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Olefin epoxidation with transition-metal catalysts in ionic liquids

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Index

Abbreviations

δ	chemical shift
DCM	dichloromethane
DMF	dimethylformamide
Et_2O	diethylether
EtOH	ethanol
eq.	equivalent(s)
l	liquid
h	hour
HV	high-vacuum
L	ligand
solv.	solvent
M	molar
mbar	millibar
MHz	megahertz
min	minute(s)
mL	milliliter
m.p.	melting point
Mt	mega-tons
MTO	methyltrioxorhenium (VII)
NMR	nuclear magnetic resonance
ppm	*parts per million*
R	organic rest
r.t.	room-temperature
RTIL	*room-temperature ionic liquid*
TBHP	*tert*-butylhydroperoxide
Tf	triflate
THF	tetrahydrofuran

Glossary of ionic liquids

[emim]	1-ethyl-3-methylimidazolium
[bmim]	1-butyl-3-methylimidazolium
[omim]	1-octyl-3-methylimidazolium
[dmim]	1-n-decyl-3-methylimidazolium
[C_{12}mim]	1-n-dodecyl-3-methylimidazolium
[pmim]	1-methyl-3-(triethoxysilylpropyl)imidazolium
[hmim]	1-n-hexyl-3-methylimidazolium
[bdmim]	1-butyl-2,3-dimethylimidazolium
[Hydemim]	1-(2-hydroxy-ethyl)-3-methylimidazolium
[bPy]	*N*-butyl-pyridinium
[bmPy]	*N*-butyl-3-methylpyridinium
[oPy]	1-octyl-pyridinium
[hnmp]	*N*-methyl-pyrrolidonium
[mdhqm]	2-methyl-3,4-dihydroisoquinolinium
[tbap]	tributylpropylammonium
[tmba]	trimethylbutylammonium

A. Introduction

1. Ionic liquids

In the last decade ionic liquids (ILs) have aroused increasing interest both in industry and in academical research. The growing attention is reflected by a steadily increasing number of scientific publications and patents in this area (Figure 1). Generally, ionic liquids are compounds which are exclusively made up of ions with a melting point below 100 °C. In particular cases the term “room-temperature ionic liquid“ (RTIL) is used in the literature. These compounds are characterized by a melting point below 25 °C. ILs constitute a large, fundamental class of fluid materials that are relevant to different areas, e.g. separation technologies, manufacturing processes, solvents for synthetic procedures and catalysis.

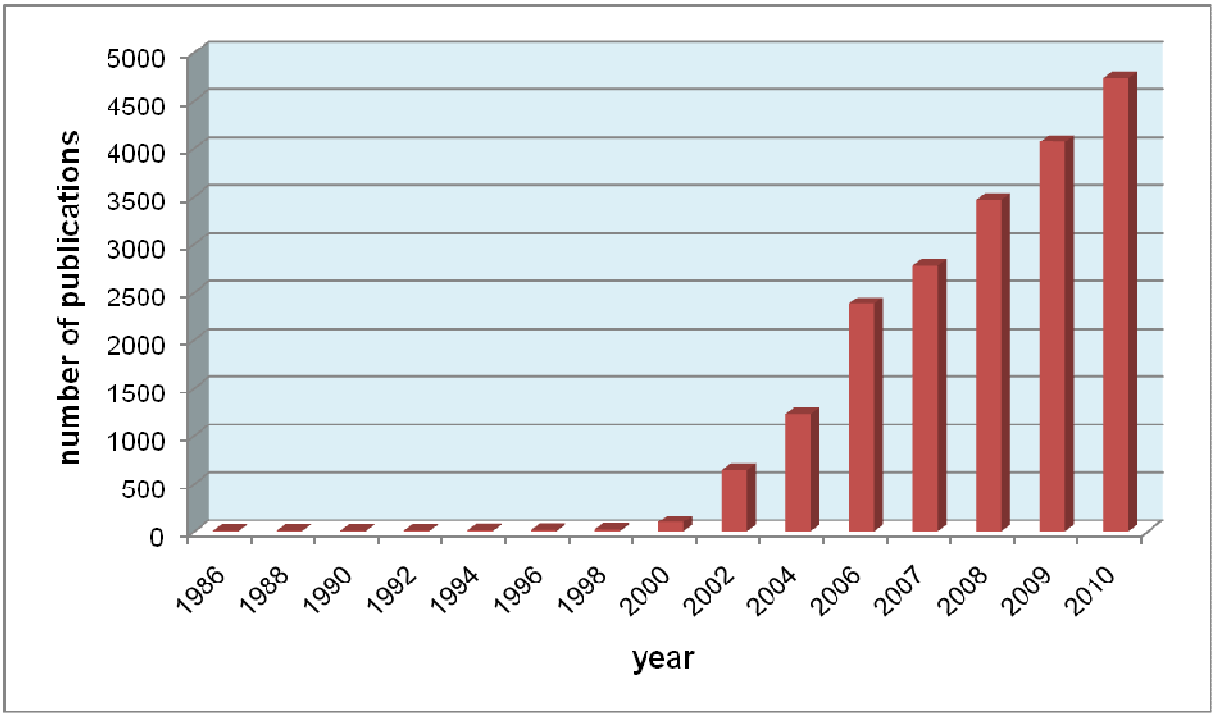


Figure 1. Number of publications and patents dealing with ionic liquids. (source: SciFinder Scholar)

Since 2000, more than 24.000 papers and about 3.500 patents dealing with ionic liquids have been published, from which about one third contains catalytic applications. Their physical properties, such as the low melting point, negligible vapor pressure, good solubility characteristics, a wide liquid range, non-flammability, a wide electrochemical window, tolerance to strong acids and excellent thermal and chemical stability render them a good alternative to volatile organic solvents.[1-10] The first compound which matches the todays` definition of an RTIL was ethylammoniumnitrate $[EtNH_3][NO_3]$ (m.p. 12 °C), which was synthesized by P. Walden in 1914.[11]

The research on ionic liquids was intensified in 1963 by the U.S. Air Force Academy with the aim of finding adequate electrolytes for thermal batteries. As a first result chloroaluminates were developed from a mixture of alkali halides and aluminium chloride.[12] With the synthesis of 1-butylpyridinium tetrachloroaluminate the era of ionic liquids has been started. For the first time, a wide range of chemists began to take interest in these new solvents.[13] Afterwards, dialkylimidazolium salts gained more and more attention; in 1992, Zaworotko *et al.* substituted the water-sensitive tetrachloroaluminate by stable tetrafluoroborate and hexafluorophosphate anions, respectively.[14] Figure 2 shows typical cations and anions which can be combined to form ionic liquids.

Today, a huge number of ILs has been synthesized for different applications both in academia and in industry. In contrast to other “green” solvents, e.g. supercritical CO_2 or perfluorinated compounds, ILs have the advantage of dissolving many organometallic complexes and show a generally immiscibility with common organic solvents.

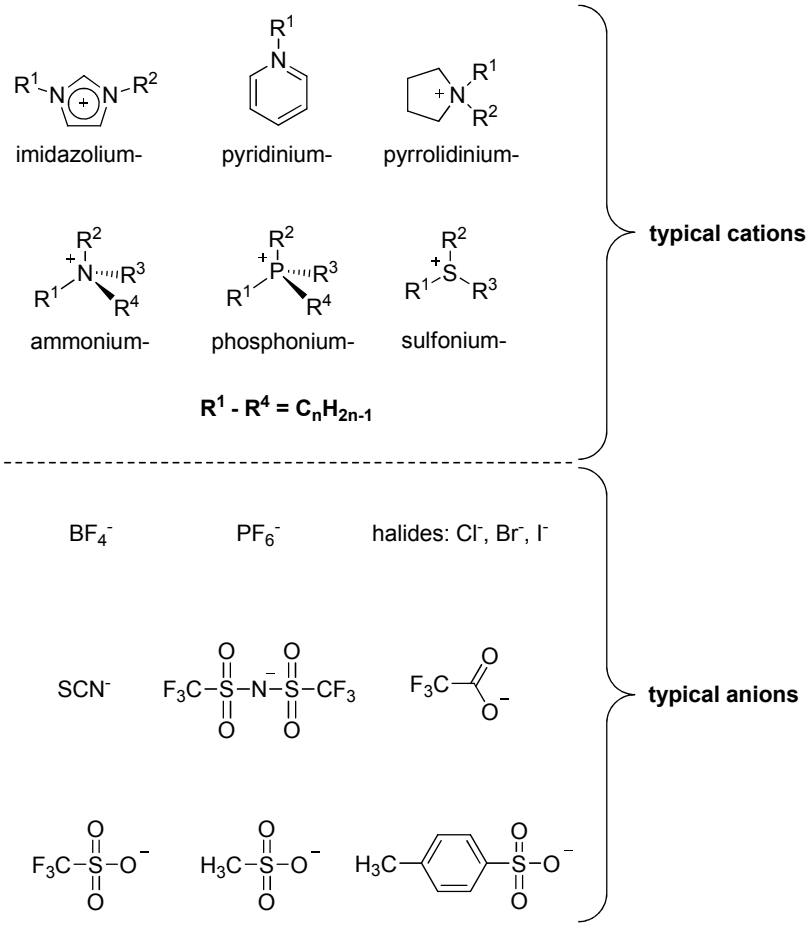
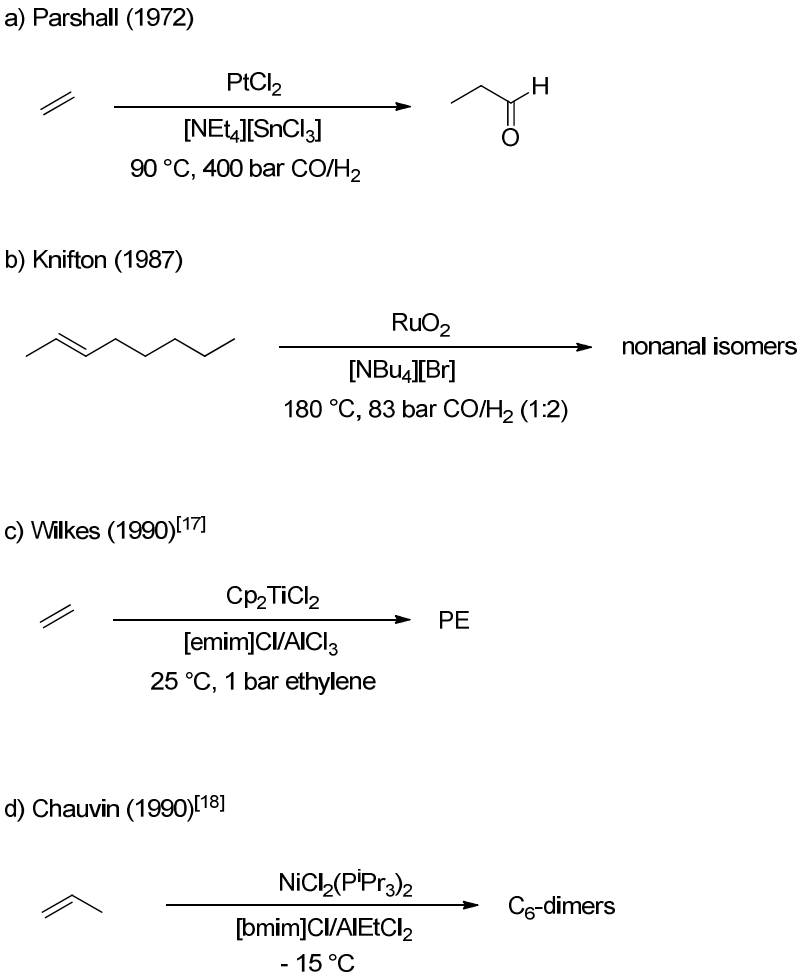


Figure 2. Typical cations and anions in ionic liquids.

The presence of a homogeneous solution is an essential, yet nontrivial requirement in homogeneous catalysis. In addition, there is a possibility to vary the composition of cation and anion, leading to different physico-chemical properties. The first example of using an ionic liquid in homogeneous transition-metal catalysis was published in 1972 by G. Parshall *et al.*, who described the Pt-catalyzed hydroformylation of ethane using $[Et_4N][SnCl_3]$ as a solvent (Scheme 1, a).[15] Afterwards, Knifton used $[Bu_4P]Br$ for the ruthenium- and cobalt-catalyzed hydroformylation of different olefins (Scheme 1, b).[16] Scheme 1 gives an overview of the first examples of homogeneous catalysis using ionic liquids as solvents.



Scheme 1. First examples of homogeneous catalysis in ILs.

1.1 Immobilization in ionic liquids

Nowadays almost all types of homogeneous catalytic reactions have been performed in ionic liquids. The negligible vapor pressure has a positive influence on the product work-up. In contrast to the use of low boiling solvents, volatile products can easily be distilled out of the reaction mixture while the catalyst is dissolved in the IL and can be recycled. Another significant advantage of using ionic liquids is the opportunity for biphasic catalysis. It is obvious that homogeneous catalysis offers

important advantages. In contrast to a heterogeneous system all metal centers are active during the reaction in the homogeneous case. Additionally, the reaction conditions (temperature, pressure) are usually much more benign and the organometallic complex is well defined with the possibility to be optimized by ligand modification. Finally, the selectivities are usually much higher than in heterogeneous systems. Despite the advantages of homogeneous catalysis, most of the industrial processes are performed by using heterogeneous catalysts. Mainly responsible for this are the difficulties of separating the dissolved catalysts when using conventional organic solvents. Thus, the idea of forming a biphasic liquid system using ionic liquids is an important approach to combine the advantages of both homogeneous and heterogeneous catalysis. In the ideal case, the organometallic complex is immobilized in the IL phase, while substrate and product are dissolved in the organic phase. When the reaction is over, the product can easily be separated by decantation or *via* a cannula. In the best case, the catalyst can be recycled and reused without further treatment. The principle of biphasic catalysis in ILs is shown in Figure 3.

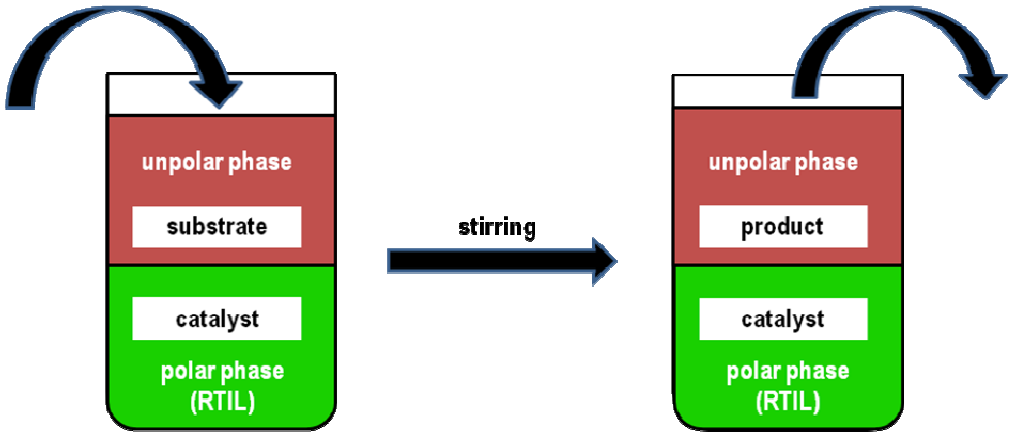
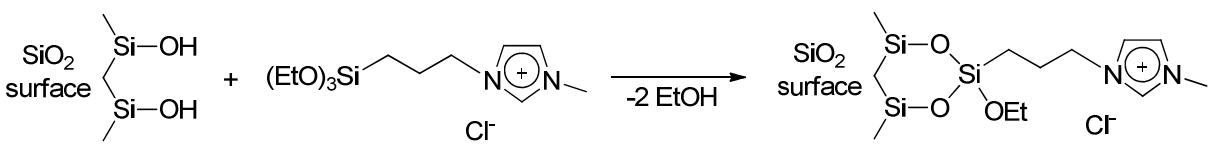


Figure 3. Principle of biphasic catalysis in ILs.

Due to the exactly tunable physicochemical properties of ionic liquids, it can even be realized to optimize the catalytic activity by an in situ extraction of catalyst poisons or reaction intermediates from the catalytic layer. However, to reach this goal more stringent, requirements have to be fulfilled by the solvent since it has to provide a specific, very low solubility for the substances which have to be extracted from the ionic liquid phase under reaction conditions. Recently, it was demonstrated that the solubility and miscibility properties of ionic liquids can be varied so widely that even mutually immiscible ionic liquids can be realized.[19] Applications of these ionic liquid–ionic liquid biphasic systems in catalysis have, however, not yet been described. Another interesting concept for immobilizing homogeneous catalysts is called SILP (supported ionic liquid phase) and was recently introduced by Mehnert and Wasserscheid.[20] In a SILP system, an ionic liquid film is immobilized on a high-surface area porous solid, e.g. silica, and the organometallic complex is dissolved in this thin IL layer. The resulting catalyst is solid with the active species being solubilized in the ionic liquid and acting as a homogeneous catalyst. In contrast to the former described liquid-liquid biphasic system a smaller amount of the IL is needed in the SILP technology. Thus, mass-transfer limitations do not play an important role, which is an important aspect especially for gas-phase reactions. Scheme 2 shows a representative route for the synthesis of a supported ionic liquid phase.



Scheme 2. Synthesis of a supported ionic liquid phase.

1.2 Important industrial applications

1.2.1 DIFASOL / DIMERSOL process

The DIFASOL process was developed by the Institute Français du Pétrole and is widely used in the dimerization of olefins (mainly propene and butene) to branched hexenes and octenes (Scheme 3). The process is based on chloroaluminate ILs and is a further development of the well-known DIMERSOL process.[21]

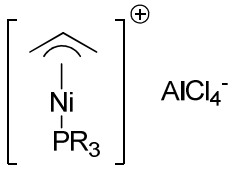
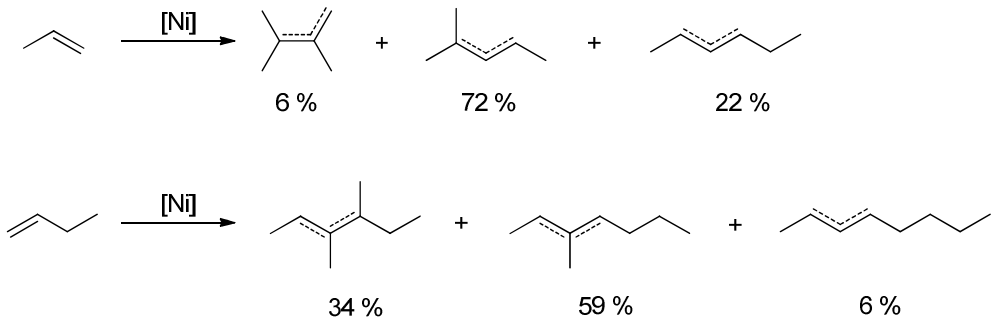


Figure 4. Structure of the cationic Ni(II) catalyst.

The used cationic Ni(II) complexes (Figure 4) are dissolved in an ionic liquid to use the following benefits:

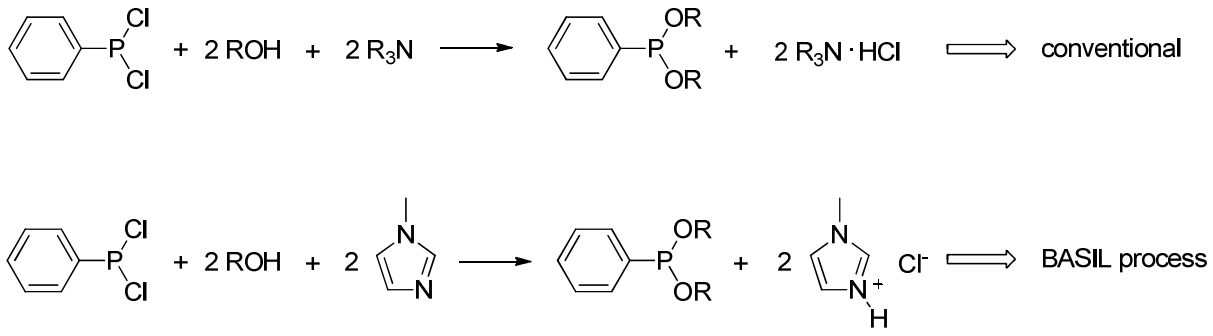
- a higher catalyst activity
- a higher catalyst stability
- a higher selectivity
- a catalyst recyclability



Scheme 3. DIFASOL process.

1.2.2 BASIL process

Probably the best-known application of ionic liquids in industry is called BASIL process (Biphasic Acid Scavenging Utilizing Ionic Liquids) and was established by BASF in 2002 (Scheme 4).[22]



Scheme 4. BASIL - vs. conventional process.

In the conventional production of alkoxyphenylphosphines, the formed HCl is scavenged with tertiary amines resulting in the corresponding ammonium salts, a thick and non-stirrable slurry. Thus, the idea to produce a liquid salt by using 1-methylimidazole as an acid scavenger was obvious. After the reaction with HCl the IL 1-methylimidazolium chloride is formed. Two liquid phases are formed during the reaction and the product can easily be separated. The ionic liquid can be transformed into the non-ionic species by simple deprotonation.

In this process, the ionic liquid is used as an auxiliary. The benefits are:

- higher chemical yield
- lower investment cost
- higher sustainability of the process
- no produced solids

1.3 Toxicity of ionic liquids

In contrast to conventional organic solvents ILs both have a negligible vapor pressure and do not emit any volatile organic compounds. These facts provide the basis for a clean manufacturing, a highly desirable goal for the chemical industry. However, even if ionic liquids do not evaporate and contribute to air pollution many of them are water soluble and can enter the environment *via* this path. Recently, toxicity studies received considerable attention and the commonly accepted opinion that ILs have low toxicity was shown to be incorrect in some cases. Jastorff et al. were the first who studied the toxic nature of different ILs in 2000.[23] In their study, which is purely based on theoretical estimations, they assumed that the longer the alkyl chains of the imidazolium cation, the higher is the bioaccumulation because of its molecular similarity to the membrane lipids. In 2007, the same group undertook more detailed studies on the (eco)toxicological behavior of 1-alky-3-methylimidazolium ILs.[24] They could prove their estimations with regard to the side chain length of the cation in all used test systems from molecular up to organismic level. Concerning the anion effect there is a divers pattern towards the different test systems. With respect to the design of safer ILs, it is suggested to use cations with a short alkyl side chain combined with BF_4^- or Cl^- as a counter ion.

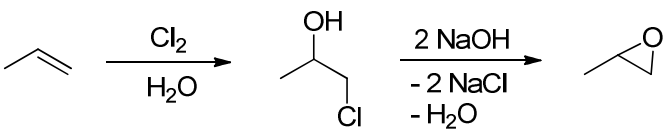
2. Epoxidation of olefins

With regard to the synthesis of fine chemicals, fragrances and pharmaceuticals, the catalytic epoxidation of olefins to their corresponding epoxides plays a very important role. The epoxides are important organic intermediates which undergo ring-opening reactions with a variety of reagents to yield mono- or

bifunctional organic products,[25] what makes them to a key raw material of a wide variety of chemicals such as glycols, glycol ethers and alkanolamines. Additionally, they can be used as building blocks for polymers (e.g. polyesters and polyurethanes). In general, epoxides can be prepared by the reaction of olefins with hydrogen peroxide, different alkyl hydroperoxides or peracids, catalyzed by transition metal complexes.[26]

2.1 Industrial processes

As far as the industrial epoxidation of olefins is concerned, two relevant products are of special interest: ethylene oxide and propylene oxide (production in 2007: 5.3 Mt and 1.8 Mt, respectively).[27] Together, they account for the immense majority of the epoxide industrial production. In industry, ethylene oxide is produced by a silver catalyzed vapor-phase oxidation of ethylene, using air or oxygen. The process, which was introduced by Union Carbide in 1937 and Shell in 1958, is promoted by alkali metals and supported on a non-porous form of α-alumina.[28] Practically, ethylene and oxygen are passed over a solid catalyst containing silver nanoparticles dispersed on α-Al_2O_3. The only drawback of this process is that it can only be applied to olefins which do not contain allylic C-H-bonds. For these compounds low yields and numerous by-products are obtained, because of competing oxidation of the allylic double bond.[29] Therefore, the chlorhydrine route (Scheme 5) is still used for the oxidation of higher olefins.



Scheme 5. The chlorhydrine process.

The chlorhydrine process is performed at a pressure of 2 - 3 bar and 30 ℃ using a water solution of chlorine as an oxidizing agent. The resulting chlorhydrine is *in situ* dehydrochlorinated to propylene oxide using basic solution of NaOH or $Ca(OH)_2$. Afterwards, the propylene oxide is distilled out of the reaction mixture to avoid direct hydration. Because of the huge amount of by-products (especially NaCl or $CaCl_2$), a direct oxidation route was independently developed by Halcon and Atlantic Richfield (ARCO) in 1967 using organic hydroperoxides as an oxidant and different high valent transition-metal catalysts.[30] Molybdenum proved to be the most efficient catalyst metal gave the highest rate and selectivity when used with TBHP. In 1983, Enichem introduced a titanium-substituted silicalite (TS-1) catalyst which has a hydrophobic surface and has proved to be effective to a variety of liquid-phase oxidation with the "greener" hydrogen peroxide.[31] Based on this process BASF, Dow and Solvay developed the HPPO (hydrogen peroxide to propylene oxide) process for the production of propylene oxide (Figure 5).[32]

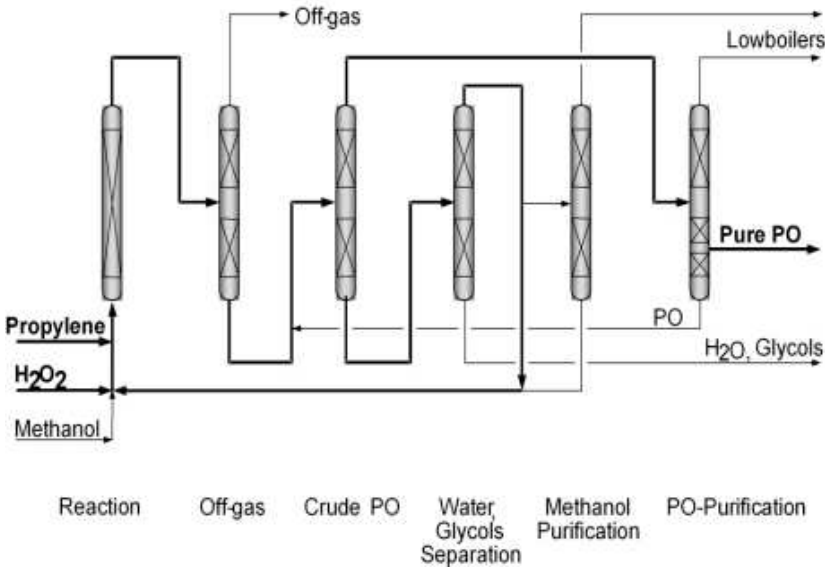


Figure 5. The BASF, Dow and Solvay plant.

In the HPPO process, propene is oxidized in a slurry containing the catalyst, hydrogen peroxide and methanol as a preferred solvent. After this reaction, propylene oxide is separated by distillation and purified. Finally, the lack of lewis-acidic sites minimizes the possibility of an epoxide ring opening reaction due to the electronic balance between titanium and silicon atoms.

2.2 Asymmetric epoxidation

The first catalyzed asymmetric epoxidation of olefins was achieved by Sharpless and Katsuki in 1979. The enantiomers of an epoxide could be produced efficiently from an allylic alcohol very efficiently with an enantiomeric excess of > 90 %. The catalytic system consists of $Ti(O^iPr)_4$, diethyl tartrate (DET) and TBHP as an oxidizing agent.[33] This achievement is known as “Sharpless epoxidation” and was honoured with the Nobel Prize in Chemistry in 2001. However, the Sharpless epoxidation is only applied in laboratory scale and has no industrial applications. Another very important catalytic system was independently introduced by Jacobsen and Katsuki in 1990.[34] By using a cationic Mn(III) salen complex (Figure 6), the reaction proved to be extraordinarily effective in the asymmetric epoxidation of cis-olefins with enantioselectivities of > 95 % ee.

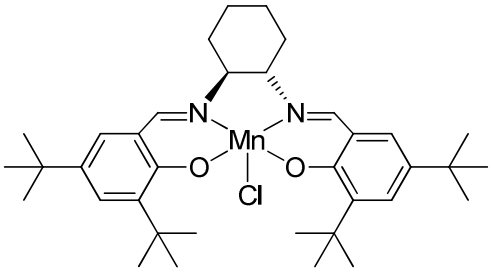
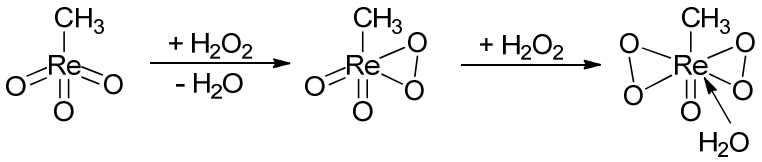


Figure 6. Jacobsen`s epoxidation catalyst.

2.3 Methyltrioxorhenium(VII) in olefin epoxidation

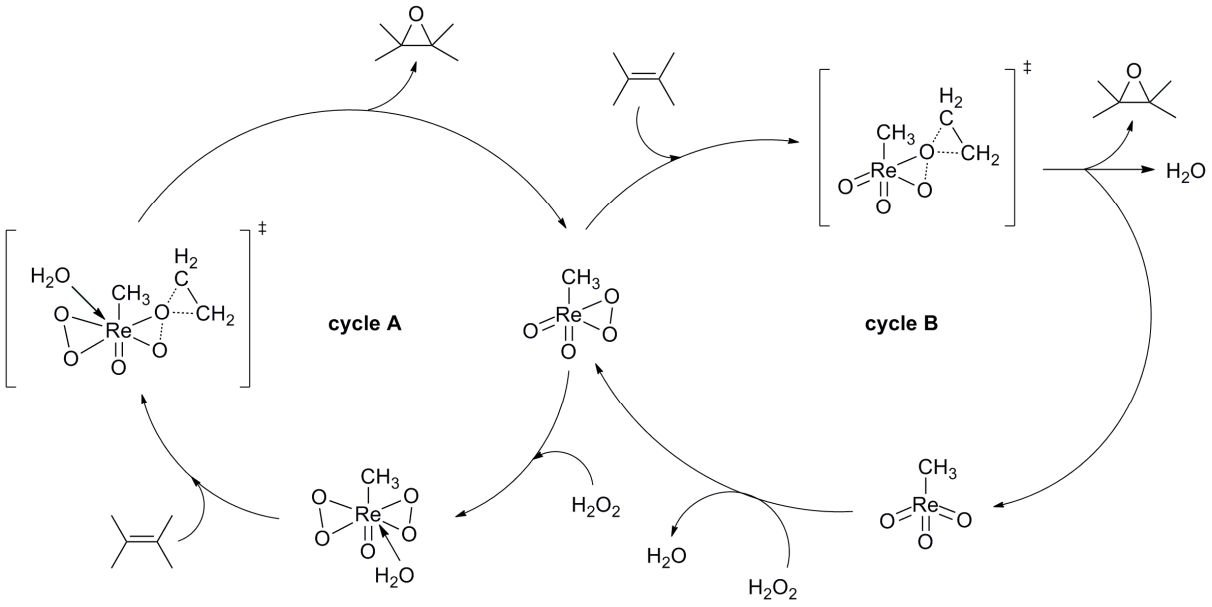
Methyltrioxorhenium (MTO) is an extremely efficient catalyst precursor for a variety of organic reactions, as has previously been demonstrated.[35] Olefin epoxidation is undoubtedly the most thoroughly examined reaction amongst the many applications of this powerful catalyst.[36] The reaction mechanism was studied in great detail - both from kinetic and theoretical points of view - by means of UV/Vis spectrophotometry and NMR spectroscopy, in the homogeneous and heterogeneous phase and in aqueous as well as organic media (Scheme 1).[37]

Scheme 6 shows the formation of the mono- and bisperoxo species of MTO after the addition of one and two equiv. of hydrogen peroxide.



Scheme 6. Formation of the mono- and bisperoxide of MTO.

The active bisperoxo species was isolated and structurally characterized by Herrmann et al.[36b] It was shown that the monoperoxo complex, which has never been isolated exists in an equilibrium with MTO and is catalytically active as well. The following Scheme 7 shows the mostly agreed mechanism for the epoxidation of olefins using the MTO / H_2O_2 system.



Scheme 7. Mechanism of the epoxidation of olefins.

For both cycles (cycle A and cycle B) a concerted mechanism is suggested where the double bond of the olefin attacks a peroxidic oxygen of the so-called “butterfly complex” $[(CH_3)Re(O_2)_2O \cdot H_2O]$.[38]

Because of the strong Lewis acidity of the d^0-Re center in MTO, there is a tendency towards ring-opening reactions of sensitive epoxidation products, leading to the formation of diols.[39] It was found that the presence of Lewis bases, for example nitrogen donor ligands, suppresses such unwanted side reactions.[40] Nevertheless, the activity of MTO-Lewis base adducts was originally found to be significantly lower than that of MTO itself.[41] However, when using a larger excess of the ligands this behavior is different.[42] Both mono- and bidentate aromatic Lewis bases with N-donor ligands show these results.[43] Many N-base adducts of MTO have been isolated and characterized and in several cases *in situ* employed for olefin epoxidation catalysis.[44] Re(V)-oxo complexes bearing Schiff base ligands have also been investigated extensively[45], and Schiff-base adducts of MTO were also synthesized and applied as epoxidation catalysts in organic solvents.[46] In the latter case, a ligand excess proved

to be unnecessary to achieve selective olefin epoxidations. Owens and Abu-Omar examined the epoxidation of different olefins using MTO as a catalyst and urea hydrogen peroxide (UHP) with the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate, [emim]BF_4, as a solvent. This oxidation system is nearly water-free, so the conversion of the substrates yields primarily the epoxides and not diols.[47] Recently, Saladino et al. published a review of reactions catalyzed by MTO in different non-conventional solvents.[48]

2.4 Molybdenum complexes in olefin epoxidation

To date, many molybdenum-based systems have been extensively studied in the catalytic epoxidation of olefins, but were found to give only moderate ee values.[49] These can be improved by performing the catalytic experiments at lower temperatures, however, leading in all cases to a significant loss of activity.[50] In the last years, [$CpMo(CO)_3R$] compounds (M = Mo, W, R=halide, alkyl) (Figure 7, a) have been thoroughly examined in epoxidation catalysis. Amongst these, *ansa*-type complexes (Figure 7, b-d), which had first been described by Eilbracht et al. in the late 1970s, aroused attention due to their potential applications in the field of asymmetric catalysis.[51-54]

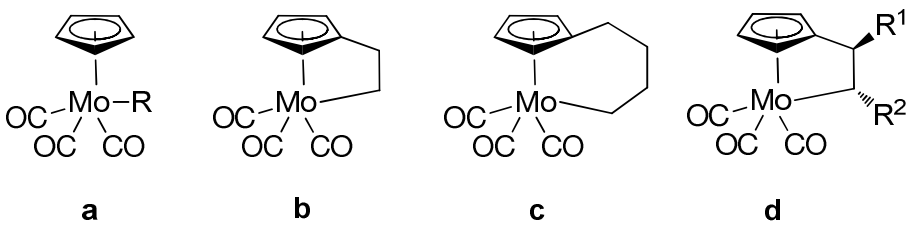


Figure 7. Structures of several $CpMo(CO)_3R$ complexes.

It is also well known that dioxomolybdenum(VI) complexes of the type $[MoO_2X_2(L)_n]$, where X is Cl, Br, CH_3 and L is a mono- or bidentate neutral N-ligand are versatile catalyst precursors for the epoxidation of olefins in the presence of TBHP as an oxidant.[55-57] Important properties, such as the solubility of the complex and the Lewis acidity of the metal center can be fine-tuned by variation of both ligands X and L of the $[MoO_2X_2L_2]$ complexes. Special interest of these type of complexes arose especially in the late 1960s when the companies Halcon and Arco used them in homogeneous phase.[30] In the following years the reaction mechanism was investigated to explain their high activity. The intensive debate over the mechanism originated mainly from the results presented by Mimoun and Sharpless.[58]

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B. Results and Discussion

1. Recent advances in oxidation catalysis using ionic liquids as solvents

This chapter originated from the following publication:

Daniel Betz, Philipp Altmann, Mirza Cokoja, Wolfgang A. Herrmann, Fritz E. Kühn, *Coord. Chem. Rev.* **2011,** *255*, 1518-1540.

