

Technische Universität München

Fachgebiet Molekulare Katalyse

Application of imidazolium based ionic liquids as solvents and catalysts in the epoxidation of olefins – Influence of the substitution pattern of the imidazolium cation on ion-pairing and catalytic activity

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"It is the brain, the little gray cells

On which one must rely.

One must seek the truth within – not without."

Agatha Christie (Hercule Poirot)

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"If I don't practice every day, the other's will."

(Phil "The Power" Taylor)

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flight to the imagination and life to everything.” (Plato)*

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„These blondes, sir, they're responsible for a lot of trouble.“
(Agatha Christie - The Labours of Hercules)

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“You want beauty“, said Hercules Poirot. “Beauty at any price.

For me, it is truth. I want always truth.” (Agatha Christie)

Deutsches Abstract

Ionische Flüssigkeiten mit Imidazoliumkationen können als Lösemittel und aktive Komponenten in der Oxidationskatalyse fungieren.

Der erste Teil dieser Arbeit beschränkt sich auf die Anwendung von ionischen Flüssigkeiten als Lösemittel für die Wiedergewinnung der aktiven Molybdänkatalysatoren in der Epoxidationskatalyse. Dabei wurde der Einfluss des Liganden der carbonylierten Ausgangsverbindung mittels NMR- und IR-Spektroskopie, sowie Röntgenkristallographie und DFT Rechnungen untersucht. Es scheint, dass je stärker die Mo–R Bindung ist, desto langsamer findet die Decarbonylierung und Bildung der aktiven Spezies statt. Deshalb ist eine einfache Korrelation der Aktivität mit der *Lewis* Azidität nicht immer möglich. Zusätzlich besitzt das Substrat einen großen Einfluss auf die Bildung der aktiven (oxo-peroxo und dioxo) Spezies.

Der zweite Teil dieser Arbeit beschäftigt sich mit der Interaktion des Imidazoliumkations mit dem Bromidanion (und dem Einfluss auf die katalytische Cycloaddition von Propylenoxid zu Propylencarbonat) und dem Perrhenatanion (und dessen Effekt in der zweiphasigen Epoxidation von Olefinen). Die Azidität des C2-Protons und die Seitenarme des Imidazoliumkations haben einen großen Einfluss auf die Reaktivität des jeweiligen Anions da sie die elektronische Umgebung, die sterische Zugänglichkeit, sowie die Löslichkeit der Katalysatoren beeinflussen. Dies ist in der Epoxidation von Olefinen deutlich sichtbar, bei der die Methylierung der C2-Position und die Einführung einer langen Alkylseitenkette zu einer eindeutigen Erhöhung der Aktivität führen. Dieser Effekt wird auch der Bildung von Mizellen im Laufe der Reaktion zugeschrieben. Mit einer optimierten Struktur des Kations konnte zum ersten Mal bewiesen werden, dass relativ einfache (und wiederverwendbare) Imidazoliumperrhenate als aktive Katalysatoren, in der heterogenen Epoxidation von Olefinen mit Wasserstoffperoxid fungieren können. In diesem Zusammenhang wurden auch die Ökotoxizität und der biologische Abbau von Ammonium- und Imidazoliumperrhenaten untersucht. Es zeigte sich, dass Imidazoliumperrhenate an sich nicht abbaubar sind und vor allem lange Seitenketten eine intrinsisch höhere Toxizität besitzen. Dabei ist das Perrhenatanion nicht schädlicher als (kommerziell eingesetzte) Standardanionen und der toxische Effekt der Imidazoliumperrhenate wird vor allem durch die Struktur des Kations gesteuert.

English Abstract

Imidazolium based ionic liquids can act as solvents in catalysis and active species in oxidation catalysis. The first part of this thesis focuses on the application of ionic liquids as solvents for the recycling of active molybdenum catalysts in epoxidation catalysis. Besides, the influence of the ligand attached to the cyclopentadienyl tricarbonyl precursor is investigated with NMR and IR spectroscopy, as well as X-Ray diffraction crystallography and DFT calculations. The stronger the Mo–R bond, the slower seems to be the decarbonylation and formation of the active species. Therefore, simple correlation between activity and *Lewis* acidity is not always possible. Additionally, the substrate has a major impact on the formation of the active (oxo-peroxo and dioxo) species.

In the second part of this thesis the interaction of the imidazolium cation with the bromide anion (and its influence on the catalytic cycloaddition of propylene oxide to propylene carbonate with carbon dioxide) and the perrhenate anion (and its effect on the biphasic epoxidation of olefins) is regarded in detail. The acidity of the C2 proton and the wing-tips of the imidazolium moiety have a great influence on the reactivity of the anion resulting from changes of the electronic environment, steric accessibility and solubility of the catalysts. Especially for the epoxidation of olefins, the methylation of the C2 position and the attachment of one long alkyl side chain lead to a high activity presumably due to the formation of micelles in the course of the reaction. For the first time it was demonstrated that relatively simple (and recyclable) imidazolium perrhenates, with an optimized cation structure, are able to act as active catalysts in the heterogeneous epoxidation of olefins with hydrogen peroxide. In this context, the (eco)toxicity and the biodegradation of different ammonium and imidazolium perrhenates were under examination showing that the imidazolium cation is not biodegradable and long alkyl side chains exhibit a distinct toxic effect. Interestingly, the perrhenate anion is comparably harmful than standard (and commercially applied) anions and the toxic effect mainly depends on the structure of the imidazolium cation.

