ₃ /CH ₃ CN/rt/45 min	95%	[58]	Low epoxide yield.
23	26a	Cyclooctene	H ₂ O ₂ /benzene/70 °C/3 h	33%	[63]	
24	26b	Cyclooctene	H ₂ O ₂ /benzene/70 °C/3 h	40%	[63]	
25	[MoO(O ₂) ₂ .2QOH] (27)	Cyclohexene	H ₂ O ₂ /NaHCO ₃ /CH ₃ CN/rt/45 min	95%	[65]	Very high TOF. The efficiency of the catalysts is a result of the compactness of the ligand QOH.
26	[MoO(O ₂)(QO) ₂] (28)	Cyclohexene	H ₂ O ₂ /NaHCO ₃ /CH ₃ CN/rt/45 min	76%	[65]	
27	[PPh ₄][MoO(O ₂) ₂ (QO)] (29)	Cyclohexene	H ₂ O ₂ /NaHCO ₃ /CH ₃ CN/rt/45 min	93%	[65]	
28	[PPh ₄][MoO(O ₂) ₂ (QO)] (30)	Cyclohexene	H ₂ O ₂ /NaHCO ₃ /CH ₃ CN/rt/45 min	71%	[65]	Efficient catalysts in regard to epoxide yield, TON and TOF.
29	[MoO(O ₂) ₂ (PyCOXH)(H ₂ O)] (31)	Cyclohexene	H ₂ O ₂ /NaHCO ₃ /CH ₃ CN/rt/1 h	97%	[66]	
30	[PMePh ₃][MoO(O ₂) ₂ (PyCO)] (32)	Cyclohexene	H ₂ O ₂ /NaHCO ₃ /CH ₃ CN/rt/1 h	99%	[66]	
31	PPh ₄ [MoO(O ₂) ₂ (HPEOH)]	Cyclooctene	H ₂ O ₂ /NaHCO ₃ /CH ₃ CN/rt/1 h	88%	[67]	Long reaction time. Using ionic liquid would provide no advantage over conventional solvents.
32	[Mo(O)(O ₂) ₂ (bipy)]	Cyclooctene	UHP/[C ₄ mim][PF ₆]/60 °C/18 h	90%	[68]	

Table 2 (Continued)

Ent.	Mo complex	Substrate	Reaction conditions	Epoxide yield	Ref.	Remarks
33	[MoO(O ₂) ₂ (4-MePyO) ₂] (34)	Cyclooctene	UHP/[C ₄ mim][PF ₆]/60 °C/18 h	83%	[68]	Relatively short reaction time. Green approach. The system could be recycled up to 10 times with consistent activity and selectivity.
34	[Mo(O)(O ₂) ₂ (dmpz) ₂]	Cyclooctene	H ₂ O ₂ /[C ₁₂ mim][PF ₆]/60 °C/2 h	99%	[69]	
35	[Mo(O)(O ₂) ₂ (py) ₂]	Cyclooctene	H ₂ O ₂ /CH ₃ Cl/60 °C/18 h	2%	[81]	The epoxide yields with bidentate ligands were markedly lower than those obtained with their monodentate counterparts.
36	[Mo(O)(O ₂) ₂ (40a) ₂]	Cyclooctene	H ₂ O ₂ /CH ₃ Cl/60 °C/18 h	86%	[81]	
37	[Mo(O)(O ₂) ₂ (40b) ₂]	Cyclooctene	H ₂ O ₂ /CH ₃ Cl/60 °C/18 h	99%	[81]	
38	[Mo(O)(O ₂) ₂ (40c) ₂]	Cyclooctene	H ₂ O ₂ /CH ₃ Cl/60 °C/18 h	71%	[81]	
39	[Mo(O)(O ₂) ₂ (40d) ₂]	Cyclooctene	H ₂ O ₂ /CH ₃ Cl/60 °C/18 h	38%	[81]	
40	[Mo(O)(O ₂) ₂ (40e) ₂]	Cyclooctene	H ₂ O ₂ /CH ₃ Cl/60 °C/18 h	17%	[81]	
41	[Mo(O)(O ₂) ₂ (40f) ₂]	Cyclooctene	H ₂ O ₂ /CH ₃ Cl/60 °C/18 h	17%	[81]	
42	[Mo(O)(O ₂) ₂ (py) ₂]	Cyclooctene	H ₂ O ₂ /solventless/60 °C/18 h	8%	[81]	The highest epoxide yield observed for complexes with functionalized pyrazole ligands (40i , 40j). Longer reaction times result in a significant decrease in epoxide selectivities.
43	[Mo(O)(O ₂) ₂ (dmpz) ₂]	Cyclooctene	H ₂ O ₂ /solventless/60 °C/18 h	31%	[81]	
44	[Mo(O)(O ₂) ₂ (40a) ₂]	Cyclooctene	H ₂ O ₂ /solventless/60 °C/18 h	23%	[81]	
45	[Mo(O)(O ₂) ₂ (40b) ₂]	Cyclooctene	H ₂ O ₂ /solventless/60 °C/18 h	31%	[81]	
46	[Mo(O)(O ₂) ₂ (40i) ₂]	Cyclooctene	H ₂ O ₂ /solventless/60 °C/4 h	88%	[81]	
47	[Mo(O)(O ₂) ₂ (40j) ₂]	Cyclooctene	H ₂ O ₂ /solventless/60 °C/4 h	99%	[81]	
48	41	Cyclooctene	H ₂ O ₂ /NaHCO ₃ /CH ₃ OH/CH ₂ Cl ₂ /rt/74.5 min	97%	[82]	Excellent epoxide yields and selectivities were observed after optimization by CCD method for all aliphatic and aromatic substrates.
49	42	Cyclooctene	TBHP/CHCl ₃ /61 °C/7 h	85%	[83]	
50	43	Cyclooctene	TBHP/CHCl ₃ /61 °C/4 h	95%	[84]	44c showed the highest activity but 44a showed the highest TOF.
51	44a	Cyclooctene	TBHP/CHCl ₃ /61 °C/1.35 h	34%	[85]	
52	44b	Cyclooctene	TBHP/CHCl ₃ /61 °C/1.35 h	60%	[85]	
53	44c	Cyclooctene	TBHP/CHCl ₃ /61 °C/1.35 h	66%	[85]	The catalyst can be reused six times, by simple magnetic separation. Poor results.
54	45	Cyclooctene	TBHP/toluene/rt/22 h	95%	[87]	
55	46	Cyclooctene	TBHP/toluene/rt/22 h	15%	[87]	
56	48	Cyclohexene	H ₂ O ₂ /CH ₂ Cl ₂ /rt/12 h	95%	[89]	

Good epoxide yields with polymeric compound of peroxido molybdenum(VI).

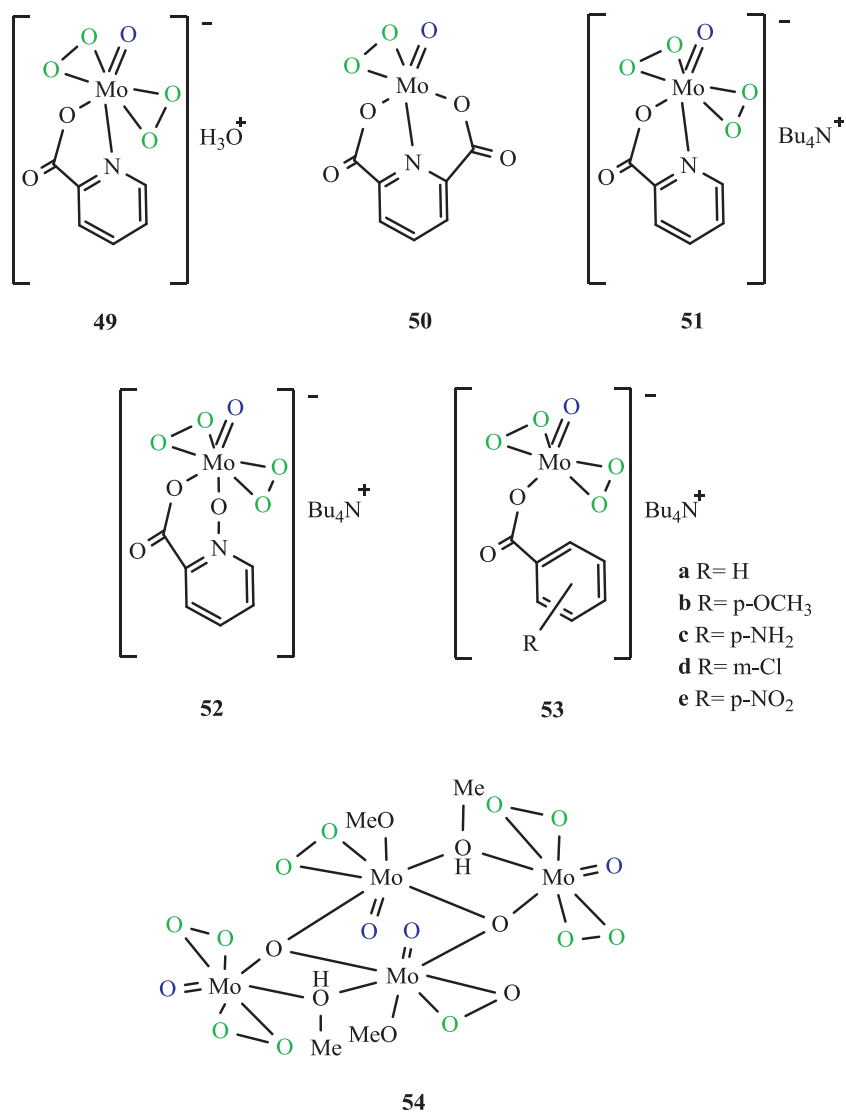


Fig. 14. The Mo(VI) oxido-bis(oxo) complexes **49–54** [90–94].