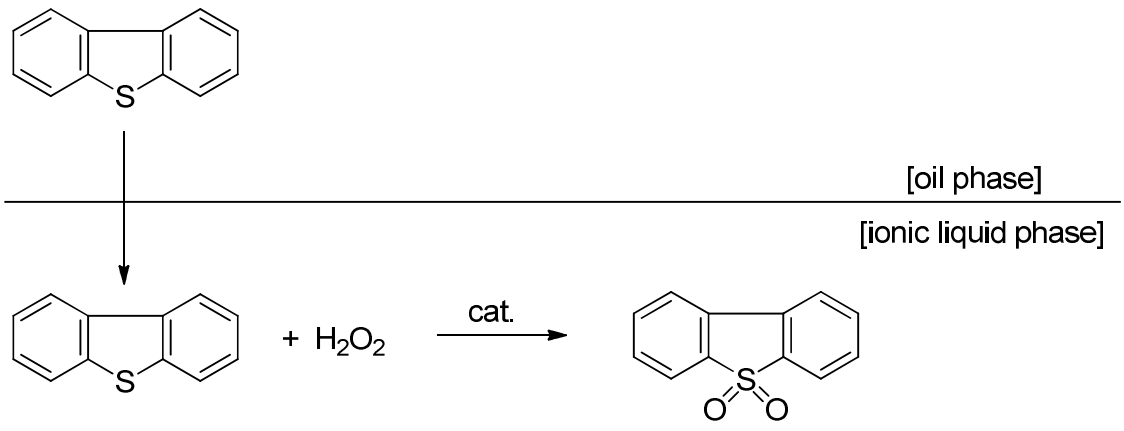
1.1 Introduction

Ionic liquids (ILs) have been used in a variety of catalytic reactions during the last decade.[1-3] They attracted considerable attention due to their physical properties, such as thermal stability, low volatility, low flash point, and high polarity. Additionally, properties such as temperature-depending miscibility with water makes them attractive alternatives to organic solvents.[4-6] Organometallic complexes, which are immiscible with hydrocarbons, are often soluble in ILs. Therefore they provide a non-aqueous alternative for two-phase catalysis, in which the catalyst is immobilized in the ionic liquid phase and can easily be separated from the product. ILs have been used for several types of reactions, such as hydrogenation, hydrosilylation and oligomerisation of olefins. Regarding oxidation reactions, Song and Roh reported the first manganese(III) (salen) complex, capable of catalyzing an asymmetric epoxidation in an ionic liquid less than a decade ago.[7] Since then, ILs have been successfully applied in olefin epoxidations, e.g. utilizing manganese(III) porphyrins as catalysts.[8-11]

The ionic liquids described in this review are used either as solvents or as extractant. In some cases they are even catalytically active themselves and do not require an additional organometallic complex as catalyst. As a result of extensive studies on oxidation catalysis in ionic liquids, several reviews have been published during the past decade.[12-14] Therefore, this review highlights the most recent results. We also excluded the very well-known oxidation catalyst methyltrioxorhenium from this work since Saladino *et al.* described its activity in non-conventional solvents in 2010.[15]

1.2 Oxidation of sulfides

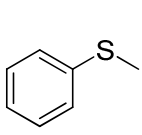
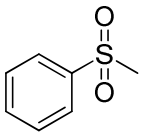
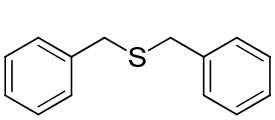
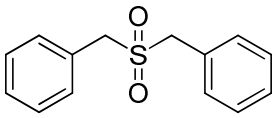
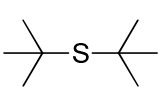
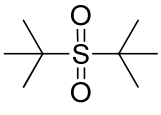
All systems described here aim on the removal of sulfur-containing compounds in diesel fuel. The removal of sulfur containing compounds is an important process in the fuel industry. Hence, research focuses on cost efficient liquid phase processes, such as the oxidation of sulfides, to remove compounds from fuels, which are corrosive for car engines and potentially problematic for the environment. Several research teams have focused on the sulfide oxidation in ionic liquids. The involved ionic liquids were used both as reaction media and as extractants, which dissolve the formed sulfones. Scheme 1 shows the reaction principle.

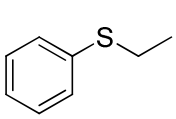
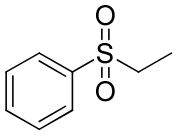
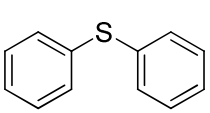
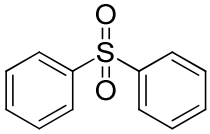
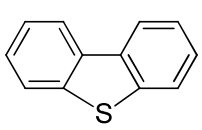
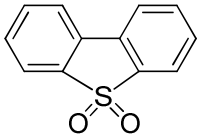
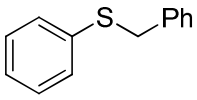
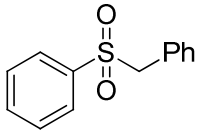
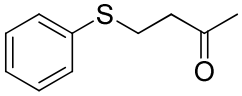
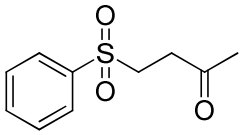
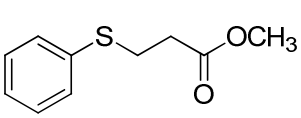
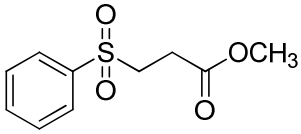
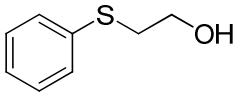
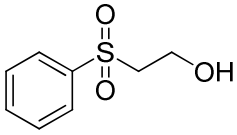
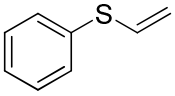
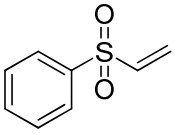
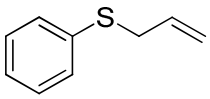
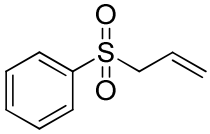
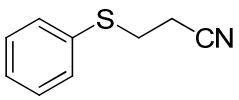
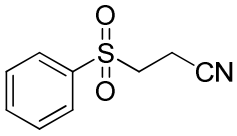
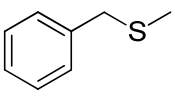
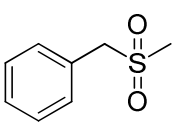


Scheme 1. The general process of the oxidative desulfurization in ILs.

The extraction of sulfur-containing compounds from diesel oil by ionic liquids could be an attractive alternative to common desulfurization by hydrotreating. The efficiency of the extraction increases if the S-species are previously oxidized to the corresponding sulfoxides and sulfones.[16] Reddy and Verkade described the oxidation of organic sulfides into sulfones by using $Ti_4[(OCH_2)_3CMe]_2(i\text{-}OPr)_{10}$. The reaction was investigated both in methanol (MeOH) and in three different RTILs ([emim]BF_4, [bmim]BF_4 and [bmim]PF_6) as solvents. H_2O_2 was used as oxidant and the reaction was performed at room temperature. Under these conditions, only sulfones but no sulfoxides were found. The activities in the different RTILs are very similar and the authors found for some substrates an acceleration of about 30 % compared with MeOH as a solvent. Additionally, the catalyst could be recycled by simply extracting the product using diethyl ether. The catalytic system could be reused for six cycles without a loss of activity. Table 1 shows the product yields in [bmim]BF_4. The velocity of the oxidation reaction is in good accordance with the steric hindrance of the substituents at the sulfur atom.[17]

Table 1. Oxidation of sulfides with 5 mol % of $Ti_4[(OCH_2)_3CMe]_2(i\text{-}PrO)$ in [bmim]BF_4 at r.t.

Entry	Substrate	Product	Time [h]	Yield [%]
1			10 min	95
2			2.5	93
3			1	93

4			2	98
5			2	91
6			2	89
7			2	90
8			1.5	90
9			2	91
10			3	91
11			2.5	87
12			2	91
13			2	91
14			1	94

Li *et al.* investigated three different ionic liquids based on iron chloride in the catalytic oxidation/desulfurization (ODS) systems for removal of benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT). The authors stated that the system [bmim]Cl/$FeCl_3$/H_2O_2 is able to remove 99 % of DBT under mild reaction conditions. As can be seen in Table 2, [bmim]Cl/$FeCl_3$ and [omim]Cl/$FeCl_3$ ionic liquids show higher ability to remove sulfur than $Et_3NHCl/FeCl_3$.[18, 19]

Table 2. Oxidative desulfurization of DBT in different ionic liquids at r.t.

Entry	IL	Yield [%]
1	[bmim]Cl/$FeCl_3$	99
2	[omim]Cl/$FeCl_3$	87
3	$Et_3NHCl/FeCl_3$	37

Reaction conditions: m(DBT)/m(IL) = 3:1, t = 10 min.

In addition, the authors studied the recycling of the [bmim]Cl/$FeCl_3$ system. They observed only a small drop from 99 to 91 % after six cycles. However, if the IL phase was extracted with CCl_4 after each run, no loss in activity could be found after nine cycles.[18, 19]

The same group investigated the desulfurization with a catalytic system containing $Na_2MoO_4 \cdot 2\ H_2O$, H_2O_2, and [bmim]BF_4. When using DBT as a model compound, a sulfur removal of 99 % was reached. The same reaction without the ionic liquid leads to a desulfurization of 4 %. The authors stated that without the IL, most of H_2O_2 decomposed at the applied temperature. Hence, the IL acts as an extractant, as reaction medium and as stabilizing agent. Table 3 shows the different investigated systems with their corresponding oxidative desulfurization yields. [20, 21]

Table 3. Different investigated systems with their corresponding yields [%] in the desulfurization of DBT.

Entry	Type of IL	IL [%]	IL+H_2O_2 [%]	IL+Na_2MoO_4+H_2O_2 [%]
1	[bmim]BF_4	16	32	99
2	[omim]BF_4	21	35	68
3	[bmim]PF_6	15	39	70
4	[omim]PF_6	20	45	78
5	[bmim]TA	15	31	49
6	[omim]TA	21	32	37

Reaction conditions: T = 70 °C, t = 3 h, 5 mol % catalyst.

Table 4 displays the oxidative desulfurization with different Mo catalysts. Li *et al.* found that the reaction including molybdenum salts as catalysts was more efficient in polar ILs than in acidic ones, since they exhibit a lower electrolyte strength.[20]

Table 4. The reactivity of different Mo catalysts for desulfurization.

Entry	Catalyst	Yield [%]
1	Na_2MoO_4	99
2	H_2MoO_4	94
3	$(NH_4)_6Mo_7O_{24}$	98
4	$H_3PMo_{12}O_{40}$	93
5	$(NH_4)_3PMo_{12}O_{40}$	98
6	$Na_3PMo_{12}O_{40}$	99

Reaction conditions: T = 70 °C, t = 3 h, 5 mol % catalyst in [bmim]BF_4.

Leaching experiments were also performed and it was observed that in case of Na_2MoO_4 1.2 mg (0.9 %) leach in one liter of the substrate phase. This amount could be completely removed by extraction with water (2 x 10 mL). Li *et al.* investigated the catalytic activity of V_2O_5 for the oxidative desulfurization of fuels.[22] The best results were obtained when a combination of H_2O_2 and V_2O_5 in [bmim]BF_4 was used. In this case, the removal of sulfur was about 99 %. The oxidation of methylphenylsulfide was performed at 35 °C by using TBHP or UHP as an o xidizing agent and 2.5 mol % of the catalyst. The authors stated that during the reaction, V_2O_5 was oxidized by H_2O_2 to the peroxovanadium compound which oxidizes the sulfides to the corresponding sulfones. Without any ionic liquid the sulfur removal was lower than 3 %. The same group studied the oxidative desulfurization of fuels by phosphotungstic acid ($H_3PW_{12}O_{40}$) and different decatungstates, respectively.[23-25] The reaction with phosphotungstic acid was performed in different ILs and H_2O_2 as an oxidant. The results are summarized in Table 5 and 6, clearly pointing out the advantage of the [bmim]-type ILs in combination with the used catalysts.

Table 5. Different investigated systems with their corresponding yields [%] in the desulfurization of DBT with phosphotungstic acid.

Entry	Type of IL	IL	IL+H_2O_2	IL+$H_3PW_{12}O_{40}$+H_2O_2
1	[bmim]BF_4	14	26	98
2	[omim]BF_4	18	27	65
3	[bmim]PF_6	12	27	98
4	[omim]PF_6	18	35	64

Reaction conditions: T = 30 °C, t = 1 h, 1 mol % catalyst.

Table 6. Different decatungstate catalysts with their corresponding DBT desulfurization yields [%].

Entry	Catalyst	Yield [%]
1	$[(C_4H_9)_4N]_4W_{10}O_{32}$	98
2	$[(CH_3)_4N]_4W_{10}O_{32}$	97
3	$[(C_2H_5)_3NC_7H_7]_4W_{10}O_{32}$	66
4	$Na_4W_{10}O_{32}$	95

Reaction conditions: T = 60 °C, t = 0.5 h, 1 mol % catalyst in [bmim]PF_6.

Both investigated catalytic systems leads to almost quantitative yields at a catalyst concentration 1 mol %. By the same group [$WO(O_2)_2$ · Phenantroline · H_2O], [$MoO(O_2)_2$ · Phenantroline] and Peroxophosphomolybdate catalysts were dissolved in ILs, e.g. [bmim]BF_4, [omim]BF_4, [bmim]PF_6, and [omim]PF_6 to oxidize DBT with hydrogen peroxide under moderate conditions. The sulfur removal of DBT-containing model oil reached 99 % at 70 ℃. The catalytic oxid ation system containing $WO(O_2)_2$ · Phen · H_2O, H_2O_2, and [bmim]BF_4 can be recycled four times without a significant decrease in activity.[26, 27]

Li and co-workers further investigated the desulfurization of dibenzothiophene by a combination of both chemical oxidation and solvent extraction.[28] Benzyltrimethylammonium chloride · 2 $ZnCl_2$ is a low-cost ionic liquid and was used as an extractant for oxidative desulfurization of DBT in *n*-octane. DBT was oxidized to the corresponding sulfone by peracetic acid, in situ prepared from H_2O_2 and acetic acid. With this system, the desulfurization yield of DBT was 94 % at 30 min and 99 % after 50 min at room temperature. According to the authors, the metal-containing ionic liquid could be recycled six times without a significant decrease in activity.

In addition to the described systems there are several reports on the investigation of Brønsted-acidic ionic liquids which are themselves acting as oxidative desulfurization catalysts. Zhao *et al.* used the Brønsted acidic ionic liquid N-methyl-pyrrolidonium tetrafluoroborate ([hnmp]BF_4) as a catalyst for the oxidative desulfurization of DBT in the presence of H_2O_2 as an oxidant.[29, 30] It was found that a coordination compound was generated between hydrogen peroxide and the cation of the ionic liquid, which results in the formation of hydroxyl radicals. The sulfur-containing compounds were first dissolved in the IL and then oxidized by the radicals. Due to the high polarity the formed sulfones could only be detected in the IL phase. Table 7 shows the recyclability of the investigated system.

Table 7. Results of the recyclability.

Cycle	Yield [%]	Cycle	Yield [%]
1	100	7	100
2	100	8	98
3	99	9	95
4	99	10	97
5	100	11	95
6	100	12	93

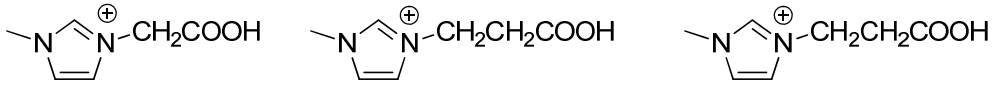
Reaction conditions: T = 60 °C, t = 2 h, V_{oil}/V_{IL} = 1:1.

The same group studied the desulfurization of thiophene with a non-fluorinated and environmentally benign IL $(C_4H_9)_4NBr \cdot 2\ C_6H_{11}NO$ as an active catalyst.[31, 32] A combination of hydrogen peroxide and acetic acid acts as an oxygen source for the reaction. After the oxidation the formed sulfoxide, sulfone and sulfate are more polar and could be extracted by the ionic liquid. A desulfurization level of up to 99 % was

obtained after 30 min and 40 ℃. An advanced oxidation process was studied by Zhao and coworkers as well.[33] In this case they used a combination of ozone and hydrogen peroxide leading to the formation of hydroxyl radicals. In contrast to applying ozone alone (64 % yield), this combination led to an increased oxidation of DBT of 99 % DBT at 50 ℃ after a reaction time of 1 50 min. [bmim]BF_4 was investigated as a reaction medium and extractant. The authors stated that the reaction became faster with increasing temperature but a higher concentration of ozone was also required.

The same reaction was investigated by the group of G. Gao. In this case they used the Brønsted acidic ionic liquid [hmim]BF_4 as a catalyst for the oxidative desulfurization of DBT in the presence of H_2O_2 as an oxidant.[34]

The deep oxidative desulfurization in the presence of H_2O_2 and UV irradiation without any catalyst at room temperature and atmospheric pressure was investigated by Zhao *et al*. The sulfur removal reached up to 99.5 % within 8 h. Without UV irradiation the yield was around 52 % after 12 h. [bmim]PF_6 was used as the extraction media.[35] Gui and coworkers studied some task-specific ionic liquids which contain carboxyl groups in their cations. Figure 1 shows the structure of the ionic liquids. In the following case the ILs act as both catalyst and extractant.



A: X = HSO_4^-
B: X = $H_2PO_4^-$

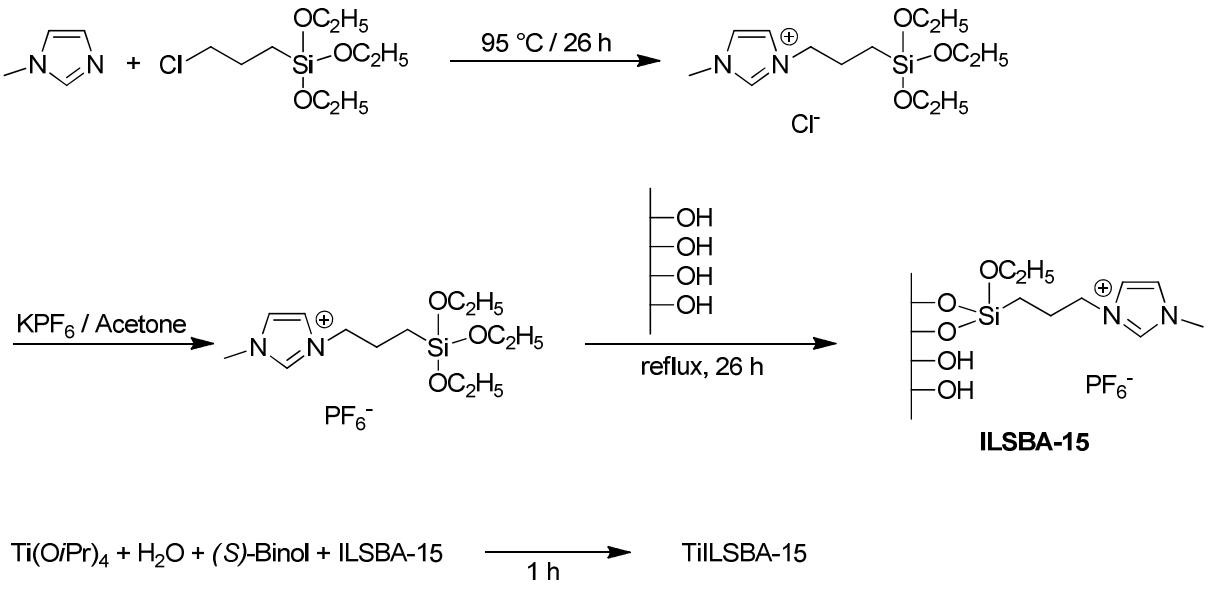
C: X = Cl

E: X = HSO_4^-
F: X = $H_2PO_4^-$

Figure 1. Structure of the task-specific ionic liquids.

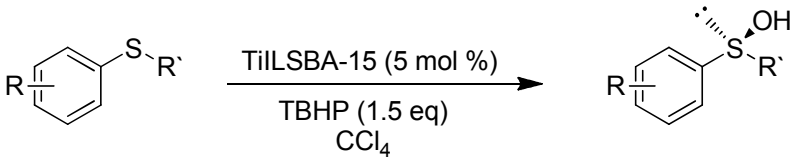
The oxidation potential of DBT with H_2O_2 as an oxidant decreases in the following order: E > F > C > A > B. The maximum yield was 97 % with compound E as

catalyst.[36] The group of Halligudi investigated a Ti-binol complex, supported on an ionic liquid-phase for enantioselective sulfide oxidation.[37] The principle of synthesising the “SILP”-type catalyst (SILP = supported ionic liquid-phase) is shown in Scheme 2.



Scheme 2. Preparation of the TiILSBA-15 catalyst.

TiILSBA-15 was synthesized and the XRD patterns of both SBA-15 and TiILSBA-15 could be associated with a *p6mm* hexagonal symmetry and the mesoporous structure of the support has not changed after the immobilization. The activity in the enantioselective oxidation of sulfides (Scheme 3) with different substrates and aqueous TBHP as an oxidizing agent was investigated (Table 8).



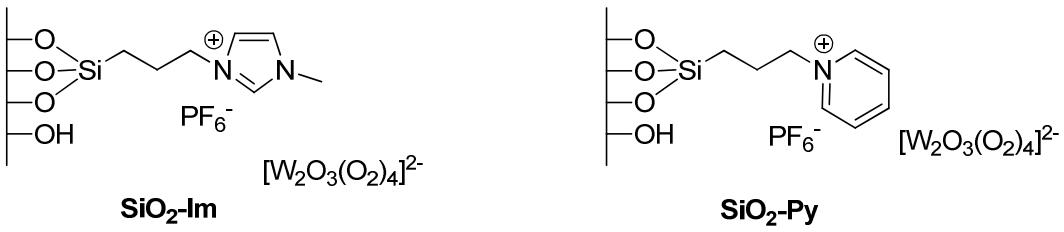
Scheme 3. Enantioselective oxidation of different sulfides.

Table 8. Catalytic results in the oxidation of different sulfur-containing compounds.

Entry	R	R`	Yield [%]	ee [%]
1	H	Me	59	99.9
2	4-Me	Me	62	99.5
3	4-Br	Me	58	99.2
4	4-Cl	Me	61	96.7
5	3-Br	Me	57	99.2
6	4-NO_2	Me	54	88.3
7	H	Et	63	77.2
8	4-OMe	Me	55	99.9
9	4-F	Me	59	98

The authors used different solvents for this reaction and found out that CCl_4 gave the best enantiomeric excess. In order to test the stability of the catalytic system the authors recycled the catalyst eight times by simple filtration after each run. They found a decrease of both the yield from 62 % to 56 % and ee values from 99.2 % to 98.2 %. Less than 0.1 ppm of Ti leached into the organic phase.

Jun-Fa and coworkers investigated two different peroxotungstates immobilized on ionic liquid-modified silica, which are depicted in Scheme 4.



Scheme 4. Different peroxotungstates investigated by Jun-Fa *et al*.

Depending on the ratio of catalyst, H_2O_2 and sulfide the authors could change the selectivity either to the formation of sulfoxides (1.5:110:100) or to the formation of sulfones (2:250:100). With both catalysts the sulfoxides could be prepared with yields between 80 % and 95 %, the sulfones between 79 % and 99 % respectively.[38]

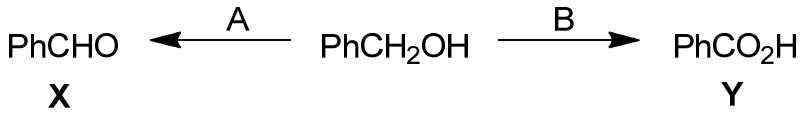
In the work of D. Zhao *et al.*, several pyridinium-based ionic liquids were employed as phase-transfer catalysts for the phase-transfer catalytic oxidation of dibenzothiophene. A mixture of H_2O_2 and formic acid was used as an oxidant. The best results were obtained with [bPy]HSO_4 at 60 °C. The desulfurization reached a maximum of 93 % within an hour. The [bPy]HSO_4 could be recycled for five cycles without a significant loss of activity.[39] A very similar system was studied recently by H. Liu and coworkers. They used [bmim]HSO_4 as a Brønsted acidic ionic liquid. This substitution leads to an increased activity in desulfurization of 99.6 % at room-temperature and after a reaction time of 90 min.[40] The group of D. Zhao optimized the oxidative desulfurization by using a quaternary ammonium coordinated ionic liquid $(C_4H_9)_4NBr \cdot 2\ C_6H_{11}NO$ as a catalytic solution. The catalytic performance reached up to 99 % in case of the oxidation and removal of DBT under the best conditions. The authors stated that with increasing temperature from 20 °C to 50 °C the yields also increased. This is caused by a reduced viscosity of the ionic liquid. With a further increase to 70 °C the yields decreased because of the decomposition of H_2O_2.

1.3 Oxidation of alcohols

In recent years many research efforts in field of the oxidation of alcohols in ionic liquids have been undertaken, for example the application of photooxidation or the reaction using reusable resins.[41, 42] In 2007, Shen and coworkers were the first

to investigate the copper-bisisoquinoline based selective oxidation of alcohols to the corresponding aldehydes and ketones by using RTILs as solvent and O_2 as an oxidant.[43] The authors stated that the catalytic activity in ionic liquids was enhanced in comparison to conventional organic solvents. The oxidation of different alcohols has been studied, including primary, secondary, allylic, and benzylic alcohols. In all cases, both the selectivity and the yield were higher than 80 %. The authors found that even air can be used instead of oxygen. Jiang and Ragauskas investigated the aerobic oxidation of alcohols to acids or aldehydes, respectively.[44] Following this method, it is possible to obtain the acid by simple addition of Cu(II) 2-ethylhexanoate as a cocatalyst.

Table 9. Recyclability of the aerobic oxidation of benzyl alcohol under the two different conditions.

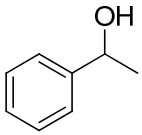
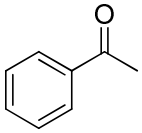
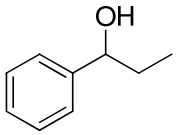
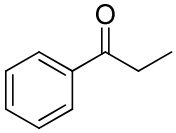
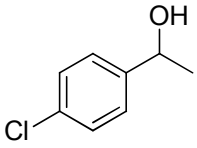
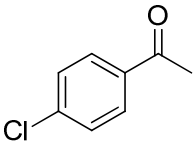
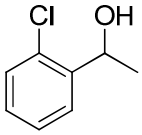
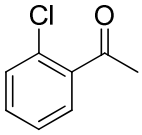
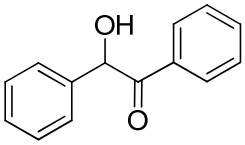
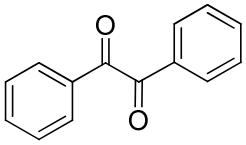
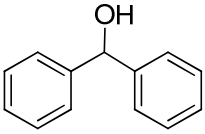
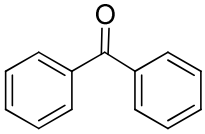
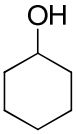
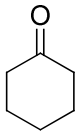


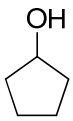
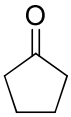
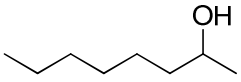
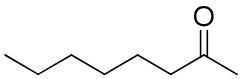
Cycle	Time [h]	Condition	Yield [%]	
			X	Y
1st	8	A	90	
	12	B		89
2nd	8	A	84	
	12	B		88
3rd	10	A	83	
	15	B		76

Reaction conditions A: 2 mmol benzyl alcohol, 2 mol % $VO(acac)_2$, 6 mol % DABCO, 1 bar O_2, 0.3 g of $[bmim]PF_6$, 95 °C; reaction conditions B: 2 mmol benzyl alcoh ol, 2 mol % $VO(acac)_2$, 2 mol % Cu(II) 2-ethylhexanoate, 6 mol % DABCO, 1 bar O_2, 0.3 g of [hmim]OTf, 95 °C for the specific time.

Table 9 shows the results and the recyclability of the catalytic system. In 2007 Liu *et al.* used $Cu(acac)_2$ for the oxidation of secondary alcohols with TBHP as an oxygen source.[45] They investigated different RTILs to find the ideal reaction conditions. The best results were achieved with imidazolium-type ionic liquids – especially with [bmim]PF_6. Subsequently, different substrates have been investigated in this RTIL.

Table 10. Oxidation of secondary alcohols with 3 mol % $Cu(acac)_2$ as a catalyst.

Entry	Substrate	Product	Time [h]	Yield [%]
1			5	91
2			5	91
3			5	93
4			5	41
5			5	94
6			5	93
7			5	65

8			15	66
9			15	58

To prove the recyclability of the catalytic system, the oxidation of 1-phenylpropan-1-ol to the corresponding acetophenone was tested in five subsequent runs. The yield decreased from 91 % in the first cycle to 84 % in the fifth cycle. Later, Han and coworkers employed the same substrates for the oxidation with a novel copper Schiff-base complex (see Figure 2).[45, 46]

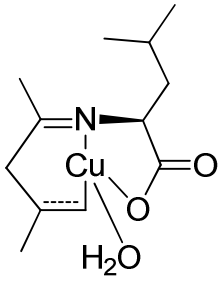
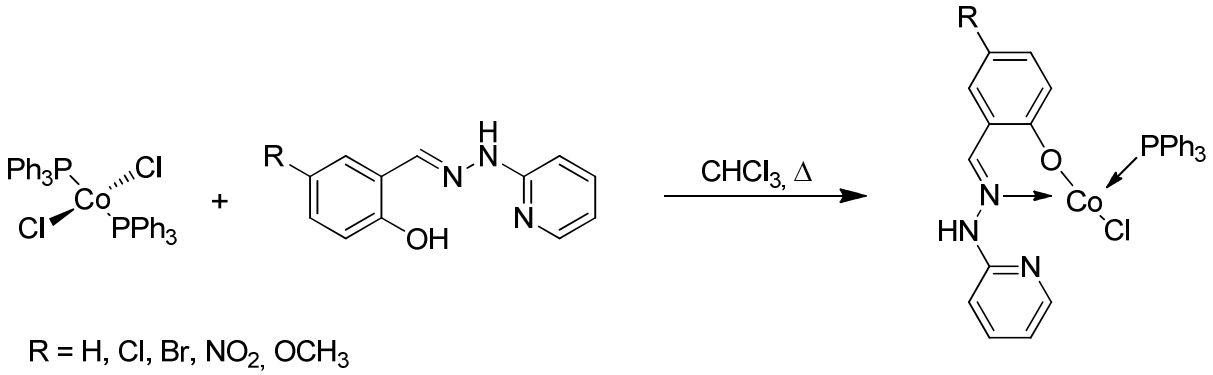


Figure 2. Structure of the Cu-Schiff-base catalyst.

The authors found that in this case, the BF_4-type RTIL leads to the highest conversion. In addition, the selectivity of the formation of the corresponding acid reaches up to 98 %. The authors also stated that with TBHP the reaction works best, instead of using H_2O_2 or NaOCl as an oxidizing agent. Finally, the reaction of the aromatic alcohols was faster than the aliphatic alcohols.

The catalytic oxidation with Ni(II)-Schiff-base catalysts in an [emim]-based IL and NaOCl as an oxidizing agent was published by Bhat and coworkers.[47] They investigated different substrates and reached yields of > 61 % after 15 min at room

temperature. The same group published analogous Co(II)-complexes (Scheme 5). A difference in the catalytic activity between the Ni(II) and the Co(II) catalysts could not be observed. The authors further stated that the activity is strongly influenced by the bulkiness of the substituent R in the ligand.[47, 48]



Scheme 5. Synthesis of the Co(II) catalysts.

A. Shaabani *et al.* investigated the oxidation of alkyl arenes and alcohols to the corresponding carbonyl compounds in ionic liquids. A variety of metallo-phthalocyanines and ionic liquids were used and the best results were obtained by using Co(II) phthalocyanine, [bmim]Br and an oxygen pressure of 0.1 atm. For the oxidation of alkyl arenes at 100 ℃, yields between 74 % and 93 % were obtained, between 80 % and 92 % for the oxidation of alcohols respectively.[49] The same catalyst was used in a tetrasulfonated type for the oxidative deprotection of trimethylsilyl ether to the corresponding carbonyl compound. In [bmim]Cl yields of up to 80 % could be obtained.[50] The groups of Hajipour and Ruoho worked on this reaction in the presence of a catalytic amount of [bmim]Br (10 mol %). They found a efficient method to obtain the carbonyl compounds under solvent-free conditions by using potassium persulfate as an oxidant. After a reaction time of 15 min they got a maximum yield of 90 %.[51] Fadini and coworkers studied the manganese(III) catalyzed cleavage of vicinal diols. When applying ILs in this reaction, the yields

increased between 10 % and 60 % compared to conventional solvents. With a concentration of [Mn(salen)(Py)](OAc) of 5 mol % at a temperature of 60 %, a quantitative oxidative C-C bond cleavage of 1,1,2,2-tetraphenyl-1,2-ethanediol could be obtained after 2 h and with oxygen as oxidant.[52]

In 2008, Liu *et al.* studied the oxidation activity of different transition-metal salts by dissolving an equimolar amount of it in a *so-called* TEMPO-IL (TEMPO = 2,2,6,6-tetramethylpiperidine N-oxyl; Fig. 3).[53, 54]

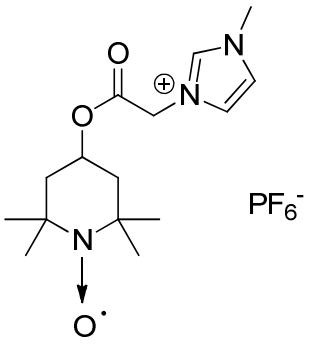


Figure 3. Structure of a TEMPO-IL.

While $Co(OAc)_2$, $CoCl_2$, $FeCl_3$, $Mn(OAc)_2$ and $NiCl_2$ show no activities as catalysts of the oxidation of benzyl alcohol, CuCl exhibits a high catalytic activity, yielding benzaldehyde in 94 %. Table 11 shows all the investigated substrates.

Table 11. TEMPO-IL/CuCl catalyzed oxidation of alcohols.

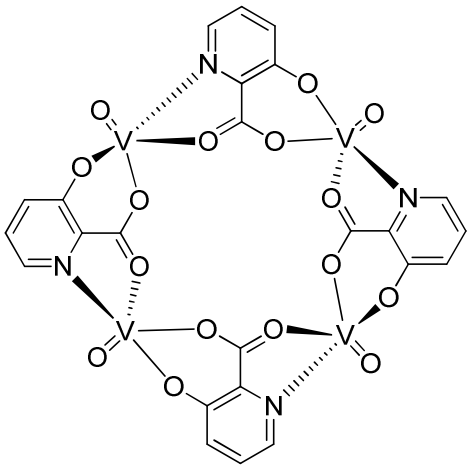
Entry	Substrate	Temp. [°C]	Conversion [%]	Yield [%]
1	benzyl alcohol	40	67	55
2	benzyl alcohol	65	99	94
3	cinnamyl alcohol	65	99	84

4	4-nitrobenzyl alcohol	100	96	84
5	4-chlorbenzyl alcohol	75	99	88
6	4-methoxybenzyl alcohol	65	99	91
7	diphenyl carbinol	65	94	85
8	2-phenylethanol	65	54	30
9	furfuryl alcohol	65	40	-
10	cyclohexanol	65	-	-
11	lauryl alcohol	65	23	-

After the reaction, the IL phase was distilled and reused for five cycles without a loss of activity. In 2008, Liu *et al.* used the same catalytic system and found out that the addition of molecular sieve MS3A results in a remarkable faster reaction rate.[55] The authors stated that the acceleration results from the property of the MS3A to act as a Brønsted base and it is independent on the water content of the reaction mixture.

Lei and coworkers studied a highly chemoselective oxidation of benzylic alcohols in the presence of aliphatic alcohols to the corresponding hydroxyl benzyl aldehydes and ketones in a [bmim]PF_6-H_2O-mixture. The reaction is an effective catalytic oxidation system, which leads to high yields using *N*-chlorosuccinimide (NCS)/NaBr/TEMPO-IL. The [bmim]PF_6, together with the catalyst TEMPO-IL could be recycled for ten subsequent runs without any loss of activity neither in terms of yield nor selectivity of the product.[56] Another effective system with a TEMPO functionalized imidazolium salt, a carboxylic acid substituted imidazolium salt and $NaNO_2$ for the aerobic oxidation of alcohols was established by He and coworkers.[57]

Ogawa *et al.* compared the catalytic activity of tetranuclear vanadium(IV) complex bearing 3-hydroxypicolic acid (hpic) as ligand (Figure 4) in organic solvents and [bmim]BF_4.[58]



$(VO)_4(hpic)_4$

Figure 4. Structure of the vanadium(IV) catalyst.

The authors stated that commercially available vanadium complexes are not active in the oxidation of benzyl alcohol. However, with 0.5 mol % [$(VO)_4(hpic)_4$] in acetonitrile (MeCN) a yield of 62 % was reached with a selectivity of 100 % to the corresponding aldehyde. In protic solvents (EtOH) the yields are even higher (up to 71 %) but the selectivity is decreased because the aldehyde is further oxidized to the corresponding acid. The oxidation of benzhydrol to benzophenone was also investigated under an atmosphere of oxygen and [bmim]BF_4 as solvent. Benzophenone was formed with a yield of 64 %.

In 2008, Halligudi and coworkers investigated the selective oxidation of alcohols by a heteropoly molybdovanadophosphoric acid ($H_5PMo_{10}V_2O_{40}$) supported ionic liquid-phase catalyst.[59] The compound was immobilized on a mesoporous silica SBA-15. The authors obtained high activity in both primary and secondary alcohols to the corresponding aldehydes and ketones, respectively. The catalyst showed no activity with respect to the oxidation of the ketone and the aldehyde to the carboxylic acid. The authors performed the catalytic reactions in an autoclave under air pressure.

Table 12 shows the results of the oxidation of 1-(naphthylen-2-yl) ethanol under different conditions.

Table 12. Oxidation of 1-(naphthylen-2-yl) ethanol under variable conditions.

Parameter	Yield [%]
pressure [atm]	
2	60
2.7	93
3.4	99
temperature [℃]	
80	79
90	92
100	99
catalyst loading [%]	
20	26
30	58
40	99
50	99
60	91

The experiments were performed by dissolving the catalyst in MeCN and adding a radical initiator (AIBN or TBHP). At an oxygen pressure of 1 atm the yield was only 40 % (increasing at higher pressure). With regard to the temperature the authors stated that no conversion was obtained at 50 ℃. Under the best conditions the authors investigated the activity of different substrates which are depicted in the following Table 13.

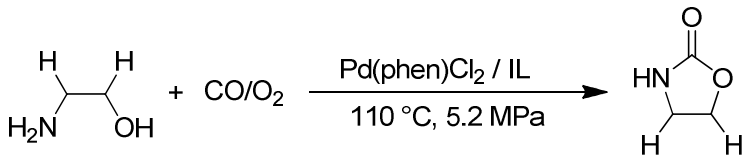
Table 13. Variation of the substrates.

Entry	Substrate	Time [h]	Yield [%]
1	1-(Naphthylen-2-yl) ethanol	7	99
2	Diphenylmethanol	7	99
3	Cyclohexanol	6	99
4	Phenylethanol	6	99
5	2-Hexanol	5	98
6	2-Phenylpropanol	7	93
7	4-Methoxy phenylethanol	6	98
8	4-Methyl phenylethanol	6	96
9	4-Chloro phenylethanol	6	98
10	4-Bromo phenylethanol	6	98
11	4-Nitro phenylethanol	6	94
12	Benzoin	7	95
13	Menthol	6	96
14	[1,7,7]Trimethylbicyclo [2,2,1]heptan-2-ol	8	95
15	3,5,5-Trimethylcyclohex-2-enol	7	94
16	Benzyl alcohol	12	98
17	1,3-Butanediol	8	83
18	Geraniol	10	97
19	Cinnamyl alcohol	13	98
20	Pyridin-2-methanol	11	96

Reaction conditions: T = 100 ℃; air pressure: 3.4 atm; catalyst concentration: 0.02 mol %.