List of Abbreviations

Bz	benzyl
Bz ^{F5}	pentafluorobenzyl
Cp	cyclopentadienyl
DFT	density functional theory
EO	ethylene oxide
HFIP	hexafluoroisopropanol
IL	ionic liquid
MTO	methyltrioxorhenium
NHC	<i>N</i> -heterocyclic carbene
NMR	nuclear magnetic resonance
PO	propylene oxide
RTIL	room temperature ionic liquid
SIP	supramolecular ion pair
TSIL	task-specific ionic liquid
TBHP	<i>tert</i> -butyl hydroperoxide
UHP	urea hydrogen peroxide
xs.	excess

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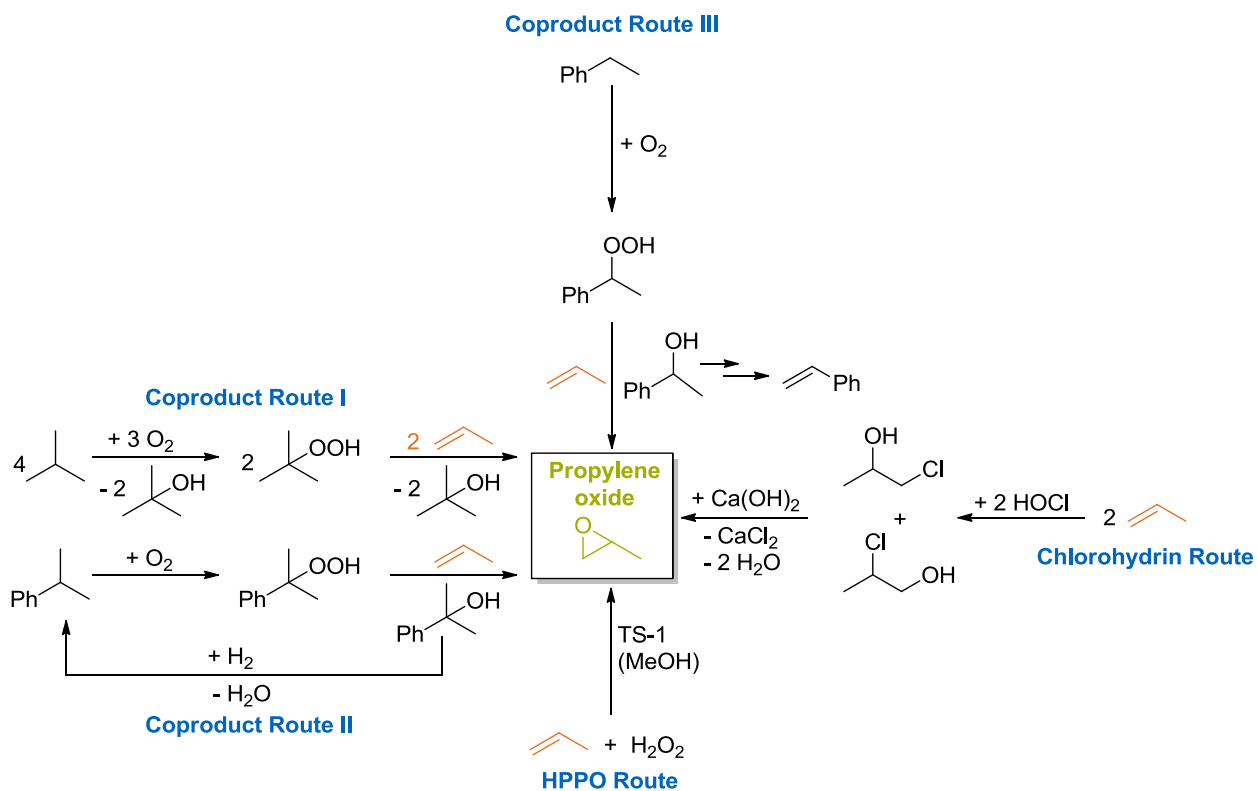
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I. Introduction

I. Introduction

I.1 Epoxidation catalysis in industry

Epoxidation reactions are key processes for the synthesis of a variety of bulk chemicals such as polyurethanes, polyglycols and polyamides as well as fine chemicals (pharmaceuticals, surfactants).¹⁻⁶ The industrial relevant epoxides ethylene (EO) and propylene oxide (PO) are synthesized by means of heterogeneous catalysis (silver on alumina for ethylene oxide and a gold-doped titanium for propylene oxide). A main challenge regarding the industrial production of PO is that a direct epoxidation in high yields is not possible with oxygen or air without suitable mediators.⁷ The commonly applied processes for the industrial production of EO and PO are summarized in scheme I.1.1.^{1, 3, 4, 7-9}



Scheme I.1.1 Different routes for the industrial synthesis of PO.⁷

For simple molecules heterogeneous catalysis is advantage as usually cheap oxidants (air, oxygen or hydrogen peroxide) can be applied and the recycling of the catalyst is more facile (compared to homogeneous systems) enabling high turnover numbers (TONs).

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However, the substrate scope is limited, especially concerning pharmaceuticals which require stereoselective transformations. Moreover, usually low activities, which are indicated by low turnover frequencies (TOFs) are quite common for heterogeneous reactions. Molecularly defined homogeneous catalysts were developed by Sharpless, Jacobsen, Katsuki and Kochi. In order to overcome the disadvantage of a limited substrate scope chiral ligands like tartrates and salen-type ligands were applied in these cases, thereby enabling asymmetric epoxidation reactions.^{2, 10-14} This development led to an explicit improvement in the synthesis of natural products and fine chemicals.¹¹ A brief overview of the main advantages and disadvantages of catalysis in homogeneous and heterogeneous phase is given in figure I.1.1.