coordination. These complexes were tested in the stoichiometric oxidation of different primary and secondary alcohols in DCE solvent. The complex **52** was 50-fold more reactive than complex **51** toward cyclohexanol. Using complex **52** complete conversion of cyclohexanol to cyclohexanone required 6 h at 50 °C. No overoxidation to the corresponding carboxylic acid was observed. With the exception of geraniol, complex **52** showed excellent chemoselectivity for alcohols and double bonds remained unaffected under oxidative conditions. In the case of geraniol oxidation, both 2,3-epoxygeraniol and geranial were formed. Also in the presence of other functional groups, the oxidation of the alcoholic function proceeds smoothly by complex **52** [93]. The epoxy rings, pyridine nitrogen, carbon-carbon triple bonds, carbamates, and amides did not compete with the oxidation of the OH group. The presence of a basic group greatly diminished the yields of the carbonyl product, for instance the use of 1-methylpiperidin-3-ol led to the lowest conversion obtained (20% conversion in 24 h). This behavior may be attributed to the ability of the substrate to displace the picolinate-*N*-oxide ligand of the complex.

Two anionic Mo(VI) peroxide complexes, $[(\text{Bu}_4\text{N})][\text{MoO}(\text{O}_2)_2(\text{R}-\text{C}_6\text{H}_5\text{CO}_2)]$ **53a–e** and $[(\text{Bu}_4\text{N})_2][2\text{MoO}(\text{O}_2)_2(\text{MeOH})_2(\text{MoO}(\text{O}_2)\text{O})_2(\text{MeO})_2]$ **54** (Fig. 14), are efficient stoichiometric oxidants for the oxidation of alcoholic

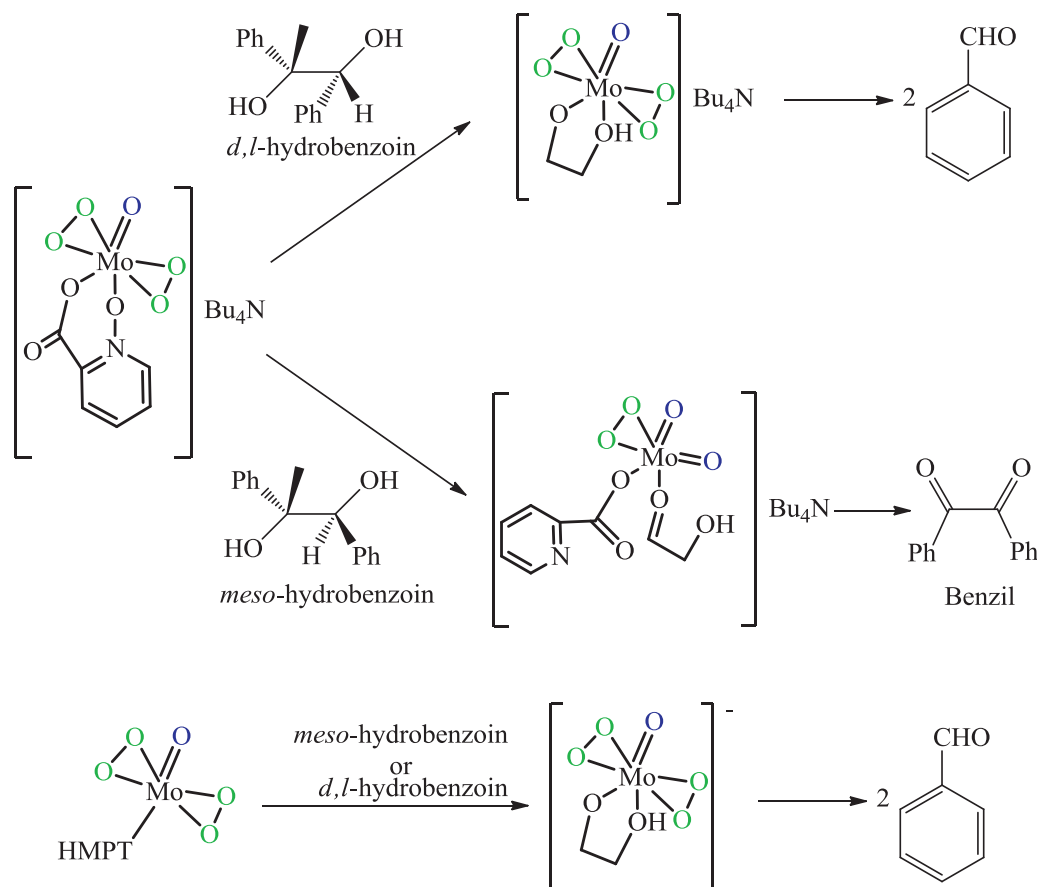
function in reaction conditions similar to those used for complexes **49–52** [94]. The corresponding oxidation rates and pseudo-first order kinetic constants of complexes **50–53** and **1c** have also been obtained (Table 3). A differentiation among these complexes can be made by comparing those whose seventh coordination site is free (**1c** and **53**), with those in which it is occupied by a ligand (**50–52**). The yield and the reaction rate observed for complex **1c** show that the presence of a free or easily removable coordination

Table 3

The oxidation of cyclohexanol by complexes **1c** and **50–53**, in DCE, at 60 °C, 24 h [94].

Oxidant	Cyclohexanone yield (%)	$k_1 \times 10^4 \text{ (s}^{-1}\text{)}^a$
1c	35	3
50	n.r	–
51	95	0.2
52	100	46
53a	100	50
53b	100	57
53c	100	82
53d	95	37
53e	100	23

^a k_1 = Pseudo-first order kinetic constant.



Scheme 8. The oxidation of *meso*- and *d,l*-hydrobenzoin with **52** and **1c** [84].

site on the Mo complexes cannot be the only requisite that makes them effective oxidants for the alcoholic function. Complexes **53a–e**, which contain monodentate ligands, are effective oxidants. Therefore, the presence of a bidentate ligand also cannot be the key feature. There remains, then, only one reasonable possibility: the most important feature of peroxide molybdenum complexes as oxidant of alcohols is their anionic character [94]. The electron-donating substituents on ligand (**53c**) increase the anionic character of the oxidant and accelerate the oxidation rates whereas the electron-accepting substituents (**53e**) decrease it. The availability of a free coordination site on molybdenum centre plays a role but is a less stringent requisite.

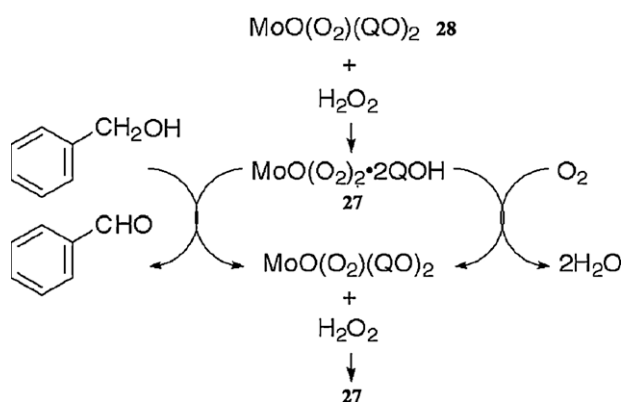
The molybdenum complexes **52** and $[\text{MoO}(\text{O}_2)_2(\text{HMPA})]$ **1c** are efficient stoichiometric oxidants for the oxidation of 1,2-diols [95]. With these complexes, the oxidation of two isomeric glycols, *meso*- and *d,l*-hydrobenzoin in DCE at 60 °C under air atmosphere led to the formation of two products (benzil and benzaldehyde). The product distribution is dependent on the nature of both the substrates and the oxidants. Benzil was the major product of the oxidation by the anionic complex **52** in the case of *meso*-hydrobenzoin (1.4 benzil/benzaldehyde ratio), but when *d,l*-hydrobenzoin oxidized with complex **52**, the major product was benzaldehyde rather than benzil (0.2 benzil/benzaldehyde ratio). In contrast, the oxidation of *meso*- and *d,l*-hydrobenzoin with neutral complex **1c**, mainly afforded benzaldehyde product (respectively, 0.01 and 0.002 benzil/benzaldehyde ratio). The kinetic results show that the two products obtained from two different intermediates.