The authors were able to find the conditions (T = 100 ℃, pressure: 3.4 atm and c = 0.02 mol %) which led to high yields of 83-99 % in all investigated substrates.

Li and Xia studied the biphasic oxidative cyclocarbonylation of β–aminoalcohols and 2-aminophenol to their corresponding 2-oxazolidinones. $Pd(phen)Cl_2$ acts as the catalyst which is stabilized by [bmim]I. Scheme 6 shows the oxidation reaction.



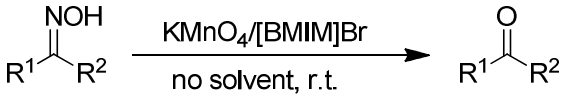
Scheme 6. Oxidative cyclocarbonylation of ethanolamine.

The best results were obtained by using [bmim]I as an ionic liquid with a TOF of 3288 h^{-1} and a conversion of 94 %.[60] The selective oxidation of alcohols in high conversion and selectivity using 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$)/ MCM-41 in ionic liquids was studied by Shen *et al*. The best performance of the photocatalytic system was obtained with a catalyst loading of 30 %, [omim]BF_4 as solvent and oxygen as oxidant. The yields were between 90 % and 99 %. The immobilization resulted in a amorphous phase with a BET surface of 632 m^2/g, a pore volume of 0.53 cm^2/g with a pore diameter of 29.7 Å.[61]

The immobilization of perruthenate (RuO_4^-) on 1-vinyl-3-butyl imidazolium chloride leads to an active catalyst for the aerobic oxidation of benzyl alcohol to benzyl aldehyde. The catalytic reaction was done in supercritical CO_2, toluene and dichloromethane at 80 ℃. Han *et al.* could demonstrate that the catalyst was very active and highly selective. The reaction rate in CO_2 depended strongly on pressure and reached a maximum at about 14 MPa.[62]

1.4 Oxidation of oximes

Compounds such as aldoximes and ketoximes are derivatives of carbonyl compounds and are, for example, used for the characterization and protection of carbonyl compounds. The regeneration of the carbonyl species is achieved by oxidation of the corresponding oximes.[63, 64] Safaei-Ghomi *et al.* investigated the oxidation of oximes with $KMnO_4$ as an oxidizing agent (Scheme 7).[65]



Scheme 7. The oxidation of various oximes with $KMnO_4$.

The best results could be obtained with a 1 : 0.7 : 0.4 ratio of oxime : IL : $KMnO_4$ at room temperature. The authors stated that the RTIL inhibits the further oxidation of the carbonyl compound to the respective carboxylic acid. In all the examined substrates yields > 81 % are obtained. The results for various oximes are listed in Table 14.

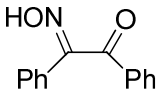
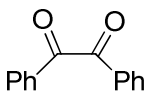
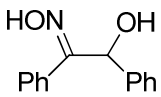
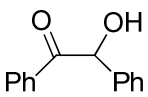
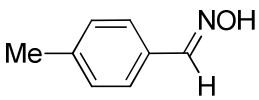
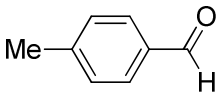
Table 14. Oxidation of oximes with $KMnO_4$ and [bmim]Br.

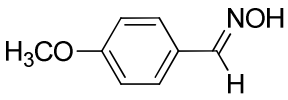
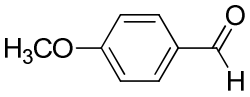
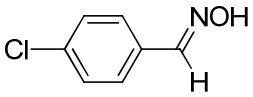
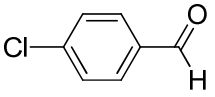
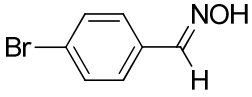
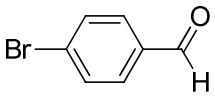
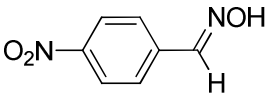
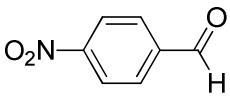
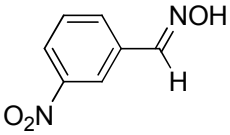
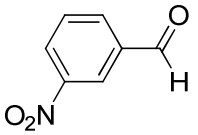
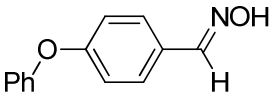
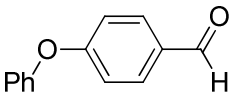
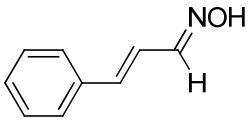
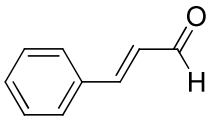
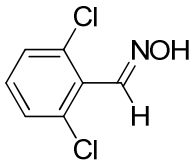
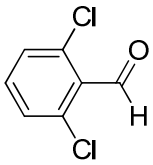
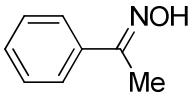
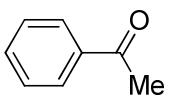
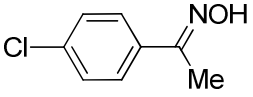
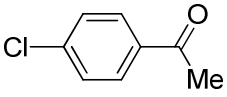
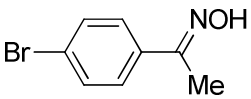
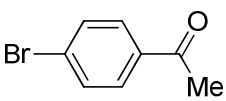
Entry	R^1	R^2	Time [min]	Yield [%]
1	C_6H_5	H	40	95
2	4-$O_2NC_6H_4$	H	9	> 98
3	3-$O_2NC_6H_4$	H	18	95
4	4-$MeOC_6H_4$	H	53	91
5	3-$MeOC_6H_4$	H	42	94
6	2,4-$(MeO)_2NC_6H_3$	H	73	89
7	4-ClC_6H_4	H	12	94
8	4-BrC_6H_4	H	17	97

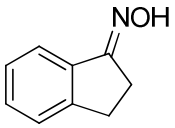
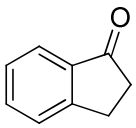
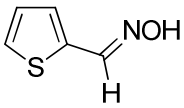
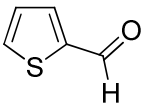
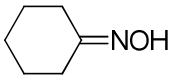
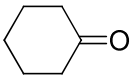
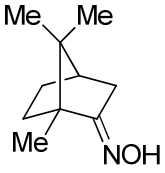
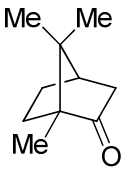
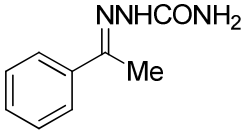
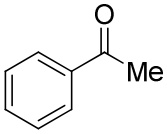
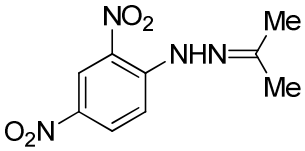
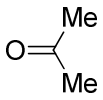
9	2,6-$Cl_2NC_6H_3$	H	23	91
10	2,4-$Cl_2NC_6H_3$	H	10	> 98
11	4-MeC_6H_4	H	50	93
12	2-MeC_6H_4	H	41	95
13	3-MeC_6H_4	H	60	91
14	C_6H_5	C_6H_5	55	81
15	C_6H_5	CH_3	52	92
16	4-ClC_6H_4	CH_3	32	93
17	4-BrC_6H_4	CH_2Br	17	93
18	2-HOC_6H_4	CH_3	28	90

In 2009, Shaabani and Farhangi investigated the aerobic cleavage of oximes in imidazol-based ionic liquids with phthalocyanin (Pc) catalysts.[66] The best results are obtained with Co-Pc catalysts and [bmim]Br as solvent. Table 15 gives an overview of the examined substrates.

Table 15. Oxidation of oximes with Co-Pc/[bmim]Br at 70 ℃.

Entry	**Substrate**	**Product**	**Time [min]**	**Yield [%]**
1			60	90, 88, 87
2			60	91
3			30	89

4			50	92
5			40	93
6			40	92
7			30	80
8			30	88
9			40	91
10			50	86
11			70	83
12			80	82
13			60	87
14			40	85

15			150	85
16			200	80
17			40	88
18			180	70
19			4 days	87
20			4 days	70

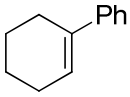
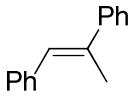
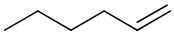
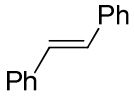
In addition, it was shown that the catalyst can be reused after extraction of the product with just a minor activity loss (see Table 15, Entry 1). Another advantage of using Co-Pc/RTIL in contrast to conventional methods is the performance under neutral conditions. Application of RTILs is also suitable for acid-sensitive functional groups.

1.5 Oxidation of olefins

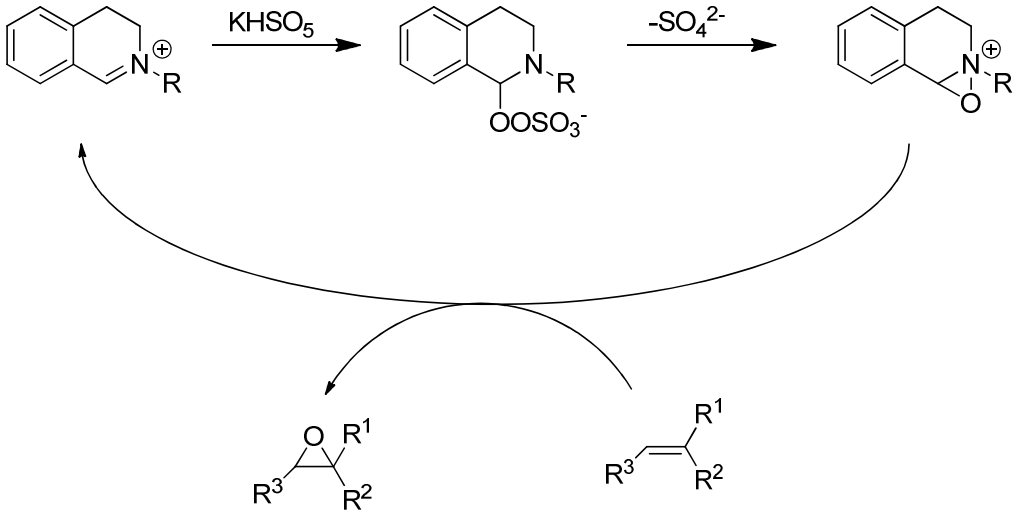
In 2008, Welton *et al.* used a number of ionic liquids as co-solvents for the catalytic epoxidation of alkenes with Oxone® ($KHSO_5$) and *N*-alkyl-3,4-dihydroisoquinolinium salts.[67] Because of the possible oxidation of imidazolium

based ILs, pyridinium cations were preferred. Welton *et al.* found that epoxidations carried out in water soluble ILs are not more efficient than those performed in MeCN. The results of the epoxidation of different substrates by 2-methyl-3,4-dihydroisoquinolinium tetrafluoroborate [mdhqm]NTf_2 catalysts are depicted in Table 16.

Table 16. Catalytic epoxidation of olefins with [mdhqm]NTf_2.

		Conversion [%] (TON)	
Entry	**Substrate**	**MeCN/H_2O (1:1)**	**[bmim]OTf/H_2O (1:1)**
1		92 (19)	100 (20)
2		75 (15)	63 (13)
3		66 (13)	6 (1)
4		18 (4)	14 (3)
5		0	0

The 2-methyl-3,4-dihydroisoquinolinium cation is a compound which is able to catalyze the olefin epoxidation without an involved metal. The mechanism is shown in Scheme 8.



Scheme 8. Olefin epoxidation without an involved metal-containing catalyst.

The authors tried a range of ILs as a co-solvent for the oxidation of 1-phenyl-cyclohexene at room temperature. Interestingly, in water immiscible ILs the epoxidation does not take place. With water miscible ILs the authors described conversions of 63 % in case of [bmim]OTf and 53 % with [bmim]BF_4 to the corresponding epoxide. The authors explained this phenomenon with phase-transfer problems of the HSO_5^- in the case of the biphasic system. In recent years, there were some publications dealing with the catalytic epoxidation of olefins with different molybdenum compounds as catalysts. Valente *et al.* described dioxomolybdenum(VI) complex bearing an anionic N,O oxazoline ligand (Figure 5).[68]

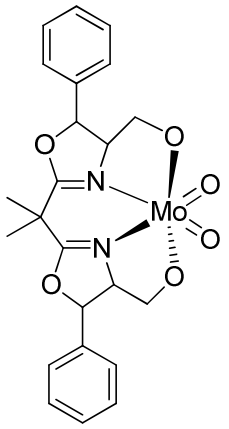
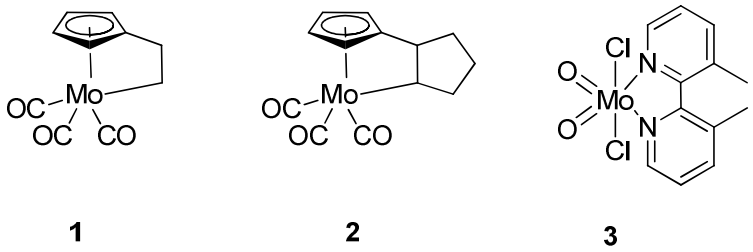


Figure 5. The investigated dioxomolybdenum(VI) complex.

The authors investigated different solvents, including ILs. They found a better solubility of the Mo(VI) complex in the more polar solvent [bmPy]BF_4 compared to [bmPy]PF_6 which led finally to a higher conversion of *trans*-β-methylstyrene in the polar solvent ([bmPy]BF_4: 31 %; [bmPy]PF_6: 1 % after 24 h). The selectivity was 100 % when using an IL as solvent; only the desired epoxide was obtained. The recyclability of the systems containing [bmim]BF_4 or [bmPy]BF_4 was studied as well and they could find out that in contrast to [bmim]BF_4 the catalyst leaching out of the IL when using [bmPy]BF_4. Kühn *et al.* recently investigated three different Mo(VI) catalysts (Figure 6) for the oxidation of *cis*-cyclooctene in ionic liquids.[69, 70]



1 **2** **3**

Figure 6. The investigated Mo complexes.

In contrast to the most other studies, the catalytic test reactions were performed at room temperature. The best results were obtained using [bmim]NTf_2 as a solvent. With **1** and **2**, quantitative yields were obtained after 1 h and a concentration of 1 mol %. With a loading of catalyst **2** of 0.05 mol %, the turnover frequency reached an impressively high value of > 44 000 h^{-1}. This is the highest value which has so far been reported for this type of reaction.

Recycling experiments led to only a minor loss of activity (80 % at the 3rd run). Compound **3** gave a moderate yield of 43 % after 24 h (1 mol %) and a TOF of around 110 h^{-1}. In addition a series of [$MoO_2X_2L_2$] (L = 4,4`-bis-methoxycarbonyl-2,2`-bipyridine, 5,5`-bis-methoxycarbonyl-2,2`-bipyridine, 4,4`-bis-ethoxycarbonyl-

2,2`-bipyridine, 5,5`-bis-ethoxycarbonyl-2,2`-bipyridine; X = Cl) was investigated by the same group. The activity of the epoxidation of cis-cyclooctene with TBHP in different room-temperature ionic liquids was approximately four times higher compared with conventionally used dichloromethane.[71]

Abrantes and coworkers used an amino acid-functionalized CpMo complex (Figure 7) for the epoxidation of *trans*-β-methylstyrene in [bmim]BF_4.[72]

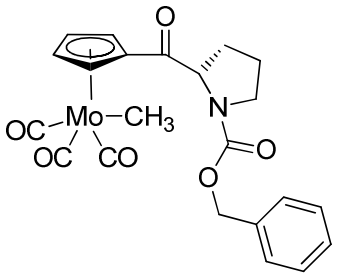
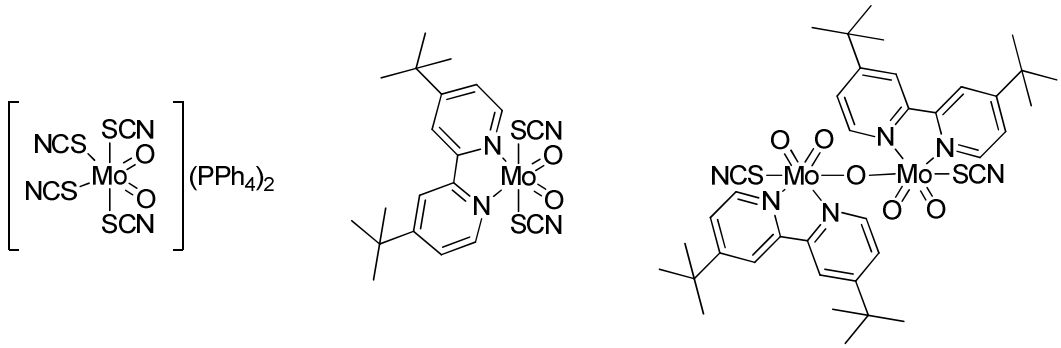


Figure 7. Amino acid-functionalized CpMo complex.

The reaction was studied at room-temperature with a catalyst concentration of 1 mol %, TBHP as oxidant. The authors found that the catalyst was completely dissolved in the IL and the organic phase remained colorless during the whole reaction. However, they could not improve the ee, which was below 5 % (independent from the solvent) and a quite low yield of 10 % after 24 h was obtained, which is lower than in an aprotic solvent (77 %). Pillinger and coworkers studied three different molybdenum compounds which are depicted in Figure 8.[73]



4 **5** **6**

Figure 8. Mo complexes used for the epoxidation of olefins by Pillinger *et al*.

The authors mentioned the poor solubility of complex **4** in the IL. This explains the lowest yield compared to catalysts **5** and **6** in the same solvent (see Table 17).

Table 17. Catalytic results of **4**-**6** in ILs.

Entry	Catalyst	Solvent	Selectivity [%]	Yield [%]	TOF [h^{-1}]
1	**4** (1st run)	[bmPy]BF_4	54	67	97
2	**4** (2nd run)	[bmPy]BF_4	92	74	50
3	**5**	[bmPy]PF_6	50	22	52
4	**5** (1st run)	[bmPy]BF_4	83	74	57
5	**5** (2nd run)	[bmPy]BF_4	88	78	56
6	**6** (1st run)	[bmPy]BF_4	93	85	62
7	**6** (2nd run)	[bmPy]BF_4	94	86	31

Reaction conditions: substrate: cyclooctene, T = 55 °C, t = 24 h, oxidant: TBHP, 1 mol % catalyst.

Interestingly, the authors stated that they found the same kinetic profile for **5** when using an aqueous TBHP solution. A comparison between the two runs reveals a loss in activity, which is probably due to the increasing concentration of *tert*-BuOH with time in the ionic liquid. In 2009, Wang and coworkers used $MoO(O_2)_2 \cdot 2QOH$ (QOH =

8-quinilinol) (Figure 9) for the epoxidation of a technical mixture of methyl oleate and methyl linoleate in [bmim]BF_4, [Hydemim]BF_4, and [bmim]PF_6.[74]

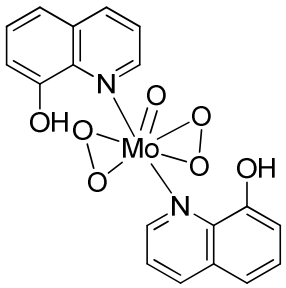


Figure 9. Oxo-bisperoxo Mo catalyst.

For the investigated substrate mixture, especially [bmim]BF_4 and [Hydemim]BF_4 showed high activities. Table 18 shows the conversions, selectivities and TOFs of the investigated ionic liquids.

Table 18. Epoxidation of methyl oleate and methyl linoleate catalyzed by $MoO(O_2)_2 \cdot 2QOH$.

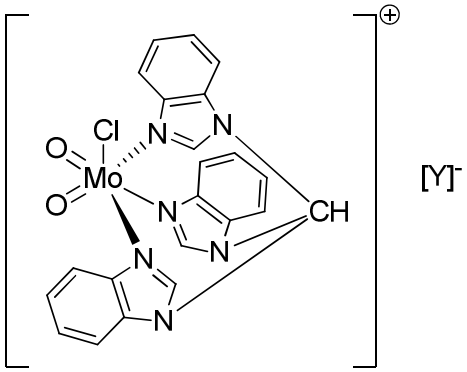
Entry	**Solvent**	**Conversion [%]**		**Selectivity [%]**	**TON(TOF)**
		methyl oleate	methyl linoleat		
1	no solvent	55	31	90	3690 (1845)
2	[bmim]BF_4	92	78	93	7812 (3906)
3	[bmim]PF_6	75	44	94	5358 (2679)
4	[Hydemim]BF_4	96	89	95	8740 (4370)
5	CH_3CN / 30% CH_3CN	85	63	92	6624 (3312)
6	70%[Hydemim]BF_4	94	84	95	8360 (4180)

7	C_2H_5OH / 30% C_2H_5OH	81	45	93	5580 (2790)
8	70%[Hydemim]BF_4	90	74	95	7695 (3848)

Reaction conditions: T = 30 °C, t = 2 h, oxidant: H_2O_2, 0.01 mol % catalyst, co-catalyst: $NaHCO_3$.

The authors obtained the best results when using ILs with BF_4 counter ions. The polar character of these species may play a key role in the epoxidation reaction. The positive effect concerning the activity of the catalyst was confirmed by the addition of [Hydemim]BF_4 to an organic solvent. Both the conversion and the selectivity to the corresponding epoxide increased. In addition, the catalytic system could be recycled for at least five runs (by washing with diethyl ether and drying) without any loss of selectivity and just a minor drop in conversion of methyl oleate (87 %) and methyl linoleate (82 %).

In 2010, Gonçalves *et al.* described different cationic molybdenum(VI) dioxo complexes containing weakly coordinating anions for the cyclooctene epoxidation (Figure 10).[75]



Y = Cl (**7**), BF_4 (**8**), PF_6 (**9**)

Figure 10. Cationic Mo-catalyst.

The catalysts were used at 55 ℃ in different solvents (DCE, [bmim]BF_4, [bmPy]BF_4, [bmim]PF_6 and [bmPy]PF_6). The performance with DCE as a solvent results in yields

between 61 % and 98 % after 24 h with a selectivity of 100 %. In all solvents complex **9** is less soluble than **7** and **8**, resulting in the lowest conversions.

In contrast to compound **9**, **7** could be completely dissolved in all ILs. Compound **8** was completely dissolved in the BF_4-type ILs, but was poorly soluble in PF_6-type ILs. The different solubility of the catalysts is obviously the most important factor concerning the activity. Table 19 shows the results of the catalytic reactions.

Table 19. Epoxidation of cyclooctene catalyzed by **7**-**9**.

Entry	Solvent	Catalyst	Conversion [%]	TOF [h^{-1}]
1	DCE	7	96	201
		8	98	168
		9	61	69
2	[bmim]BF_4	7	78	76
		8	75	91
		9	40	15
3	[bmPy]BF_4	7	80	64
		8	81	102
		9	40	15
4	[bmim]PF_6	7	91	142
		8	45	67
		9	42	22
5	[bmPy]PF_6	7	94	163
		8	51	73
		9	40	19

The authors stated that the reaction proceeds as a heterogeneous process, because the organic phase remained colorless, while the IL phase is yellow, because of the active species being formed. The authors additionally compared the results when using different oxidants in the oxidation of cyclooctene (Table 20).

Table 20. Catalytic epoxidation of cyclooctene with **7** in [bmim]PF_6 using different oxidants.

Entry	Oxidant	Conversion [%]	TOF [h^{-1}]
1	TBHP (decane)	91	142
2	TBHP (aq)	50	18
3	H_2O_2 (aq)	38	-
4	UHP	92	16

In the case of water-free oxidants (TBHP in decane, UHP) the reactions are significantly faster, most presumably because of the coordinating properties of water which finally leads to a less active catalytic species. Interestingly, even when applying aqueous TBHP or H_2O_2 the authors did not observe any diol formation.

The catalytic system **7**/[bmim]PF_6/TBHP was finally used to investigate the epoxidation of different olefins. Cyclooctene gave the best results under the applied conditions (91 %). It is followed by norbornene (55%), cyclohexene (37%) and styrene ≈ α-pinene (15 %).

Tsang *et al.* described the palladium-catalyzed oxidation of styrene using different multicarboxylic acid appended imidazolium ILs (Figure 11) as reaction medium.[76]

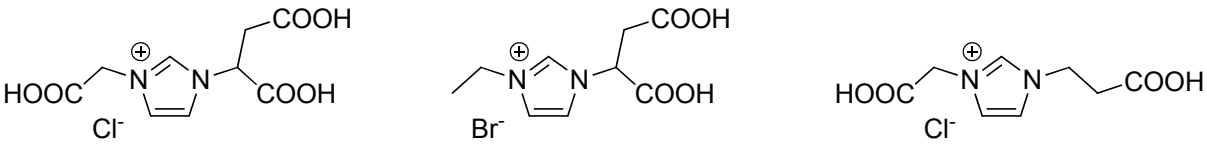


Figure 11. Multicarboxylic acid containing ILs applied by Tsang *et al*.

The treatment of the ionic liquids with the precatalyst $PdCl_2$, led to the formation of a species containing the $PdCl_4^{2-}$ or $PdCl_2Br_2^{2-}$ anion, which was shown to be an active catalyst of the selective catalytic oxidation of styrene to acetophenone with hydrogen peroxide as oxygen source. Compared with neat $PdCl_2$, the investigated system requires less $PdCl_2$ and is more active. The turnover frequency reached a maximum of 146 h^{-1}, a conversion of 100 % with a selectivity of 93 %. The same reaction without an IL led to a TOF of 21 h^{-1} with a conversion of 25 % and a selectivity of 86 % to acetophenone. Table 21 shows the results of the investigated systems.

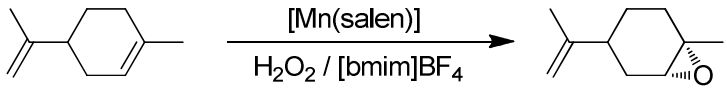
Table 21. Oxidation of styrene catalyzed by $PdCl_2$/IL.

Entry	IL	Conversion [%]	Selectivity [%]	TOF [h^{-1}]
1	-	25	86	21
2	**10**	100	93	146
3	**11**	84	92	116
4	**12**	80	92	92

Reaction conditions: T = 55 ℃; catalyst concentrat ion = 0.1 mol %.

After investigating all the possible combinations the authors found that the reaction temperature was the most important factor for the rate of the oxidation, independent of the nature of the cation and anions. A great advantage of the multicarboxylic acid

containing ILs compared to [bmim]BF_4 is the possibility of reusing the catalytic system. With [bmim]BF_4, the selectivity decreased to < 20 % after the 3rd cycle. The catalyst could be recycled ten times without a loss of both activity and selectivity. The group of Lu studied an ionic manganese porphyrin catalyst, which is embedded in [bPy]BF_4 in the oxidation of different styrene derivatives. They found a good activity and recyclability compared to the neutral complex. The derivatives was converted into the corresponding epoxides in selectivities between 57 % and 100 %.[77, 78] The asymmetric epoxidation of limonene was investigated by the group of Bernardo-Gusmão. They used Jacobsens Mn(salen) catalyst and hydrogen peroxide as an oxygen source (Scheme 9).



Scheme 9. Oxidation of limonene catalyzed by Jacobsens catalyst.

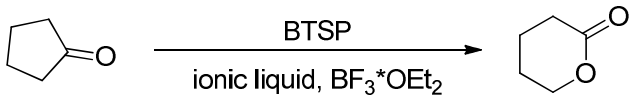
The catalytic procedure was performed in [bmim]BF_4 and resulted in a high diastereomeric excess of 74 % to the respective 1,2-epoxi-*p*-ment-8-enes, while the conversion was 70 %.[79] Also a Mn(salen) catalyst was used for the oxidation of styrene with molecular oxygen to benzaldehyde.[80] Besides studies of kinetics, reaction temperature and reaction pressure, three ionic liquids ([bmim]PF_6, [hmmim]CF_3COO and [bmim]BF_4) were tested as solvents in the oxidation. [bmim]BF_4 turned out to be the best solvent in this reaction.

Another salen catalyst was investigated recently by Li and coworkers. They modified a Cu(salen) catalyst with an ionic pyridinium tag in the backbone of the salen-ligand. This complex was studied in the allylic oxidation of cyclohexene with molecular

oxygen. The authors state that because of the highest nucleophilicity, Cu[salen-Py]X_2 with X = PF_4 showed the highest catalytic activity.[81]

1.6 The Baeyer-Villiger reaction

In 2008 Slupska *et al.* reported the oxidation of various ketones with bis(trimethylsilyl)peroxide (BTSP) in ionic liquids (Scheme 10).[82]



Scheme 10. Baeyer-Villiger reaction.

The lactonisation of cyclopentanone was performed in an organic solvent (dichloromethane (DCM)) and in different ionic liquids to compare solvent influences (Table 22). These catalytic examinations were carried out with $BF_3 \cdot OEt_2$ as acid catalyst (200 mol%), showing yields up to 20 % higher yields in all used ionic liquids compared to dichloromethane. The lower yields of [bmim]HSO_4 and [bmim]BF_4 compared to the other ionic liquids were explained by the relatively fast decomposition of BTSP in these solvents. The necessity of adding an extra catalyst to the reaction mixture in order to obtain the desired product, together with the decomposition experiments, leads the authors to the conclusion that the rate of BTSP-decomposition is slower than the rate of the oxidation reaction only if a co-catalyst is present. The comparison of different catalysts ($BF_3 \cdot OEt_2$, $AlCl_3$, $SnCl_3$) in [bmim]NTf_2 and dichloromethane lead to similar results for the ionic liquid, while the differences between the catalysts in dichloromethane are much more pronounced (Table 22).

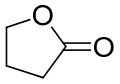
The only catalyst free oxidation of cyclic ketones could be carried out in [bmim]OTf (Table 23). The reason for that is, due to the authors, the influence of the OTf^- anion. To proof their statement catalysis was successfully performed in dichloromethane together with NaOTf (Table 23). The proposed reaction mechanism is shown in Scheme 11.

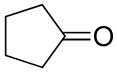
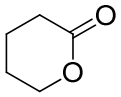
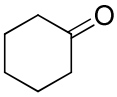
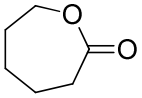
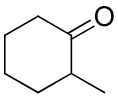
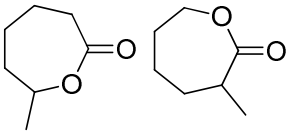
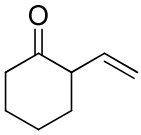
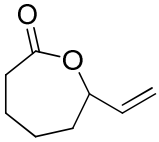
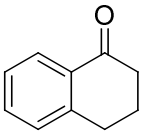
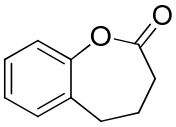
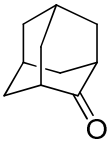
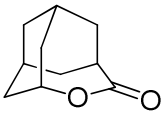
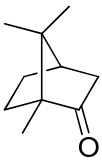
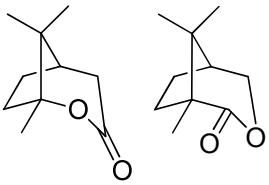
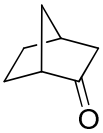
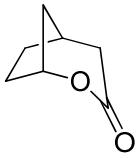
Table 22. Oxidation of cyclopentanone to δ-valerolactone.

Entry	Solvent	Catalyst	Yield [%]
1	[bmim]NTf_2	$BF_3 \cdot OEt_2$	95
2	[bmim]HSO_4	$BF_3 \cdot OEt_2$	80
3	[bmim]BF_4	$BF_3 \cdot OEt_2$	78
4	[bmim]OTf	$BF_3 \cdot OEt_2$	99
5	dichloromethane	$BF_3 \cdot OEt_2$	73
6	dichloromethane	$AlCl_3$	55
7	dichloromethane	$SnCl_3$	90
8	[bmim]NTf_2	$AlCl_3$	87
9	[bmim]NTf_2	$SnCl_3$	94

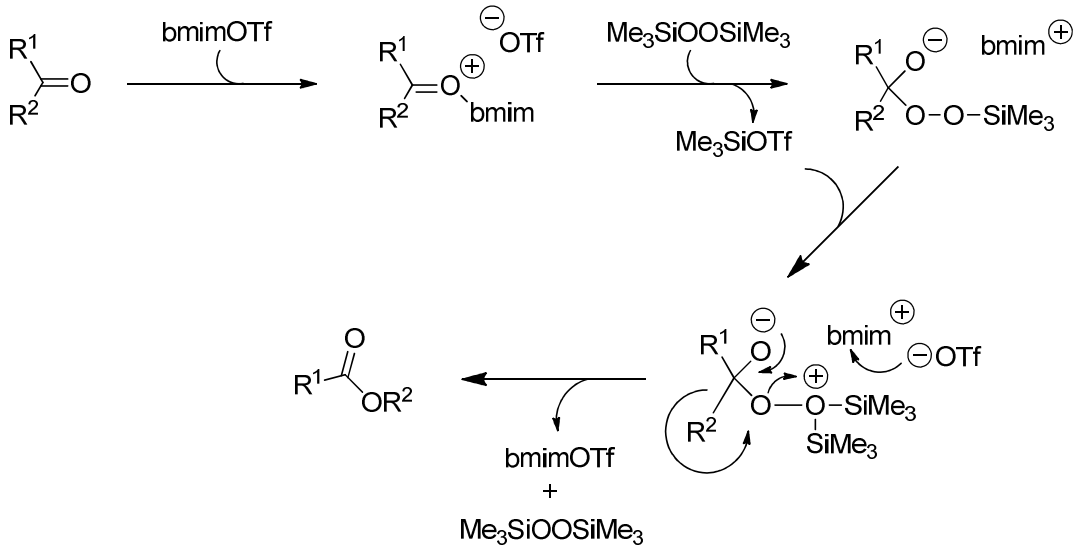
Reaction conditions: cyclopentanone (0.5 mmol), BTSP (1 mmol), catalyst (1 mmol), solvent (2 mL), reation time: 5 h, r.t., yield determined by GC.

Table 23. Oxidation of ketones in [bmim]OTf.

Entry	Ketone	Lactone	Time [h]	Temp. [℃]	Yield [%]
1			1	25	98

2			2	25	95
3			2	25	94
4			2	25	96
5			8	40	94
6			10	40	41
7			24	40	(87)
8			15	40	(89)
9			8	25	99

Reaction conditions: ketone (0.5 mmol), BTSP (1 mmol), [bmim]OTf (2 ml); yield determined by GC; isolated yields in parenthesis. [a] *dichloromethane (2 mL); NaOTf (1.1 mmol).*

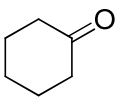
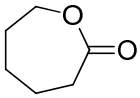
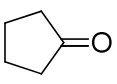
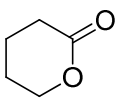
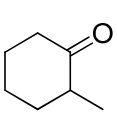
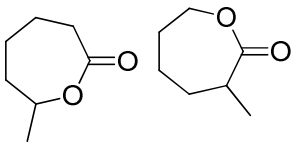


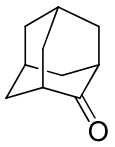
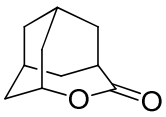
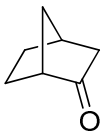
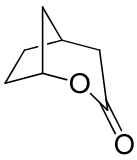
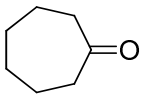
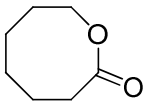
Scheme 11. Proposed reaction mechanism of the Baeyer-Villiger oxidation of ketones by BTSP in the presence of [bmim]OTf.

In further studies, Chrobok studied the Baeyer-Villiger reaction with molecular oxygen as an oxygen source in the presence of benzaldehyde[83], as this combination showed good results in previous examinations.[84] During this reaction benzaldehyde is converted to benzoic acid. The addition of a radial initiator such as 1,1'-azobis(cyclohexanecarbonitrile) (ACHN) increases the reaction rate of the lactonisation by a factor of four. The optimal concentration of ACHN was found to be 0.033 mol/L and the best substrate to benzaldehyde ratio was 1:2. The addition of Fe_2O_3 as a co-catalyst does not accelerate the reaction. The catalytic performance in different ionic liquids and with different substrates is summarized in Table 24.

The ionic liquids could be recovered via extraction methods after the reaction, this is possible, whether they are hydrophilic or hydrophobic. The same ionic liquids could be used for four runs without activity loss.

Table 24. Lactonisation of various ketones with oxygen[a].

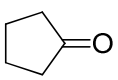
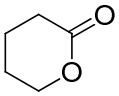
Entry	Ketone	Lactone	Solvent	Conversion [%]	Yield lactone [%]
1			$[bmp]NTf_2$	95	89
2	:	:	$[tmba]NTf_2$	95	88
3	:	:	$[bmim]BF_4$	90	85
4	:	:	$[emim]OSO_3Me$	85	76
5	:	:	$[bmim]CF_3COO$	80	72
6	:	:	[bmim]OTf	62	55
7	:	:	$[bmim]NTf_2$	96	90
8			$[bmim]NTf_2$	99	85
9			$[bmim]NTf_2$	99	95

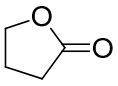
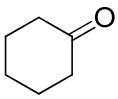
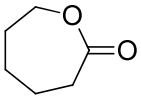
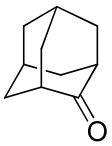
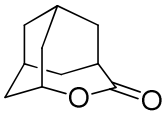
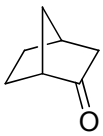
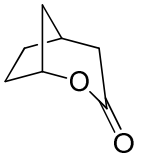
10			[bmim]NTf_2	100	96
11			[bmim]NTf_2	100	94
12			[bmim]NTf_2	49	40

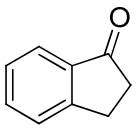
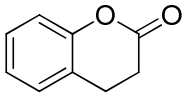
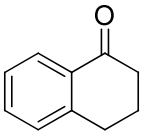
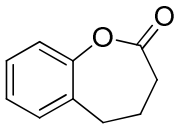
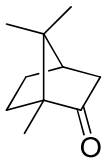
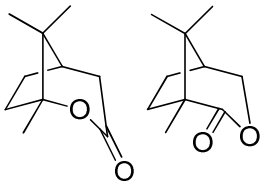
Reaction conditions: Ketone (3 mmol); benzaldehyde (6 mmol); ACHN (0.033 mol/L); solvent (2 mL); 90 ℃; yields determined by GC.