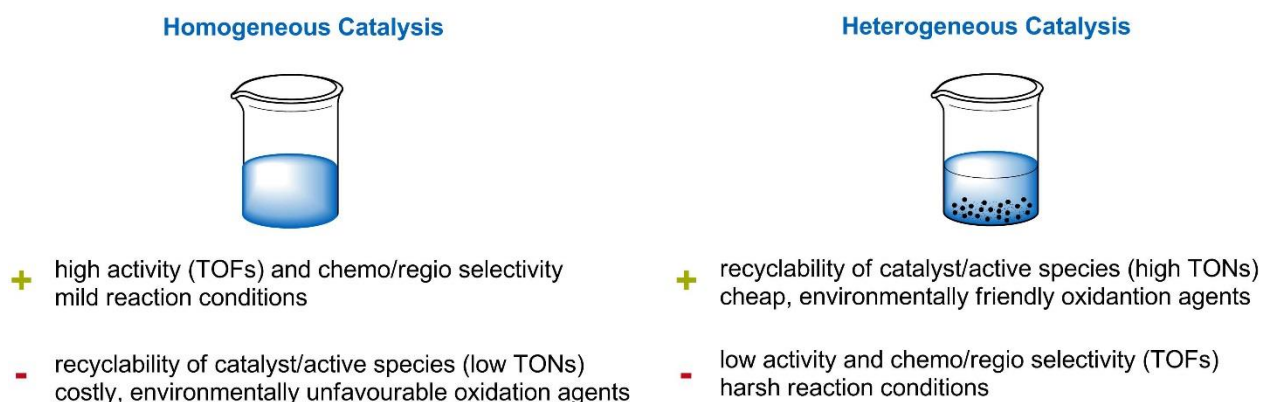


Figure I.1.1 Overview of advantages and disadvantages of homogeneous and heterogeneous catalysis.

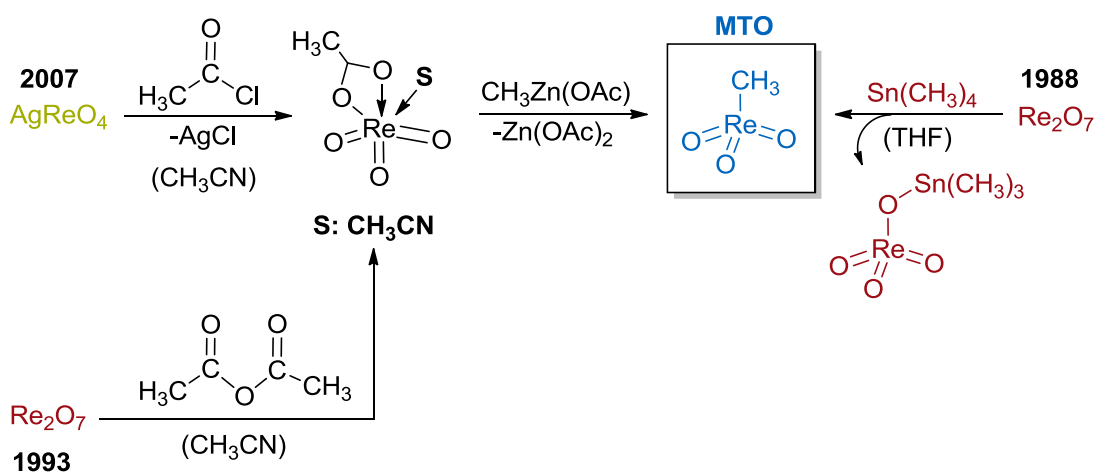
Still challenging in homogeneous epoxidation catalysis is the use of unusual (and typically) costly oxidants such as iodosyl benzene and *tert*-butyl hydroperoxide (TBHP), relatively high catalyst loadings and (still in some parts) a limited substrate scope.¹² The necessity of a molecular catalyst which combines the advantages of a heterogeneous catalyst (such as high TONs, cheap and environmentally friendly oxidants and catalysts) with the abilities of homogeneous catalytic systems (high TOFs, broad substrate scope, mild reactions conditions) still remains. Further, a long term objective in homogeneous catalysis is the introduction of chiral ligand motifs to the, usually catalytically active, metal center particularly designed for a certain “target” olefin. Changes in the steric and electronic structure of the ligand could be used to influence the catalytic activity (e.g. via solubility), stability (immobilization with suitable linkers) and stereoselectivity (via sterically demanding ligands).

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I.2 Homogeneous epoxidation reactions with Methyltrioxorhenium

The history of methyltrioxorhenium (MTO) started with its accidental discovery in 1979 by Beattie and Jones. It was rather seen as mere lab curiosity, which was isolated as decomposition product of trimethyldioxorhenium (VII) in low yields.¹⁵ Its application in oxidation catalysis started a decade later when Herrmann and co-workers found a high yielding synthetic pathway which has been improved in the past decade leading to a relatively cheap, simple, non-toxic and high-yielding synthesis of MTO (Scheme I.2.1).¹⁶⁻