Benzil is formed when glycol coordinates to the molybdenum center as a monodentate ligand, while benzaldehyde originates from a complex in which the substrate is present as a bidentate chelating ligand (Scheme 8). Hence the different product

distributions observed may be rationalized on the basis of the chelating ability of substrate and the availability of free coordination sites at the metal. Because of steric factor, *d,l*-hydrobenzoin is a better chelating ligand than the *meso*-isomer. As a consequence, *d,l*-hydrobenzoin acts as a chelating ligand and benzaldehyde should be formed. On the other hand, taking into account that complex **1c** already has a free coordination site and a second one that is occupied by the easily removable HMPT ligand, the experimental finding that the complex **1c** mainly affords benzaldehyde as product. The complexes **52** and **1c** discussed oxidized almost 3 equivalent of substrate, suggesting the involvement of air dioxygen in reaction.

In the presence of $[\text{MoO}(\text{O}_2)_2(\text{BPHA})_2]$ **21a** as a stoichiometric oxidant, a series of primary and secondary alcohols were easily oxidized to the corresponding carbonyl compounds in good to excellent yields. The oxidation of cyclododecanol to cyclododecanone proceeded with excellent activity (97% conversion) and a selectivity of 100% in 4 h. With changing substrate to linear dodecanol the conversion decreased to 63% in 13 h, but the selectivity to carbonyl compound remained constant. The reaction condition was similar to the oxidation of allylic alcohols except the reaction temperature was 85 °C [59].

A solution obtained by dissolving MoO_3 in a moderate excess of H_2O_2 reacts with QOH to give $[\text{MoO}(\text{O}_2)_2(\text{QO})_2]$ **28**, but when the same reaction is conducted with a large excess of H_2O_2 , an anionic complex is formed, which reacts with PPh_4Cl to give the corresponding salt $[\text{MoO}(\text{O}_2)_2(\text{QO})][\text{PPh}_4]$ **29**. Both neutral and anionic complexes catalyzed the oxidation of several alcohols (including aromatic, cyclic and linear ones) to their corresponding aldehydes with H_2O_2 , O_2 or $\text{H}_2\text{O}_2 + \text{O}_2$ as an oxidant [96,97]. Increasing the O_2 concentration in the reaction medium shifts the equilibrium of the reaction, $2\text{H}_2\text{O}_2 \rightleftharpoons 2\text{H}_2\text{O} + \text{O}_2$ to the backward, so the



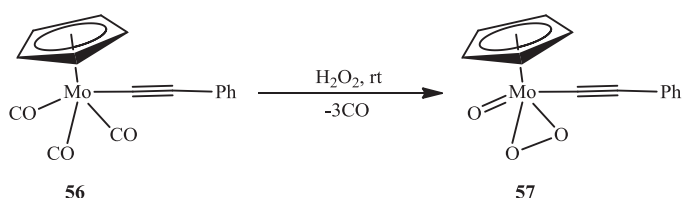
Scheme 9. The catalyst precursor **28** and the active catalyst **27** in the oxidation of alcohols. Figure was reproduced from ref. [96], with permission of the copyright holders.

combination of H_2O_2 and O_2 was more potential oxidant than H_2O_2 . Oxidation of cyclohexanol in refluxing acetonitrile using complex **28** as a catalyst and $\text{H}_2\text{O}_2 + \text{O}_2$ as an oxidant afforded the cyclohexanone in a yield of 34% (TON = 700). The higher aldehyde yields obtained in the case of benzylic and allylic alcohols (benzyl alcohol: 59%, cinnamyl alcohol: 66%) [96]. However, due to obtaining a mixture of respective aldehydes and carboxylic acids, the selectivity for oxidation of aliphatic alcohols was low. In the presence of AIBN and benzoquinone as radical scavengers, the conversions did not decrease at all. The radical mechanism ruled out by this data. Considering all experimental results, a probable mechanistic pathway was provided in which $[\text{Mo}(\text{O}_2)_2(\text{QO})_2]$ **28** was a catalyst precursor and $\text{Mo}(\text{O}_2)_2 \cdot 2\text{QOH}$ **27** was the active catalyst (Scheme 9) [96].

In accordance with previous studies [94], the anionic complex **29** was a more efficient catalyst for the alcohol oxidation than the neutral complex **28** [97]. In identical reaction condition, the oxidation of cyclohexanol using $[\text{Mo}(\text{O}_2)_2(\text{QO})][\text{PPh}_4]$ **29** as a catalyst and $\text{H}_2\text{O}_2 + \text{O}_2$ as an oxidant afforded cyclohexanone in a yield of 84% (TON = 840). The selectivity results were the same as those of the complex **28**.

In 2005, Wei et al. reported that the bis-quaternary phosphonium peroxidomolybdate $\text{Ph}_3\text{P}(\text{CH}_2)_2\text{PPh}_3[\text{Mo}(\text{O}_2)_2(\text{C}_2\text{O}_2)]$ **55** is an effective catalyst in the oxidation of alcohol under the water–organic biphasic system [98]. When the mixture of complex **55**, 30% aqueous H_2O_2 , and benzyl alcohol (in a ratio of 1:120:100) was stirred vigorously in air and at 90°C for 8 h, benzoic acid obtained in 49% yield. In this case, bis-quaternary phosphonium cation which possessing lipophilic nature, can catch peroxido $\text{Mo}(\text{VI})$ anion carrying active oxygen into organic phase where the oxidation reaction takes place. In the absence of bis-quaternary phosphonium cation, the oxidation of benzyl alcohol at the same condition gave benzaldehyde in a poor yield.

A novel procedure of oxidizing alcohols was recently reported by Umbarkar et al. using in situ generated oxido-peroxido molybdenum species **57** that is formed by the reaction of tricarbonyl acetylide precursor **56** with 30% hydrogen peroxide (Scheme 10) [99]. The oxidation of primary alcohols with H_2O_2 as an environ-



Scheme 10. In situ generation of oxido-peroxido $\text{Mo}(\text{VI})$ acetylide complex **57** [99].

mentally benign oxidant and 1 mol% **56** at 80°C was investigated and after 8 h, high conversion of benzyl alcohol (86%) with very high selectivity (92%) to benzaldehyde was observed. No additional solvent was used. As 30% H_2O_2 is used as an oxidant the remaining 70% water acts as a solvent. At the end of reaction, the aldehyde forms a separate organic phase from the aqueous phase containing the Mo catalyst. So catalyst **57** readily separated, recycled and reused for five cycles. The benzyl alcohol conversion did not decrease significantly and the aldehyde selectivity remained constant (1st run: 86% conversion, 5th run: 84% conversion). Higher conversion was obtained for benzyl alcohol with electron-donating substituents such as *p*-methyl, *p*-methoxy and 3,5-dimethoxy (83–90%) and lower conversion was obtained for benzylalcohol with electron-withdrawing substituents such as *p*-nitro, *p*-chloro, an 2,4-dichloro benzylalcohols (60–78%). But this catalyst was not capable for oxidizing aliphatic alcohols such propanol, butanol, and octanol.

A mechanism for the oxidation of various alcohols to aldehydes using catalyst **56** was suggested by comparison with the literature reports (Scheme 11) [97,100]. Molybdenum acetylide complex **56** on treatment with H_2O_2 forms corresponding oxido-peroxido complex **57**. When alcoholic substrate approaches the catalyst, the peroxido ring opens by abstracting alcohol OH proton. The carbon proton abstraction followed by liberation of water molecule and aldehyde leads to the formation of $\text{Mo}(\text{VI})$ dioxido complex which after further treatment with H_2O_2 regenerates the compound **57**. During this mechanism, the alcohol substrate coordinates to Mo center.