Another method to reuse ionic liquids is the heterogenization of [pmim]HSO_4 on a silica support (Scheme 12).[85] The tethering of the catalyst (HSO_4^-) is obtained via cation-anion interaction. The Baeyer-Villiger reaction was performed with H_2O_2 (68 %) at 50 ℃ in dichloromethane as solvent, the data are given in Table 25.

Table 25. Baeyer-Villiger reaction with different ketones and a heterogenized ionic liquid.

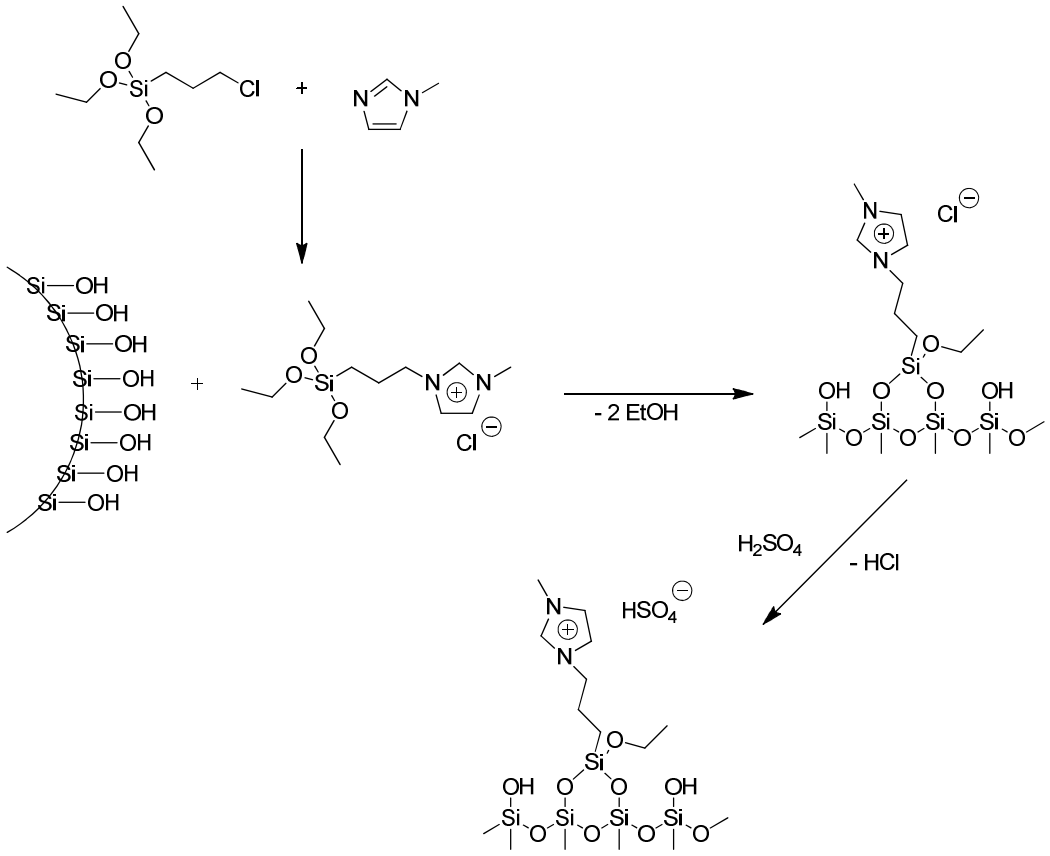
Ketone	**Lactone**	**Catalyst [g]**	**Conversion [%]**	**Yield [%]**
		-	31	6
:	:	0.4 (silica support)	30	5
:	:	0.4 ($pmimHSO_{4SiO2}$)	86	60

:	:	0.4 ($pmimHSO_{4SiO2}$)	75	55
:	:	0.4 ($pmimHSO_{4SiO2}$)	98	75
:	:	0.2 ($pmimHSO_{4SiO2}$)	60	45
:	:	0.6 ($pmimHSO_{4SiO2}$)	98	74
:	:	0.4 ($pmimHSO_{4SiO2}$)	98	65
:	:	0.4 ($pmimCl_{SiO2}$)	30	6
:	:	0.8 ($tbapHSO_{4SiO2}$)	95	72
		0.4 ($pmimHSO_{4SiO2}$)	100	96
		0.4 ($pmimHSO_{4SiO2}$)	86	64
		0.4 ($pmimHSO_{4SiO2}$)	95	(89)
		0.4 ($pmimHSO_{4SiO2}$)	95	(88)

		0.4 (pmimHSO$_{4SiO2}$)	81	(75)
		0.4 (pmimHSO$_{4SiO2}$)	78	(74)
		0.4 (pmimHSO$_{4SiO2}$)	64	60

Reaction conditions: Ketone (1 mmol); H_2O_2 (68 %); dry dichloromethane (2 mL); 50 ℃; yield determined by GC; isolated yields in parentheses.

Recycling experiments showed no loss of activity and 90 % of the catalyst could be recovered after each of the four runs.



Scheme 12. Heterogenization of [pmim]HSO_4 on a silica support.

1.7 Oxidation of nitrotoluene

The oxidation of nitrotoluene and derivatives to their corresponding nitrobenzoic acids with molecular oxygen in ionic liquids was first reported in 2009.[4] Shan *et al.* performed the oxidation in a biphasic system containing an aqueous sodium hydroxide solution and different ionic liquids. As catalyst for the oxidation of *para*-nitrotoluene (PNT), different metallo-phthalocyanine complexes were tested (Table 26). The special behavior of the chosen ionic liquid ([omim]BF_4), to be miscible with water at temperatures higher 70 °C and immiscible below, lead to an easy separation of product and catalyst. The reaction was performed at 90 °C in homogeneous phase. After cooling down the reaction mixture, the water and the ionic liquid phases separate, whereas the product is soluble only in the aqueous phase and catalyst and substrate in the ionic liquid. The catalyst was recycled by simple extraction methods and was reused for at least five more runs without loss of activity (Table 26, Entry 11: cat. used for 6 times). Other substrates used were *ortho*- (ONT), *meta*- (MNT), di-nitrotoluene (DNT) and toluene. As it can be seen from the data in Table 26, MNT and toluene show no activity due to their relatively low deprotonation ability in alkali aqueous solution which plays a major role in the reaction pathway towards benzoic acid.[86] The major role of NaOH can be seen in a decrease of the yield with decreasing NaOH concentration (compare Table 26, Entries 1 and 5).

Table 26. Oxidation of nitrotoluenes by molecular oxygen.

Entry	Substrate	Ionic liquid	Catalyst [mg]	NaOH [g]	$P(O_2)$ [MPa]	Yield [%]
1	PNT	$[omim]BF_4$	$Fe^{II}Pc$; 10	1.5	2	92
2	PNT	$[omim]BF_4$	$Fe^{II}Pc$; 10	1.5	2	89
3	PNT	$[omim]BF_4$	$Cu^{II}Pc$; 10	1.5	2	70
4	PNT	$[omim]BF_4$	$Fe^{II}Pc$; 5	1.5	2	85
5	PNT	$[omim]BF_4$	$Fe^{II}Pc$; 10	1	2	70
6	PNT	$[omim]BF_4$	$Fe^{II}Pc$; 10	1.5	2.5	93
7	PNT	$[omim]BF_4$	$Fe^{II}Pc$; 10	1.5	1.5	84
8	PNT	$[omim]Tf_2N$	$Fe^{II}Pc$; 10	1.5	2	13
9	PNT	$[dmim]BF_4$	$Fe^{II}Pc$; 10	1.5	2	72
10	PNT	-	$Fe^{II}Pc$; 10	1.5	2	-
11	PNT	$[omim]BF_4$	$Fe^{II}Pc$; 10	1.5	2	92
12	ONT	$[omim]BF_4$	$Fe^{II}Pc$; 10	1.5	2	93
13	MNT	$[omim]BF_4$	$Fe^{II}Pc$; 10	1.5	2	-
14	DNT	$[omim]BF_4$	$Fe^{II}Pc$; 10	1.5	2	93
15	Toluene	$[omim]BF_4$	$Fe^{II}Pc$; 10	1.5	2	-

Reaction conditions: 0.2 mmol substrate; 10 ml ionic liquid; 5 ml water; 90 ℃; 12 h.

1.8 Carbonylation

In 2008, ionic liquids were used as solvents for copper catalyzed carbonylation of methanol to dimethyl carbonate (DMC) by Liu and coworkers.[87] Besides DMC, the main product, three other by-products were detected: dimethoxymethane (DMM), dimethylether (DME) and methylformate. Amongst these byproducts, DME reaches

normally the highest yields. The different ionic liquids and catalysts as well as the space-time yield (STY), conversion and selectivities are listed in Table 27. The catalysis was usually performed with 1 mmol catalyst, 4 g MeOH, 2 g ionic liquid and 2.4 MPa CO and O_2 (ratio 2:1) at room temperature. A model system containing 1 mmol CuCl, 4 g MeOH, 2 g [bPy]BF_4 and 2.4 MPa CO/O_2 (ratio 2:1) at 120 ℃ was chosen to study different reaction parameters. After 4 h the conversion of MeOH stopped and no differences regarding selectivity were observed. Higher gas pressures (from 2.4 MPa to 6.0 MPa) of CO and O_2 lead to higher conversions of MeOH (from 19.8 % to 37.1 %) while the selectivity of DMC remained stable at nearly 100 %. With temperatures higher than 120 ℃, higher conversions could be reached, however, the selectivity of DMC also decreases. An increase of the ratio of CO to O_2 hampers the reaction more instead of increasing the selectivity of DMC.

Table 27. Oxidative carbonylation of methanol.

Catalyst	**Ionic liquid**	**Conversion [%]**	**Selectivity of DMC [%]**	**Selectivity of DMM [%]**	**Selectivity of DME [%]**	**STY [g(DMC)/ g(cat)·h]**
CuCl	-	9	97.3	2.8	-	2.3
CuCl	[bPy]BF_4	17	97.8	2.3	-	4.6
CuCl	[oPy]BF_4	17	98.3	1.8	-	4.6
CuCl	[bdmim]BF_4	14	99.2	0	-	3.8
CuCl	[bPy]Cl	14	87	0	9.7	3.5
CuCl	[bmim]Cl	4	70.3	5.3	25.8	0.8
CuCl	[emim]BF_4	7	81.2	5.3	14.5	1.5
CuCl	[omim]BF_4	9	93.5	2.4	4.5	2.3
CuCl	[bPy]PF_6	5	32.4	9.1	58.5	0.5

CuCl	[omim]PF_6	8	53.2	5.5	43	1.2
CuCl	[bdmim]PF_6	7	51.6	5	45	1
$CuCl_2 \cdot 2H_2O$	-	15	93.3	5.4	-	2.2
$CuCl_2 \cdot 2H_2O$	[bPy]BF_4	17	99.1	1	-	2.6
$CuBr_2$	-	11	90.1	9.2	1.3	1.2
$CuBr_2$	[bPy]BF_4	17	97.1	0.5	2.6	1.9
CuBr	-	9	96.9	3.4	-	1.6
CuBr	[bPy]BF_4	17	96.3	3.2	0.8	3.1
CuI	-	1	78.5	22.6	-	0.1
CuI	[bPy]BF_4	11	96.2	-	-	1.5

Reaction conditions: 1 mmol Cu catalyst; 4.0 g MeOH; 2.0 g ionic liquid; 2.4 MPa; p_{CO}/p_{O2} = 2:1; T = 120 °C; t = 2 h.

In 2010, Stricker *et al.* inserted the copper catalyst directly into the ionic liquid. [88] They prepared three different types of catalysts, tetrakis(1-dodecylimidazole)copper(I)hexafluorophosphate $[Cu(Im^{12})_4][PF_6]$, bis(1-dodecylimidazole)cuproniumdihalogenocuprate $[Cu(Im^{12})_2][CuX_2]$ and $[dmim]_n[CuX_{2n}]$ for the carbonylation of methanol. With the applied conditions, the catalysis showed better conversions and similar selectivities compared to the results of Liu and coworkers (Table 28).

Table 28. Synthesis of DMC.

Entry	Catalyst	Conversion [%]	Selectivity [%]
1	$[Cu(Im^{12})_4][PF_6]$	31	58
2	$[Cu(Im^{12})_2][CuCl_2]$	60	83
3	$[Cu(Im^{12})_2][CuBr_2]$	62	89
4	$[CuCl + 4\ Im^{12}]$	48	78

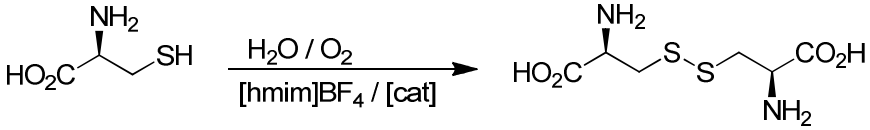
5	[CuCl + 4 Im[1]]	45	73

Reaction conditions: 5 mol% Cu (total); MeOH (30 mmol); p(O_2) (3 bar); p(CO) (50 bar); 4 h; 120 °C.

Another carbonylation was carried out by Ma *et al*. who synthesized methyl phenyl carbamate (MPC) from aniline.[89] With an immobilized catalyst consisting of selenium and [bmim]BF_4 on mesoporous silica conversions higher than 74 % were obtained. The selectivity was 99 % and the catalyst could be reused for four times without loss in activity.

1.9 Oxidation of cysteine

In 2010, Shan *et al*. reported the catalytic oxidation of cysteine to cystine with iron-, and copper-phthalocyanine complexes in the presence of molecular oxygen in the ionic liquid [hmim]BF_4 (Scheme 13).[5]



Scheme 13. Oxidation of cysteine to cystine.

The yields of cystine in dependence of different catalyst types and concentrations as well as of varying oxygen pressure are given in Table 28. The iron(II) catalyst showed the best performance and oxygen pressure above 2 MPa leads to increase of activity. This is presumably a consequence of a limited solubility of oxygen in ionic liquids. Without ionic liquids, the reaction gave only 13 % yield, demonstrating the effect of this reaction medium. The catalysts were recycled by making use of the temperature

dependent miscibility of ionic liquids with water (compare **Oxidation of nitrotoluene**). The miscibility at temperatures higher 80 °C lead to a homogeneous phase of aqueous solution and ionic liquid in which the catalysis took place. After cooling down the phases separated and the educt remained in the water phase while the catalyst is in the ionic liquid phase. The solid product was filtered off. The sixth catalytic run (Table 29, Entry 11) showed almost the same activity as the first one (Table 29, Entry 1).

Table 29. Oxidation of cysteine to cystine.

Entry	Ionic liquid [g]	Catalyst [mg]	$p(O_2)$ [MPa]	Yield [%]
1	[hmim]BF_4 (1)	$Fe^{II}Pc$ (10)	2	98
2	[hmim]BF_4 (1)	$Fe^{II}Pc$ (10)	2	89
3	[hmim]BF_4 (1)	$Cu^{II}Pc$ (10)	2	82
4	[hmim]BF_4 (1)	$Fe^{II}Pc$ (15)	2	98
5	[hmim]BF_4 (1)	$Fe^{II}Pc$ (5)	2	70
6	[hmim]BF_4 (1)	$Fe^{II}Pc$ (10)	2.5	98
7	[hmim]BF_4 (1)	$Fe^{II}Pc$ (10)	1.5	84
8	[hmim]Tf_2N (1)	$Fe^{II}Pc$ (10)	2	23
9	[dmim]BF_4 (1)	$Fe^{II}Pc$ (10)	2	32
10	-	$Fe^{II}Pc$ (10)	2	14
11	[hmim]BF_4 (1)	$Fe^{II}Pc$ (10)	2	96

Reaction conditions: cysteine (2 mmol); water (4 mL); T = 80 °C; t = 12 h.

1.10 Oxidation of cyclohexane

The oxidation of cyclohexane with metal-containing zeolits was studied by Wang *et al.* using TS-1 (titanium silicate) and various ZSM-5 zeolits.[90, 91] The oxidation was carried out with TBHP as oxidant because H_2O_2 lead to low conversions (Table 30). The yield displays a mixture of cyclohexanol, cyclohexanone and with ZSM-5 catalysts cyclohexyl hydroperoxide (CHHP). Temperature screenings revealed 90℃ as the optimal temperature and the best ratio of substrate and oxidant was found to be 1:2. Iron turned out to be the most active metal for the oxidation of cyclohexane and recycling of the catalyst by decantation lead to no decrease in activity after four runs.

Table 30. Oxidation of cyclohexane.

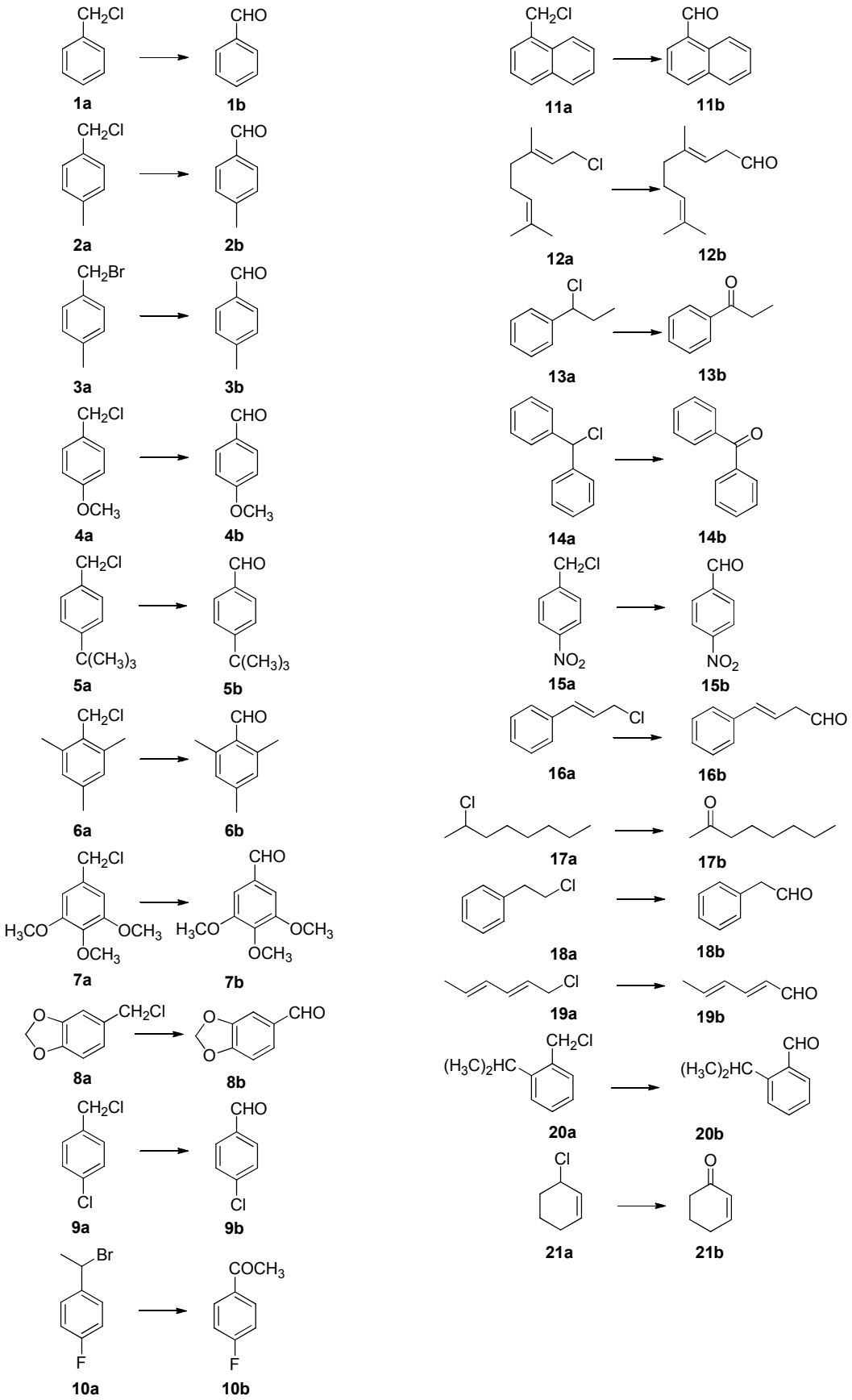
Entry	Catalyst	Solvent	Yield [%]
1	TS-1	Acetone	3
2	TS-1	-	1
3	TS-1	[emim]BF_4	7
4	TS-1	[emim]BF_4	10
5	TS-1	[emim]BF_4	13
6	TS-1	[emim]BF_4	13
7	HZSM-5	-	1

8	HZSM-5	Acetone	2
9	FeZSM-5	Acetone	3
10	HZSM-5	[emim]BF_4	15
11	NiZSM-5	[emim]BF_4	15
12	CoZSM-5	[emim]BF_4	14
13	MnZSM-5	[emim]BF_4	15
14	FeZSM-5	[emim]BF_4	21
15	CuZSM-5	[emim]BF_4	10

Reaction conditions: 0.15 g catalyst; 27.8 mmol cyclohexane; 55.6 mmol TBHP (80 % in H_2O); 5 mL ionic liquid; 90 °C.

1.11 Oxidation of halides

The oxidation of halides to ketones and aldehydes with H_5IO_6 proceeded better if ionic liquids were doted to the reaction mixture (Table 31).[92] Further studies dealt with V_2O_5 as catalyst in ionic liquids (Table 32).[93] The different oxidized species for both ways are shown in Scheme 14.



Scheme 14. Oxidation of various halides.

Table 31. Oxidation of halides in ionic liquids.

Entry	Ionic liquid	Product	Time [h]	Yield [%]
1	-	**1b**	4	42
2	[bmim][$FeCl_4$]	**1b**	2	75
3	[hmim][$FeCl_4$]	**1b**	2	78
4	[omim][$FeCl_4$]	**1b**	2	83
5	[dmim][$FeCl_4$]	**1b**	2	91
6	[C_{12}mim][$FeCl_4$]	**1b**	2	94
7	[C_{12}mim][$FeCl_4$]	**2b**	1.5	93
8	[C_{12}mim][$FeCl_4$]	**3b**	1.5	93
9	[C_{12}mim][$FeCl_4$]	**4b**	1.5	95
10	[C_{12}mim][$FeCl_4$]	**5b**	1.5	96
11	[C_{12}mim][$FeCl_4$]	**6b**	1.5	98
12	[C_{12}mim][$FeCl_4$]	**7b**	1.5	98
13	[C_{12}mim][$FeCl_4$]	**8b**	1.5	95
14	[C_{12}mim][$FeCl_4$]	**9b**	2	92
15	[C_{12}mim][$FeCl_4$]	**10b**	2.5	91
16	[C_{12}mim][$FeCl_4$]	**11b**	1.5	97
17	[C_{12}mim][$FeCl_4$]	**12b**	2	96

18	$[C_{12}mim][FeCl_4]$	**13b**	2	93
19	$[C_{12}mim][FeCl_4]$	**14b**	2.5	95
20	$[C_{12}mim][FeCl_4]$	**15b**	2.5	90
21	$[C_{12}mim][FeCl_4]$	**16b**	2	94
22	$[C_{12}mim][FeCl_4]$	**17b**	3	88
23	$[C_{12}mim][FeCl_4]$	**18b**	3	90

Reaction conditions: organic halide (10 mmol); H_5IO_6 (11 mmol); 30 ℃; ionic liquid (0.4 mmol).

Table 32. Oxidation of organic halides with H_5IO_6/V_2O_5.

Entry	Catalyst	Ionic liquid	Product	Time [h]	Yield [%]
1	V_2O_5	-	**2b**	10	53
2	-	$[bmpy]PF_6$	**2b**	6	48
3	V_2O_5	$[bmim]BF_4$	**2b**	7	74
4	V_2O_5	[bmim]Cl	**2b**	8	68
5	V_2O_5	[hmim]OTf	**2b**	6	76
6	V_2O_5	$[hmim]PF_6$	**2b**	6	83
7	V_2O_5	$[bpy]PF_6$	**2b**	3	89
8	V_2O_5	$[bmpy]PF_6$	**2b**	3	97
9	V_2O_5	$[bmpy]PF_6$	**1b**	3	92

10	V_2O_5	[bmpy]PF_6	**3b**	5	93
11	V_2O_5	[bmpy]PF_6	**4b**	3	98
12	V_2O_5	[bmpy]PF_6	**5b**	3	96
13	V_2O_5	[bmpy]PF_6	**6b**	3	98
14	V_2O_5	[bmpy]PF_6	**7b**	3	99
15	V_2O_5	[bmpy]PF_6	**8b**	3	96
16	V_2O_5	[bmpy]PF_6	**9b**	6	89
17	V_2O_5	[bmpy]PF_6	**10b**	8	87
18	V_2O_5	[bmpy]PF_6	**11b**	3	96
19	V_2O_5	[bmpy]PF_6	**12b**	3	93
20	V_2O_5	[bmpy]PF_6	**13b**	6	91
21	V_2O_5	[bmpy]PF_6	**14b**	6	94
22	V_2O_5	[bmpy]PF_6	**15b**	10	87
23	V_2O_5	[bmpy]PF_6	**16b**	3	92
24	V_2O_5	[bmpy]PF_6	**17b**	24	63
25	V_2O_5	[bmpy]PF_6	**18b**	24	75
26	V_2O_5	[bmpy]PF_6	**19b**	3	90
27	V_2O_5	[bmpy]PF_6	**20b**	3	95
28	V_2O_5	[bmpy]PF_6	**21b**	6	89

Reaction conditions: Organic halide (10 mmol); V_2O_5 (0.3 mmol); H_5IO_6 (12 mmol); ionic liquid (5 mL); 50 ℃.

1.12 α-Tosyloxilation of ketones

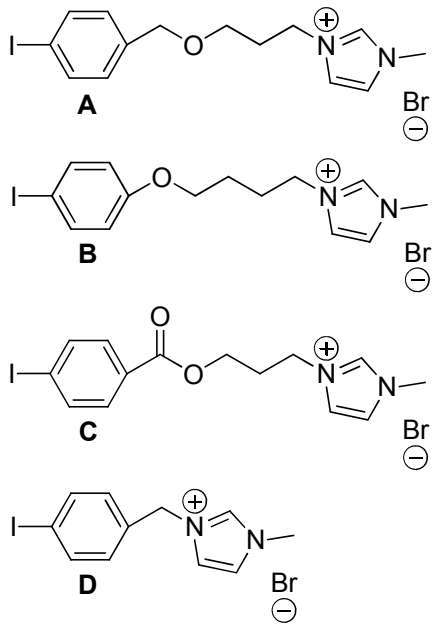
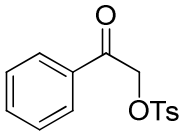
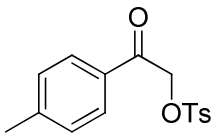
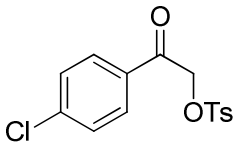
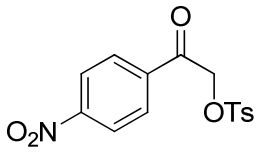
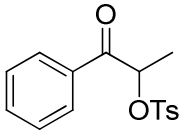
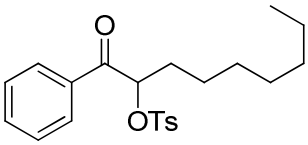
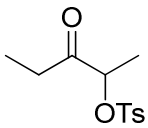
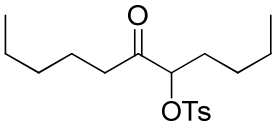


Figure 12. IL-supported PhI **A**-**D**.

The oxidation of various ketones was carried out in [emim]OTs as solvent as well as small amounts of IL-supported PhI **A**-**D** (Figure 12) together with *m*-chloroperbenzoic acid (MCPBA) and *p*-toluenesulfonic acid (PTSA · H_2O).[94] The different products and yields are summarized in Table 33. After extraction of the products and oxidants the ionic liquids were reused twice with small losses in activity.

Table 33. Tosyloxidation of ketones.

Entry	Product	Yields [%]			
		A	**B**	**C**	**D**
1		82	83	80	70

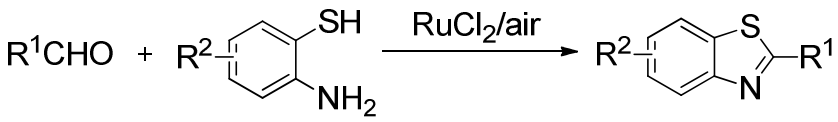
2		60	58	39	48
3		77	76	67	67
4		65	70	72	71
5[a]		83	75	63	70
6[a]		81	75	52	56
7		57	64	61	69
8		57	66	62	53

Reaction conditions: Substrate (1 mmol); MCPBA (1.3 equiv); PTSA · H_2O (1.1 equiv); ***A****,* ***B****,* ***C*** *or* ***D*** *(0.1 equiv); [emim]OTs (2 mL); 50 ℃; 5 h;* [a] *PTSA · H_2O (0.5 equiv).*

1.13 Synthesis of thiazoles

Additionally to tosyloxylation the condensation of acetophenone and thioamides to thiazoles was studied by Akiike *et al*. Applying the same conditions as used in the tosyloxilation, yields between 37 % and 72 % were reached.[94]

Wang *et al.* studied the oxidative reaction of 2-aminothiophenol and aldehydes to thiazoles with air as oxidant (Scheme 15).[95]



Scheme 15. Oxidative condensation towards thiazoles.

The experimental data is summarized in Table 34. Extraction of the ionic liquid with diethyl ether and reuse of the IL for three times lead only to a slight decrease of yield. Moreover, the authors applied their catalytic procedure to synthesize 5-heteroaryl-substituted-2'-deoxyuridines.

Table 34. Thiazole formation.

Entry	R^1	R^2	Solvent	Catalyst (0.05 eq)	Time [h]	Yield [%]
1	C_6H_5	H	THF	$RuCl_3$	3	68
2	C_6H_5	H	CH_3CN	$RuCl_3$	3	62
3	C_6H_5	H	Toluene	$RuCl_3$	3	50
4	C_6H_5	H	dichloromethane	$RuCl_3$	3	61
5	C_6H_5	H	$[bmim]PF_6$	-	3	trace
6	C_6H_5	H	:	$InCl_3$	2	trace
7	C_6H_5	H	:	$CeCl_3$	2	trace
8	C_6H_5	H	$[bmim]BF_4$	$RuCl_3$	0.5	75
9	C_6H_5	H	$[bmmim]PF_6$	:	:	63

10	C_6H_5	H	[bmim]PF_6	:	:	78
11	C_6H_5	H	:	:	:	83
12	4-BrC_6H_4	H	:	:	:	85
13	4-$CH_3OC_6H_4$	H	:	:	:	80
14	4-CNC_6H_4	H	:	:	:	85
15	2-BrC_6H_4	H	:	:	1	81
16	2-$NO_2C_6H_4$	H	:	:	0.5	82
17	2-ClC_6H_4	H	:	:	1	81
18	3-$NO_2C_6H_4$	H	:	:	0.5	86
19	3-BrC_6H_4	H	:	:	:	84
20	3-$CH_3C_6H_4$	H	:	:	:	79
21	C_6H_5	4-Cl	:	:	:	83
22	4-$NO_2C_6H_4$	4-Cl	:	:	:	88
23	4-BrC_6H_4	4-Cl	:	:	:	83
24	4-$CH_3OC_6H_4$	4-Cl	:	:	:	82
25	3-ClC_6H_4	4-Cl	:	:	:	83
26	3-BrC_6H_4	4-Cl	:	:	:	80
27	2-$NO_2C_6H_4$	4-Cl	:	:	:	80
28	2-ClC_6H_4	4-Cl	:	:	1	80
29	2-BrC_6H_4	4-Cl	:	:	1	79

30	N-propyl	H	:	:	2	75
31	N-propyl	4-Cl	:	:	2	76
32	C_6H_5	3-Cl	:	:	4	62
33	4-$NO_2C_6H_4$	3-Cl	:	:	3	75
34	3-$CH_3C_6H_4$	3-Cl	:	:	4	60
35	2-$NO_2C_6H_4$	3-Cl	:	:	6	43
36	4-BrC_6H_4	4-CH_3	:	:	2	80
37	3-$CH_3C_6H_4$	4-CH_3	:	:	2	78

Reaction conditions: Starting materials (1 mmol); solvent (1 mL).

1.14 Conclusion and perspective

Clearly, ionic liquids attract more and more attention in many fields of catalytic applications. This broadening attractivity ranges from well examined reactions, like the oxidative desulfurization of organic compounds, to more uncommon reactions, e.g. the oxidation of oximes. In any case, ionic liquids are usually able to improve the performance of the catalytic reaction. They could therefore certainly act as substitutes for conventional organic solvents, in some cases even as “catalysts” themselves or as extraction media for the separation of products. The transfer of ionic liquids from lab-scale application to industrial processes would be desirable especially from the “green” chemical point of view and will probably happen in the future due to their significant advantages as well. Particularly the recycling of the catalytic system might play a key role with regard to sustainability, provided IL is environmentally neutral or benign.

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2. Methyltrioxorhenium

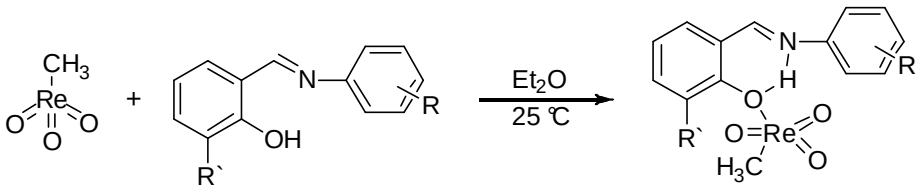
This chapter originated from the following publication:

Daniel Betz, Fritz E. Kühn, in: *e-Eros (Encyclopedia of Reagents for Organic Synthesis, L. A. Parquette (ed.), Wiley-VCH*, **2010,** 1-8.

2.1 Epoxidation of Alkenes

The use of aromatic N-donor ligands in significant excess (ca.10–12:1) together with MTO leads to higher activities and selectivities in epoxidation catalysis than with MTO alone.[1] This behavior is displayed both with mono- and bidentate aromatic Lewis bases with N-donor ligands.[2]

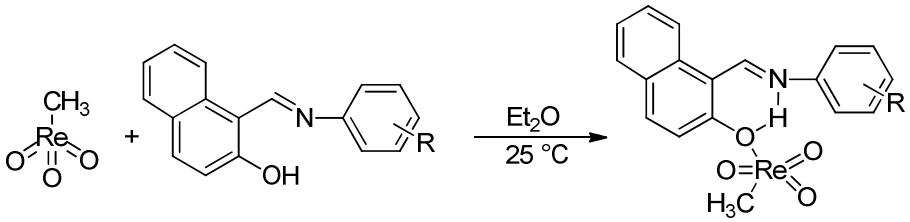
In the meantime, many N-ligand adducts of MTO have been isolated, characterized and applied for the epoxidation of olefins as catalysts.[3] Other donor adducts of MTO, despite being mentioned sporadically in the literature, have never been examined to the same extent with respect to their applicability as epoxidation catalysts.[4] Rhenium complexes with Schiff-base ligands derived from salicylaldehyde and mono- or diamines have received attention due to their applications in catalysis and nuclear medicine. Re(V) oxo complexes bearing Schiff-base ligands have been investigated extensively.[5] Kühn *et al.* described the following Schiff-base adducts of MTO (Scheme 1) and applied them as epoxidation catalysts.[6]



R`= H, R = H; R`= H, R = *p*-CH_3; R`= H, R = *p*-Cl;
R`= H, R = *p*-$OCH_3$; R`= -OCH_3, R = *p*-CH_3

Scheme 1. Formation of a MTO/Schiff-base complex.

The -OCH_3 group on the Schiff base seems to destabilize the resulting complex under oxidative conditions, other Schiff bases lead to active and highly selective epoxidation catalysts. An excess of ligand, however, always leads to rapid decomposition of the catalyst. Given the ready availability and stability of the title complexes, together with the good catalytic activity and high selectivity of some of them, they appear to be good alternatives to less stable MTO/N-donor complexes as epoxidation catalysts. The Schiff base adducts of MTO can also be prepared and applied in situ. In contrast to N-donor adducts, no pronounced ligand excess is necessary to achieve high yields and selectivities in olefin epoxidation catalysis. In addition to the compounds of Scheme 1 other Schiff-base complexes (Scheme 2) have been synthesized and investigated on their catalytic activity.[7]

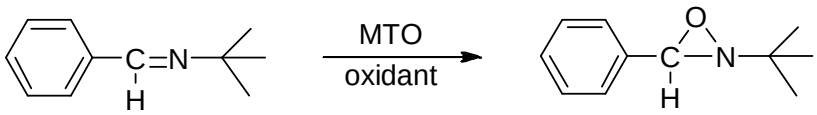


R = H; R = *p*-CH_3; R = *o*-CH_3 + *m*-CH_3; R = *o*-Cl

Scheme 2. Schiff-based complexes investigated by Kühn *et al.*

2.2 Oxidation of Aldimines

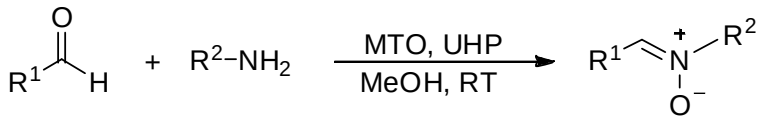
MTO were found to be an efficient catalyst for the oxygenation of various aldimines to the corresponding oxaziridines (Scheme 3) in excellent yields under mild conditions using solid peroxides like UHP, SPC and SPB as oxidants. Among the rhenium-based catalysts studied, MTO was found to be the most efficient in this reaction. The use of solid peroxides offers nearly water free atmosphere, making the reactions more selective towards the oxaziridines rather than ring opening products.[8]



Scheme 3. Oxidation of an aldimine.