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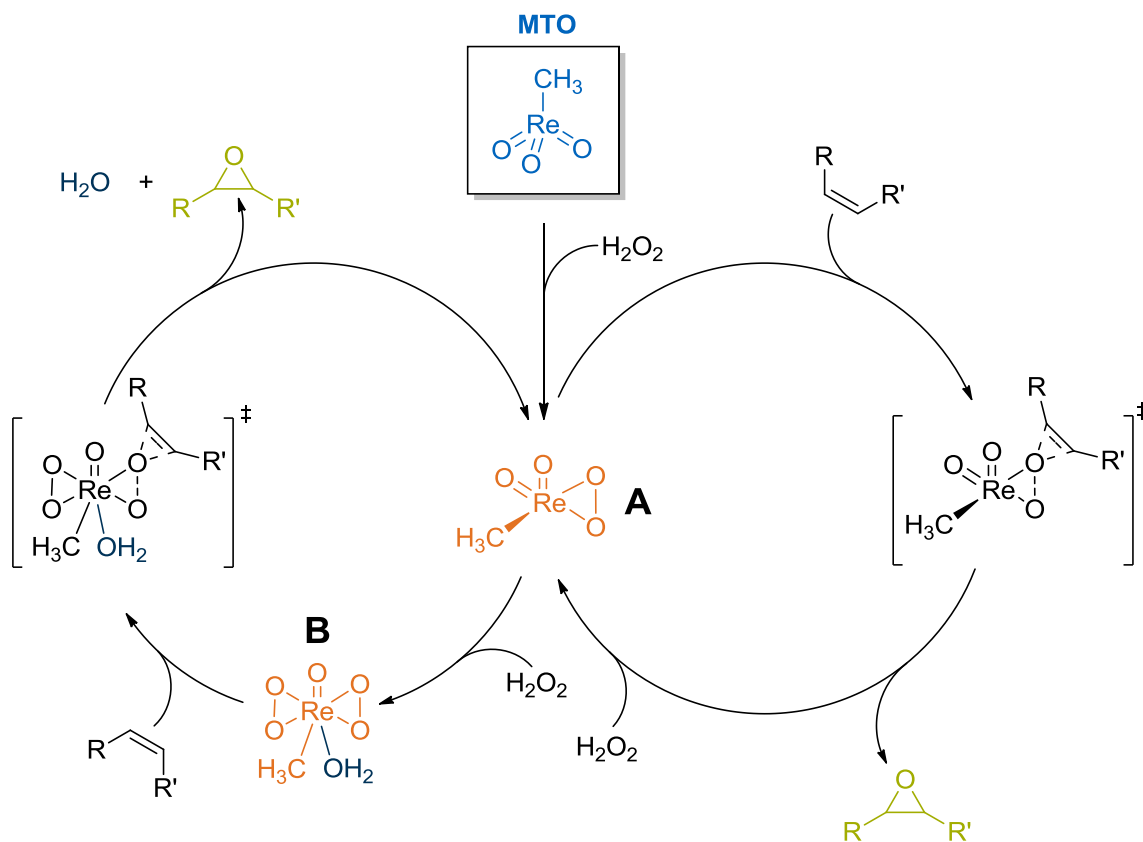


Scheme I.2.1 Synthetic routes for the synthesis of MTO in the past decades.

Since the early 1990s, several groups applied MTO in the oxidation of several substrates, e.g. alkenes,²²⁻²⁴ alkynes,²⁵ sulfur compounds,^{26, 27} phosphines,²⁸ halides²⁹ and organo-nitrogen³⁰ compounds. Especially its potential in epoxidation catalysis was revealed. The mechanism of the epoxidation reaction was investigated by the groups of Herrmann and Espenson by applying catalytic and stoichiometric amounts of MTO and different quantities of hydrogen peroxide as oxidant of choice (Scheme I.2.2).^{31, 32} With low excess or stoichiometric amounts of oxidant, MTO reacts to the monoperoxo complex $[(\text{CH}_3)\text{Re}(\eta^2\text{-O}_2)\text{O}_2]$ (**A**) which could only be identified applying *in-situ* spectroscopic methods. To date, it was not possible to crystallize or isolate this species. Excess of peroxide leads to the formation of the bisperoxo complex $[(\text{CH}_3)\text{Re}(\eta^2\text{-O}_2)_2\text{O}]\text{-L}$ (**B**) which could be identified with several ligands using *in-situ* spectroscopy and X-Ray diffraction crystallography. According to Espenson and Herrmann both complexes take part in the

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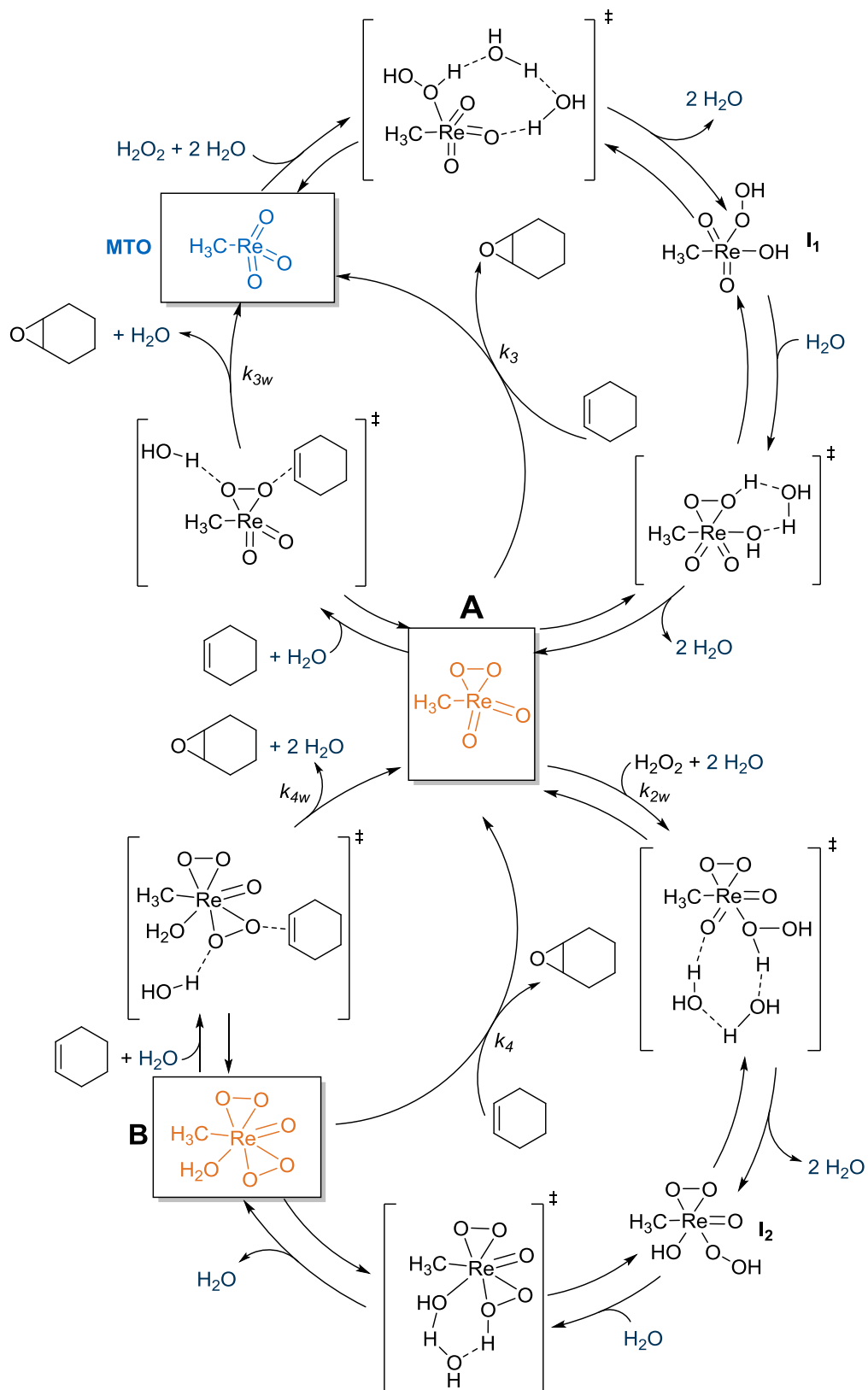
epoxidation of olefins, but only the bisperoxo species is able to transfer one oxygen atom to the olefin without additional oxidant.