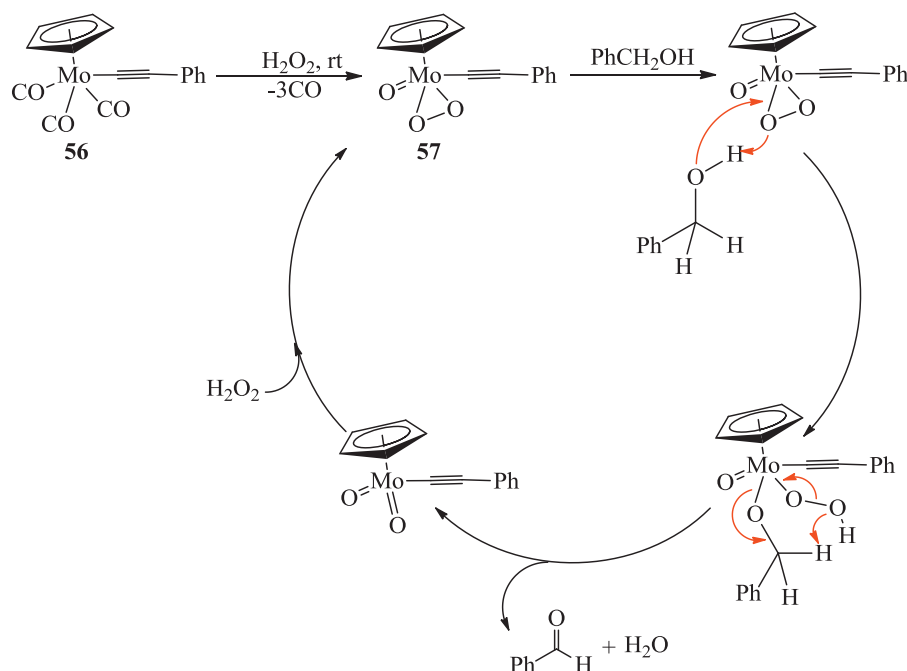
Bhattacharyya used the $\text{PPh}_4[\text{Mo}(\text{O}_2)_2(\text{HPEOH})]$ **33** (Fig. 10) in peroxidic oxidation of various alcohols to their corresponding aldehydes or ketones with H_2O_2 as an oxidant in CH_3CN as a solvent at refluxing condition [67]. The complex catalyzed the oxidation of several alcohols (including aromatic, cyclic and linear ones) to their corresponding aldehydes. However, the catalyst was not selective in the oxidation of linear aliphatic alcohols: for example, 1-butanol gave a mixture of aldehyde and carboxylic acid in a 3:1 ratio (aldehyde/carboxylic). The higher selectivity in the case of aromatic alcohols is due to the fact that only in the aromatic case resonance stabilization of $\text{C}=\text{O}$ bond makes it reasonably immune against overoxidation [101–103]. With increase in chain length of the aliphatic alcohols the rate of catalytic oxidation decreased but the selectivity of aldehyde increased (from 56% in methanol to 98% in 1-dodecanol).

The results of stoichiometric (Table 4) and catalytic oxidation (Table 5) of alcohols by oxido-peroxido molybdenum(VI) complexes are summarized at the end of this chapter. For further details about the reaction conditions, the reader is referred to the original publication.

4. Oxidation of alkanes

In view of their importance as intermediates in organic synthesis, many methods for selective oxidation of alkanes have been documented in the literature [104–107].

In 1999, Bhattacharyya reported that complex $[\text{Mo}(\text{O}_2)_2(\text{QO})_2]$ **28** is an active catalyst for homogeneous and selective oxidation of toluene, *o*-xylene and *p*-xylene to give benzoic acid (95%, TON = 1310), phthalic acid (76%, TON = 1047) and *p*-toluic acid (88%, TON = 1021) respectively, with H_2O_2 (0.038 mol) + O_2 as an oxidant in refluxing acetonitrile (reaction time: 6 h) [108]. The benzoic acid yield was reduced to 72% when only H_2O_2 (0.076 mol) was used as an oxidant and trace when exclusively O_2 was used. Analytical and infrared data showed that reaction of compound **28** with an excess of H_2O_2 ($\text{Mo}:\text{H}_2\text{O}_2 \approx 1:4$) leads to formation of $[\text{Mo}(\text{O}_2)_2 \cdot 2\text{QOH}]$ **27**. These observations led to conclude that com-



Scheme 11. The mechanism for the oxidation of various alcohols proposed by Umbarkar and coworkers. Reproduced from ref. [99], with permission of the copyright holders.

pound **28** may be the catalyst precursor and compound **27** the active catalyst in the oxidation of methylbenzenes (Scheme 12). In the presence of a radical scavenger such as benzoquinone no oxidation occurred, suggesting the intervention of a radical pathway. As mentioned before [96], the same catalyst was proposed to promote the oxidation of alcohols through a non radical mechanism. In addition, compound **28** was stoichiometrically reacted with toluene in refluxing acetonitrile for 4 h to give benzoic acid (72%), with *o*-xylene to give phthalic acid (55%) and with *p*-xylene to give *p*-toluic acid (61%).

The oxido-bisperoxido Mo(VI) complex **58** (Fig. 15) synthesized by the reaction of MoO_3 with H_2O_2 and dmpz was studied by Punniyamurthy and coworkers [109]. This complex exhibited the excellent catalytic activity for the selective oxidation of benzylic

C–H bonds of alkylbenzenes to the corresponding alcohols and ketones in moderate to good yields using H_2O_2 in acetonitrile under atmospheric oxygen. The oxidation of diphenylmethane occurred selectively and afforded a 3:2 mixture of diphenylmethanol and benzophenone in 62% yield when the reaction was allowed to reflux for 12 h. Allylbenzene, butylbenzene, ethylbenzene and tetralin as a substrates containing secondary C–H bonds, were oxidized to a mixture of the corresponding alcohols and ketones in high yields (64–84%), but toluene and xylenes due to the high strength of the C–H bond were less reactive (23–37%). In the case of allylbenzene no double bond oxidation was observed. The oxidation of methylphenyl acetate gave the corresponding α -keto ester as the sole product (82%). The yield of products was extremely

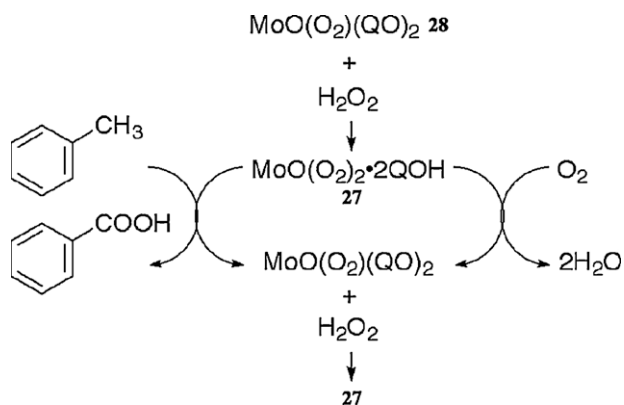
Table 4
Summary of the results of the stoichiometric oxidation of alcohols by Mo(VI) oxido-peroxido complexes.

Ent.	Mo complex	Substrate	Reaction conditions	Ketone yield	Ref.	Remarks
1	$\text{H}[\text{MoO}(\text{O}_2)_2(\text{C}_5\text{H}_4\text{NCO}_2)]$ (49)	2-octanol	$\text{CD}_3\text{OD}/50^\circ\text{C}/29\text{ h}$	75%	[90]	49 oxidizes up to 1.7 mol of substrates.
2	$[\text{MoO}(\text{O}_2)_2(\text{HMPT})(\text{H}_2\text{O})]$ (1c.H}_2\text{O})	2-octanol	$\text{CD}_3\text{OD}/50^\circ\text{C}/29\text{ h}$	17%	[90]	Low ketone yield, long reaction time.
3	$[\text{MoO}(\text{O}_2)_2(\text{HMPT})]$ (1c)	cyclohexanol	$\text{DCE}/60^\circ\text{C}/24\text{ h}$	35%	[94]	The reaction rate is strongly dependent on anionic character of complex and the availability of a free coordination site on molybdenum centre. The highest reaction rate was achieved with 53e.
4	$[(\text{Bu})_4\text{N}][\text{MoO}(\text{O}_2)_2(\text{C}_5\text{H}_4\text{NCO}_2)]$ (51)	cyclohexanol	$\text{DCE}/60^\circ\text{C}/24\text{ h}$	95%	[94]	
5	52	cyclohexanol	$\text{DCE}/60^\circ\text{C}/24\text{ h}$	99%	[94]	
6	53a	cyclohexanol	$\text{DCE}/60^\circ\text{C}/24\text{ h}$	99%	[94]	
7	53b	cyclohexanol	$\text{DCE}/60^\circ\text{C}/24\text{ h}$	99%	[94]	High ketone yield obtained within relatively short reaction time but in high temperature.
8	53c	cyclohexanol	$\text{DCE}/60^\circ\text{C}/24\text{ h}$	99%	[94]	
9	53d	cyclohexanol	$\text{DCE}/60^\circ\text{C}/24\text{ h}$	95%	[94]	
10	53e	cyclohexanol	$\text{DCE}/60^\circ\text{C}/24\text{ h}$	99%	[94]	
11	$[\text{MoO}(\text{O}_2)(\text{BPHA})_2]$ (21a)	2-octanol	$\text{DCE}/85^\circ\text{C}/5\text{ h}$	95%	[59]	

Table 5

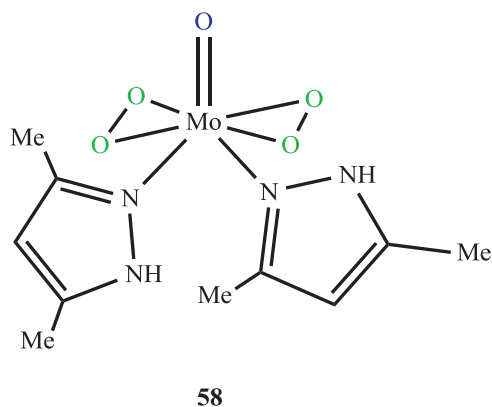
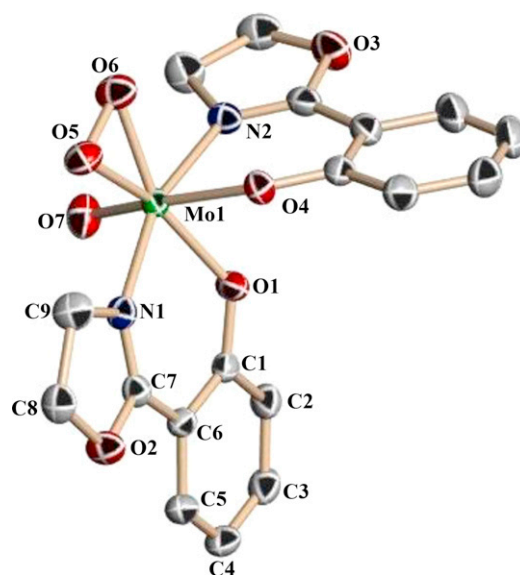
Summary of the results of the catalytic oxidation of alcohols by Mo(VI) oxido-peroxido complexes.