2.3 Oxidation of primary Amines

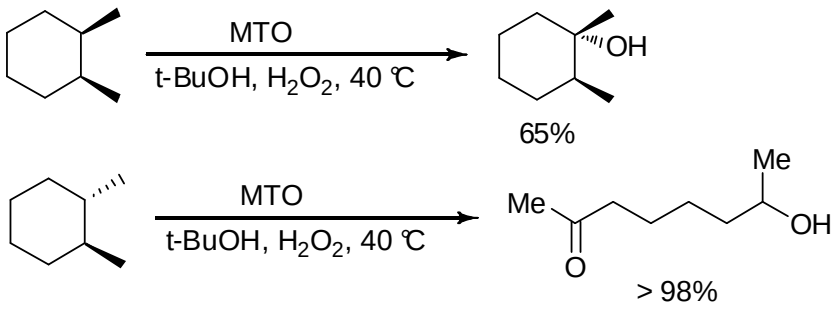
Goti *et al.* described a one-pot condensation/oxidation of primary amines and aldehydes (Scheme 4) using urea–hydrogen peroxide (UHP) as stoichiometric oxidant in the presence of methyltrioxorhenium as catalyst affords nitrones in a simple and regioselective manner. From a sustainability point of view, this one-pot synthesis is simple to perform, takes place under mild conditions, has high atom economy and releases water as the only by-product.[9]



Scheme 4. MTO catalyzed formation of nitrones.

2.4 Oxidation of Methyl substituted Cyclohexane

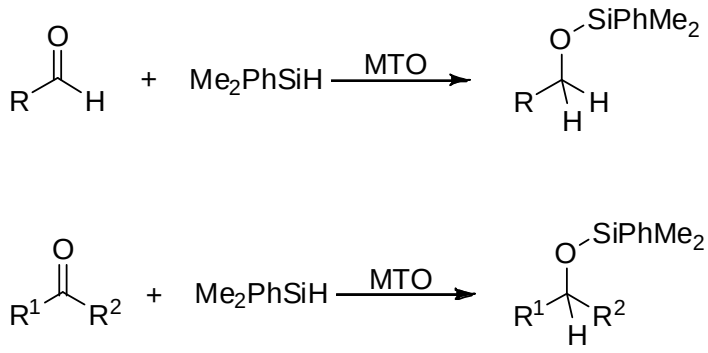
Methyltrioxorhenium is a versatile catalyst for the oxidative fictionalization of cyclohexane derivatives with H_2O_2 as oxygen donor. Interestingly, there is a difference between the two stereoisomeric cis- and trans- configurations (Scheme 5).[10]



Scheme 5. Functionalization of cyclohexane derivatives.

2.5 Hydrosilylation of aliphatic and aromatic Aldehydes

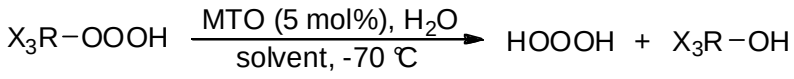
In 2003, Toste and co-workers reported the use of the dioxo rhenium(V) derivative $[ReO_2I(PPh_3)_2]$ as catalyst for the hydrosilylation of aldehydes and ketones.[11] Based on these results Romão et al. investigated the activity of Re(VII) species in the same reaction. They pointed out that methyltrioxorhenium(VII) is the most active and versatile catalyst for the hydrosilylation of aliphatic and aromatic aldehydes and ketones (Scheme 6).[12] Methyltrioxorhenium is an effective catalyst reaching total conversion of the aldehyde to the silylated ether after 5 h at 80 ℃.



Scheme 6. Hydrosilylation of aldehydes and ketones.

2.6 Transformation of Hydrotrioxides

Hydrotrioxides, ROOOH, have already been found to be key intermediates in the reaction of ozone with alcohols, ethers, acetals, hydrocarbons, and organometallic hydrides.[13] Corey *et al.* have presented evidence that triethylsilyl hydrotrioxide, $Et_3SiOOOH$, generated by the low-temperature ozonization of triethylsilane, is an excellent source of singlet oxygen ($O_2(^1\Delta_g)$).[14] Tuttle and co-workers found that, under certain conditions, HOOOH is also formed in modes yields during the decomposition of some silyl hydrotrioxides in organic oxygen bases as solvents.[15] The same group reported that HOOOH is formed nearly quantitatively in the low-temperature MTO-catalyzed transformation of dimethylphenylsilyl hydrotrioxide in various solvents (acetone-d_6, methyl acetate, *tert*-butyl methyl ether) (Scheme 7). They found that other silyl hydrotrioxides, as well as some acetyl hydrotrioxides investigated, react similarly.[16]



R = Si, C; X = Me, Et, n-Bu, Ph

Scheme 7. Transformation of hydrotrioxides.

2.7 References

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3. Epoxidation of α-Pinene Catalyzed by Methyltrioxorhenium(VII): Influence of Additives, Oxidants and Solvents

This chapter originated from the following publication:

Typhène Michel, Daniel Betz, Mirza Cokoja, Volker Sieber, Fritz E. Kühn

J. Mol. Catal. A: Chem. **2011**, *340*, 9-14.

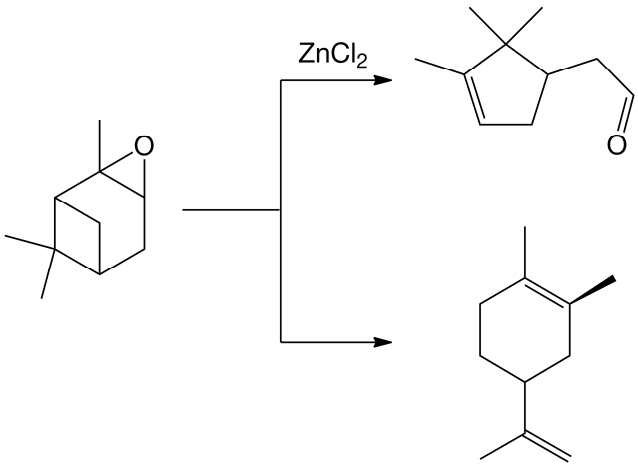
3.1 Abstract

The epoxidation of α-pinene employing methyltrioxorhenium as catalyst is examined. The influence of mono- and bidentate Lewis basic additives (e.g. ^{t}butylpyridine, 4,4'-dimethyl-2,2'-bipyridine, Schiff-bases) is investigated. Additionally the impact of the oxidant (H_2O_2 in water or urea-hydrogen peroxide (UHP)) on the catalytic performance is studied. The effect of the solvent is also examined in order to determine the optimal conditions for the epoxidation of α-pinene. The best and straightforwardly applicable result is obtained when a ratio α-pinene : MTO : UHP : ^{t}butylpyridine of 200 : 1 : 600 : 40 is applied at 0 °C in nitromethane. In this case, α-pinene oxide is formed with 95 % yield after 3 h with a turnover frequency (TOF) of 610 h^{-1}.

3.2 Introduction

α-Pinene is a monoterpene which is an important ingredient of some flavoring plants such as mint, lavender and ginger. It is extracted from turpentine oil (350.000 t/year), which is a product of the paper pulp industry.[1] α-Pinene is

particularly utilized as starting material in terpene chemistry to obtain flavors and fragrances. It is also an intermediary species in the synthesis of Taxol®, an anticancer drug.[2-4] The epoxidized product of α-pinene, α-pinene oxide is used to synthesize campholeic aldehyde an intermediate in the synthesis of the sandalwood fragrance.[1] α-Pinene oxide is additionally employed in the synthesis of *trans*-carveol, which is an important component for perfume bases and food flavor compositions (Scheme 1).[5]



Scheme 1. Reaction of α-pinene oxide to campholeic aldehyde and to *trans*-carveol.

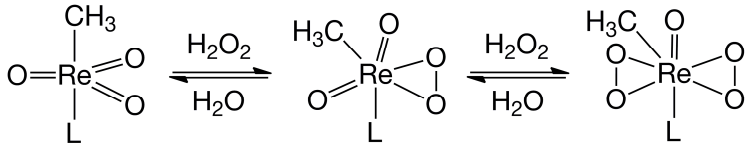
The epoxidation of α-pinene in homogeneous phase has been studied in some detail in the past. Among the homogeneous catalysts applied for this reaction, methyltrioxorhenium[6-8] (MTO) is among the most widely used ones. However, in almost all cases the epoxidation suffers from either low conversion or low yield because of the formation of α-pinene diol as byproduct. Using the MTO-Lewis base adducts as catalysts does neither prevent diol formation nor does it improve the epoxide yields.[9-10] A change of the oxidant to urea hydrogen peroxide (UHP) and addition of the base (+)-2-aminomethylpyrrolidine does not lead to a better selectivity according to the literature reports.[11] The reported conversion is still

very low (< 7 %), when MTO is anchored to a polymers such as poly(vinylpyridine) (PVP) or poly(vinylpyridine N-oxide) (OPVP).[12] Although some reports claim that with MTO as catalyst, nearly quantitative yields of α-pinene oxide can be reached[13], we were unable to reproduce these results. Accordingly, the need for a straightforward, unproblematic procedure towards α-pinene oxide still remains. A wide range of other metals has been applied for the epoxidation of α-pinene. Molybdenum(VI) complexes have been studied for this reaction.[14-20] Co(III) supported material on hexagonal mesoporous silica (HMS) or Co supported by zeolite (NaCoY93) were investigated.[21-22] The synthesis of α-pinene oxide was also carried out with [Cu(pyridine)$_2$Cl$_2$] and the[CrO_3(2,2'-bipyridine)] as catalysts.[23] Lipase activity towards epoxidation of α-pinene has been studied.[24-25] [Ru(salophen)Cl-PSI] (PSI = polystyrene-bound imidazole) with $NaIO_4$ has also been employed for the formation of α-pinene oxide.[26] The epoxidation of α-pinene using (N,N-bis(salicylidene)ethylenediamine)Ti-salan complex is reported to lead to 85 % epoxide yield after 7 h reaction time.[27] Based on these results, we set out to re-examine MTO as catalyst in the presence of Lewis basic additives, since such MTO based systems proved to be superior to other catalyst systems in many epoxidation reactions, provided optimal conditions were found.

Additionally, MTO requires H_2O_2 as oxidant (Scheme 3), which has the advantage of being environmentally benign and cheap in comparison to other conventional oxidants used in epoxidations, e.g. meta-chloroperoxybenzoic acid (mCPBA).

Nevertheless, due to the high Lewis acidity of the Re(VII) center in presence of H_2O (the by-product formed during the oxidation), ring opening of (sensitive) epoxides to diols occurs. It was shown that employing Lewis basic additives (Lewis base ligands) decreases the acidity of the rhenium center[8] and allows the synthesis of sensitive epoxides.[9, 28-33] Particularly the use of pyridine and some of

its derivatives, as well as Schiff base ligands leads in many cases to both good activity and high selectivity towards epoxidation of olefins.[34-42]



Scheme 2. Reaction of a MTO-Lewis base complex with H_2O_2 forming a mono- and bis(peroxo) complex, L=electron donor ligand.[9, 28-33]

In this work, we investigated the optimal and reproducible conditions for the epoxidation of α-pinene with MTO as catalyst. For this purpose, several mono- and bidentate base adducts were applied. Additionally, to eliminate potential problem sources, the effect of using different oxidants and reaction media, including ionic liquids, was examined.

3.3 Experimental

Starting materials

Hydrogen peroxide was used 35 % in water (Aldrich). (1R)-(+)-α-pinene was purchased from Aldrich. Urea Hydrogen Peroxide (UHP) contained 35 wt. % H_2O_2 (Acros organics). Methyltrioxorhenium and the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM]PF_6 were synthesized according to literature procedures.[43-46]

Gas chromatography

Gas chromatography was performed using a DB23 column (30 m, 0.25 mm, 0.25 µm film thickness). The isothermal temperature profile is: 60 ℃ for the first 2

min, followed by a 10 ℃/min temperature gradient to 105 ℃ for 10 min, then by 4 ℃/min to 155 ℃ and finally 20 ℃/min to 260 ℃. The injector temperature was 320 ℃. Chromatography grade helium was used as the carrier gas.

Epoxidation of α-pinene in different solvents

Method A:

MTO was dissolved in the solvent and the solution brought to the appropriate reaction temperature. The ligand, the two standards (mesitylene: 100 µL and ethylbenzene: 100 µL), and the oxidant (H_2O_2 35 % or UHP) were added to the solution. α-Pinene was then added to the reaction. The different catalyst:ligand:oxidant ratios are given in Table 1. Samples were taken after 5 min, 10 min, 15 min, 30 min, 60 min, 90 min, 3 h, 5 h and 24 h. For each sample, 200 µL of the reaction mixture was taken and mixed with a catalytic amount of MnO_2 to decompose excess H_2O_2. The mixture was then filtered through $MgSO_4$ in order to remove H_2O. CH_2Cl_2 (1.8 mL) was then added and the solution was analyzed by GC or stored in the freezer for some hours.

Table 1. Summary of the different ratios employed in the epoxidation of α-pinene.

Entry	α-pinene ratio	MTO ratio (mmol)	^{t}butylpyridine ratio	H_2O_2 ratio	CH_2Cl_2 (mL)
1	100	1 (0.048)	5	300	2.3
2	100	1 (0.048)	10	300	2.3
3	100	1 (0.048)	20	300	2.3
4	100	1 (0.048)	20	150	1.2

In this method, the samples are not stable, consequently, it is important to measure them directly in GC or to store them in the freezer. It is not possible to do several reaction in the same time. Consequently, a new method was found to stabilized the GC samples and allowed measurement over night.

Method B:

MTO was dissolved in the solvent and the solution brought to the appropriate reaction temperature. The ligand, the two standards (mesitylene: 250 µL and ethylbenzene: 250 µL), and the oxidant (H_2O_2 35 % or UHP) were added to the solution. α-pinene was then added to the reaction. The different catalyst:ligand:oxidant ratios are given in Table 2. Samples were taken after 5 min, 30 min, 2 h, 5 h and 24 h. For each sample, 1.5 mL of the reaction mixture was taken and mixed with a catalytic amount of MnO_2 to decompose excess H_2O_2. The mixture was then filtered and extract 4 times with 1.5 mL of water to remove MTO. The organic layer was then dried over $MgSO_4$ and filtered. 0.18 mL (for H_2O_2) or 0.2 mL (for UHP) was taken from this solution and diluted with 1.3 mL of CH_2Cl_2. The solution was then analyzed by GC.

Table 2. Summary of the different ratios employed in the epoxidation of α-pinene.

Entry	α-pinene ratio	MTO ratio (mmol)	Ligand[a] ratio	H_2O_2 ratio	Solvent[b] (mL)
1	100	1 (12)	20	150	7.6
2	100	0.5 (6)	10	150	7.6
3	100	0.1 (1.2)	2	150	7.6
4	100	1 (6)	20	150	7.8

Entry	α-pinene ratio	MTO ratio (mmol)	Ligand[a] ratio	UHP ratio	Solvent[b] (mL)
5	100	1 (12)	20	150	8.4
6	100	0.5 (6)	20	150	8.4
7	100	1 (12)	20	300	8.4
8	100	0.5 (6)	20	300	8.4

[a] ^{t}butylpyridine, 4,4'dimethyl-2,2'-bipyridine or two Schiff-bases. [b] CH_2Cl_2, $MeNO_2$, $CHCl_3$ or THF.

Epoxidation of α-pinene in ionic liquids

MTO (0.024 mmol) and ^{t}butylpyridine (5 equiv.) were dissolved in 1-butyl-3-methylimidazoliumhexafluorophosphate ([bmim]PF_6) (0.2 mL). In a separate flask, mesitylene (100 µL), ethylbenzene (100 µL) and α-pinene (100 equiv.) were mixed together and a blank sample was taken from this solution. UHP or aqueous H_2O_2 (300 equiv.) was then added to the ionic liquid followed by the solution of α-pinene. The sampling time is the same as for conventional solvents. At defined times, 41 µL of the organic phase was poured in a vial containing MnO_2 in order to destroy excess oxidant, dried over $MgSO_4$ and filtered. 2 mL of CH_2Cl_2 were then added and the sample was analyzed by GC.

3.4 Results and Discussion

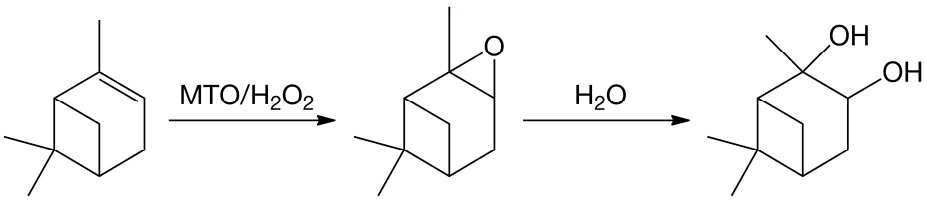
Optimization of the conditions for the epoxidation of α-pinene

a) Lewis base concentration and temperature effects

In a previous work, optimal conditions for cyclooctene epoxidation with the

system MTO/^{t}butylpyridine/H_2O_2 were determined.[35] The best result was obtained when a molar ratio cyclooctene :MTO : ^{t}butylpyridine : H_2O_2 of 100 : 1 : 5 : 300 in CH_2Cl_2 at 25 ℃ was applied.

This condition was applied to the epoxidation of α-pinene. However, the formation of α-pinene diol was observed. From this observation it was deduced that α-pinene oxide appears to be more acid sensitive than cyclooctene oxide, being easily transformed to α-pinene diol in the presence of MTO and water (Scheme 3).



Scheme 3. Reaction from α-pinene to α-pinene diol in presence of MTO/H_2O_2 and water.

Accordingly, the Lewis acitity of the system has to be reduced by addition of a propper Lewis-base. Due to the beneficial effects of excess Lewis-base, originating from the weak Re-N interaction.[47] An excess of ^{t}butylpyridine was applied. To strengthen the base effect the reaction temperature was kept low.

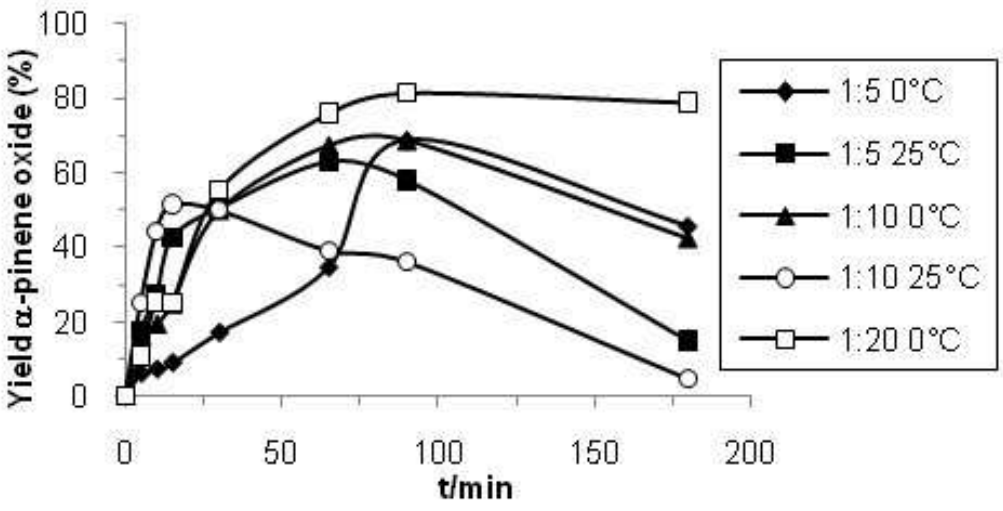


Figure 1. Kinetics of the α-pinene epoxidation with different molar ratios of MTO : ^{t}butylpyridine at 0 ℃ and 25 ℃, ratio α-pinene : MTO : H_2O_2 is 100 : 1 : 300 in CH_2Cl_2.

All kinetic curves depicted in Figure 1, show a feature which has not yet been described in detail in the previous reports on α-pinene epoxidation. The formation of α-pinene oxide is fast at the beginning of the reaction but after some time, the product yield not only becomes stagnant but decreases, reflecting the somewhat slower reaction to the respective diol becoming dominant. The formation of α-pinene diol is observed for all MTO : ^{t}butylpyridine ratios. However, a ratio of 1 : 20 at 0 ℃ leads to the highest yield of α-pinene oxide observed. Besides, the diol formation is less pronounced in comparison to the other cases. Thus, in the following reactions, the molar ratio between MTO and the ligands was kept at 1 : 20 and the reactions were performed at 0 ℃.

b) Oxidant concentration effects

Another method to reduce the diol formation is to decrease the concentration of H_2O_2 in the reaction (see Figure. 2).

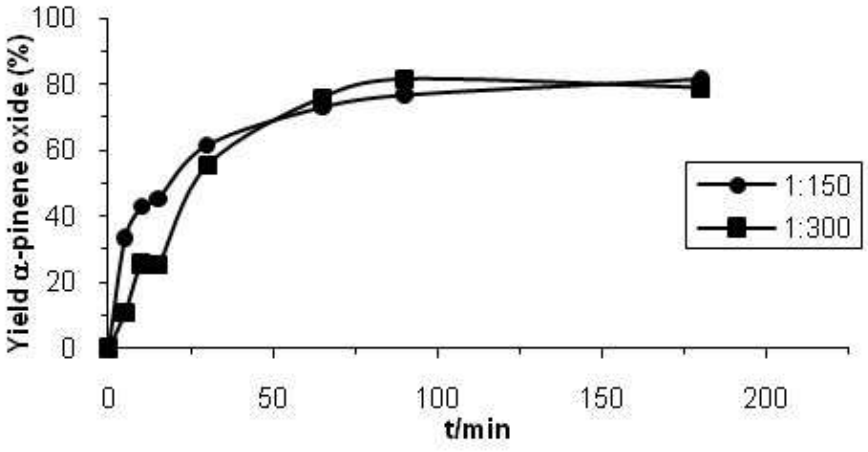


Figure 2. Kinetics of the α-pinene epoxidation at 0℃ with a molar ratio of α-pinene : MTO : ^{t}butylpyridine 100 : 1 : 20 at different MTO : H_2O_2 ratios in CH_2Cl_2.

In the case of a molar MTO : H_2O_2 ratio of 1 : 300 the epoxide yield reaches a maximum (82 %) after 1.5 h (conversion α-pinene = 96 %) and then decreases, whereas in the case of a ratio of 1 : 150, the conversion is somewhat slower and reaches a maximum epoxide yield after 3 h (81 %) (conversion α-pinene = 84 %). Follow up diol formation is largely suppressed in the latter case. It is therefore more economical to use the lower concentration of hydrogen peroxide for the epoxidation of α-pinene.

c) Catalyst concentration effects

The concentration of MTO was decreased to establish the minimum concentration of catalyst needed to perform this reaction without activity loss. The ratio α-pinene : ^{t}butylpyridine : H_2O_2 used was 10 : 2 : 15.

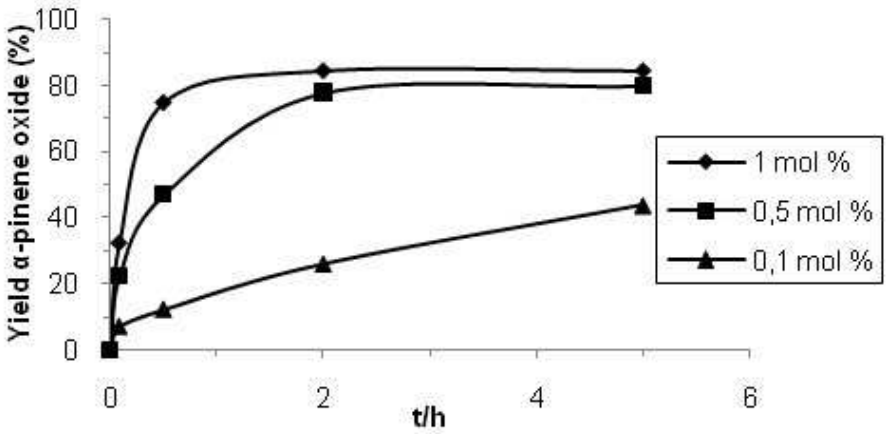


Figure 3. Kinetics of the epoxidation of α-pinene at 0 ℃ with MTO concentrations in CH_2Cl_2.

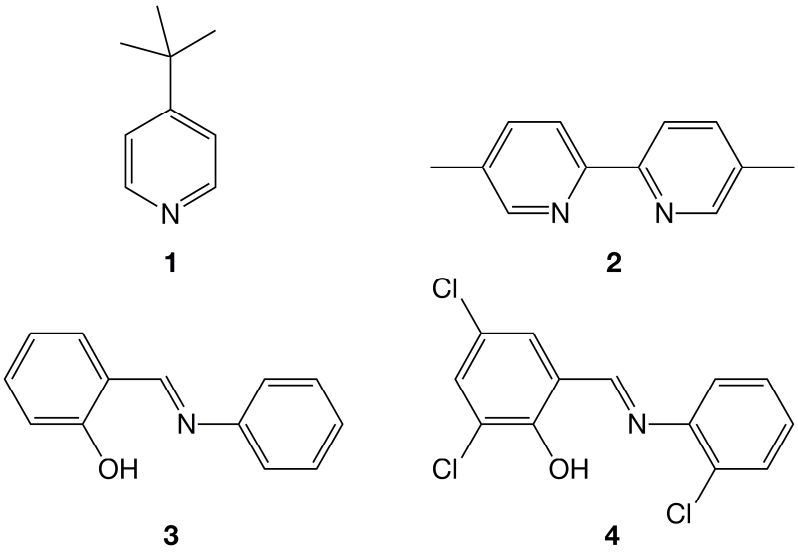
Decreasing the concentration of MTO in the reaction from 1 mol % to 0.5 mol % leads to quite similar results (Figure 3). The formation of α-pinene oxide is slightly higher after 2 h with 1 mol % (84 % yield) than with 0.5 mol % (77 % yield). Yet, the long-term activity (> 1 d) of the catalyst is decreasing for concentrations below

1 mol %; the activity decreases more significantly when the concentration of MTO in the reaction is reduced to 0.1 mol %. To ensure both maximum yield and good activity the concentration of MTO was kept at a 1 mol % level for all following reactions. The poor activity at a catalyst concentration of 0.1 mol % may be due to several effects: First, MTO can decompose to methanol and perrhenate to a higher degree in the presence of large excess of oxidant.[31] Second, the Lewis base can also be oxidized in the presence of H_2O_2.[43-44, 48] Oxygen donor adducts of MTO, however, which are formed during this ligand oxidation process are less active than N-base adducts.[43-44, 48] Third, impurities of oxidant and solvent have a stronger impact on catalyst deactivation when very low catalyst amounts are applied. In practical applications, however, a rigorous cleaning of the ingredients of the reaction mixture might be counterproductive with respect to reaction efficiency and costs.

Ligand-, oxidant-, and solvent- influence on the epoxidation of α-pinene

a) Ligand effects

The influence of a bidentate ligand (4,4'-dimethyl-2,2'-bipyridine), two different Schiff base ligands (2-[(E)-(phenylimino)methyl]phenol and 2,4-dichloro-6-[[(2-chlorophenyl)imino] methyl]phenol) on the α-pinene oxide yield was examined (Scheme 4). The epoxidation of α-pinene was originally performed with a ratio substrate : MTO : ligand : H_2O_2 (100 : 1 : 20 : 150) in CH_2Cl_2 at 0 ℃. The results are summarized in Table 3.



Scheme 4. Lewis base ligands used in this study: 4-tert-butylpyridine (1), 4,4'-dimethyl-2,2'-bipyridine (2), 2-[(E)-(phenylimino)methyl]phenol (3) and 2,4-dichloro-6-[[(2-chlorophenyl) imino]methyl]phenol (4).

Table 3. Comparison of the influence of ligands 1-4 on the epoxidation of α-pinene.

Ligand	Yield α-pinene oxide (Time)	TOF (h^{-1})	Observation
1	85% (5h)	390	Minor α-pinene diol formation
2	81% (5h)	200	Minor α-pinene diol formation
3	6% (5h)	20	α-pinene diol as main product
4	11% (5h)	20	α-pinene diol as main product

The activity of the catalytic system MTO : ^{t}butylpyridine (1) : H_2O_2 (TOF = 390 h^{-1}) is higher than the catalytic system MTO : 4,4'-dimethyl-2,2'bipyridine (2) : H_2O_2 (TOF = 200 h^{-1}). Moreover, the formation of α-pinene diol is less pronounced

when ^{t}butylpyridine (1) is employed as Lewis basic additive, compared to 4,4'-dimethyl-2,2'-bipyridine (2). In contrast to pyridine-based Lewis bases, Schiff-base ligands 3 and 4 lead to a low selectivity in the formation of α-pinene oxide (Table 3). The main product formed is α-pinene diol in both examined cases. Consequently, ^{t}butylpyridine (1) appears to be the best of the examined ligands as additive for the epoxidation of α-pinene. It was thus used for the following experiments.

b) Oxidant effect

In all the previous experiments, α-pinene diol formation was observed. It was thus important to investigate other oxidants, which might prevent this unwanted follow-up reaction. Several reports describe the utilization of urea hydrogen peroxide (UHP) as an alternative oxidant to aqueous H_2O_2 in metal complex catalyzed olefin epoxidation reactions when acid sensitive epoxides are formed.[49-50] Accordingly, UHP was used as an alternative oxidant.

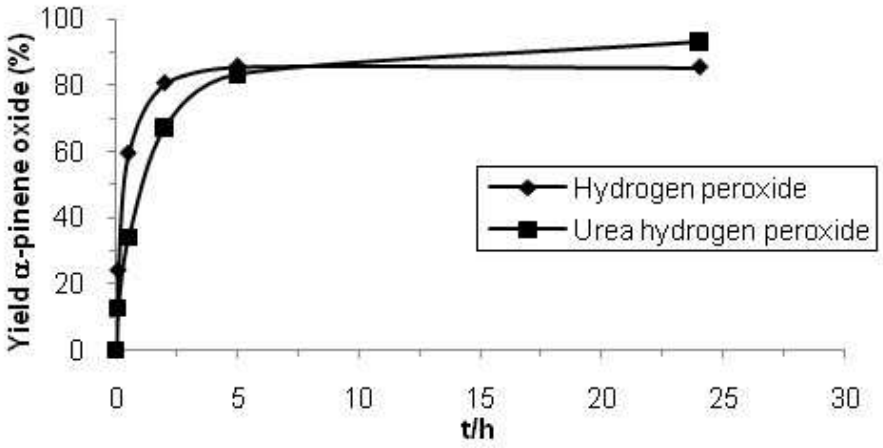


Figure 4. Kinetics of the α-pinene epoxidation in CH_2Cl_2 at 0 °C employing a ratio α-pinene : MTO : ^{t}butylpyridine : oxidant (100 : 1 : 20 : 150) with different oxidants.

The catalytic reaction undertaken with the system MTO : UHP has approximately the same activity as the MTO : H_2O_2 system (see Figure 4). However, the formation of α-pinene diol is only observed when H_2O_2 is used. UHP as oxidant does not lead to byproduct formation. However, the use of UHP can be problematic due to its solubility: it is barely soluble in most common organic solvents. Therefore, the real concentration of UHP in solution is hardly predictable, and the reaction cannot be described as really homogeneous. Based on these considerations, both UHP and H_2O_2 have certain advantages as oxidants for the epoxidation of α-pinene and will be used in the following experiments.

c) Solvent effects

Nitromethane, the ionic liquid ([bmim]PF_6), $CHCl_3$ and THF were selected as solvents. Sharpless et al. demonstrated that the use of nitromethane and dichloromethane as solvent leads to similar efficiency in the epoxidation of cyclohexene.[33] Previous work on epoxidation reactions in ionic liquid shows in many cases a yield improvement compared to organic solvents.[36, 51-56]

Table 4. Comparison of the influence of H_2O_2 and UHP in different solvents.[a]

		Yield % (TOF h^{-1})	
Entry	Solvent	H_2O_2	UHP
1	CH_2Cl_2	85 (400)	93 (150)
2	$MeNO_2$	51 (330)	63 (290)
3	$CHCl_3$	87 (100)	83 (100)
4	THF	47 (170)	29 (120)

[a] Reaction conditions: Ratio α-pinene:MTO:^{t}butylpyridine:oxidant (100:1:20:150) after 24 h reaction time.

The epoxidation of α-pinene is favored when dichloromethane is used as solvent at 0 °C. The use of other solvents such as nitromet hane, chloroform or THF leads to lower formation of α-pinene oxide. However, the turnover frequenties measured for dichloromethane and nitromethane are close (see Table 4). In the case of the ionic liquid [bmim]PF_6, the measurements proved to be problematic due to the significant amount of solid residue. Nevertheless, α-pinene diol appears to be the main product formed according to GC analysis. In the following experiments, dichloromethane and nitromethane were further used as solvent. The conditions of α-pinene epoxidation were optimized for H_2O_2 as oxidant. So far, the best efficiency is obtained with either H_2O_2 or UHP as oxidant with a ratio of α-pinene : MTO : ^{t}butylpyridine : oxidant of 100 : 1 : 20 : 150. This condition leads to the formation of α-pinene oxide in 85 % yield after 5 h. Further experiments were done to determine the optimal conditions of the epoxidation of α-pinene employing UHP as oxidant. For this purpose, the concentration of UHP was increased and the concentration of MTO was decreased.

Table 5. Optimization of α-pinene epoxidation employing UHP as oxidant.

	Ratio MTO: UHP[a] Yield % (TOF h^{-1})			
Solvent	100:1:20:150	200:1:40:300	100:1:20:300	200:1:40:600
CH_2Cl_2	83 (150)	80 (450)	93 (200)	83 (210)
$MeNO_2$	65 (290)	84 (420)	96 (270)	100 (610)

[a] samples taken after 5 h.

As depicted in Table 5, increasing the concentration of UHP from 150 equiv. to 300 equiv. leads to higher formation of α-pinene oxide. Moreover, the formation of α-pinene diol is not observed in all these experiments. Decreasing the concentration of catalyst in the reaction leads to similar efficiency in nitromethane.

From this set of experiments, the optimal condition for the epoxidation of α-pinene was found to be a ratio α-pinene : MTO : ^{t}butylpyridine : UHP of 100 : 0.5 : 20 : 300 in nitromethane at 0 °C. Formation of α-pinene oxide occurs with 95 % yield after 3 h and quantivative yield after 5 h with a TOF of 610 h^{-1}.

3.5 Conclusion

MTO based catalytic systems were examined and optimized for practically applicable laboratory scale epoxidation of α-pinene. The major challenge of this reaction is the usually unwanted formation of diol that had not been sufficiently addressed in previous reports. While Schiff-bases as additives do not suppress diol formation, the bidentate N-donor ligand 4,4'-dimethyl-2,2'-bipyridine allows to reach good activities. However, the latter ligand is also not able to completely supress the formation of α-pinene diol. The epoxidation of α-pinene can be acchieved with either H_2O_2 or UHP as oxidant. However, the condition, which leads to the best result employed MTO as catalyst, ^{t}butylpyridine as ligand and UHP as oxidant. It leads to the formation of α-pinene oxide in high yield (95 % after 3 h) and to an acceptable TOF of 610 h^{-1}. No formation of α-pinene diol is observed in this case. This result is straightforwardly obtained when applying a α-pinene : MTO : ^{t}butylpyridine : UHP ratio of 100 : 0.5 : 20 : 300 in $MeNO_2$ at 0 °C.

3.6 Acknowledgements

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4. Epoxidation in Ionic Liquids: A Comparison of Rhenium(VII) and Molybdenum(VI) Catalysts

This chapter originated from the following publication:

Daniel Betz, Wolfgang A. Herrmann, Fritz E. Kühn, *J. Organomet. Chem.* **2009**, *694*, 3320-3324.

4.1 Abstract

Complexes of the type (dimethyl-bpy)MoO_2Cl_2 and Schiff/Lewis-base complexes of methyltrioxorhenium (MTO), being efficient homogeneous catalysts for the epoxidation of olefins, have been examined with respect to their catalytic performance at 55 °C and 25 °C in systems employing room temperature ionic liquids (RTILs) of composition [bmim]NTf_2, [bmim]PF_6, [bmim]BF_4 and [omim]PF_6 as solvents. The performance in the cyclooctene epoxidation was observed to be strongly dependent on the water content of the system and the catalyst solubility in the RTIL. MTO based systems prove to be superior with respect to lower energy consumption, higher stability and higher product yields compared to the investigated Mo(VI) system under the conditions applied.

4.2 Introduction

In the last decade room temperature ionic liquids (RTILs) have been used in a variety of catalytic reactions.[1] Their unique physical properties, such as low volatility, low flash point, thermal stability and high polarity make them an attractive alternative to organic solvents.[2] Inorganic or organometallic complexes, sometimes immiscible

with hydrocarbons, are often soluble in RTILs. RTILs provide therefore a non-aqueous alternative for two-phase catalysis, in which the catalyst is immobilized in the ionic liquid phase and is easily separated from the products. RTILs have been used for several types of reactions, such as hydrogenation, hydrosilylation and oligomerization of olefins. Song and Roh reported the first manganese(III) (salen) complex, capable of catalyzing an asymmetric epoxidation in an ionic liquid less than a decade ago.[3] Since then, RTILs have been successfully applied in olefin epoxidation with manganese(III) porphyrins.[4] A series of imidazolium-based RTILs have been tested in this work as solvents for the catalytic cyclooctene epoxidation.