Scheme I.2.2 Mechanism of the catalytic epoxidation of olefins with MTO and hydrogen peroxide as oxidant of choice.

A recent study by Scott et al. demonstrated the important role of water in this epoxidation mechanism with cyclohexene as substrate.³³ Water evidently accelerates the formation of the monoperoxo and bisperoxo complexes involving hydrogen bonding via an outer sphere mechanism. As a consequence a distinct increase of the activity in the epoxidation of cyclohexene was observed (Scheme I.2.3). This observation, 25 years after the first mechanistic proposal, shows that still not every aspect of the catalytic mechanism is clear and that hydrogen bonding is an important factor. This should further be considered for other homogeneous or heterogeneous epoxidation catalysts applying hydrogen peroxide as oxidant.

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Scheme I.2.3 Influence of water on the formation of the active complexes **A** and **B** in the epoxidation of cyclohexene by Scott et al.³³

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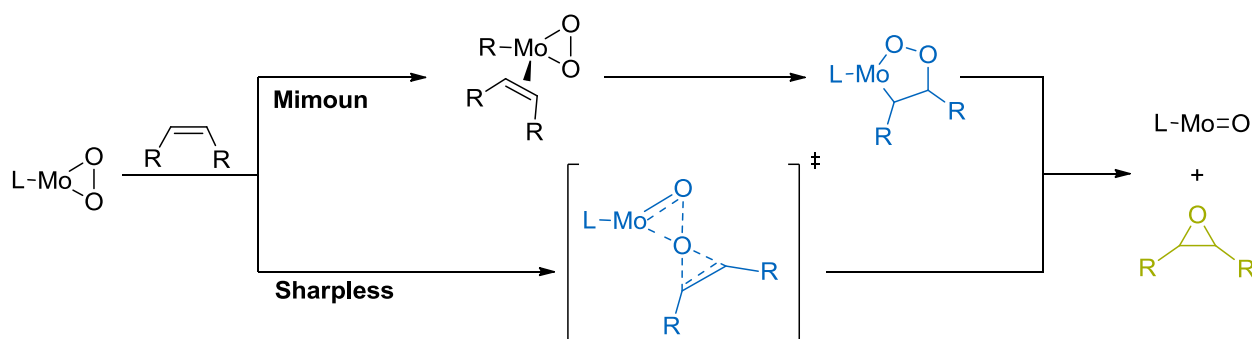
With methyltrioxorhenium as catalyst high turnover frequencies up to **40 000 h⁻¹** were reached with *cis*-cyclooctene as substrate , an excess pyrazole as *Schiff base* and hexafluoroisopropanol (HFIP) as solvent in epoxidation catalysis.³⁴ MTO was additionally applied in the epoxidation of more sophisticated olefins, including 1-octene,³⁴ styrene,³⁵ (+)-limonene,³⁶ α -pinene,³⁷ camphene,³⁸ pseudo-cumene^{39, 40} and the industrial relevant propene,⁴¹ proofing its general applicability in epoxidation catalysis.

The high catalytic activity of MTO (and related homogeneous epoxidation catalysts) can be attributed to the *Lewis* acidity of its metal center. Attempts to enhance the *Lewis* activity by introducing a trifluoromethyl group, failed although several DFT studies predicted that a fluorinated derivative of MTO should be stable.⁴²⁻⁴⁵

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I.3 Homogeneous epoxidation reactions with molybdenum based catalysts

The application of molybdenum-containing catalysts for epoxidation reactions started in the early 1970s after the development of the Halcon/ARCO process where molybdenum hexacarbonyl acts as pre-catalyst for the epoxidation of propylene. The catalytically active species is formed *in-situ* after oxidative decarbonylation of the carbonyl precursor. First mechanistic proposals were given by the groups of Sharpless⁴⁶ and Mimoun^{47, 48} (Scheme I.3.1).