Ent.	Mo complex	Substrate	Reaction conditions	Ketone/aldehyde yield	Ref.	Remarks
1	[MoO(O ₂)(QO) ₂] (28)	Cyclohexanol	H ₂ O ₂ /CH ₃ CN/78 °C/16 h	30%	[96]	The selectivity for oxidation of aliphatic alcohols was low.
2	[MoO(O ₂)(QO) ₂] (28)	Cyclohexanol	O ₂ /CH ₃ CN/78 °C/16 h	8%	[96]	
3	[MoO(O ₂)(QO) ₂] (28)	Cyclohexanol	H ₂ O ₂ +O ₂ /CH ₃ CN/78 °C/16 h	34%	[96]	
4	[MoO(O ₂) ₂ (QO)][PPh ₄] (29)	Cyclohexanol	H ₂ O ₂ /CH ₃ CN/78 °C/24 h	81%	[97]	In regard to ketone yield, anionic complex 29 was a more efficient catalyst than the neutral complex 28 .
5	[MoO(O ₂) ₂ (QO)][PPh ₄] (29)	Cyclohexanol	H ₂ O ₂ +O ₂ /CH ₃ CN/78 °C/19 h	84%	[97]	
6	55	Cyclohexanol	H ₂ O ₂ /80 °C/12 h	33%	[98]	Under identical conditions, the oxidation of benzyl alcohol leads to the formation of benzoic acid in 49% yield. A 7% yield of benzoic acid was obtained as a side-product. The catalyst was not selective in the oxidation of linear aliphatic alcohols.
7	57	Benzylalcohol	H ₂ O ₂ /80 °C/8 h	79%	[99]	
8	PPh ₄ [MoO(O ₂) ₂ (HPEOH)] (33)	Cyclohexanol	H ₂ O ₂ /CH ₃ CN/78 °C/24 h	81%	[67]	

**Scheme 12.** The catalyst precursor **28** and the active catalyst **27** in the oxidation of methylbenzenes. Figure was reproduced from ref. [108], with permission of the copyright holders.

lowered when the reactions were carried out under a nitrogen atmosphere.

In 2012, Bagherzadeh et al. reported [110] the synthesis of a new mononuclear oxido-peroxido complex of molybdenum(VI) with the formula [MoO(O₂)(phox)₂] **59** and characterized it by X-ray structure analysis (Fig. 16), elemental analysis, infrared, UV–visible and ¹H, ¹³C NMR spectroscopy. The oxidation of cyclohexane,

**Fig. 15.** The oxido-bis(oxazolinone) Mo(VI) complex **58** reported by Punniyamurthy and coworkers [109].**Fig. 16.** Molecular structure of complex **59**. Figure was reproduced from ref. [110], with permission of the copyright holders.

toluene and ethylbenzene in acetonitrile solution at room temperature catalyzed by complex **59** gave within 12 h respectively cyclohexanone, benzaldehyde and acetophenone as the main product, as well as smaller amounts of cyclohexanol, benzylalcohol and 1-phenylethanol (Table 6). The efficiency of catalysts towards all the substrates was almost the same with maximum conversion, TON, and selectivity. complex **59** is one of the rare catalysts that can perform the hydrogen peroxide oxidation of alkanes in room temperature.

A summary of published results for stoichiometric and catalytic oxidation of alkanes by Mo(VI) oxido-peroxido complexes is given in Table 6. For further details about the reaction conditions, the reader is referred to the original publication.

5. Oxidation of sulfides

Many molybdenum complexes catalyze the oxidation of organic sulfides to sulfoxides. Organic sulfides have electron-rich sulfur atoms which undergo electrophilic oxidation giving sulfoxide; upon further oxidation sulfones are formed. Selective oxidation

Table 6
Summary of published results for the oxidation of alkanes by Mo(VI) oxido-peroxido complexes.

Ent.	Mo complex	Application	Substrate	Reaction conditions	Product (yield)	Ref.	Remarks
1	[MoO(O ₂)(QO) ₂] (28)	Homogeneous catalyst	Toluene	H ₂ O ₂ /CH ₃ CN/78 °C/10 h	Benzoic acid (72%)	[108]	Good TON of 1300.
2	[MoO(O ₂)(QO) ₂] (28)	Homogeneous catalyst	Toluene	H ₂ O ₂ +O ₂ /CH ₃ CN/78 °C/6 h	Benzoic acid (95%)	[108]	
3	[MoO(O ₂)(QO) ₂] (28)	Stoichiometric oxidant	Toluene	CH ₃ CN/78 °C/4 h	Benzoic acid (72%)	[108]	Non radical mechanism.
4	58	Homogeneous catalyst	Toluene	H ₂ O ₂ +O ₂ /CH ₃ CN/78 °C/12 h	Benzyl Alcohol (37%)	[109]	The yield of products was lowered when the reactions were carried out under a nitrogen atmosphere.
5	[MoO(O ₂)(phox) ₂] (59)	Homogeneous catalyst	Toluene	H ₂ O ₂ /CH ₃ CN/rt/12 h	Benzaldehyde (51%)	[110]	One of the rare catalysts that can perform the hydrogen peroxide oxidation of alkanes in room temperature.
6	[MoO(O ₂)(phox) ₂] (59)	Homogeneous catalyst	Cyclohexane	H ₂ O ₂ /CH ₃ CN/rt/12 h	Cyclohexanone (53%)	[110]	
7	[MoO(O ₂)(phox) ₂] (59)	Homogeneous catalyst	Ethylbenzene	H ₂ O ₂ /CH ₃ CN/rt/12 h	Acetophenone (48%)	[110]	

of sulfides to sulfoxides is a valuable transformation for organic synthesis since sulfoxides are highly important intermediates in the preparation of various chemically and biologically active compounds. Furthermore, sulfoxidation catalysis has assumed special relevance in the deep desulfurization of fuels, due to environmental constraints [111–113].

Beside oxidation of alkenes, Di Furia and Modena used MoO(O₂)₂L (L = HMPT **1c**, L = HBPT **18b**) (Figs. 1 and 6) as a catalyst for the selective oxidation of *p*-ClC₆H₄SCH₃ to the corresponding sulfoxide [54]. The catalytic oxidations were carried out in a two-phase system consisting of DCE and aqueous H₂O₂ at 40 °C. Using [MoO(O₂)₂(HMPT)] **1c** or [MoO(O₂)₂(HBPT)] **18b** the oxidation was complete within 10 min. The tungsten(VI) analogue, a more effective catalyst in the olefins epoxidation, appeared to be less efficient under otherwise identical conditions (75% conversion). In 1988, Di Furia and coworkers also explored the possibility of the complexes **51** and **52** (Fig. 14) for the stoichiometrically oxidation of sulfides and sulfoxides [114]. Both complexes were active in the oxidation of various sulfides in DCE solvent and gave quantitative yields of corresponding sulfoxide at 40 °C. Quantitative yields of the sulfones were obtained when compounds **51** and **52** were applied as an oxidant for the oxidation of sulfoxides.

As mentioned before [94], in the oxidation of alcohols in dichloroethane, catalyst **52** was almost 30-fold more reactive than catalyst **51**. However, in the oxidation of sulfide to sulfoxide and sulfoxide to sulfone, the second-order rate constants for catalysts **51** and **52** were identical. These results suggest that in contrast with the alcohol oxidation, association of the substrate with MoO(O₂)₂ is not essential for oxidation of sulfide and sulfoxide. In agreement with this conclusion no noticeable effect on the reaction rate was observed when HMPT, which is more nucleophilic than the organic sulfides and sulfoxides examined, was added to the reaction mixture. NMR spectroscopy has also confirmed that during oxidation, ligands dissociation does not occur. Therefore, the oxidation of sulfur base compounds proceeds via an external nucleophilic attack of substrates to the peroxido ligands of molybdenum complexes. In fact, the oxidation rates increase with increasing nucleophilicity of the substrates, i.e. dibutyl sulfide > methylphenyl sulfide > diphenyl sulfide. The anionic nature of the peroxido Mo complexes accounts for their reduced ability as electrophilic oxidants, as compared with neutral peroxido species. The neutral MoO(O₂)(HMPT) **1c** complex was 1000-fold more reactive than catalysts **51** and **52** [114].