4.2.1 MTO derivatives as catalysts

Methyltrioxorhenium (MTO) is an extremely efficient catalyst precursor for a variety of organic reactions, as has been previously demonstrated, mainly by the research groups of J. H. Espenson and W. A. Herrmann.[5] Olefin epoxidation is yet the best examined of the many applications of this versatile catalyst.[6] The reaction mechanism has been studied in great detail, both from a kinetic and theoretical point of view in homogeneous and heterogeneous variations of the reaction.[7] Due to its Lewis acidity, MTO promotes ring-opening reactions of sensitive epoxidation products, which lead to the formation of diols.[8] It was recognized quite early that the presence of Lewis bases, for example nitrogen donor ligands, suppresses unwanted side reactions.[9] Nevertheless, the activity of MTO–Lewis base adducts was originally found to be significantly lower than that of MTO itself.[10] The use of aromatic N-donor ligands in 5 – 12 fold excess however, leads to higher activities and selectivities in epoxidation catalysis than with MTO alone.[11] Both mono- and bidentate aromatic Lewis bases with N-donor ligands display this behavior.[12] Many N-base adducts of MTO have been isolated and characterized and in several cases *in situ* employed for

olefin epoxidation catalysis.[13] Re(V)-oxo complexes bearing Schiff base ligands have also been investigated extensively [14], and Schiff-base adducts of MTO were also synthesized and applied as epoxidation catalysts in organic solvents.[15] In the latter case ligand excess proved to be unnecessary to achieve selective olefin epoxidations. Owens and Abu-Omar examined the epoxidation of different olefins using MTO as a catalyst and urea hydrogen peroxide (UHP) with the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate, [emim]BF_4, as a solvent. This oxidation system is nearly water-free, so the conversion of the substrates yields primarily the epoxides and not diols.[16]

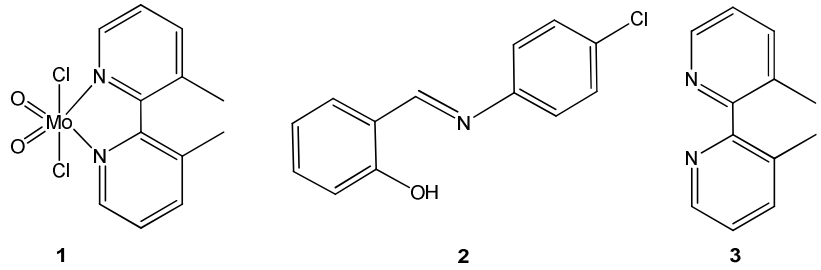
4.2.2 Molybdenum systems as catalysts

Molybdenum(VI) complexes are also versatile catalysts for the epoxidation of olefins. It has been shown that compounds of the type $MoO_2X_2L_2$ (L = Lewis base) and Cp`$Mo(CO)_3Cl$ can be used as olefin epoxidation catalysts or catalyst precursors. The latter compounds are undergoing oxidation *in situ* with TBHP to the Mo(VI) catalyst. Cp`$Mo(CO)_3R$ (R = alkyl or ansa-alkyl) complexes show a catalytic activity comparable to their chloro analogues.[17] The by-product of the oxidation of olefins with TBHP in the presence of Mo(VI) dioxo complexes is t-BuOH, which decreases the velocity of the catalytic reaction with increasing concentration.[18a-c] The Cp`$Mo(CO)_3R$ catalysts (Cp` = Cp, Cp*; R = Cl, Me) were investigated in RTILs and it was observed that among all examined catalysts the best epoxid yields are obtained for [bmim]NTf_2-containing systems.[19] Valente et al. examined two other Mo(VI) catalysts - MoO_2Me_2(p-tolyl-(CH_3-DAB)) and the cationic complex [$MoO_2Cl(Bn_3Me_3$-tame)]BF_4 (tame = *tert*-amylmethylether) - for the epoxidation of olefins. Both catalysts lead to the highest yields when using [bmim]NTf_2 as a solvent.[20] Among

the large variety of RTILs available in the literature, in this study RTILs of the imidazolium salt type were chosen with different anions as solvents due to their high oxidation stability as well as their ease of accessibility in terms of synthesis.[2, 21]

4.3 Results and discussion

Compound **1**, a very simple and straightforward Lewis base adduct of dichloro dioxo molybdenum(VI) (see Scheme 1), was used as a catalyst for olefin epoxidation. Compound **2** and **3** (same ligand as in compound **1**) were added to the reaction solution together with MTO to form the active catalysts *in situ*. Such an *in situ* formation of MTO based catalysts is well established in the literature (see above). Table 1 shows the results of the catalytic epoxidation of cis-cyclooctene with the molybdenum system **1**.



Scheme 1. Structures of the investigated complexes.

Table 1. Catalytic results for compound **1** as the catalyst with different RTILs as solvents under laboratory atmosphere with water equilibrated RTILs and TBHP as oxidizing agent.

solvent	yield [%] after 4 h	yield [%] after 24 h	TOF[a] (mol/mol*h)
[bmim]BF_4	21	27	36
[bmim]PF_6	26	33	55
[omim]PF_6	22	30	64
[bmim]NTf_2	31	43	113

[a] *Determined after 5 min reaction time.*

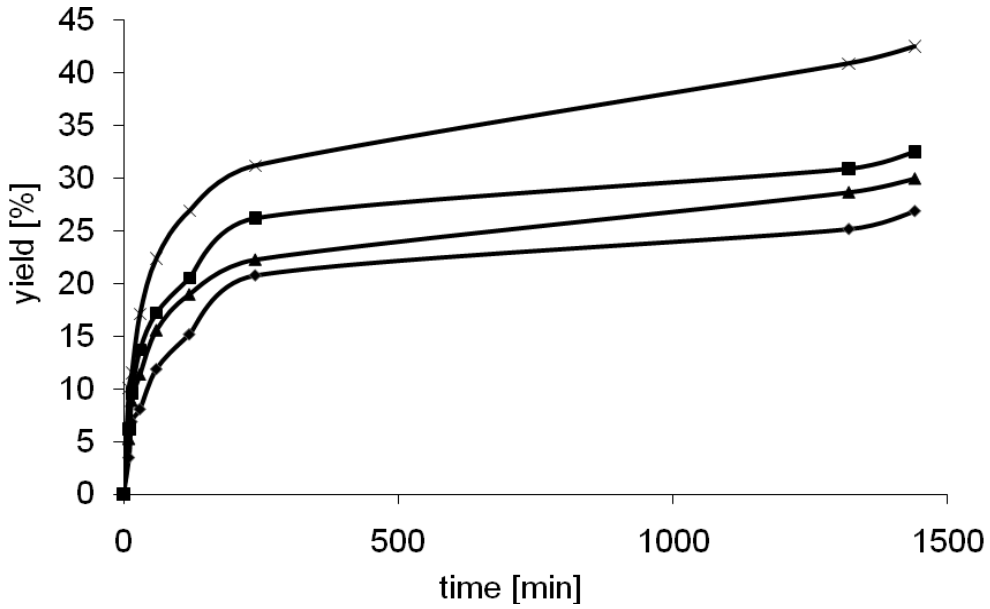


Figure 1. Kinetics of cyclooctene epoxidation in the presence of the complex **1** using $[bmim]BF_4$ (◆), $[bmim]PF_6$ (■), $[bmim]NTf_2$ (×) or $[omim]PF_6$ (▲) as solvents.

In all examined cases for epoxidation reactions catalyzed by Mo systems in RTILs the reaction leads to the highest yields when using $[bmim]NTf_2$ as solvent (Table 1, Figure 1). The low water content of this RTIL[2] allows a longer survival of the water sensitive Mo(VI) species. However, compared to the performance under solvent free conditions (Figure 2) the yields obtained for compound **1** in ionic liquids are not particularly impressive. This is, most likely, due to phase transfer problems between the viscous RTIL and the substrate and in particular to the mentioned instability of Mo(VI) in water-containing systems, leading to catalyst decomposition. According to its high water content, $[bmim]BF_4$ leads to the lowest product yield. The progress of reactions is quite independent from the different solvents, which can be deduced from the general shape of the curves in figure 1.

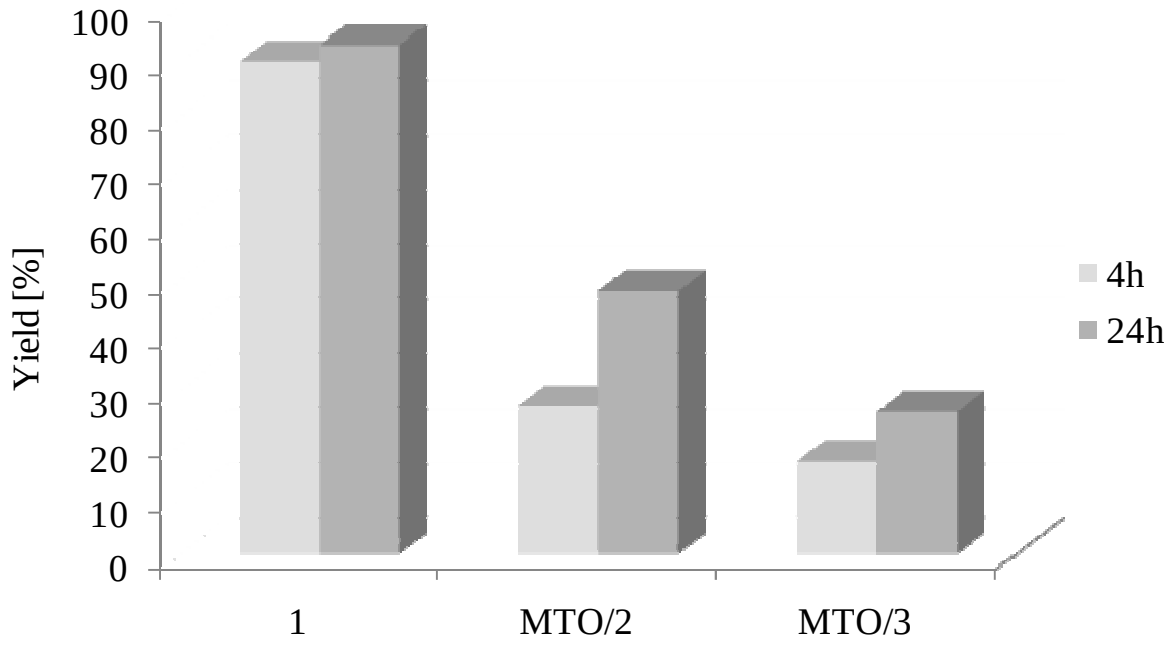


Figure 2. Catalytic results for compounds **1**, MTO/**2** and MTO/**3** as the catalyst under solvent free condition in laboratory atmosphere.

In addition to the molybdenum system, two MTO derivatives have been investigated. The influence of a Lewis base ligand was to be evaluated in comparison to the previous examinations that had been executed with MTO alone. The respective ligand is added directly to the solution and readily forms a complex with MTO as described in the literature.[12b, 15a] The catalytic activity of both MTO complexes was examined as mentioned for the molybdenum system.

Table 2. Catalytic results for MTO with compound **2** and **3** with different solvents under laboratory atmosphere with water equilibrated RTILs and H_2O_2 as oxidizing agent.

	MTO/**2**			MTO/**3**		
solvent	**yield [%] after 4 h**	**yield [%] after 24 h**	**TOF[a] (mol/mol*h)**	**yield [%] after 4 h**	**yield [%] after 24 h**	**TOF[a] (mol/mol*h)**
[bmim]BF_4	69	80	451	41	63	122
[bmim]PF_6	77	95	479	59	81	374
[omim]PF_6	50	81	402	29	52	51
[bmim]NTf_2	64	85	230	49	73	210

[a] *Determined for the first 5 min of reaction time.*

By comparing complexes of MTO with ligand **2** and MTO with ligand **3** a clear trend can be observed. In all cases the MTO/**2** system leads to higher yields compared with MTO/**3**. Both catalytic systems have the highest activity when [bmim]PF_6 is used as solvent. Interestingly, the addition of the Schiff-base has a considerable effect on the activity of the catalyst when the reaction is taking place in [bmim]PF_6. In this work it was found that the cyclooctene oxide yield rises by 25 % after 24 h in comparison to pure (Lewis base ligand free) MTO. Figures 3 and 4 give more details concerning the progress of reaction. Furthermore it should be mentioned that in all RTILs the MTO adducts produce a higher yield of cyclooctene oxide than the pure MTO. This fact does not surprise, because ring-opening reactions are suppressed with the ligated system. However, with MTO alone diol formation occurs.

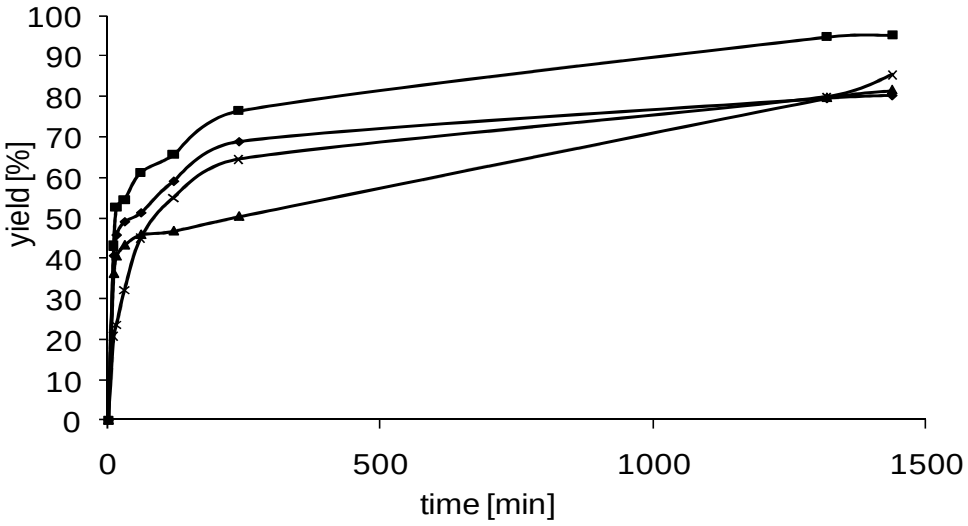


Figure 3. Kinetics of cyclooctene epoxidation in the presence of the complex **2** using [bmim]BF_4 (◆), [bmim]PF_6 (■), [bmim]NTf_2 (×) or [omim]PF_6 (▲) as solvents.

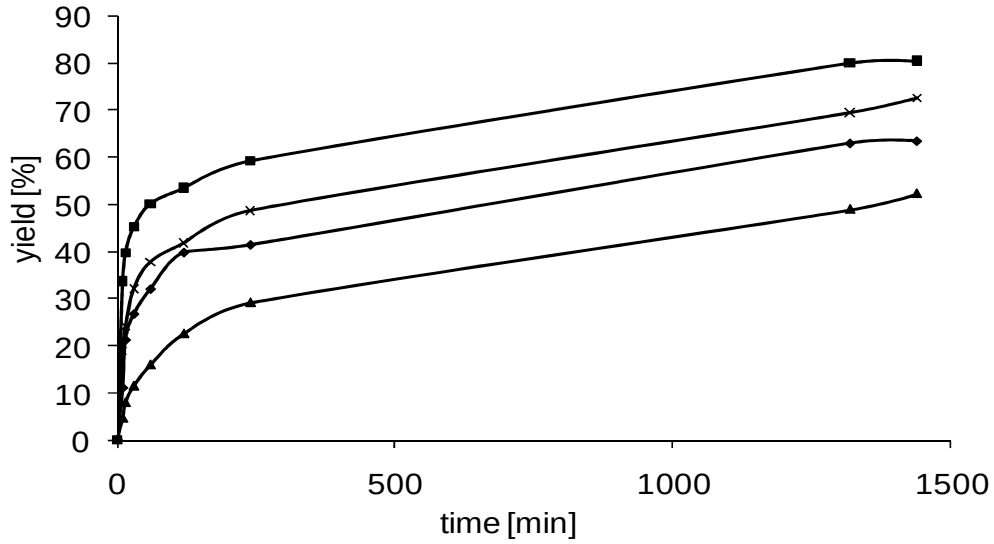


Figure 4. Kinetics of cyclooctene epoxidation in the presence of the complex **3** using [bmim]BF_4 (◆), [bmim]PF_6 (■), [bmim]NTf_2 (×) or [omim]PF_6 (▲) as solvents.

In summary, [bmim]PF_6 is the most appropriate solvent for both examined base adducts of MTO, leading to the highest yields among the systems studied. The use of RTILs in this reaction is meaningful, as higher yields were obtained in all cases compared to solvent-free systems. It should be finally mentioned that the catalytic reactions with the molybdenum system are performed at 55 ℃ with TBHP as oxidizing agent while the base adducts of MTO we applied at room temperature and with H_2O_2 as oxidant. In addition, all RTILs were water equilibrated and the reactions are performed under laboratory atmosphere. This fact leads to a very convenient and straight forward procedure. Interestingly, comparison between the yields of **1** and MTO/**3** shows that the rhenium system leads to much higher conversion although the ligand is the same. Furthermore, the water content of the RTIL, being very important for the water sensitive Mo(VI) catalyst **1** is not a concern for the MTO based systems, which produce water as byproduct of the epoxidation with H_2O_2 anyway.

4.4 Experimental part

All preparations were performed under laboratory atmosphere. TBHP was purchased from Aldrich as 5.0–6.0 M solution in n-decane and used after drying over molecular sieves to remove the water (< 4 % when received). ^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained using a 400-MHz Bruker Avance DPX-400 spectrometer. Catalytic runs were monitored by GC methods on a Hewlett–Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphadex 120 and a Hewlett–Packard integration unit HP 3396 Series II.

4.4.1 Synthesis of ionic liquids

The RTILs [bmim]PF_6, [omim]PF_6, [bmim]NTf_2 and [bmim]BF_4 were prepared and purified as described in the literature.[2, 21a] Their spectroscopic data are in accordance with the data reported previously. MTO was prepared according to literature procedures [22] and MoO_2Cl_2 was purchased from Sigma-Aldrich.

4.4.2 Catalytic reactions

All catalytic reactions were performed under laboratory atmosphere and the course of the yield was monitored by GC analysis. During the first 30 min of the reaction samples were taken every 5 min, afterwards every 30 min. After reacting for 24 h, magnetic stirring was stopped. If the two phases could be easily recognized, the samples were taken from the upper phase. If not, 2 mL of n-hexane was added and the mixture was stirred until two layers could be clearly seen (after allowing the mixture to settle). The samples were treated with a catalytic amount of MnO_2 to destroy remaining peroxide. Then, methylene chloride was added to get the right concentration for the GC analysis. Finally the sample was treated with a catalytic amount of $MgSO_4$ to remove residual water. The resulting slurry was filtered and the

filtrate injected into a GC column. The yield of cyclooctene was calculated from calibration curves recorded prior to the reaction course.

Cyclooctene epoxidation with the Mo(VI) system: After preheating the oil bath to 55 ℃, the reaction vessel was charged with cis-cyc looctene (800 mg, 7.3 mmol) and internal standard mesitylene (0.5 g). Afterwards TBHP (2.65 mL, 5.5 M in n-decane) and RTIL (0.5 mL) were added and the mixture was stirred for 10 min. With the addition of the catalyst (73 µmol, 1 mol %) the catalytic reaction was started. Cyclooctene epoxidation with the Re(VII) systems: The reaction vessel was charged with cis-cyclooctene (800 mg, 7.3 mmol) and internal standard mesitylene (0.5 g). Afterwards H_2O_2 (1.62 mL, 30 % aqueous solution) and RTIL (0.5 mL) were added and the mixture was stirred for 10 min. With the addition of MTO (73 µmol, 1 mol %) and the ligand (73 µmol) the catalytic reaction was started.

4.5 Conclusion

For the epoxidation of cyclooctene in ionic liquids four different RTILs were examined as solvents for the catalysts. They served as solvents for catalytic reactions with MTO and base adducts as catalysts. Additionally, a molybdenum(VI) system was investigated for sake of comparison. Since the MTO- and Mo-catalyzed epoxidations are well examined in the literature, this work may provide further insight into the recommendability of replacing the conventional solvent DCM by ionic liquids in lab scale reactions. The MTO containing catalysts in [bmim]PF_6 (particularly the MTO/**2** system) show the highest yield, which turns out to be higher than in conventionally used DCM or in solvent free epoxidation systems. Moreover, the easy product separation in case of the biphasic system may contribute larger scale applications. The reaction with the molybdenum system as catalyst leads to the

highest yield in [bmim]NTf_2, correlating well with published Mo systems, which in all cases gave the highest yields in [bmim]NTf_2.[19] This is due to the low water content in this RTIL which prolongs the life time of the water sensitive Mo(VI) species. However, under the applied conditions – which require no further precautions and can be easily executed under lab atmosphere the MTO/**2**/H_2O_2/[bmim]PF_6 system is the most efficient one.

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5. Highly soluble dichloro, dibromo and dimethyl dioxo molybdenum(VI)-bipyridine complexes as catalysts for the epoxidation of olefins

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Alev Günyar, Daniel Betz, Markus Drees, Eberhard Herdtweck, Fritz E. Kühn, *J. Mol. Catal. A: Chem.* **2010**, *331*, 117-124.

5.1 Abstract

The reaction of solvent substituted $MoO_2X_2(S)_2$ (X = Cl, S = THF; X = Br, S = DMF) complexes with one equivalent of bidentate nitrogen donor ligands at room temperature leads within a few minutes to the quantitative formation of complexes of the type $[MoO_2X_2L_2]$ (L = 4,4´-bis-methoxycarbonyl-2,2´-bipyridine, 5,5´-bis-methoxycarbonyl-2,2´-bipyridine, 4,4´-bis-ethoxycarbonyl-2,2´-bipyridine, 5,5´-bis-ethoxycarbonyl-2,2´-bipyridine). Treatment of the complexes $[MoO_2Cl_2L_2]$ with Grignard reagents at low temperatures yields dimethylated complexes of the formula $[MoO_2(CH_3)_2L_2]$. $[MoO_2Br_2$(4,4´-bis-ethoxycarbonyl-2,2'-bipyridine)], $[MoO_2Br_2$(5,5´-bis-methoxycarbonyl-2,2´-bipyridine)] and $[MoO_2Br_2$(5,5´-bis-ethoxycarbonyl-2,2´-bipyridine)] have been exemplary examined by single crystal X-ray analysis. The complexes were applied as homogenous catalysts for the epoxidation of cyclooctene with *tert*-butyl hydroperoxide (TBHP) as oxidising agent under solvent-free conditions. The complexes containing L = Cl have been additionally investigated with room-temperature ionic liquids (RTILs) as solvents. The catalytic activity of the $[MoO_2X_2L_2]$ complexes in olefin epoxidation with *tert*-butyl hydroperoxide is on average very good.

The main advantage of the synthesised complexes in comparison to previously reported complexes is their high solubility. This good solubility is apparently the reason that the catalytic potential of the compounds can unfold. The turnover frequencies (TOFs) in RTILs are even higher, showing the performance of the catalysts under optimised conditions.

5.2 Introduction

Molybdenum(VI) complexes are applied as homogeneous catalysts in industrial processes for the epoxidation of propylene with alkyl hydroperoxides as oxygen source since many years.[1] Epoxides are important organic intermediates undergoing ring-opening reactions with a variety of reagents to yield mono- or bifunctional organic products.[2,3] In general, epoxides can be prepared by the reaction of olefins with hydrogen peroxide or alkyl hydroperoxides, catalyzed by transition metal complexes.[1b-c,4] Among the variety of efficient catalysts known today for olefin epoxidation are several organometallic and inorganic oxides containing a metal in its highest oxidation state.[5] It is well known that complexes of the type $[MoO_2X_2(L)_n]$ (X = Cl, Br, CH_3; L = mono- or bidentate neutral N-ligand) are versatile catalyst precursors for the epoxidation of olefins in the presence of *tert*-butyl hydroperoxide (TBHP).[6-8] Treatment of $[MoO_2X_2]$ species (X= halide, OR, $OSiR_3$) with Lewis bases (L or L_2), such as pyridine, 2,2-bipyridine, 1,10-phenanthroline and 4,4`-*tert*-butyl-2,2`-bipyridine, and with donor solvents such as acetonitrile and THF, leads to adducts of composition $[MoO_2X_2L_2]$.[5,9-11] In the presence of TBHP as oxygen source some of these complexes have shown quite good catalytic activities. TBHP is one of the industrially preferred oxygen sources, partly because it is a mild and selective oxidant, not particularly corrosive or hazardous, and the by-product of the reaction, *tert*-butyl alcohol, can be separated and recycled for use in other

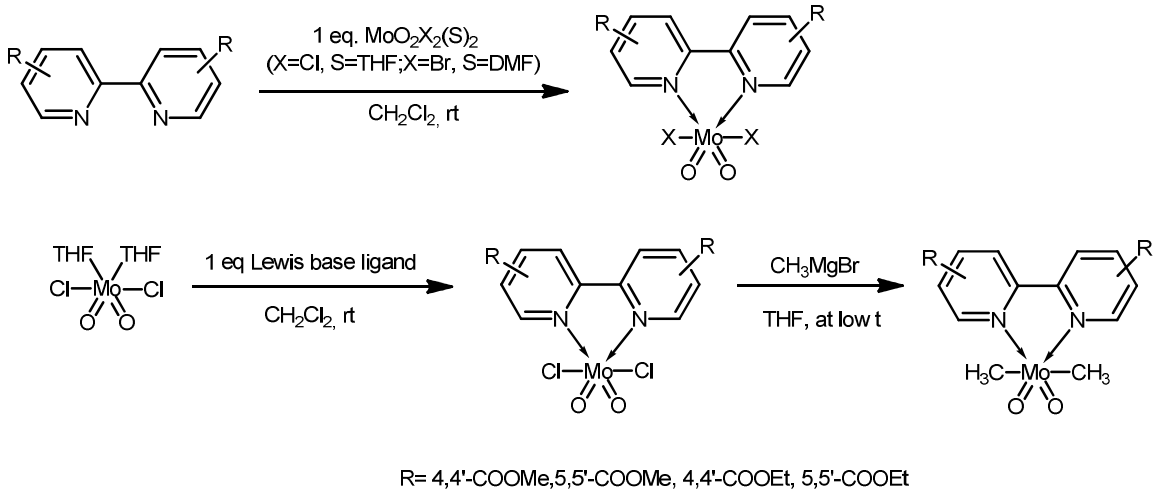
industrial processes.[12] Important properties, such as the solubility of the complex and the Lewis acidity of the metal centre can be fine-tuned by variation of both ligands X and L of the $[MoO_2X_2L_2]$ complexes.

Dioxomolybdenum(VI) halides and related compounds are useful precursors for the synthesis of other molybdenum complexes via oxygen or halogen/ligand abstraction or substitution.[13-16] The usual route to bromo complexes consists of reacting anhydrous $[MoO_2Br_2]$ with the appropriate ligand in aprotic solvents.[17] However, $[MoO_2Br_2]$ is not readily available[18,19] and has accordingly limited the coordination chemistry of this dibromodioxomolybdenum(VI) family. Another synthetic procedure is based on the reaction of aqueous solutions of molybdates in hydrobromic acid with the neutral ligands.[20] However, the procedure has not been extended to the synthesis of related species. Thus, the number of dioxomolybdenum(VI) bromide adducts that has been reported is low in comparison to those of $[MoO_2Cl_2]$.[17]

In this work the synthesis of well soluble compounds is described, since most of the $[MoO_2X_2(bipy)]$ compounds reported so far are only fairly soluble in most organic solvents. This low to moderate solubility appears to be responsible for the fact that $[MoO_2X_2L_2]$-type catalysts are usually regarded as inferior to other, related homogeneous epoxidation catalysts, such as CH_3ReO_3 (MTO) or $[CpMoO_2R]$ derivatives,[5] although the $[MoO_2X_2L_2]$ compounds would be both cheaper and more easily accessible than the former compounds. Furthermore, the electronic contribution of the different functional groups in different positions at the bipyridine rings and the implications of these differences on the catalyst activity are examined.

5.3 Results and Discussion

The synthesis of a series of dioxodichloromolybdenum(VI) bipyridine derived complexes has been described previously. In these cases the ligands had different functional groups at different positions on the bipyridine rings.[24] Among the complexes described previously is [MoO_2Cl_2(4,4´-bis-ethoxycarbonyl-2,2´-bipyridine)], which is also included in this paper as complex **4** for sake of comparison. For the present work the reaction of a variety of bipyridine derived ligands, which should lead to good complex solubility has been synthesised and applied. Scheme 1 shows the synthesis routes for the Mo(VI) complexes.

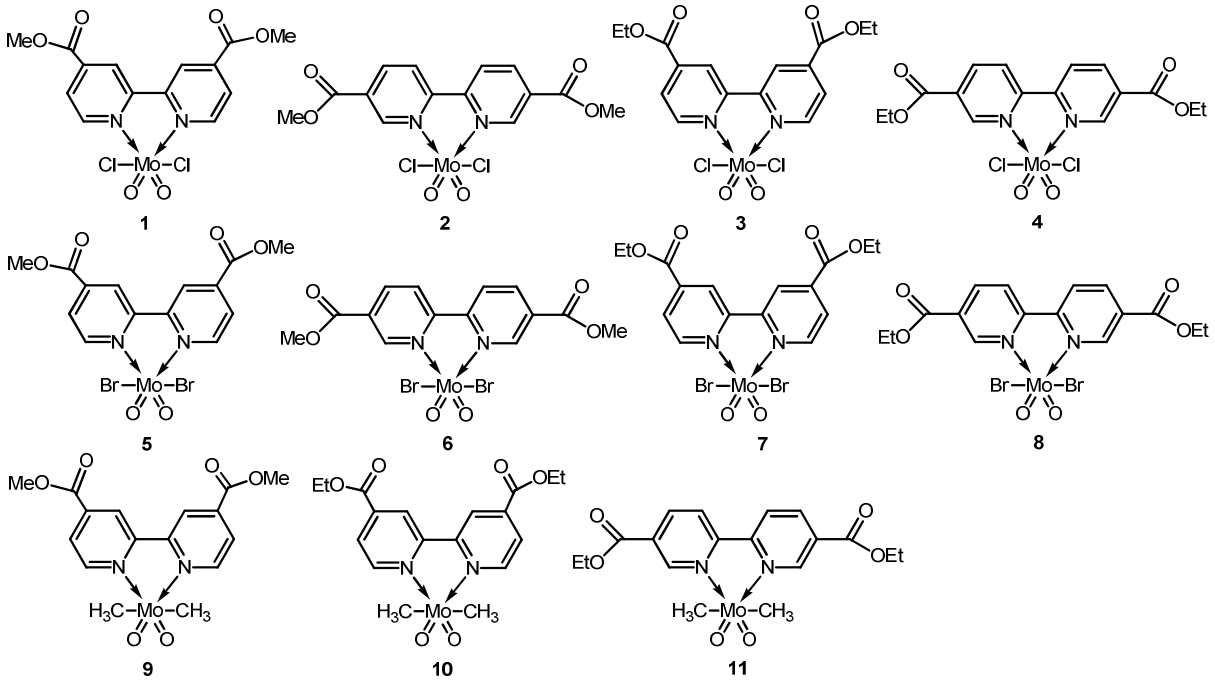


Scheme 1. Synthesis route for Mo(VI) complexes.

Synthesis and spectroscopic characterisation of complexes 1-11

The dichlorodioxo molybdenum(VI) complexes **1**, **2**, **3**, **4** (Scheme 2) were obtained as white microcrystalline powders in yields between 94 and 98 % by addition of 1 equiv. of the bidentate Lewis base ligands to a solution of the adduct [$MoO_2Cl_2(THF)_2$] in CH_2Cl_2 at room temperature. The bromides are readily prepared from [$MoO_2Br_2(DMF)_2$] and the corresponding Lewis base ligands for compounds **5**, **6**, **7**, **8**

(Scheme 2) according to described procedures.[25] When synthesizing the complexes **9**-**11**,[6a] the dichlorides do not need to be isolated prior to Grignard reagent addition. In some cases this isolation of the intermediates has negative effects on the overall yield of the final dialkyl products. Therefore, the whole process consists of dissolving $[MoO_2Cl_2(THF)_2]$ in CH_2Cl_2, treatment with the corresponding bidentate ligand and reaction of the *in situ* formed complex with the required amount of CH_3MgBr at low temperature. After warming to room temperature, the resulting solution is evaporated to dryness and the residue is treated with water under aerobic conditions. The resulting solution is extracted with dichloromethane. The dichloromethane phase is dried and the residue recrystallized to give the alkyl complexes **9**-**11** (Scheme 2) in yields between 32 and 79 %. All compounds are stable under laboratory atmosphere and can be handled in air.



Scheme 2. Structures of complexes **1**-**11**.

FT-IR spectroscopic data for complexes **1**-**11** are in consistence with other Lewis-base adducts of bis(halogeno)dioxomolybdenum described before.[25] The symmetric

and asymmetric IR stretching vibrations for the *cis*-dioxo unit of the complexes are in the expected range between 900 and 950 cm^{-1} (Table 1). The corresponding force constants of the Mo=O bonds can be derived from the υ (Mo=O) values. The M=O vibrations of the complexes are always shifted to higher wave numbers compared to their precursor, $[MoO_2X_2]$. This is an indication for comparatively strong metal–Lewis base ligand interactions. Additionally, this trend is reflected in the calculated force constants (see Table 1). A comparison of the observed IR- values for the complexes **9** - **11** (Table 1) indicates that the replacement of a halide by a methyl group weakens the equatorial metal - ligand bonds. The observed stretching vibrations as well as the calculated force constants (Table 1) show for both complex series, **1, 5, 9; 2, 6, 10; 3, 7, 11**, that there is a slight increase of Mo=O bond strength in the order $-CH_3$ < Br < Cl, in accordance with the inductive effects of these three ligands. The differences appear to be significant (the tendency is same in all three series of compounds), but not particularly pronounced.

Table 1. Selected FT-IR (KBr), calculated force constants *f* (Mo=O) for $MoO_2Cl_2L_2$ and ^{95}Mo NMR spectroscopic data for complexes **1**-**11**.

	υ(Mo=O) [cm^{-1}]			*f* (Mo=O	Decomp.Tem	δ(^{95}Mo)	Deuterated
Comple	$υ_{as}$	$υ_s$	$υ_{average}$	mdyn Å$^-$	ºC	ppm	solvent
1	918	951	935	7.00	275	Not determined	Not determined
2	910	942	926	6.88	290	201	$CDCl_3$
3	914	950	932	6.97	250	202	$CDCl_3$
4	911	945	928	6.91	275	191	CD_3NO_2
5	912	946	929	6.92	250	249	$CDCl_3$
6	906	938	922	6.82	275	249	$CDCl_3$
7	911	948	930	6.93	250	253	$CDCl_3$
8	911	943	927	6.89	275	246	$CDCl_3$
9	900	934	917	6.74	210	449	$CDCl_3$
10	898	932	915	6.71	200	449	$CDCl_3$
11	900	932	916	6.73	225	461	$CDCl_3$

The ^{1}H NMR spectra of complexes **1**-**11** were measured at room temperature using $CDCl_3$ as solvent. In general, the spectroscopic data for these complexes are in good agreement with those obtained for previously described MoO_2X_2–Lewis-base adducts.[25] Except for compounds **9**-**11** the protons are solely situated in the Lewis base. The chemical shift of the ligand protons is reported in the supporting information and compared to the chemical shifts observed for the protons of the free ligand. As stated above, the important feature of the most of the dioxomolybdenum(VI) complexes studied previously is that they are of low to moderate solubility in most common organic solvents.[24] However, the complexes synthesised in this work are generally of better solubility. The chemical shifts of the -CH_3 ligands of compounds **9**-**11** appear in the range between 0.57 and 0.61 ppm in ^{1}H NMR spectroscopy, in agreement with the values as previously reported for similar complexes.[6c]

The differences in the ^{95}Mo NMR shifts[25] between the different bipyridine ligated complexes is comparatively small, only a few ppm in each case with the same ligand X (X= Cl, Br, -CH_3). The difference in the chemical shift between Cl and Br is ≈ 50 ppm, between Br and -CH_3 ligands it is nearly 200 ppm. Complexes of the composition $[MoO_2Cl_2L_2]$ generally display their ^{95}Mo NMR signals between 160 and 220 ppm, whereas the bromine derivatives show their ^{95}Mo signals between 170 and 280 ppm. The methyl complexes of formula $[MoO_2(CH_3)_2L_2]$ described in the literature display ^{95}Mo NMR shifts between 370 and 520 ppm. Methyl complexes with N-bidentate heterocyclic aromatic ligands display their signals in the low-field region of this range between 370 and 450 ppm.[6c] The obtained ^{95}Mo NMR spectra for the complexes synthesised are summarised in Table 1; The $[MoO_2Cl_2L_2]$ complexes show their signals around 200 ppm, the $[MoO_2Br_2L_2]$ complexes exhibit their signals between 246 and 253 ppm and the $[MoO_2(CH_3)_2L_2]$ complexes display their signals in

the range between 449 and 461 ppm, which is in consistence with the literature reported results summarised above.[6c]

Thermogravimetric analyses (TGA) were performed for all compounds (see Table 1). The onset of the first decomposition temperature for the compounds range between 200-290 ºC. The synthesised dimethyldioxomolybdenum(VI) complexes are less stable than the dihalogenodioxomolybdenum(VI) complexes. In the case of methoxycarbonyl groups placed in the 4,4´-positions on the bipy-ring the decomposition temperature increases in the order **9** < **5** < **1**. Related to ethoxycarbonyls - regardless of the position of the functional groups located on the bipy-ring - both bromo and chloro molybdenum(VI) complexes have similar stability whereas in the case of complexes with methoxycarbonyl groups, dichlorodioxomolybdenum(VI) complexes are more stable than dibromodioxomolybdenum (VI) complexes. From the mass loss of the first decomposition step it can be concluded that in all cases one ligand X is lost first, triggering the follow-up decomposition of the whole molecule.

Crystal structures of complexes 6, 7, 8

Single crystals of compounds **6**, **7**, and **8** were obtained and examined by X-ray crystallography (see Figure 1, S1, S2, and S3).