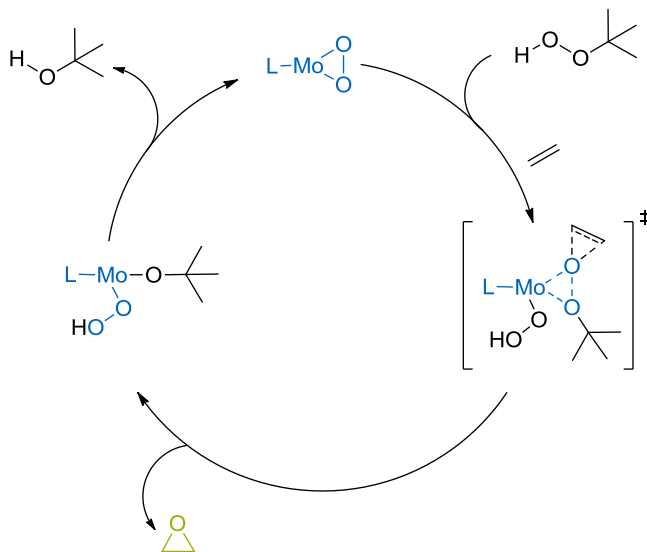


Scheme I.3.1 Proposed mechanism by Mimoun and Sharpless et al. for the epoxidation of olefins with molybdenum peroxo compounds.

Mimoun et al. proposed a multi-step mechanism involving the coordination of the olefin to the metal center. Subsequently the olefin is inserted into the metal-peroxo bond forming a five-membered metallacycle as intermediate, which is followed by elimination of the epoxide. The proposal of Sharpless includes the formation of a spiro-like transition state without direct interaction of the olefin with the metal center. This mechanism is in accordance with a DFT study conducted in 1995 by the group of Thiel and co-workers. In this study *tert*-butyl hydroperoxide (TBHP) was used as typical oxidant, since most molecular molybdenum based catalysts suffer from decomposition in the presence of water (Scheme I.3.2).⁴⁹ Typical already oxidized molybdenum catalysts are e.g. mononuclear organomolybdenum complexes and related compounds like dimethyl-dioxo-molybdenum(VI)-bipyridine (for homogeneous catalysis)⁵⁰⁻⁵² or polyoxomolybdates (in heterogeneous catalysis).⁵³ Molybdenum tricarbonyl or NHC dicarbonyl complexes proved to be suitable precursors due to a better stability towards air and moisture in comparison to the oxidized catalysts. Especially cyclopentadienyl tricarbonyl derivatives

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of the type $[\eta^5\text{-C}_5\text{R}'_5\text{Mo}(\text{CO})_3\text{R}'']$ ($\text{R}' = \text{H}, \text{CH}_3, \text{Bz}$; $\text{R}'' = \text{Cl}, \text{CH}_3, \text{CF}_3$)⁵⁴⁻⁵⁷ are well examined in literature. This includes studies on their activity in epoxidation catalysis, and mechanistic considerations using theoretical calculations to analyze the formation of possible intermediates and active species.⁵⁸⁻⁶⁰



Scheme I.3.2 Proposed mechanism Thiel et al. for the epoxidation of ethylene with TBHP as oxidant.

Relatively similar energy barriers for different active species imply that it is difficult to suggest one certain mechanism without further analytic evidence (including X-Ray crystallography and *in-situ* NMR and IR spectroscopy). Distinct advantages of these compounds compared to methyltrioxorhenium are the cheaper metal price of molybdenum, the possibility of recycling and easy derivatization or insertion of ligands. While it was so far not possible to introduce a trifluoromethyl group in MTO, it was possible to synthesize $[\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{CH}_3]$ and its fluorinated derivative $[\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{CF}_3]$ and compare their activity in epoxidation catalysis.⁵⁷ This example showed that a simple correlation between *Lewis* acidity and activity in epoxidation catalysis is not always possible. The fluorinated compound is more *Lewis* acidic and a higher activity is expected. However, the decarbonylation is very slow under standard conditions, so that the methylated compound is more active. After decarbonylation and isolation of the oxo-peroxo species the fluorinated compound is far more active and its true potential is revealed.^{57, 58} Revealing the possible reasons for the slow decarbonylation of the fluorinated tricarbonyl complex is also part of this thesis. For at least a decade the