In 1995, Carofiglio investigated the enantioselective oxidation of sulfides by hydrogen peroxide in water in the presence of catalytic amounts of Na₂MoO₄ and of functionalized βCDs **60a–d** as

chiral ligands (Fig. 17) [115]. Under these conditions an oxido-bisperoxido molybdenum(VI) complex, which is the real oxidant, is formed. In all cases good to excellent yields (62–98%) of methyl phenyl sulfoxide were obtained at 20 °C after 2 h. The enantioselectivities were in the range 17–60% (*R*-enantiomer) depending on the nature of the ligand and on the experimental conditions. The aqueous methanol solution of MoO(O₂)₂**60a** catalyst showed the highest yield (98%) and enantiomeric excess (60% of (*R*)-sulfoxide). Under the same conditions, using unfunctionalized βCD leads to the formation of racemic sulfoxide.

In 2001, Cass and coworker reported the grafting of the oxido-peroxido Mo(VI) complexes [MoO(O₂)(PyO)(H₂O)] **61** and [MoO(O₂)(Pyrazole)(H₂O)] **62** (Fig. 18) on silica gel and their use for stoichiometric oxidation of sulfides to give the corresponding sulfoxides [116]. The oxidations were carried out in methanol/acetonitrile (1:1, v/v) at –10 °C. Several sulfides (aromatic sulfides, ketosulfides, sulfinyl acid and esters, and olefinic sulfides) underwent oxidation and produced the corresponding sulfoxides (83–97% sulfoxide yield, 3–23 h). Notably, functionalized sulfides were chemoselectively oxidized, that is, only the sulfur

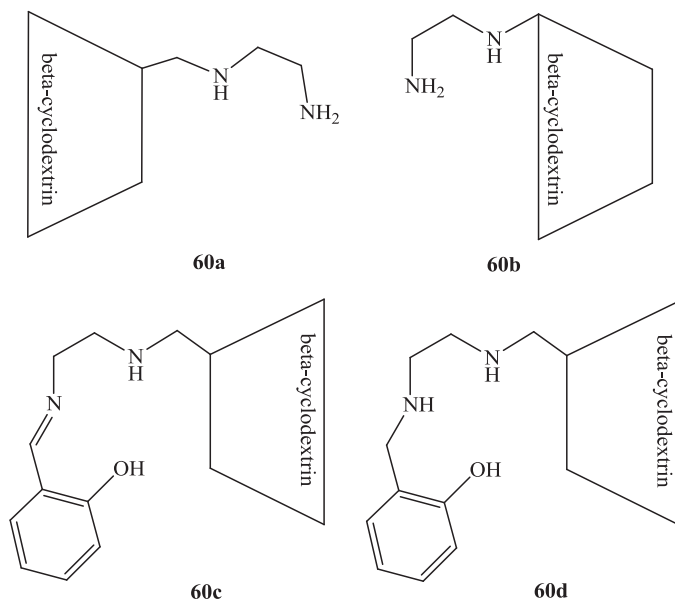


Fig. 17. The functionalized βCDs ligands used by Carofiglio [115].

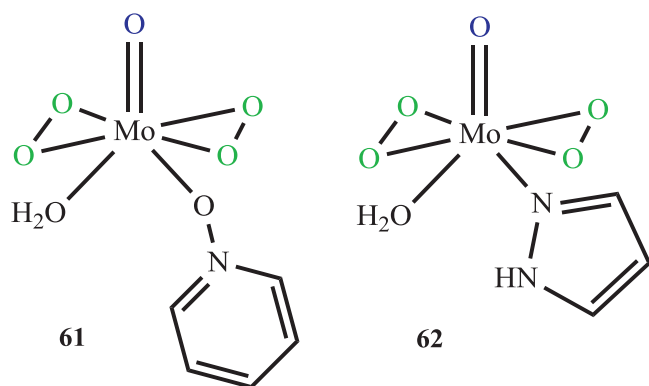


Fig. 18. The oxido-peroxido Mo(VI) complexes developed by Cass et al. [116].

atom was oxygenated, whereas olefin, ketone, and ester groups remained intact. The choice in the solvent used was significantly influence the selectivity. In methanol/acetonitrile (1:5, v/v) solvent, the main products were sulfones.

The complex **62** reacts 2-fold faster than complex **61**. However, trace amount of sulfones were detected for the reaction of complex **62** with all substrates when the reactions were carried out at 0 °C. In the presence of unsupported complexes, the main product is sulfone, but by coating the complexes on silica gel, sulfoxides were obtained in very high yields. *To investigate the reusability of supported complexes, the reconstituted complex 62 was successfully used for the oxidation of benzyl phenyl sulfide affording the corresponding sulfoxide in 95% isolated yield.*

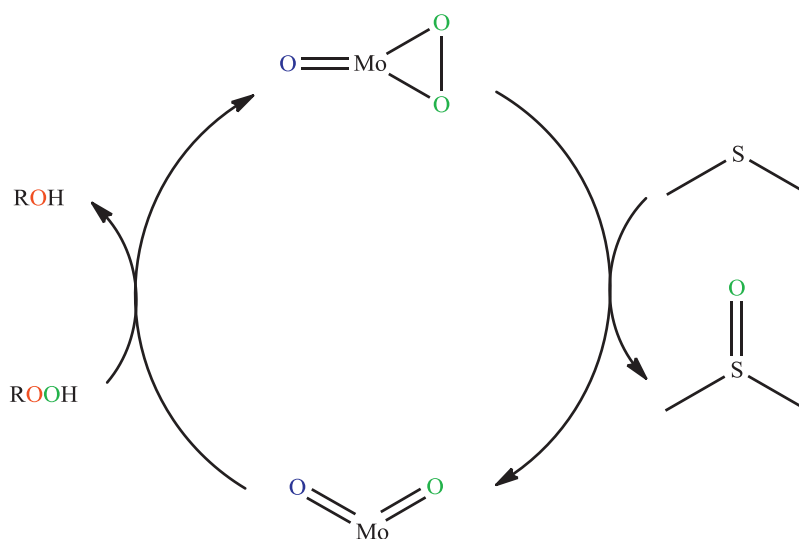
The catalytic potentiality of [MoO(O₂)(QO)₂] **28**, [PPh₄][MoO(O₂)₂(QO)] **29**, and PPh₄[MoO(O₂)₂(HPEOH)] **33** (Fig. 10) in the oxidation of sulfides with H₂O₂ as an oxidant in CH₃CN at refluxing condition was also studied by Bhattacharyya [67,96,97]. Using catalyst **33** in the oxidation of methyl ethyl sulfide, the corresponding sulfoxide was obtained as the main product with 96% yield, together with 4% yield of sulfone within 1 h. In the same reaction condition, dimethyl sulfide and ethylbenzyl sulfide rapidly convert to sulfone [67]. Similarly, the oxidation of dimethyl sulfide with H₂O₂ was catalyzed by complex **28**, yielding the dimethyl sulfone with TON up to 2845 and yields up to 85%. The use of O₂ instead of H₂O₂ resulted in the selective formation of DMSO in 21% yield (TON=665) [96]. Among these

three catalysts, **28**, **29**, and **33**, the anionic complex **29** exhibited the lowest catalytic activity [97].

In 2012 bagherzadeh et al. used the complex **41** (Fig. 12) as a catalyst for the oxidation of various types of structurally diverse substrates arylalkyl, diaryl, dibenzyl, benzylphenyl and dialkyl sulfides by UHP as an oxidant [82]. The reaction conditions fully optimized by a rotatable CCD and were as follows: The molar ratios for catalyst:substrate:UHP was 1:93:167 and reactions were performed in the (70:30) mixture of CH₃OH/CH₂Cl₂ (1.2 mL) under air at room temperature within 35.25 min. With this optimized condition, very good chemical yields of sulfoxides depending on the nature of the sulfide, in the range of 79–100% (TON = 74–93), were obtained for all cases. Lower yields were obtained for dialkylsulfide, such as dioctylsulfide with 79% conversion. In contrast with the olefin epoxidation, no addition of NaHCO₃ co-catalyst was required.

Then the catalytic activity of complex [MoO(O₂)(phox)₂] **59** (Fig. 16) was evaluated through the oxidation of several sulfides (arylalkyl sulfides, diaryl sulfides and dialkyl sulfides) with 70% aqueous TBHP in CH₃CN at room temperature [117]. Selective oxidation of sulfides occurred to afford sulfoxide with high yields (66–99%) within 30 min, without any by-products such as sulfone, which could arise from the over oxidation of sulfide. Interestingly, even using two and three equivalents of TBHP, selectivity did not decrease and methylphenyl sulfoxide was still the sole product. The oxidation of methylphenyl sulfide with UHP under identical reaction conditions, afforded the complete conversion in lower time (5 min), but with low selectivity (78%) to the sulfoxide. A mechanism of the epoxidation was suggested for the oxidation of sulfides catalyzed by complex **59** (Scheme 13). In this mechanism, the reaction starts with nucleophilic attack of the uncoordinated sulfide on one oxygen atom of the peroxido ligand, yielding sulfoxide and generating the related molybdenum(VI) dioxido complex. The **59** is then regenerated with reaction of dioxido complex and ROOH oxidant, which reenters the cycle. Very recently, Calhadro et al. have shown by using DFT studies that the oxidation of sulfides by CpMoO(O₂)Cl **39** complex takes place with the same mechanism [118].