All obtained structures exhibit the central molybdenum atom, situated in a distorted octahedron formed by two trans-located bromo, two cis-oriented oxo ligands, and two nitrogen atoms of the chelating bipyridine ligand. The distortion of the octahedron results from the displacement of the molybdenum atom away from the centre towards the two oxo ligands. The Mo–O bond lengths in these complexes range from 1.688(2)-1.704(2) Å, the lengths of the Mo–Br bonds are found within the range of

2.5155(5)-2.5306(5) Å, and the Mo–N bond lengths vary between 2.321(2) Å and 2.350(2) Å. All these values are expected for the respective Mo–E bond lengths.[26]

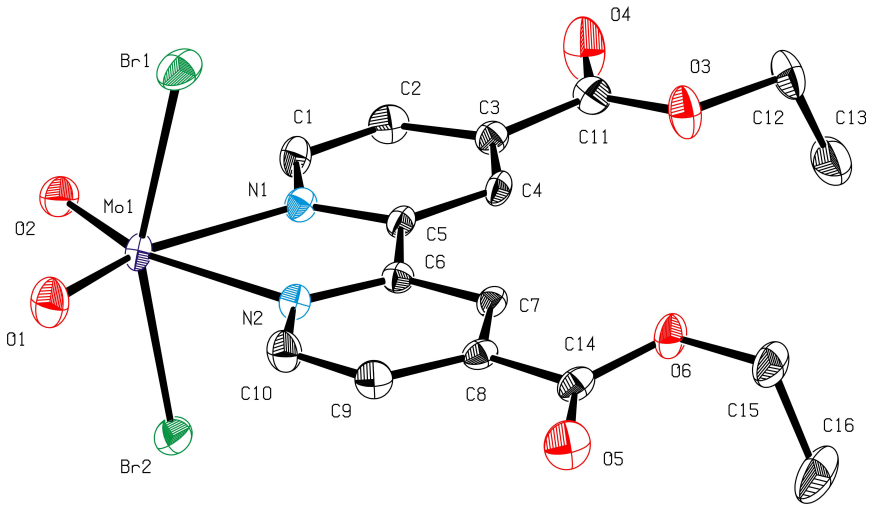


Figure 1. ORTEP style plot of compound **7** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Mo1−Br1 2.5269(4), Mo1−Br2 2.5 197(4), Mo1−O1 1.700(2), Mo1−O2 1.696(2), Mo1−N1 2.328(2), Mo1−N2 2.321(2); Br1−Mo1−Br2 159.22(1), Br1−Mo1−O1 96.80(7), Br1−Mo1−O2 95.75(6), Br1−Mo1−N1 81.14(5), Br1−Mo1−N2 80.13(5), Br2−Mo1−O1 95.82(7), Br2−Mo1−O2 96.38(6), Br2−Mo1−N1 81.74(5), Br2−Mo1−N2 82.73(5), O1−Mo1−O2 106.65(10), O1−Mo1−N1 161.93(9), O1−Mo1−N2 93.27(9), O2−Mo1−N1 91.42(8), O2−Mo1−N2 160.03(8), N1−Mo1−N2 68.67(7).

DFT calculation of formation energies

Density functional calculations were carried out to get more information of the thermodynamic behaviour of the complexes. They show overall similar thermodynamic values. Reaction enthalpies for the formation of the complexes out of solvent-free $[MoO_2X_2]$ range between -14 and -17 kcal/mol for X = $-CH_3$, between -20 and -23 kcal/mol for X = Cl and between -23 to -26 for X = Br. Entropic considerations come more strongly into account when looking at the complete ligand exchange of the $[MoO_2X_2(THF)_2]$ complexes with the relevant bidentate bipy ligand. The free energy of these substitutions vary from -10 kcal/mol to -16 kcal/mol for all

substituents X (-CH_3, Cl, Br) of the Mo centre. It can also be seen that substituents in the 4,4'-position lead to complexes that are more stable (ca. 2 kcal/mol) in comparison to the corresponding 5,5'-substituted compounds. The difference between -OMe and -OEt as bipy functionalised group is negligible.

5.4 Catalytic epoxidation of *cis*-cyclooctene

The epoxidation of cyclooctene using TBHP as oxidant in the presence of complexes **1**-**11** at 55 ºC yields cyclooctene oxide as the only product. Two series of experiments with different molar ratio of catalyst: substrate: oxidant (1 : 100 : 150 and 1 : 1000 : 1500) were undertaken in order to compare the catalytic potential of the systems. The details of the catalytic reactions are given in the experimental section. Control experiments confirm that epoxidation does not take place in the absence of catalyst. The time-dependent curves obtained for compounds **1**-**11** are typical for $[MoO_2X_2L_2]$-type complexes used as epoxidation catalysts with TBHP.[6,25] Initially the reaction is fast, indicating that the active oxidising species are formed rapidly after addition of the peroxide to the reaction medium. Progressively, the reaction rate decreases, when the reaction is nearly complete, due to an increasing lack of substrate (Figure 2). All examined compounds show high catalytic activity. Only complexes **5** and **6** show an induction period. Compounds **5** and **6** dissolve very slowly after addition of TBHP leading to a slow reaction in the beginning, whereas the other complexes dissolve immediately. After the catalyst has totally dissolved, the reaction is fast in all cases. The activities of the examined catalysts are in the range of 1600-2000 h^{-1}, (Table 2) and yields 95 % within 30 min. These results differ from literature data where the halide complexes, particularly the –Cl compounds, were found to be significantly more active (for cyclooctene epoxidation) than the methyl

derivatives under reaction conditions identical to those used in the present work.[6c,25,26] In the light of the results presented here it can be assumed that these lower activities of the -CH_3 complexes are mainly due to solubility problems. Furthermore, in some cases the TOFs have been calculated differently (not at the steepest slope of the olefin epoxide formation curves), the reported numbers can therefore be regarded as 'lower limits' not as realistic turnover frequencies.

When changing the catalyst: substrate: oxidant ratio from 1 : 100 : 150 to 1 : 1000 : 1500, the activities lower except for complex **8**. In the latter case the TOF increases slightly from 1970 h^{-1} to 2310 h^{-1}. It appears that optimal activities for the system have been reached when applying a 1 : 100 : 150 catalyst : substrate : oxidant ratio. Lowering the reaction temperature to 25 ºC also lowers the activity. In the case of compound **3**, the TOF decreases from ca. 1884 h^{-1} (at 55 ºC) to ca. 230 h^{-1} (at 25 ºC) (Figure 2).

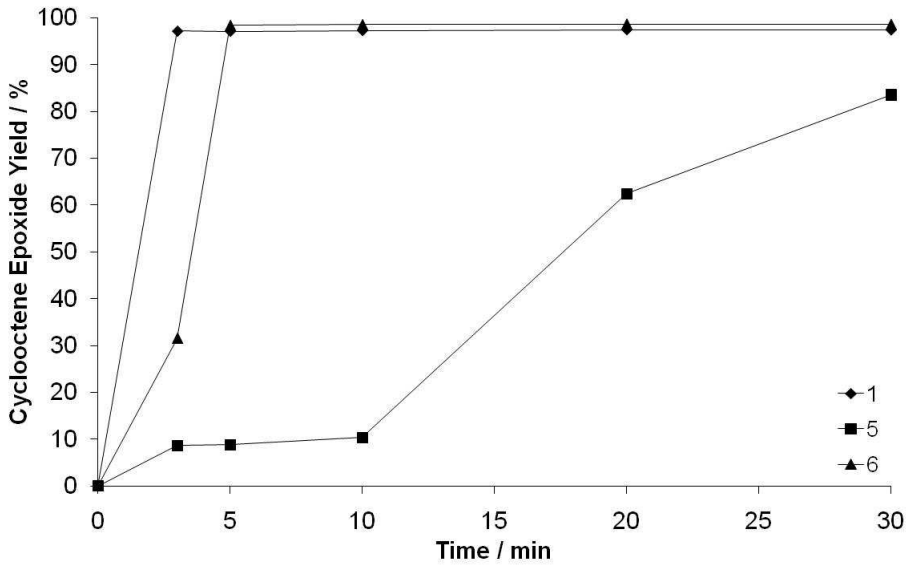


Figure 2. Time dependent yield of cyclooctene oxide in the presence compounds **1**, **5** and **6** as catalysts at 55 ºC with 1 mol % catalyst concentration between 0-30 min. The curve for compound **1** is typical for the remaining compounds **2**-**4**, **7**-**11**.

A further set of experiments was performed to explore the stability of the complexes under catalytic conditions. After 24 h reaction time, when the product yield reaches ≈ 100%, more substrate and TBHP were added to the reaction mixture. The catalyst was still active and the reaction reaches more than 90 % product yield within 4 hours, albeit somewhat slower in catalysing the reaction (Figure 3). This is most probably caused by the excess of *tert*-butyl alcohol present in the reaction mixture hindering the reaction process. This phenomenon is already known from related complexes and has been ascribed to an adduct formation of the catalyst with the by-product *t*-BuOH, rather than a catalyst decomposition.[6b]

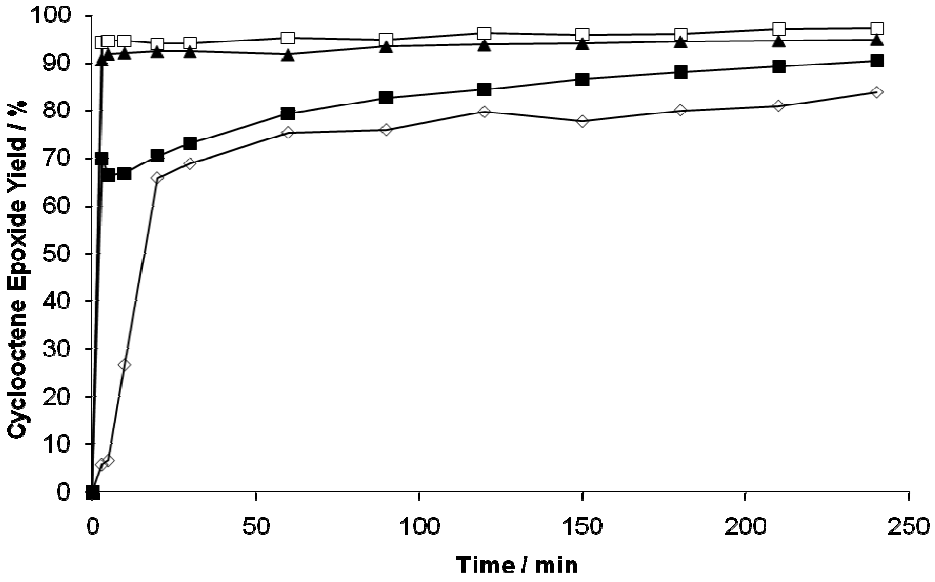


Figure 3. Time dependent yield of cyclooctene oxide with compound **8** as catalyst. (□: catalyst: substrate: oxidant ratio 1 : 100 : 150 at 55ºC, ▲: catalyst: substrate: oxidant ratio 1 : 1000 : 1500 at 55ºC, ■: 2nd run catalyst: substrate: oxidant ratio 1: 100: 150 at 55ºC, ◊: catalyst: substrate: oxidant ratio 1 : 100 : 150 at r.t.).

Table 2. The TOF values for $[MoX_2O_2L_2]$ type complexes **1**-**11** using cyclooctene as substrate. The TOFs of all complexes have been calculated at the time interval of highest conversion.

Compound	TOF [h^{-1}]
1	1950
2	1940
3	1880
4	1910
5	310
6	2010
7	1600
8	1970
9	1960
10	1900
11	1950

5.5 Catalytic epoxidation of *cis*-cyclooctene with RTILs as solvents

The chloride-containing complexes are investigated additionally in RTILs ([bmim]PF_6, [omim]PF_6, [bmim]NTf_2 and [bmim]BF_4) as solvents. In contrast to the catalysis without an additional solvent this catalysis was performed at room-temperature and with a catalyst: substrate: oxidant ratio from 1 : 1000 : 1500. The catalyst was dissolved in the RTIL and this solution was added to the reaction solution. Since the catalytically active Mo(VI) species are water-sensitive, the activity of the system depends on the water-content of the ionic liquid. [bmim]NTf_2 has the lowest water-content of all the investigated RTILs[27], leading to the highest activity in this solvent. The TOFs in [bmim]NTf_2 are considerably higher than the TOF under solvent free conditions (see Table 3).

Table 3. TOF values [h^{-1}] for [$MoO_2Cl_2L_2$] type complexes **1**-**4**, using cyclooctene as substrate and a RTILs as solvent. The TOFs of all complexes have been calculated for the time interval of highest conversion (c = 0.1 mol %).

Compound	[BMIM]NTf_2	[BMIM]BF_4	[BMIM]PF_6	[C_8MIM]PF_6
1	5390	280	1360	5390
2	8090	30	320	7110
3	7910	250	2490	5240
4	3430	660	430	2990

A reduction of the concentration of compound **2** to 0.05 mol % in [bmim]NTf_2 even leads to a TOF of 10080 h^{-1}. Another advantage of the performance in RTILs is the possibility to reuse the catalyst. After the reaction a phase separation ionic liquid/product takes place and the product can be easily removed quantitatively via a cannula. Additionally, oil pump vacuum allows the removal of *t*-BuOH from the RTIL phase. Since both starting reagents and epoxide are not present in the RTIL it can be concluded that the conversion of cyclooctene is achieved by a biphasic reaction and not by a homogeneous reaction. Addition of substrate and oxidising agent restarts the reaction. This catalytic procedure was repeated three times without any loss of activity and consequently without any leaching effects. Figure 4 shows the kinetics of the compounds **1**-**4** in [bmim]NTf_2.

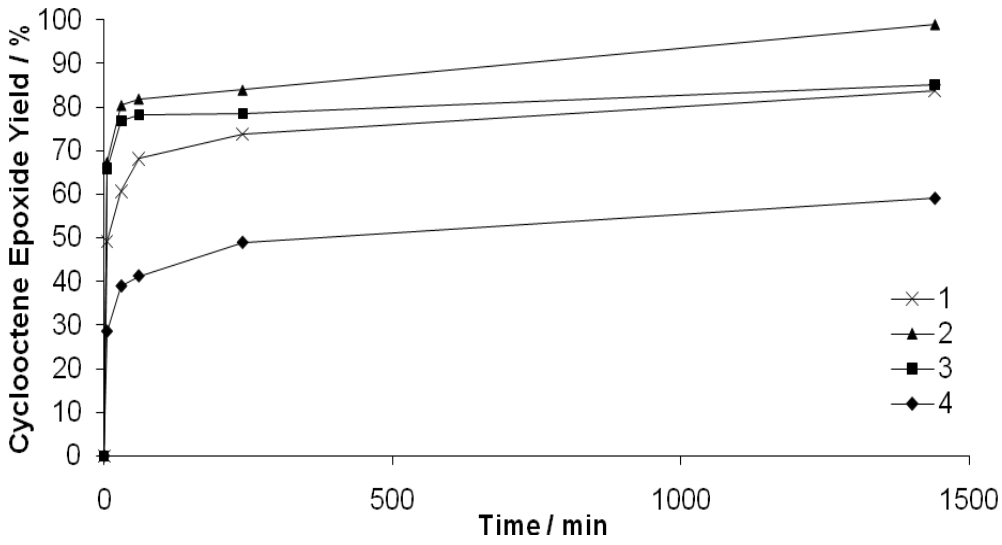


Figure 4. Time dependent yield of cyclooctene oxide in the presence of $[MoO_2Cl_2L_2]$ and compounds **1-4** as catalysts at room temperature with 0.1 mol % catalyst concentration and [bmim]NTf_2 as solvent.

5.6 Experimental

General: All preparations and manipulations were carried out under an oxygen- and water-free argon atmosphere with standard Schlenk techniques. $[MoO_2Cl_2]$, TBHP (5.5 M solution in decane, stored over molecular sieve) was purchased from Aldrich, 4,4'-dicarboxy-2,2'-bipyridine and 5,5'-dicarboxy-2,2'-bipyridine were purchased from HetCat and used as received. Solvents were dried by standard procedures, distilled, and kept under argon over molecular sieves (hexane, THF, and diethyl ether over Na/benzophenone ketyl, dichloromethane, chloroform over CaH_2, methanol and ethanol over Mg/I_2). $[MoO_2Br_2(DMF)_2]$ was prepared according to published procedures.[21] Elemental analyses were performed with a Flash EA 1112 series elemental analyzer. ^{1}H, ^{13}C and ^{95}Mo NMR spectra were

measured in $CDCl_3$ with a 400 MHz Bruker Avance DPX-400 spectrometer. IR spectra were recorded with a Perkin Elmer FT-IR spectrometer using KBr pellets as the IR matrix. Catalytic runs were monitored by GC methods on a Varian CP-3800 instrument equipped with a FID and a VF-5ms column. Thermogravimetric analyses were performed using a Netzsch TG209 system at a heating rate of 10 K min^{-1} under argon. X-ray structure determination[22] was carried out on an area detecting system (APEX II, κ–CCD) at the window of a rotating anode (Bruker AXS, FR591) and graphite monochromated MoK_α radiation (λ = 0.71073 Å). Raw data were corrected for Lorentz polarization, and, arising from the scaling procedure, for latent decay and absorption effects. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimising $\Sigma w(F_o^2-F_c^2)^2$ with SHELXL-97 weighting scheme. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for Crystallography.

Warning: TBHP (in decane) is toxic, possibly mutagen and a strong oxidiser. It is a combustible liquid and is readily absorbed through the skin and must be stored below 8 ℃.

Ligand synthesis

Appropriate 2,2'-bipyridine ligand precursors (1.0 g, 4.5 mmol) in methanol (17 ml) was added into concentrated sulfuric acid (2 ml) which is placed into an ice bath. After refluxing for overnight, the solution was poured into water (42 ml) forming a

white slurry. The pH value of the slurry was adjusted to 8 with 25% (w/v) ammonia solution. The product was then extracted with chloroform, dried over magnesium sulfate and evaporated to dryness.

4,4'-bis-methoxycarbonyl-2,2'-bipyridine: Yield 0.76 g (2.8 mmol, 62%). ^{1}H NMR (400 MHz, $CDCl_3$, 20 ℃, ppm): δ=8,94 (s, 2H, py-$H^{6,6´}$), 8.84 (d, $^{3}J_{H,H}$ = 5.1 Hz, 2H, py-$H^{3,3´}$), 7.88 (dd, $^{3}J_{H,H}$ = 5.1 Hz, 2H, py-$H^{5,5'}$), 3.98 (s, 6H, CH_3).

4,4'- bis-ethoxycarbonyl-2,2'-bipyridine: Yield 0.95 g (3.2 mmol, 71%). ^{1}H NMR (400 MHz, $CDCl_3$, 20 ℃, ppm): δ=8.93 (s, 2H, py-$H^{6,6´}$), 8.84 (d, $^{3}J_{H,H}$= 4.9 Hz, 2H, py-$H^{3,3´}$), 7.89 (dd, $^{3}J_{H,H}$= 4.9 Hz, 2H, py-$H^{5,5´}$), 4.44 (q, $^{3}J_{H,H}$= 7.2 Hz, 4H, CH_2), 1.42(t, $^{3}J_{H,H}$= 7.8 Hz, 6H, CH_3).

5,5'- bis-methoxycarbonyl-2,2'-bipyridine: Yield 0.72 g (2.6 mmol, 58%). ^{1}H NMR (400 MHz, $CDCl_3$, 20 ℃, ppm): δ=9.28 (d, $^{3}J_{H,H}$= 1.66 Hz, 2H, py-$H^{3,3´}$), 8.57 (dd, $^{3}J_{H,H}$= 8.35 Hz, 2H, py-$H^{6,6´}$), 8.43 (dd, $^{3}J_{H,H}$= 8.26 Hz, 2H, py-$H^{4,4´}$), 3.98 (s, 6H, CH_3).

5,5'- bis-ethoxycarbonyl-2,2'-bipyridine: Yield 0.9 g (3 mmol, 67%). ^{1}H NMR (400 MHz, $CDCl_3$, 20 ℃, ppm): δ=9.28 (s, 2H, py-$H^{3,3´}$), 8.56 (d, $^{3}J_{H,H}$= 8.2 Hz, 2H, py-$H^{6,6´}$), 8.42 (dd, $^{3}J_{H,H}$= 8.6 Hz, 2H, py-$H^{4,4´}$), 4.43 (q, $^{3}J_{H,H}$= 7.3 Hz, 4H, CH_2), 1.42 (t, $^{3}J_{H,H}$= 7.7 Hz, 6H, CH_3).

Complex synthesis

Synthesis of complexes 1-4: The complex $[MoO_2Cl_2(THF)_2]$ was dissolved in CH_2Cl_2 (5 mL) and treated with one equiv. of ligands that were also dissolved in CH_2Cl_2 (10 mL). The resulting solutions were each stirred for one hour. The solvent

was removed in vacuo, and the product washed with diethyl ether (2 x 5 mL) and dried under vacuum.

[MoO_2Cl_2(4,4´-bis-methoxycarbonyl-2,2´-bipyridine)](1) [$MoO_2Cl_2(THF)_2$] (0.96 mmol). Yield: 0.45 g (95%). Color: white. Selected IR (KBr): v(cm^{-1}) = 1726 (vs), 1563(s), 1435(s), 1020(w), 951(vs), (Mo═O_{sym}), 918 (vs) (Mo═O_{asym}). ^{1}H NMR (400 MHz, $CDCl_3$, 20 ℃, ppm): δ=9.72 (d, $^3J_{H,H}$=5.5 Hz, 2H, py-$H^{6,6´}$), 8.90 (s, 2H, py-$H^{3,3´}$), 8.28 (d, $^3J_{H,H}$=5.5 Hz, 2H, py-$H^{5,5´}$), 4.10 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 ℃, ppm): δ=163.7 (C=O), 153.2 (py-$C^{4,4´}$), 150.3 (py-$C^{2,2´}$), 142.1 (py-$C^{6,6´}$), 126.8 (py-$C^{3,3´}$), 122.7 (py-$C^{5,5´}$), 54.0 (CH_3). Anal. Calc. For $C_{14}H_{12}Cl_2MoN_2O_6$ (471.10): C 35.69, H 2.57, N 5.95. Found C 34.88, H 2.65, N 5.70.

[MoO_2Cl_2(5,5´-bis-methoxycarbonyl-2,2´-bipyridine)](2) [$MoO_2Cl_2(THF)_2$] (1.75 mmol). Yield: 0.77 g (94%). Color: white. Selected IR (KBr): v(cm^{-1}) = 1730 (vs), 1608(s), 1431(vs), 1045(s), 942(vs), (Mo═O_{sym}), 910 (vs) (Mo═O_{asym}). ^{1}H NMR (400 MHz, $CDCl_3$, 20 ℃, ppm): δ=10.14 (d, 2H, py-$H^{3,3´}$), 8.79 (dd, $^3J_{H,H}$=8.2 Hz, 2H, py-$H^{6,6´}$), 8.41 (d, $^3J_{H,H}$=8.4 Hz, 2H, py-$H^{4,4´}$), 4.05(s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 ℃, ppm): δ=163.3 (C=O), 153.5 (py-$C^{2,2´}$), 151.7 (py-$C^{6,6´}$), 142.0 (py-$C^{4,4´}$), 130.0 (py-$C^{5,5´}$), 123.2 (py-$C^{3,3´}$), 53.4 (CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 ℃, ppm): δ=201 ppm. Anal. Calc. For $C_{14}H_{12}Cl_2MoN_2O_6$ (471.10): C 35.69, H 2.57, N 5.95. Found C 36.16, H 2.88, N 5.67.

[MoO_2Cl_2(4,4´-bis-ethoxycarbonyl-2,2´-bipyridine)](3) [$MoO_2Cl_2(THF)_2$] (1.01 mmol). Yield: 0.53 g (98%). Color: white. Selected IR (KBr): v(cm^{-1}) = 1730(vs), 1616(w), 1487(w), 1093(w), 950(vs) (Mo═O_{sym}), 914(vs) (Mo═O_{asym}). ^{1}H NMR (400 MHz, $CDCl_3$, 20 ℃, ppm): δ=9.67 (d, $^3J_{H,H}$=5.5 Hz, 2H, py-$H^{6,6´}$), 8.88 (s, 2H, py-$H^{3,3´}$), 8.27 (d, $^3J_{H,H}$=5.5 Hz, 2H, py-$H^{5,5´}$), 4.55 (q, $^3J_{H,H}$= 7.1 Hz, 4H, CH_2), 1.48 (t, $^3J_{H,H}$=

7.8 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 ℃, ppm): δ=163.2 (C=O), 153.1 (py-$C^{4,4´}$), 150.3 (py-$C^{2,2´}$), 142.5 (py-$C^{6,6´}$), 126.8 (py-$C^{3,3´}$), 122.7 (py-$C^{5,5´}$), 63.4 (CH_2), 14.4 (CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 ℃): δ=202 ppm. Anal. Calc. For $C_{16}H_{16}Cl_2MoN_2O_6$ (499.15): C 38.50, H 3.23, N 5.61. Found C 37.64, H 3.17, N 5.41.

[MoO_2Cl_2(5,5´-bis-ethoxycarbonyl-2,2´-bipyridine)](4): [$MoO_2Cl_2(THF)_2$] (1.00 mmol) Yield: 0.5g (94%) color: white. Selected IR (KBr): v(cm^{-1}) = 1730(vs), 1607(s), 1471(w), 1059(w), 945(vs) (Mo═O_{sym}), 911(vs) (Mo═O_{asym}). ^1H NMR (400 MHz, CD_3NO_2, 20 ℃, ppm): δ = 9.96 (s, 2H, py-$H^{3,3´}$), 8.88 (dd, $^3J_{H,H}$ =8.6 Hz, 2H, py-$H^{6,6´}$), 8.73 (d, $^3J_{H,H}$ =8.1 Hz, 2H, py-$H^{4,4´}$), 4.51 (q, $^3J_{H,H}$= 7.3 Hz, 4H, CH_2), 1.44 (t, $^3J_{H,H}$ =7.8 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, CD_3NO_2, 20 ℃, ppm): δ =164.9 (C=O), 154.7 (py-$C^{2,2´}$), 153.3 (py-$C^{6,6´}$), 143.8 (py-$C^{4,4´}$), 132.2 (py-$C^{5,5´}$), 126.1 (py-$C^{3,3´}$), 69.2 (CH_2), 14.6 (CH_3). ^{95}Mo NMR (26 MHz, CD_3NO_2, 20 ℃): δ = 191 ppm. $C_{16}H_{16}Cl_2MoN_2O_6$ (499.15): calc. C 38.50, H 3.20, N 5.61; found C 38.65, H 3.27, N 5.18.

Synthesis of complexes 5-8: The complex [$MoO_2Br_2(DMF)_2$] was dissolved in CH_2Cl_2 (5 mL) and treated with one equiv. of ligands that were also dissolved in CH_2Cl_2 (10 mL). The resulting solutions were each stirred for one hour. The solvent was removed in vacuo, and the product washed with diethyl ether (2 x 5 mL) and dried under vacuum.

[MoO_2Br_2(4,4´-bis-methoxycarbonyl-2,2´-bipyridine)](5) [$MoO_2Br_2(DMF)_2$] (0.46 mmol). Yield: 0.25 g (98%). Color: yellow. Selected IR (KBr): v(cm^{-1}) = 1733 (vs), 1619(w), 1486(w), 1073(w), 946(vs), (Mo═O_{sym}), 912 (vs) (Mo═O_{asym}). ^1H NMR (400 MHz, $CDCl_3$, 20 ℃, ppm): δ=9.77 (d, $^3J_{H,H}$=6.2 Hz, 2H, py-$H^{6,6´}$), 8.90 (s, 2H, py-$H^{3,3´}$), 8.27 (d, $^3J_{H,H}$=4.7 Hz, 2H, py-$H^{5,5´}$), 4.10 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$,

20 ℃, ppm): δ=163.7 (C=O), 153.5 (py-$C^{4,4´}$), 150.5 (py-$C^{2,2´}$), 142.1 (py-$C^{6,6´}$), 126.8 (py-$C^{3,3´}$), 122.9 (py-$C^{5,5´}$), 54.0 (CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 ℃): δ=249 ppm. Anal. Calc. For $C_{14}H_{12}Br_2MoN_2O_6$ (560.00): C 30.03, H 2.16, N 5.00. Found C 29.83, H 2.30, N 5.05.

[MoO_2Br_2(5,5´-bis-methoxycarbonyl-2,2´-bipyridine)](6) [$MoO_2Br_2(DMF)_2$] (0.60 mmol). Yield: 0.32 g (95%). Color: yellow. Selected IR (KBr): ν(cm^{-1}) = 1729 (vs), 1607(s), 1429(s), 1058(w), 938(vs), (Mo═O_{sym}), 906 (vs) (Mo═O_{asym}). ^{1}H NMR (400 MHz, $CDCl_3$, 20 ℃, ppm): δ=10.18 (d, 2H, py-$H^{3,3´}$), 8.80 (dd, $^3J_{H,H}$=8.3 Hz, 2H, py-$H^{6,6´}$), 8.42 (d, $^3J_{H,H}$=8.3 Hz, 2H, py-$H^{4,4´}$), 4.05 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 ℃, ppm): δ=163.3 (C=O), 153.7 (py-$C^{2,2´}$), 151.8 (py-$C^{6,6´}$), 142.1 (py-$C^{4,4´}$), 130.0 (py-$C^{5,5´}$), 123.4 (py-$C^{3,3´}$), 53.6 (CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 ℃): δ=249 ppm. Anal. Calc. For $C_{14}H_{12}Br_2MoN_2O_6$ (560.00): C 30.03, H 2.16, N 5.00. Found C 29.74, H 2.34, N 4.98.

[MoO_2Br_2(4,4´-bis-ethoxycarbonyl-2,2´-bipyridine)](7) [$MoO_2Br_2(DMF)_2$] (0.40 mmol). Yield: 0.24 g (97%). Color: yellow. Selected IR (KBr): ν(cm^{-1}) = 1729(vs), 1616(w), 1461(w), 1093(w), 948(vs) (Mo═O_{sym}), 911(vs) (Mo═O_{asym}). ^{1}H NMR (400 MHz, $CDCl_3$, 20 ℃, ppm): δ=9.74 (d, $^3J_{H,H}$=5.7 Hz, 2H, py-$H^{6,6´}$), 8.88 (s, 2H, py-$H^{3,3´}$), 8.25 (d, $^3J_{H,H}$=5.8 Hz, 2H, py-$H^{5,5´}$), 4.55 (q, $^3J_{H,H}$= 7.2 Hz, 4H, CH_2), 1.49 (t, $^3J_{H,H}$= 7.8 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 ℃, ppm): δ=163.5, (C=O), 153.8 (py-$C^{4,4´}$), 150.7 (py-$C^{2,2´}$), 142.8 (py-$C^{6,6´}$), 127.1 (py-$C^{3,3´}$), 123.2 (py-$C^{5,5´}$), 63.8 (CH_2), 14.8 (CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 ℃): δ=253 ppm. Anal. Calc. For $C_{16}H_{16}Br_2MoN_2O_6$ (588.06): C 32.68, H 2.74, N 4.76. Found C 32.69, H 3.02, N 4.90

[MoO_2Br_2(5,5´-bis-ethoxycarbonyl-2,2´-bipyridine)](8): [$MoO_2Br_2(DMF)_2$] (0.46 mmol) Yield: 0.25 g (91%) color: yellow. Selected IR (KBr): ν(cm^{-1}) = 1723 (vs),

1609(w), 1470(w), 1061(w), 943(vs), (Mo═O_{sym}), 911 (vs) (Mo═O_{asym}). ^{1}H NMR (400 MHz, $CDCl_3$, 20 ℃, ppm): δ = 10.16 (d, 2H, py-$H^{3,3´}$), 8.79 (dd, $^{3}J_{H,H}$ =8.4 Hz, 2H, py-$H^{6,6´}$), 8.42 (d, $^{3}J_{H,H}$ =8.1 Hz, 2H, py-$H^{4,4´}$), 4.52 (q, $^{3}J_{H,H}$= 7.1 Hz, 4H, CH_2), 1.47 (t, $^{3}J_{H,H}$= 7.8 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 ℃, ppm): δ =163.2 (C=O), 154.1 (py-$C^{2,2´}$), 152.3 (py-$C^{6,6´}$), 142.3 (py-$C^{4,4´}$), 130.9 (py-$C^{5,5´}$), 123.7 (py-$C^{3,3´}$), 63.4 (CH_2), 14.8 (CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 ℃): δ = 246 ppm. $C_{16}H_{16}Br_2MoN_2O_6$ (588.06): calc. C 32.68, H 2.74, N 4.76; found C 32.06, H 2.73, N 4.54

Synthesis of complexes 9-11. A solution of $[MoO_2Cl_2(THF)_2]$ in THF (15 ml) was treated with one equiv. of ligands that were also dissolved in THF (10 mL). The colour of the solution changed immediately to yellow and the reaction mixture was stirred for further 30 min. To this solution, 2.1 equiv. CH_3MgBr were slowly added at −20ºC. The reaction mixture was allowed to warm-up to room temperature and was stirred for 2h. The dark brown suspension was taken to dryness and distilled water was added. The product was extracted with dichloromethane and the organic phase was dried over anhydrous $MgSO_4$. The solvent removed in vacuo and the residue was recrystallised from CH_2Cl_2 / Et_2O / hexane.

$[MoO_2(CH_3)_2$(4,4´-bis-methoxycarbonyl-2,2´-bipyridine)] (9). $[MoO_2Cl_2(THF)_2]$ (0.53 mmol). Yield: 0.18 g (79%). Color: yellow. Selected IR (KBr): ν(cm^{-1}) = 1731 (vs), 1612(w), 1441(w), 1064(w), 934(vs), (Mo═O_{sym}), 900 (vs) (Mo═O_{asym}). ^{1}H NMR (400 MHz, $CDCl_3$, 20 ℃): δ=9.76 (d, $^{3}J_{H,H}$=5.5 Hz, 2H, py-$H^{6,6´}$), 8.90 (s, 2H, py-$H^{3,3´}$), 8.11 (dd, $^{3}J_{H,H}$=5.6 Hz, 2H, py-$H^{5,5´}$), 4.08 (s, 6H, O-CH_3), 0.57 (s, 6H, Mo-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 ℃, ppm): δ=163.7 (C=O), 153.5 (py-$C^{4,4'}$), 150.5 (py-$C^{2,2´}$), 142.1 (py-$C^{6,6´}$), 126.8 (py-$C^{3,3´}$), 122.9 (py-$C^{5,5´}$), 54.0 (CH_3), 22.4 (Mo-CH_3). ^{95}Mo

NMR (26 MHz, $CDCl_3$, 20 ℃): δ=449 ppm. Anal. Calc. For $C_{16}H_{18}MoN_2O_6$ (430.26): C 44.66, H 4.22, N 6.51. Found C 45.74, H 4.81, N 6.16.

[$MoO_2(CH_3)_2$(4,4'-bis-ethoxycarbonyl-2,2'-bipyridine)] (10). [$MoO_2Cl_2(THF)_2$] (1.02 mmol). Yield: 0.14 g (32%). Color: yellow. Selected IR (KBr): v(cm^{-1}) = 1729(vs), 1613(w), 1467(w), 1099(w), 932(vs) (Mo═O_{sym}), 898(vs) (Mo═O_{asym}). ^{1}H NMR (400 MHz, $CDCl_3$, 20 ℃): δ=9.75 (d, $^3J_{H,H}$=6.0 Hz, 2H, py-$H^{6,6'}$), 8.90 (s, 2H, py-$H^{3,3'}$), 8.10 (d, $^3J_{H,H}$=5.8 Hz, 2H, py-$H^{5,5'}$), 4.53 (q, $^3J_{H,H}$= 7.2 Hz, 4H, CH_2), 1.48 (t, $^3J_{H,H}$= 7.9 Hz, 6H, CH_3), 0.57 (s, 6H, Mo-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 ℃, ppm): δ=163.7 (C=O), 152.2 (py-$C^{4,4'}$), 149.9 (py-$C^{2,2'}$), 140.8 (py-$C^{6,6'}$), 125.1 (py-$C^{3,3'}$), 122.5 (py-$C^{5,5'}$), 63.2 (CH_2), 14.5 (CH_3), 22.3 (Mo-CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 ℃): δ=449 ppm. Anal. Calc. For $C_{18}H_{22}MoN_2O_6$ (458.32): C 47.17, H 4.84, N 6.11. Found C 46.31, H 4.72, N 5.92.

[$MoO_2(CH_3)_2$(5,5'-bis-ethoxycarbonyl-2,2'-bipyridine)](11): [$MoO_2Cl_2(THF)_2$] (0.60 mmol) Yield: 0.14 g (51%) color: yellow. Selected IR (KBr): v(cm^{-1}) = 1725 (vs), 1604(w), 1470(w), 1057(w), 932(vs), (Mo═O_{sym}), 900 (vs) (Mo═O_{asym}). ^{1}H NMR (400 MHz, $CDCl_3$, 20 ℃): δ = 10.16 (d, $^3J_{H,H}$ =1.2 Hz, 2H, py-$H^{3,3'}$), 8.69 (dd, $^3J_{H,H}$ =8.4 Hz, 2 H, py-$H^{6,6'}$), 8.41 (d, $^3J_{H,H}$ =8.7 Hz, 2H, py-$H^{4,4'}$), 4.50 (q, $^3J_{H,H}$= 7.1 Hz, 4H, CH_2), 1.45 (t, $^3J_{H,H}$= 8.8 Hz, 6H, CH_3), 0.61 (s, 6H, Mo-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 20 ℃, ppm): δ =163.5 (C=O), 152.6 (py-$C^{2,2'}$), 150.9 (py-$C^{6,6'}$), 140.0 (py-$C^{4,4'}$), 129.2 (py-$C^{5,5'}$), 122.8 (py-$C^{3,3'}$), 62.6 (CH_2), 14.5 (CH_3), 21.7 (Mo-CH_3). ^{95}Mo NMR (26 MHz, $CDCl_3$, 20 ℃): δ = 461 ppm. $C_{18}H_{22}MoN_2O_6$ (458.32): calc. C 47.17, H 4.84, N 6.11; found C 46.01, H 4.95, N 5.35.

Synthesis of the ionic liquids

The RTILs [bmim]PF_6, [omim]PF_6, [bmim]NTf_2 and [bmim]BF_4 were prepared and purified as described in the literature.[23] Their spectroscopic data are in accordance with the data reported previously.

Catalytic reactions

Without solvent: Cis-cyclooctene (7.3 mmol), mesitylene (2.00 g, internal standard), and 1 mol % of compounds **1-11** (73 μmol, catalyst) were mixed in the reaction vessel under air at 55 ºC. With the addition of TBHP (11 mmol, 5.5M in decane) the reaction was started under vigorous stirring. The course of the reaction was monitored by quantitative GC analysis. Samples were taken in regular time intervals, diluted with CH_2Cl_2, and treated with a catalytic amount of $MgSO_4$ and MnO_2 to remove water and to destroy the excess of peroxide. The resulting slurry was filtered and the filtrate injected into a GC column. The conversion of cyclooctene and the formation of the according oxide were calculated from calibration curves (r^2 = 0.999) recorded prior to the reaction course.