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commonly synthesized molybdenum metal complexes were not able to compete with MTO in terms of activity. This changed with the development of ansa-cyclopentadienyl molybdenum complexes of the type $[\text{Mo}(\eta^5\text{-C}_5\text{H}_4(\text{CH})(\text{CH}_2)_n\text{-}\eta^1\text{-(CH)})(\text{CO})_3]$.⁶¹⁻⁶³ With the ionic liquid $[\text{C}_4\text{C}_{1\text{im}}][\text{NTf}_2]$ (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) as solvent it was possible to achieve TOFs of up to **44 000 h⁻¹** for the epoxidation of *cis*-cyclooctene and high activities for other more sophisticated olefins.⁶¹ However, the original goal, to introduce a stereocenter next to the molybdenum atom and the modification of the cyclopentadienyl ring system to achieve high enantioselectivity in epoxidation catalysis, was not accomplished. It was assumed that the additional ring strain might lead to the observed poor stabilities of the complexes.⁶⁴ *N*-heterocyclic carbene (NHC) ligands were also applied for the synthesis of molybdenum cyclopentadienyl complexes. Advantages are their higher complex stability due to their strong σ -donating and poor π -accepting character.^{65, 66} Ansa-bridged cyclopentadienyl-imidazolylidene molybdenum complexes were first synthesized by Royo et al.⁶⁷ These complexes are all active in epoxidation catalysis with the main disadvantage of a rather enhanced induction period, compared to the tricarbonyl complexes. Hor and Zhao et al. reported the synthesis of a series of neutral dicarbonyl complexes of the type $[\text{CpMo}(\text{CO})_2(\text{NHC})\text{X}]$ ($\text{X} = \text{halide}$), and an ionic complex of the type $[\text{CpMo}(\text{CO})_2(\text{IMes})(\text{NCCH}_3)][\text{BF}_4]$ ($\text{IMes} = 1,3\text{-bis}(2,4,6\text{-trimethylphenyl})\text{imidazol-2-ylidene}$).⁶⁸ With the latter compound it was possible to achieve TOFs of over **3400 h⁻¹**. An additional, but also quite ineffective triazolylidene NHC based catalyst, has been reported in 2013, which was applied as pre-catalyst in epoxidation catalysis using ionic liquids as solvents.⁶⁹ In 2014 Kühn et al. demonstrated that already high activities (in terms of TOFs) can be achieved with NHC based molybdenum complexes which are able to challenge the highly active MTO. By applying the neutral complex $[\text{CpMo}(\text{CO})_2(\text{ImPyMes})(\text{NCCH}_3)][\text{BF}_4]$ in the epoxidation of *cis*-cyclooctene it was possible to reach a TOF of ca. **53 000 h⁻¹**.⁷⁰ Although it was possible to oxidize several other substrates like 1-octene, styrenes and stilbenes it was, so far, not possible to oxidize further sophisticated substrates, which is already feasible with MTO as catalyst (see chapter 1.II).^{2, 71, 72} Similar to MTO it was also not possible to achieve enantiometric excesses using chiral catalysts and prochiral substrates. A definite reason is still under discussion but a conceivable explanation might be that, for most complexes, the chiral groups are too far located from the active molybdenum metal center.

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I.4 Iron complexes as cheap alternatives in homogeneous epoxidation catalysis

Iron NHC complexes in general are used in several catalytic reactions.⁷³ Complexes of this class recently also proved to be active in homogeneous epoxidation catalysis.^{74, 75} In comparison to rhenium and molybdenum based complexes, iron as active a center has the major advantage of being the most common non-toxic transition metal in the earth's crust. Thus, using iron is far more cost-efficient and potentially applicable in industry.⁷⁶ Natural systems built up with iron cofactors developed billion years ago and are able to oxidize organic compounds in usually high activities and selectivity. Therefore, the synthesis and application of iron porphyrin complexes is of high academic interest especially (in dependence on the role of the cytochrome P450 systems in nature) in epoxidation catalysis.⁷⁷ First examples were introduced over 30 years ago by Groves.⁷⁸ Since then, also nonheme based systems were developed by other groups, mainly based on amino-pyridine ligand motifs.^{76, 79-84} Some bipyrrrolidine and biperidine derived systems are also promising candidates for asymmetric epoxidation catalysis.⁸⁵⁻⁸⁸ In terms of activity, it was recently shown that NHC based iron complexes can outperform previously mentioned molybdenum and rhenium based catalysts. *Cis*-cyclooctene was epoxidized with TOFs of up to **184 000 h⁻¹** and other rather simple olefins (see Figure I.4.1) were also converted more efficiently.⁷⁴ A remarkable effect is that a small change in the oxidation state of iron (from +II to +III) lead to a more than tripled activity. Similar to the molybdenum based molecular catalysts, a definite mechanism is still under discussion. However, an iron(III) hydroperoxo species is regarded as most possible intermediate in the formation of the actual active species in several mechanistic studies.^{76, 81, 89} Therefore, iron(II) complexes seem to be disadvantageous for the application in epoxidation catalysis as, prior to the catalytic process, a one electron Fenton-type oxidation step is necessary. In the course of this reaction, radicals are produced which might lead to the observed catalyst decomposition and low selectivity.^{74, 90} The most active rhenium, molybdenum and iron based homogeneous epoxidation catalysts are shown in Figure I.4.1 including their activities and advantages as well as disadvantages.

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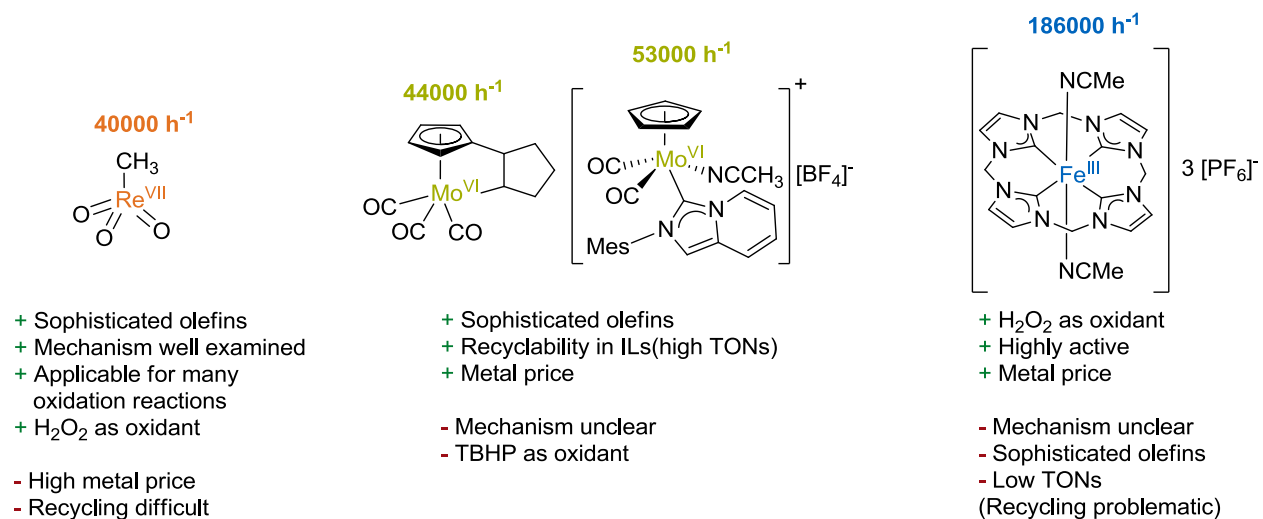


Figure I.4.1 Most active molecular rhenium, molybdenum and iron based catalysts (in terms of TOFs on top of the respective structure) for the homogeneous epoxidation of *cis*-cyclooctene (as benchmark substrate) including advantages as well as disadvantages.