At the end of this section, we summarize the results of stoichiometric and catalytic oxidation of sulfides by oxido-peroxido molybdenum(VI) complexes (Table 7). For further details about the reaction conditions, the reader is referred to the original publication.



Scheme 13. The mechanism for the oxidation of sulfides by oxido-peroxido Mo(VI) in the presence of TBHP oxidant [117,118].

Table 7Summary of the results of the stoichiometric and the catalytic oxidation of sulfides by oxido-peroxido complexes of the type $[\text{MoO}(\text{O}_2)_m(\text{L})_n]$ ($n, m = 1, 2$).

Ent.	Mo complex	Application	Substrate	Reaction conditions	Sulfoxide (sulfone) yield ^a	Ref.	Remarks
1	$[\text{MoO}(\text{O}_2)_2(\text{HMPT})]$ (1c)	Homogeneous catalyst	<i>p</i> -ClC ₆ H ₄ SCH ₃	H ₂ O ₂ /DCE/40 °C/10 min/[H ⁺]	50% (2%)	[54]	The reaction rates depend on the concentration of the catalyst so that a 5-fold increase of the metal complex leads to higher conversions in shorter reaction times.
2	$[\text{MoO}(\text{O}_2)_2(\text{HBPT})]$ (18b)	Homogeneous catalyst	<i>p</i> -ClC ₆ H ₄ SCH ₃	H ₂ O ₂ /DCE/40 °C/10 min/[H ⁺]	72% (5%)	[54]	
3	MoO(O ₂). 60a	Stoichiometric oxidant	PhSCH ₃	H ₂ O/CH ₃ OH/20 °C/2 h	98%	[115]	
4	MoO(O ₂). 60a	Stoichiometric oxidant	PhSCH ₃	H ₂ O/20 °C/2 h	91%	[115]	The enantioselectivities are strongly dependent on the ligand nature and on the experimental conditions. The highest enantioselectivity was achieved with ligand 60a in H ₂ O/CH ₃ OH solvent (60% of (<i>R</i>)-sulfoxide).
5	MoO(O ₂). 60a	Stoichiometric oxidant	PhSCH ₃	H ₂ O/DCE/20 °C/2 h	44%	[115]	
6	MoO(O ₂). 60b	Stoichiometric oxidant	PhSCH ₃	H ₂ O/CH ₃ OH/20 °C/12 h	90%	[115]	
7	MoO(O ₂). 60c	Stoichiometric oxidant	PhSCH ₃	H ₂ O/CH ₃ CN/rt/12 h	76%	[115]	
8	MoO(O ₂). 60d	Stoichiometric oxidant	PhSCH ₃	H ₂ O/CH ₃ CN/rt/12 h	89%	[115]	
9	61	Stoichiometric oxidant	PhSCH ₃	CH ₃ OH/CH ₃ CN/rt/23 h	97%	[116]	
10	62	Stoichiometric oxidant	PhSCH ₃	CH ₃ OH/CH ₃ CN/rt/12 h	92%	[116]	The choice in the solvent used was significantly influence the selectivity. Trace amount of sulfones were detected for all substrates.
11	[PPh ₄] [MoO(O ₂) ₂ (QO)] (29)	Homogeneous catalyst	CH ₃ SCH ₃	H ₂ O ₂ /CH ₂ Cl ₂ /40 °C/1 h	18% (82%)	[97]	Under these reaction conditions, using 28,29 and 33 as catalyst for hydrogen peroxide oxidation of all sulfides results in a relatively high amount of sulfone products.
12	[PPh ₄] [MoO(O ₂) ₂ (QO)] (29)	Homogeneous catalyst	CH ₃ SCH ₃	H ₂ O ₂ +O ₂ /CH ₂ Cl ₂ /40 °C/1 h	6% (94%)	[97]	
13	[MoO(O ₂)(QO) ₂] (28)	Homogeneous catalyst	CH ₃ SCH ₃	H ₂ O ₂ /CH ₂ Cl ₂ /40 °C/16 h	(85%)	[96]	
14	[MoO(O ₂)(QO) ₂] (28)	Homogeneous catalyst	CH ₃ SCH ₃	O ₂ /CH ₂ Cl ₂ /40 °C/16 h	21%	[96]	
15	[MoO(O ₂)(QO) ₂] (28)	Homogeneous catalyst	CH ₃ SCH ₃	H ₂ O ₂ +O ₂ /CH ₂ Cl ₂ /40 °C/1 h	(91%)	[96]	
16	33	Homogeneous catalyst	CH ₃ SCH ₃	H ₂ O ₂ /CH ₃ CN/78 °C/1 h	4% (96%)	[67]	
17	41	Homogeneous catalyst	PhSCH ₃	UHP/CH ₃ OH/CH ₂ Cl ₂ /rt/35 min	96% (4%)	[82]	The reaction conditions optimized by a rotatable CCD and good chemical yields of sulfoxides were obtained for all substrates.
18	[MoO(O ₂)(phox) ₂] (59)	Homogeneous catalyst	PhSCH ₃	UHP/CH ₃ OH/CH ₂ Cl ₂ /rt/5 min	78% (22%)	[117]	The oxidation with UHP afforded the complete conversion in lower time but with low selectivity to the sulfoxide.
19	[MoO(O ₂)(phox) ₂] (59)	Homogeneous catalyst	PhSCH ₃	TBHP/CH ₃ CN/rt/30 min	99%	[117]	

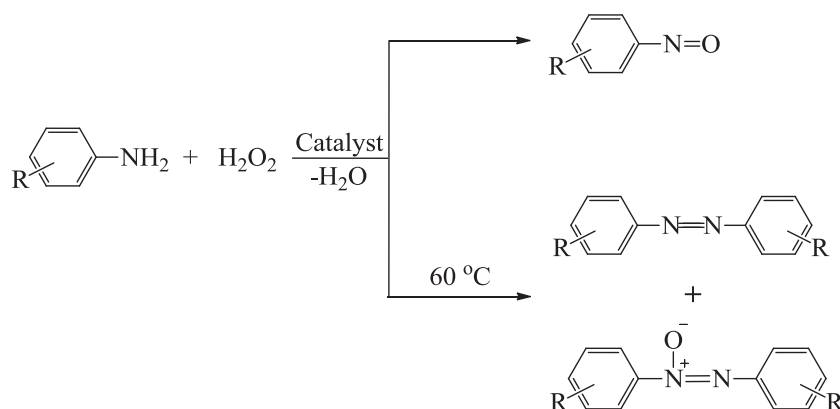
^a Values in parentheses are the corresponding sulfone yield.

6. Oxidation of amines

Nitroso compounds are useful reagents in organic synthesis and they are utilized extensively as chemical feedstocks for a wide range of useful materials such as dyes, pharmaceuticals, perfumes and

plastics. Therefore catalytic oxidation of primary aromatic amines to nitroso aromatic compounds is an important functional transformation in organic synthesis.

The first report of the amine oxidation by molybdenum peroxido complexes was by Porta et al. in 1993 [119]. The stoichiometric



Scheme 14. Oxidation of primary aromatic amines by complex **57** [121].

reactions of Mimoun type complex $[\text{Mo}(\text{O})(\text{O}_2)_2(\text{HMPT})(\text{H}_2\text{O})]$ **1c**. H_2O with primary benzylic amines, RCH_2NH_2 , yielded the corresponding nitroso compounds, $\text{RCH}=\text{NH}-\text{OH}$ in acetonitrile solvent. But the conversion was very low (10%, 30 min). Since complex/amine molar ratio was 0.2, this conversion value is not surprising. The selectivity to nitroso compound was only 13% because the oxime obtained reacted with water present in the reaction medium, to give the corresponding Schiff bases, $\text{RCH}_2\text{N}=\text{CHR}$. A few minutes after the beginning of oxidation reaction, the free HMPT ligand was detectable in the reaction mixture. This result indicating that the HMPT ligand is dissociated from Mo center allowing the subsequent coordination of the amine. This ligand displacement starts before any oxidation occurs, so it is reasonable to suggest that the oxidation mechanism starts with the initial coordination of the substrate to the metal center.

The catalytic oxidation of benzylamine to the corresponding nitroso compound by $[\text{Mo}(\text{O})(\text{O}_2)_2(\text{HMPT})(\text{H}_2\text{O})]$ **1c**. H_2O (molar ratio amine/catalyst=18) using H_2O_2 as an oxidant also was

reported [120]. The main results of reaction were: 30% conversion of the amine (after 1 h), 74% selectivity to the nitroso compound.