With RTILs: Cis-cyclooctene (7.3 mmol), mesitylene (2.00 g, internal standard), and TBHP (11 mmol, 5.5M in decane) were mixed in the reaction vessel under air at room-temperature. The reaction is started under vigorous stirring by adding compounds **1-4** (7.3 μmol, 0.1 mol %), dissolved in RTIL (0.5 ml). The course of the reaction was monitored by quantitative GC analysis. Two phases could be easily recognised and the samples were taken from the upper organic phase in regular time intervals. After diluting the samples with CH_2Cl_2 they were treated with a catalytic amount of $MgSO_4$ and MnO_2 to remove water and to destroy the excess of peroxide. The resulting slurry was filtered and the filtrate injected into a GC column. The

conversion of cyclooctene and the formation of the according oxide were calculated from calibration curves (r^2 = 0.999) recorded prior to the reaction course.

5.7 Conclusion

The dioxomolybdenum(VI) complexes [$MoO_2X_2L_2$] (X = Cl, Br, -CH_3; L = 4,4´-bis-methoxycarbonyl-2,2´-bipyridine, 5,5´-bis-methoxycarbonyl-2,2-bipyridine, 4,4´-bis-ethoxycarbonyl-2,2´-bipyridine, 5,5´-bis-ethoxycarbonyl-2,2´-bipyridine) are very active and highly selective catalysts for the homogeneous epoxidation of cyclooctene using *tert*-butyl hydroperoxide (TBHP). Cyclooctene oxide is obtained quantitatively within 1 h and the reaction solution containing the catalyst can be reused. Catalytic results show that the reaction is selective to the desired epoxide and no diol formation is observed. It is important to note that almost all of the complexes described here are highly soluble in organic solvents in contrast to many of the previously reported related complexes. This shows that the ligand L is obviously more important for the solubility than the ligand X and R.

The major advantage of using RTILs as solvents is the formation of a biphasic system, which can be easily separated. After product removal the catalysts can be reused for additional cycles without observable loss of activity. Furthermore, no leaching of the catalyst can be observed. In [bmim]NTf_2 the reactions yields the best results, correlating well with other reported Mo systems,[28] because of the low water content of this particular RTIL.

5.8 References

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6. Olefin Epoxidation with a New Class of *Ansa*-Molybdenum Catalysts in Ionic Liquids

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6.1 Introduction

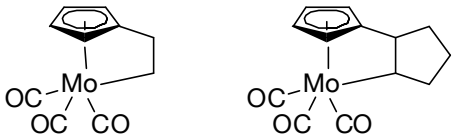
Epoxidation reactions of C=C double bonds are of high interest for the synthesis of fine chemicals such as pharmaceuticals and flavor & fragrance molecules.[1] A vast number of coordination compounds have been applied as catalysts for this type of reaction. Beside the well-known and highly active methyltrioxorhenium (MTO), several other Re(VII), Ti(IV), V(III), Mo(VI) and Mn(III) compounds have been found to catalyze olefin epoxidations.[2] Many other catalytic systems based on molybdenum and tungsten have been extensively studied and applied in asymmetric epoxidation catalysis.[3] Compounds of the type $[MoO_2X_2L_2]$ (L = Lewis base) and $[Cp`Mo(CO)_3Cl]$ can easily be transformed to catalytically active oxo-peroxo species for olefin epoxidation with tert-butyl hydroperoxide (TBHP).[4] $[Cp`Mo(CO)_3R]$ (R = alkyl) complexes show a catalytic activity comparable to their chloro analogues.[5] Among this class of compounds, we are currently exploring *ansa* complexes of the general type $[Mo(\eta^5\text{-}C_5H_4(CH(CH_2)_n)\text{-}\eta^1\text{-}CH)(CO)_3]$ as epoxidation catalysts.[6-9] We have previously reported the synthesis of new molybdenum and

tungsten *ansa*-complexes with cyclopentyl moieties and exceptionally stable bridging units and performed first studies of these compounds as epoxidation catalysts.[6f]

Herein, we report the remarkable activity of *ansa*-bridged Mo(VI) complexes for the epoxidation of different olefins in room temperature ionic liquids (RTIL) as solvents. Due to their high stability towards oxidation, imidazolium salt type RTILs are employed.[10,11] In the last decade, a plethora of catalytic reactions has been performed in RTILs as reaction media.[12] The unique physical properties of RTILs such as low volatility, low flash point, thermal stability and high polarity are an attractive alternative to organic solvents.[10] Inorganic or organometallic complexes which are insoluble in hydrocarbons are often soluble in RTILs. Ionic liquids therefore provide a non-aqueous version of two-phase catalysis, in which the catalyst is dissolved in the ionic liquid phase and can be easily separated from the product. Less than a decade ago, Song and Roh were the first to report the asymmetric epoxidation in an ionic liquid catalyzed by a manganese(III) salen complex.[13] Ever since, RTILs have been successfully applied as reaction media for olefin epoxidation, e.g. with Fe(III) porphyrin complexes, inorganic dioxomolybdenum(VI) systems, or methyltrioxorhenium (MTO) as catalyst, where the activity in RTILs is also higher than in conventional solvents or under solvent-free conditions.[14] The catalytic activities of [Cp`Mo(CO)$_3$R] compounds (Cp` = Cp, Cp*; R = Cl, Me) have as well been investigated in RTILs. Among all examined catalysts, the best epoxide yields are obtained with [bmim]NTf$_2$ as the RTIL (bmim = 1-butyl-3-methylimidazolium), as shown by both Valente *et al.* and our group.[14f,g,15]

6.2 Results and discussion

Compounds **1** and **2** (Scheme 1) were synthesized according to literature procedures[6f,9a] and tested as catalyst precursors for the epoxidation of *cis*-cyclooctene, 1-octene and *cis*-stilbene with TBHP as oxidant. All catalytic investigations were performed at room temperature and under laboratory atmosphere. The RTILs were water equilibrated. The course of the reaction was monitored via GC-MS and GC-FID, respectively.



1 **2**

Scheme 1. Compounds tested as catalysts of olefin epoxidation in ionic liquids.

In literature, cyclooctene is reported to be the most frequently used substrate for catalytic epoxidation test reactions. Compounds **1** and **2** were found to be even more active catalysts for the epoxidation of cyclooctene than the comparable [$CpMo(CO)_3CH_3$] at room temperature.[6d-f] At a catalyst concentration of 1 mol % of catalyst **1**, nearly quantitative conversions (> 90% epoxide yield) were reached after 5 min both in [bmim]NTf_2 and [bmim]PF_6 (Figure 1). The turnover frequencies (TOF) are in the range of 3000–4000 h^{-1}. With compound **2** as catalyst, the reactions proceeded somewhat slower (Figure 2). In [bmim]NTf_2, a quantitative conversion to cyclooctene epoxide was reached after 30 min, whereas in [omim]PF_6 (omim = 1-octyl-3-methylimidazolium) after 30 min the epoxide yield was 85 %; 100 % were reached after 4 h. Yet, in both cases, after 5 min reaction time, the TOFs are 3880 and 4130 h^{-1} respectively. Catalytic tests in the RTIL [bmim]BF_4 resulted in all cases in very poor yields because of the high water content of this RTIL. For this reason,

this RTIL has been excluded in the further studies. Table 1 summarizes the results of the catalytic epoxidation of *cis*-cyclooctene with 1 mol % of molybdenum compounds **1** and **2**. In order to determine the actual catalytic activity of compound **2**, the catalyst concentration was decreased. With a catalyst concentration of 0.05 mol %, the TOF rises to an exceedingly high value of 44000 h^{-1}. To the best of our knowledge, this is the highest TOF ever reported for a molecular epoxidation catalyst both in conventional solvents and in ionic liquids. Interestingly, when using compound **1** under the same conditions, the TOF is much lower.

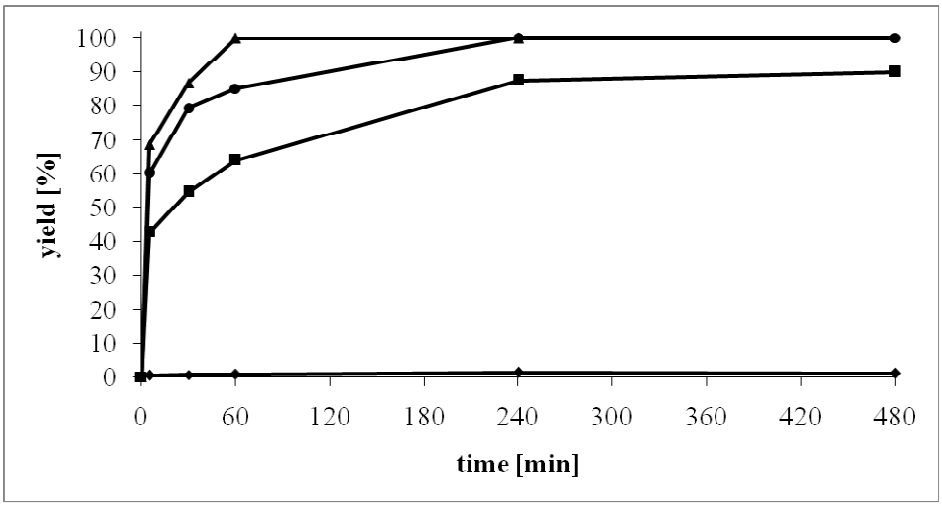


Figure 1. Reaction kinetics of cyclooctene epoxidation in the presence of **1** using [bmim]BF_4 (◆), [bmim]PF_6 (■), [bmim]NTf_2 (▲) or [omim]PF_6 (•) as solvent.

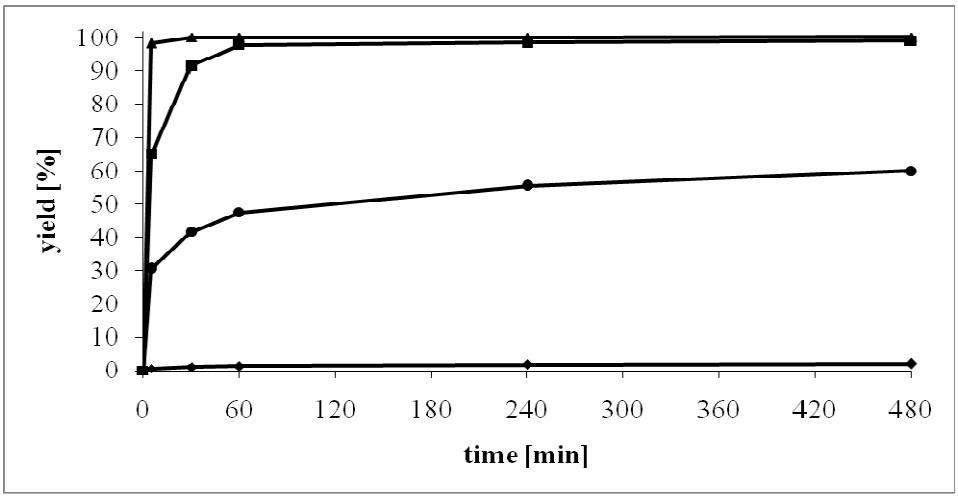


Figure 2. Reaction kinetics of cyclooctene epoxidations in the presence of **2** using [bmim]BF_4 (◆), [bmim]PF_6 (■), [bmim]NTf_2 (▲) or [omim]PF_6 (•) as solvent.

Table 1. Catalytic results for the epoxidation of cyclooctene with compounds **1** and **2** (c = 1 mol %) as catalyst precursor and different RTILs as solvent in laboratory atmosphere using water equilibrated RTILs. TBHP is the oxidizing agent.

	1			**2**		
Solvent	**Yield after 4 h [%]**	**Yield after 24 h [%]**	**TOF[a] [h^{-1}]**	**Yield after 4 h [%]**	**Yield after 24 h [%]**	**TOF[a] [h^{-1}]**
CH_2Cl_2	100	100	900	100	100	900
[bmim]BF_4	2	2	27	1	2	38
[bmim]PF_6	98	100	3100	87	94	2410
[bmim]NTf_2	100	100	3700	100	100	4130
[omim]PF_6	55	66	1540	100	100	3880

[a] *Determined after 5 min reaction time.*

A further decrease of the catalyst concentration to 0.01 mol % results in a decrease of the TOF to 8900 h^{-1}. Complex **2** was employed as homogeneous catalyst precursor in CH_2Cl_2 as solvent, which yielded in a TOF of 3800 h^{-1} at a concentration of 0.1 mol %.[6f] These results show that at a catalyst precursor concentration of 1 mol % only a fraction of the catalyst molecules is actually involved in the catalytic

process and the number of active centers is accordingly low. At a concentration of 0.05 mol %, more catalytic centers are involved so that a more realistic turnover frequency (activity) is obtained. At even lower concentrations (0.01 mol %), deactivation processes are seemingly playing a larger role. The exact nature of the deactivation is currently under investigation; there are indications that a certain amount of water in the solvent is leading to decomposition of the catalyst at low catalyst concentrations. In order to test the stability of the catalytic species and to probe the convenience of catalyst recycling in a biphasic system, the RTIL solution containing the catalyst was separated from the reaction medium by simple decantation via a cannula after the first run and a further batch of substrate and oxidant was added (see Exp. Section). We observed that the catalyst remains active for at least three catalytic runs, associated with a minor drop in the activity (to 80 %; Figure 3). Since leaching effects could not be observed and the catalyst is stable under the applied conditions, this activity drop is usually ascribed to an increasing concentration of water (from the oxidant and/or substrate) in the ionic liquid which is being added to the system after each catalytic run.

Experiments with 1-octene resulted in low to moderate yields (52 % after 24 h in the case of **1** in [bmim]NTf_2 and 28 % for **2**, respectively) which is not particularly surprising, since it is known that 1-octene is generally less prone to epoxidation than cyclooctene. Yet, no diol formation could be observed (see Table 2).

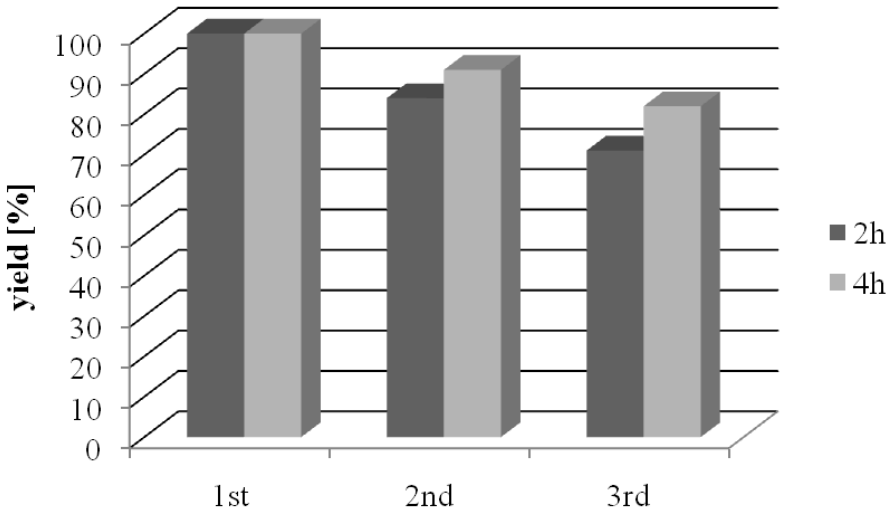


Figure 3. Epoxide yield for the first, second and third cycle after 2 h and 4 h reaction time in the presence of **2**. [bmim]NTf_2 was used as solvent (laboratory atmosphere with water equilibrated RTIL and cyclooctene as substrate).

Table 2. Catalytic results for the epoxidation of 1-octene with compounds **1** and **2** (c = 1 mol %) in different ionic liquids at laboratory atmosphere and water equilibrated RTILs and TBHP as oxidizing agent.

	1		**2**	
Solvent	Yield after 4 h [%]	Yield after 24 h [%]	Yield after 4 h [%]	Yield after 24 h [%]
CH_2Cl_2	-----	19	-----	60
[bmim]PF_6	8	17	10	19
[bmim]NTf_2	32	52	27	28
[omim]PF_6	26	35	11	19

A comparison between the biphasic catalytic system in RTILs and homogeneous catalysis in CH_2Cl_2[6d-f] shows that for the two-phase heterogeneous catalysis, the catalyst activities in [bmim]NTf_2 are significantly higher than under homogeneous conditions for compound **1**.

The catalytic epoxidation of cis-stilbene is rather challenging in epoxidation catalysis since it is difficult to prevent diol formation in this case. It is noteworthy that no diols were detected during the course of the measurements. (catalyst concentration: 1 mol %). The catalytic results are given in Table 3.

Table 3. Catalytic results for the epoxidation of *cis*-stilbene with compounds **1** and **2** (c = 1 mol %) in different solvents in laboratory atmosphere and water equilibrated RTILs. TBHP was applied as oxidizing agent.

	1			**2**		
Solvent	Yield after 4 h [%]	Yield after 24 h [%]	TOF[a] [h^{-1}]	Yield after 4 h [%]	Yield after 24 h [%]	TOF[a] [h^{-1}]
CH_2Cl_2	-----	9	-----	37	-----	-----
[bmim]PF_6	46	51	340	28	36	590
[bmim]NTf_2	64	68	1290	39	50	750
[omim]PF_6	31	33	450	23	31	270

[a] *Determined after 5 min reaction time.*

Compound **1** yielded 64% *cis*-stilbene epoxide, while compound **2** afforded 39 % epoxide after 4 h in [bmim]NTf_2. The turnover frequencies are in the range of 1300 h^{-1} (for compound **1**) and 750 h^{-1} (for compound **2**).

6.3 Conclusion

The biphasic epoxidation of selected olefins (namely *cis*-cyclooctene, 1-octene and *cis*-stilbene) with the *ansa*-compounds Mo(η^5-C_5H_4(CH_2-η^1-CH)$(CO)_3$) **1** and Mo(η^5-C_5H_4($CH(CH_2)_n$)-η^1-CH)$(CO)_3$ **2** as catalyst precursors were examined. As solvents four different RTILs ([bmim]BF_4, [bmim]PF_6, [bmim]NTf_2 and [omim]PF_6)

were used. For all investigated reactions, both the yields and the TOFs for catalysis carried out in RTILs are much higher than in all conventional solvents. The biphasic catalytic systems described herein clearly outperform previously published homogeneous catalyst systems containing compounds **1** and **2**. Quantitative yields without formation of diols were observed and TOFs up to 44000 h^{-1} were reached. In contrast to the homogeneous system the catalyst is immobilized in the ionic liquids and the product phase can be easily separated from the biphasic system. Catalyst **2** can be reused for at least three subsequent runs with only a minor loss of activity. In all cases, catalytic reactions in [bmim]NTf_2 yielded the best results, correlating well with other reported Mo systems.[14g,15] This is most likely due to the low water content of this RTIL which affects the life time of the slightly water sensitive Mo(VI) species. In accord with its high water content, [bmim]BF_4 leads to the lowest product yield. Accordingly replacing the conventional solvents CH_2Cl_2 by more sustainable ionic liquids in lab scale reactions seems to be recommendable and a scale up of such reactions appears to be promising.

Experimental Section

TBHP was purchased from Aldrich as a 5.0–6.0 M solution in n-decane and used after drying over molecular sieves in order to remove water. ^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained using a Bruker Avance DPX-400 spectrometer. Catalytic runs were monitored by GC methods on a Hewlett–Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphadex 120 and a Hewlett–Packard integration unit HP 3396 Series II.

Synthesis of ionic liquids

The RTILs [bmim]PF_6, [omim]PF_6, [bmim]NTf_2 and [bmim]BF_4 were prepared and purified as described in the literature.[10,11] Their spectroscopic data were in

accordance with the data reported previously. Compounds **1** and **2** were prepared according to literature procedures.[6f,9a]

Catalytic Reactions

All catalytic reactions were performed at laboratory atmosphere (under air at r.t.) in a reaction vessel equipped with a magnetic stirrer.

cis-cyclooctene: 800 mg (7.3 mmol) of the olefin, 500 mg mesitylene (internal standard) and 1 mol % (73 µmol) of the catalyst (**1** or **2**), 0.05 or 0.01 mol % (**2**), dissolved in 0.5 mL RTIL, was added to the reaction vessel. Afterwards, the reaction was started by adding 2.65 mL TBHP (5.5 M in n-decane).

1-octene: 800 mg (7.3 mmol) of the olefin, 500 mg mesitylene (internal standard) and 1 mol % (73 µmol) of the catalyst (**1** or **2**) was added to the reaction vessel and diluted in 0.5 mL RTIL. Afterwards, the reaction was started by adding 2.65 mL TBHP (5.5 M in n-decane).

cis-stilbene: 0.291 g (1.6 mmol) of the olefin, 0.360 g of 4-methylbenzophenone (internal standard) and 1 mol % (16 µmol) of the catalyst (**1** or **2**) was added to the reaction vessel and diluted in 0.5 mL RTIL. The reaction was started with the addition of 0.6 mL TBHP (5.5 M in n-decane).

The course of the reaction was monitored by quantitative GC analysis. Samples taken were treated with $MgSO_4$ and MnO_2 to remove water and destroy excess peroxide. Afterwards, the sample was diluted with CH_2Cl_2 and the resulting slurry was filtered and the filtrate was injected into a GC column. The conversions of *cis*-cyclooctene, 1-octene, *cis*-stilbene and the formation of their respective oxides were calculated from calibration curves (r^2 > 0.999) recorded prior to the start of the

reaction. For the second and third run the upper phase was removed from the reaction vessel by means of cannulation. Additionally, oil pump vacuum allowed the removal of *t*-BuOH from the RTIL phase. New charges of cyclooctene (0.800 g, 7.3 mmol), mesitylene (0.500 g) and TBHP (2.65 mL, 5.5 M in n-decane) were added.

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7. Olefin epoxidation with perrhenate catalysts

For a long time, it was believed that methyltrioxorhenium is only catalytically active in olefin epoxidation when hydrogen peroxide was used as oxidant. In 1993, Herrmann et al. reported that organic peroxides, such as tert-butyl hydroperoxide (TBHP), lead to deactivation of MTO.[1] In this work, this study was revisited. First, the reaction of MTO and TBHP was investigated by means of ^{17}O labeling experiments, B3LYP calculations and extensive catalytic studies.

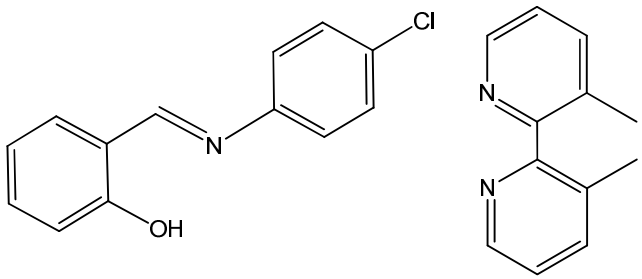
7.1 Results

Besides the well-known MTO/H_2O_2 system, the activity of MTO using TBHP as an oxidizing agent was investigated. The catalysis was performed at room temperature with an MTO : *cis*-cyclooctene : TBHP ratio of 1 : 100 : 200 and different ionic liquids as solvents. The catalytic results are shown in the table below (Table 1).

Table 1. Catalytic results of epoxidation of *cis*-cyclooctene.

solvent	yield [%] (after 4 h)	yield [%] (after 24 h)
[bmim]BF_4	31	40
[bmim]PF_6	27	43
[omim]PF_6	13	46
[bmim]NTf_2	7	32

In 2000, the MTO-catalyzed epoxidation of *cis*-cyclooctene in ionic liquids was investigated by Owens and Abu-Omar. They obtained a conversion of over 95 % using [emim]BF_4 as a solvent and the oxidizing agent UHP.[2] Although the results using TBHP were comparatively low, the possible influence of an equimolar addition of two different Lewis base ligands (Figure 1) was tested.



1 **2**

Figure 1. Investigated Lewis base ligands.

Performing the reaction under the same conditions as mentioned above led to the following results (Table 2).

Table 2. Catalytic results using 1 mol % MTO/Lewis-base ligand.

	yield [%] (after 24 h)	
solvent	**MTO/1**	**MTO/2**
[bmim]BF_4	39	32
[bmim]PF_6	56	42
[omim]PF_6	41	31
[bmim]NTf_2	48	34

It was observed that there is no significant difference between the Lewis base-free performance (Table 1) and the results obtained by the *in situ* addition of a Lewis base ligand (Table 2 and 3). This fact is rather contrary to the results, described in Chapter 4 - using H_2O_2 instead of TBHP as an oxidant. Thus, investigations on the nature of the catalytically active species were necessary. In a serie of ^{17}O NMR experiments, the concentration of the ^{17}O-labeled MTO was steadily reduced. Up to an MTO : TBHP ration of 1 : 40 a single peak at $\delta = 829$ ppm appeared, which is

referred to MTO. By a further reduction of the MTO concentration, this peak was high-field shifted to δ = 564 ppm, corresponding to the formation of a perrhenate species.

To substantiate this result, the mechanism was calculated by using a B3LYP functional. In the first instance the reaction mechanism of MTO / H_2O_2 was calculated started from the monoperoxo complex (Figure 2).

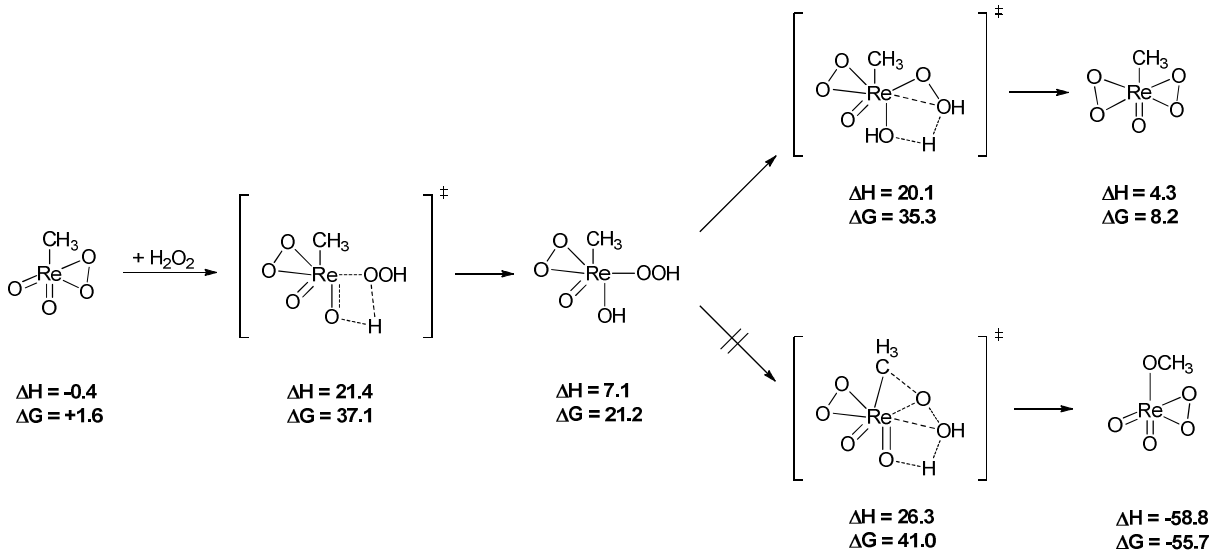


Figure 2. Results of the MTO / H_2O_2 system (all values are given in kcal/mol).

The obtained results are in good agreement with the results published by Periana *et al*.[3] The following Figure 3 shows the reaction mechanism of MTO and TBHP.

A major difference compared to the MTO / H_2O_2 system is that a Baeyer-Villiger mechanism is not possible when using TBHP. This is a result of the sterical demanding ^{t}Bu group, which avoids a possible rearrangement and subsequent formation of a monoperoxo complex. Thus, the Re-C bond is oxidized in an exergonic reaction, resulting in the formation of methoxytrioxorhenium(VII).

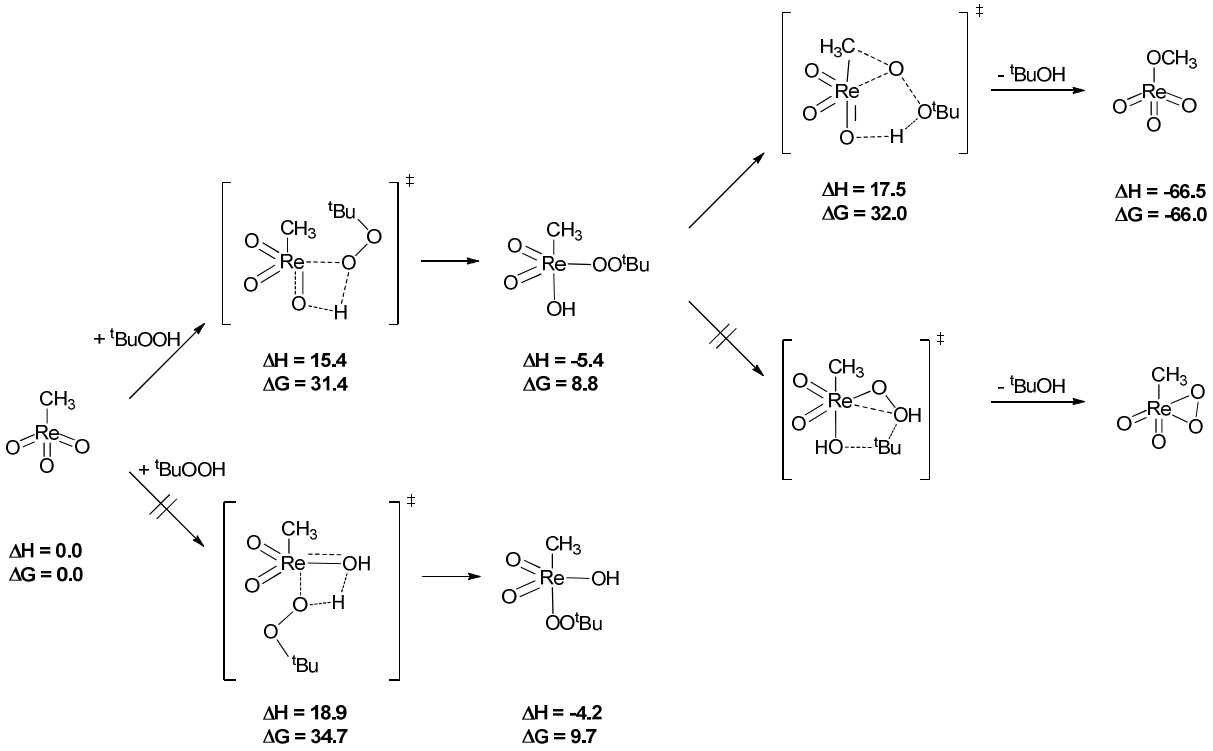


Figure 3. Results of the MTO / TBHP system (all values are given in kcal/mol).

These calculations reinforced the results, which are obtained by the labeling NMR studies. Nevertheless, to date it was unfortunately not possible to crystallize the active species what could certainly remove the last serious doubts of producing an active ReO_4^- by the reaction of MTO and an excess of TBHP.

The catalytic activity of perrhenates in ILs was verified in another dissertation project in our laboratories. The reaction of a perrhenate salt with an imidazolium based ionic liquid led to a complete ion exchange and resulted in the formation of an imidazolium perrhenate. This compound showed a very high activity leading to an almost quantitative yield of cyclooctene oxide by using H_2O_2 as an oxidant. Both IR and labeling NMR studies showed that the mechanism is completely different compared to other molecular systems using Re(VII) or Mo(VI) catalysts in organic solvents. The mechanism is based on coordination of H_2O_2 to a perrhenate anion. Weak hydrogen bonds between the Re=O group and H_2O_2 lead to an increasing O-O bond distance.

In this activated state the oxygen can be transferred to the olefin. After the reaction the system can be reused without a loss of activity by removing the coordinated water.

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C. Summary

A series of different Re(VII) and Mo(VI) catalysts have been investigated towards their activity in the epoxidation of several olefins. The main focus was the performance under biphasic conditions by using different room-temperature ionic liquids. The catalyst activities and stabilities were compared to the homogeneous phase catalysis in conventional organic solvents. In all examined epoxidation reactions catalyzed by Mo systems in RTILs, the highest yields are obtained when using [bmim]NTf_2 as solvent. The low water content of this RTIL allows a longer survival of the water sensitive Mo(VI) species. First, the catalysts **1-3** were investigated; compounds **2** and **3** were used as additional Lewis base ligands of MTO (Figure 1).

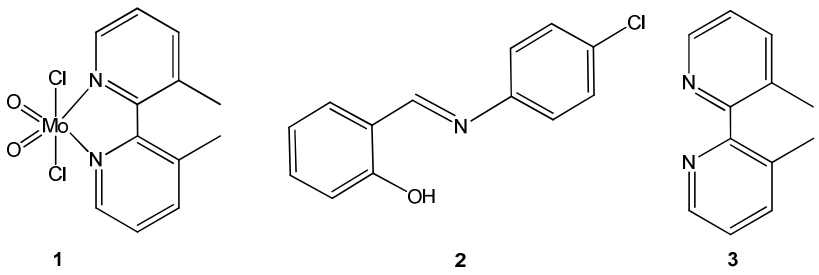


Figure 1. Molybdenum catalyst and Lewis base ligands for MTO.

Surprisingly, it was found that the MTO derivatives are also active when TBHP was used as oxidant. This led to further investigations towards the identification of the catalytically active species. By means of ^{17}O labeling studies, it was shown that upon reaction of MTO and TBHP, perrhenate was formed. Compared to the performance under solvent free conditions, the epoxide yields obtained for compound **1** in ionic liquids are not particularly impressive. Most likely, due to phase transfer problems between the viscous RTIL and the substrate and in particular to the mentioned instability of Mo(VI) in water-containing systems, leading to catalyst decomposition. According to its high water content, [BMIM]BF_4 leads to the lowest product yield with

1. The MTO containing catalysts in [bmim]PF_6 (particularly the MTO/**2** system) show the highest yield, which turns out to be higher than in conventionally used DCM or in solvent free epoxidation systems. Moreover, the easy product separation in case of the biphasic system may contribute larger scale applications. Under the applied conditions, which require no further precautions and can be easily executed under lab atmosphere the MTO/**2**/H_2O_2/[bmim]PF_6 system is the most efficient one. With regard to the epoxidation of α-pinene with an MTO / ^{t}Bu-pyridine adduct the use of [bmim]PF_6, proved to be problematic due to the significant amount of solid residue. Nevertheless, α-pinene diol appears to be the main product formed.

The following chloride-containing molybdenum complexes **4-7** (Figure 2) were investigated both under solventless conditions and in RTILs ([bmim]PF_6, [omim]PF_6, [bmim]NTf_2 and [bmim]BF_4).

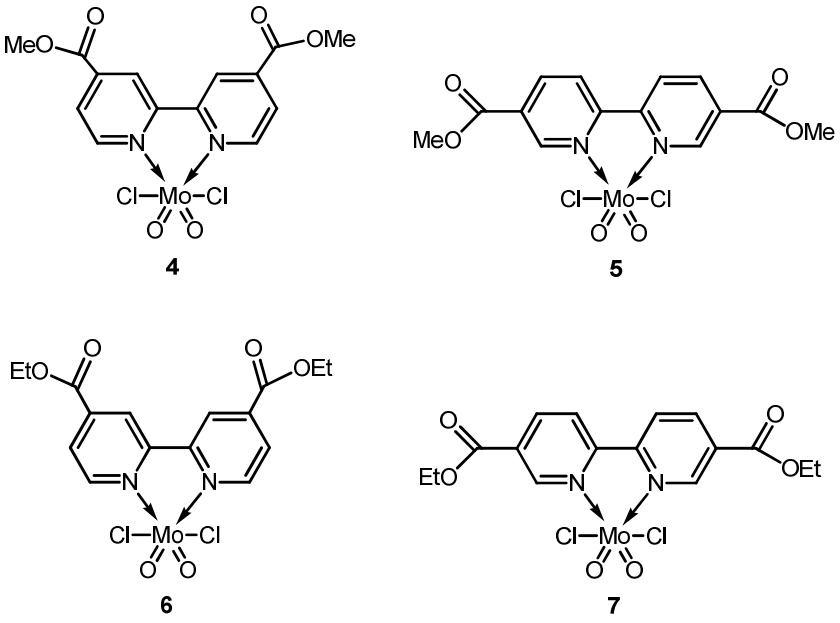
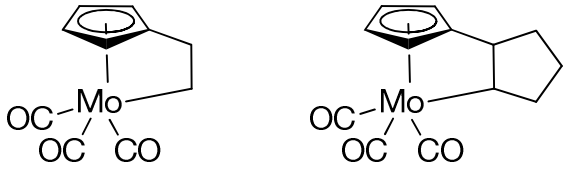


Figure 2. Chloride-containing molybdenum catalysts.

It was found that the turnover frequencies are in all cases considerably higher when using ILs than under solvent free conditions. A second advantage of the performance

in ILs is the possibility to reuse the catalyst. After the reaction, a phase separation ionic liquid/product takes place and the product can be easily removed quantitatively *via* cannulation. Additionally, oil pump vacuum allows the removal of *t*-BuOH from the IL phase. Since both starting reagents and epoxide are not present in the RTIL, it can be concluded that the conversion of cyclooctene is achieved by a biphasic reaction and not by a homogeneous reaction. This catalytic procedure was repeated three times without any loss of activity and consequently without any leaching effects. Additionally, the reaction is selective to the desired epoxide in all runs and no diol formation was observed.

Furthermore, the two different *ansa*-compounds Mo(η^5-C_5H_4(CH_2-η^1-CH)$(CO)_3$) **8** and Mo(η^5-C_5H_4($CH(CH_2)_n$)-η^1-CH)$(CO)_3$ **9** (Figure 3) were examined as precursors for the biphasic epoxidation of several olefins.



8 9

Figure 3. *Ansa*-molybdenum catalyst precursors.

For all investigated reactions, both the yields and the TOFs for catalysis carried out in RTILs were much higher than in all conventional solvents. The applied biphasic catalytic systems clearly outperform previously published homogeneous catalyst systems. In the oxidation of *cis*-cyclooctene, quantitative yields without formation of diols were observed and TOFs up to 44000 h^{-1} were reached. The product phase can be easily separated from the biphasic system. Catalyst **9** can be reused for at least three subsequent runs with only a minor loss of activity. The work shows that

accordingly replacing the conventional solvents CH_2Cl_2 by more sustainable ionic liquids in lab scale reactions seems to be recommendable and a scale up of such reactions appears to be a promising step for the future.

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