The in situ generated molybdenum acetylido oxido-peroxido complex **57** (Scheme 10) was used as a catalyst for the selective N-oxidation of primary amines to nitroso derivatives with H_2O_2 oxidant (Scheme 14) [121]. The activity of this catalyst depends on the solvent and reaction temperature. Very high aniline conversion (97%) and excellent selectivity for nitroso benzene (97%) were obtained in *t*-BuOH solvent at room temperature (TON=470). At higher temperatures azo and azoxy compounds were formed as the major products compared with the nitroso derivative. The selectivity for the nitroso compound was decreased to only 8% at 100 °C. High yields of the nitroso compounds (>80%) were found for substrates such as *p*-Me, *p*-OCH₃, and *p*-NO₂ aniline. In the case of all substrates tested, high selectivity (>74%) for the nitroso compounds was obtained.

The oxidation of aniline and 1,4-diaminobenzene was investigated by Bhattacharyya in the presence of complex

Table 8

Summary of the results of the stoichiometric and the catalytic oxidation of amines by oxido-peroxido Mo(VI) complexes.

Ent.	Mo complex	Application	Substrate	Reaction conditions	Conv.	Selectivity to nitroso compound	Ref.	Remarks
1	1c . H_2O	Stoichiometric oxidant	Benzylamine	$\text{CH}_3\text{CN}/\text{rt}/30\text{ min}$	10%	13%	[119]	The low selectivity is because of the oxime obtained reacted with water to give the corresponding Schiff base. The selectivity to nitroso compound is relatively good, but conversion is considerably low. The selectivity depends on the reaction temperature. An 18% yield of nitrobenzene was obtained as a side-product. Quinine and <i>p</i> -nitroaniline were obtained in 57% and 27% yields, respectively. Quinine and <i>p</i> -nitroaniline were obtained in 15% and 9% yields, respectively. Quinine and <i>p</i> -nitroaniline were obtained in 64% and 27% yields, respectively. A reduction in refluxing time increases the proportion of nitrosobenzene production.
2	1c . H_2O	Homogeneous catalyst	Benzylamine	$\text{H}_2\text{O}_2/\text{CH}_3\text{CN}/\text{rt}/1\text{ h}$	30%	74%	[120]	
3	57	Homogeneous catalyst	Aniline	$\text{H}_2\text{O}_2/t\text{-BuOH}/\text{rt}/12\text{ h}$	97%	97%	[121]	
4	33	Homogeneous catalyst	Aniline	$\text{H}_2\text{O}_2/\text{CH}_3\text{OH}/78^\circ\text{C}/7\text{ h}$	96%	81%	[67]	
5	28	Homogeneous catalyst	1,4-diaminobenzene	$\text{H}_2\text{O}_2/\text{CH}_3\text{OH}/78^\circ\text{C}/10\text{ h}$	84%	–	[96]	
6	28	Homogeneous catalyst	1,4-diaminobenzene	$\text{O}_2/\text{CH}_3\text{OH}/78^\circ\text{C}/10\text{ h}$	24%	–	[96]	
7	28	Homogeneous catalyst	1,4-diaminobenzene	$\text{H}_2\text{O}_2+\text{O}_2/\text{CH}_3\text{OH}/78^\circ\text{C}/10\text{ h}$	91%	–	[96]	
8	29	Homogeneous catalyst	Aniline	$\text{H}_2\text{O}_2/\text{CH}_3\text{OH}/78^\circ\text{C}/7\text{ h}$	96%	85%	[97]	
9	29	Homogeneous catalyst	Aniline	$\text{H}_2\text{O}_2+\text{O}_2/\text{CH}_3\text{OH}/78^\circ\text{C}/5\text{ h}$	99%	70%	[97]	

$\text{PPh}_4[\text{MoO}(\text{O}_2)_2(\text{HPEOH})]$ **33** (Fig. 10) as a catalyst with H_2O_2 in CH_3CN at refluxing condition [67]. With this catalytic system, aniline was oxidized to nitrosobenzene as the main product (78%) and small amount of nitrobenzene (18%). 1,4-diaminobenzene was converted to the mixture of quinine (54%) and *p*-nitroaniline (30%). Under identical conditions, the catalyst $[\text{MoO}(\text{O}_2)(\text{QO})_2]$ **28**, led to the same yields and selectivities [96]. The use of O_2 instead of H_2O_2 resulted in the same products but with significantly lower yields (15% quinine and 9% *p*-nitroaniline). In the case of both catalysts, the reduction of reflux time increases the proportion of *p*-nitroaniline and nitrobenzene produced. The anionic complex $\text{PPh}_4[\text{MoO}(\text{O}_2)_2(\text{QO})]$ **29** also can catalyze the oxidation of aniline with similar conversion and selectivity under the same conditions as in the case of catalyst **33** [97].

Table 8 is a summary of the results in both the stoichiometric and the catalytic oxidation of amines by oxido-peroxido Mo(VI) complexes. For further details about the reaction conditions, the reader is referred to the original publication.

7. Conclusions and outlook

Molybdenum(VI) oxido-peroxido complexes are probably one of the best catalysts for the oxidation reactions [13]. These complexes are one of the rare catalysts which can promote complete epoxidation of linear alkenes at room temperature in less than 3 h [82]. Another interesting feature of these complexes is their ability to act as both a catalyst and a stoichiometric oxidant. Due to high activity and selectivity of the oxido-peroxido molybdenum(VI) complexes used in different challenging catalytic processes, around the world, several important research groups maintain as priority research lines the design of new oxido-peroxido complexes and their potential applications.

The type of ligands and structure of complexes have marked effect on the catalytic (or oxidation) activity of complexes involving peroxido Mo(VI): (1) the monoperoxido complexes always show lower activity for a stoichiometric oxygen transfer to substrate than the bisperoxido complex with the same ligands [17,35]; (2) the presence of alkyl side chain on ligand increases the solubility of the complex in organic substrate and usually causes in marked increase in the catalytic activity [39,40,50,53,54,81]; (3) in the case of the epoxidation of alkenes with ROOH oxidant, electron withdrawing groups raise the Lewis acidity of the catalyst and accelerating the reaction [42]; (4) molybdenum oxido-peroxido complexes with hemilabile ligands exhibit high catalytic activity in the oxidation reactions [41,42,44,55] and (5) the anionic complexes are a more efficient catalyst for the alcohol oxidation than the neutral counterpart [94,97], but the same argument is true in reverse for the sulfide and sulfoxide oxidations [97,114]. On the other hand, the reactions were extremely sensitive to the reaction conditions. Therefore effective catalytic systems for oxidation reaction require not only optimizing the structural and chemical properties of the catalyst, but also the proper choice of oxidizing agent and solvent. Future directions of research should focus on design of new Mo oxido-peroxido complexes with desirable structural properties and optimizing reaction conditions to obtain a catalytic system with an attractive activity.

The mechanism of action of these complexes has been investigated in some detail. Today we know that the stoichiometric epoxidation occurs by a direct attack at the double bond of the olefin at one of the oxygen centers of the peroxido group [23–26]. In the case of the catalytic epoxidation, the reaction starts with coordination of oxidizing agent to the Mo(VI) center to form MoOOR ($\text{R} = \text{H}$, CH_3 , and *tert*-Bu). Then the olefin approaches towards the OOR fragment, yielding the epoxide

and concomitant elimination of ROH [41,42,44,55]. It is well accepted that the oxidation of alcohol proceeds through the coordination of substrate to the molybdenum [96,97,100] but, association of the substrate to the metal center is not essential for the oxidation of sulfide [114,117,118]. A radical mechanism has been proposed for the oxidation of alkanes [108]. Nevertheless, there are still questions to be answered. For example, why $\text{CpMoO}(\text{O}_2)\text{CH}_3$ is an effective catalyst precursor in the olefin epoxidation with TBHP [72] but $\text{CpMoO}(\text{O}_2)\text{Cl}$ complex is totally inactive under the same condition [73,74]. These questions will certainly remain at the focus for theoretical studies in the near future.

Recently, the immobilization of active oxido-peroxido molybdenum(VI) catalysts on a support was reported [83–89,116]. Some exhibited high catalytic activity and selectivity. Since the recycling of catalyst will reduce the cost of products, a recyclable oxido-peroxido Mo(VI) catalyst is an attractive candidate in the development of a cost-effective catalysis process. In this context, further research on immobilizing of oxido-peroxido Mo(VI) complex on various supports will be needed, and their suitability in the oxidation catalysis should be considered for industrial applications. The development of more benign, environmentally friendly oxidation reactions with less hazardous solvents, such as ionic liquids and aqueous solutions, is currently the major focus of a wide variety of research activities. The oxido-peroxido Mo complexes show a good activity for the oxidation of organic substrates both in ionic liquid media [68,69] and in an aqueous/organic biphasic system [53,54,60,98]. The synthesis of highly active molybdenum peroxido complexes using less toxic and readily available precursors and carrying out the oxidation reaction in environmentally friendly solvents will also make this topic of chemical research more interesting and challenging.

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