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I.5 Ionic liquids – Applications in industry

The interest in the field of ionic liquids (ILs), which are known since the 20th century in academia, has risen exponentially since the early 1990ies and has still grown fast in the last ten years (Figure 1.5.1).

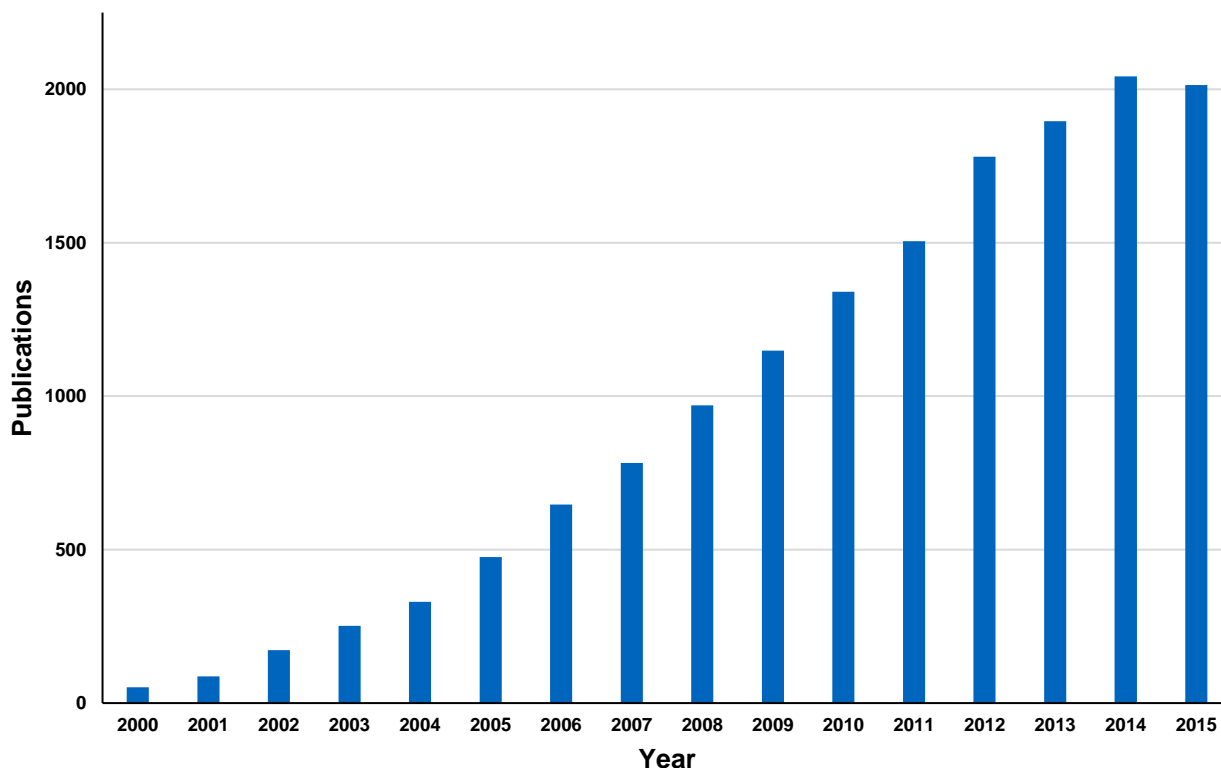


Figure I.5.1 Number of publications dealing with ionic liquids (source: Thomson Reuters – ISI Web of Science, Date: 04.04.2016, search term: „ionic liquid“).

Ionic liquids are (by definition) salts with a melting point lower than 100 °C, and are therefore often referred as “liquid salts”. ILs that are liquid at room temperature are further denoted as RTILs (room temperature ionic liquids).⁹¹ Their unique chemical and physical properties (e.g. low miscibility with non-polar, organic solvents, low flash points, thermal stability, low volatility, low toxicity for several compounds and high polarity) make ILs suitable candidates to replace conventional organic solvent systems (in academia and industry). A lot of general reviews about ionic liquids⁹¹⁻⁹⁵ as well as ionic liquids in catalysis⁹⁶⁻¹⁰¹ and their application in industry¹⁰²⁻¹⁰⁴ have been published in the last decade. Several groups, like Wasserscheid,⁹¹ Seddon,¹⁰⁵⁻¹¹³ Rogers,¹¹⁴⁻¹¹⁸ Welton^{92, 93, 96,}

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¹¹⁹⁻¹²¹ and Dupont^{95, 97} investigated ILs as reaction media in two-phase catalyzed reactions. Their fundamental research results enabled potential applications of ILs in industry and smoothed the way for this field. A distinct advantage of ILs is the possibility to synthesize and combine a vast number of cations with anions. This makes it feasible to “design” task-specific ILs” (TAILs) with the desired physicochemical behaviors (see Figure 1.5.2) by combination of the “right” anions and cations. Thereby, even small changes on the cation moiety can lead to vast differences in solubility and catalytic activity.¹²²⁻¹²⁴

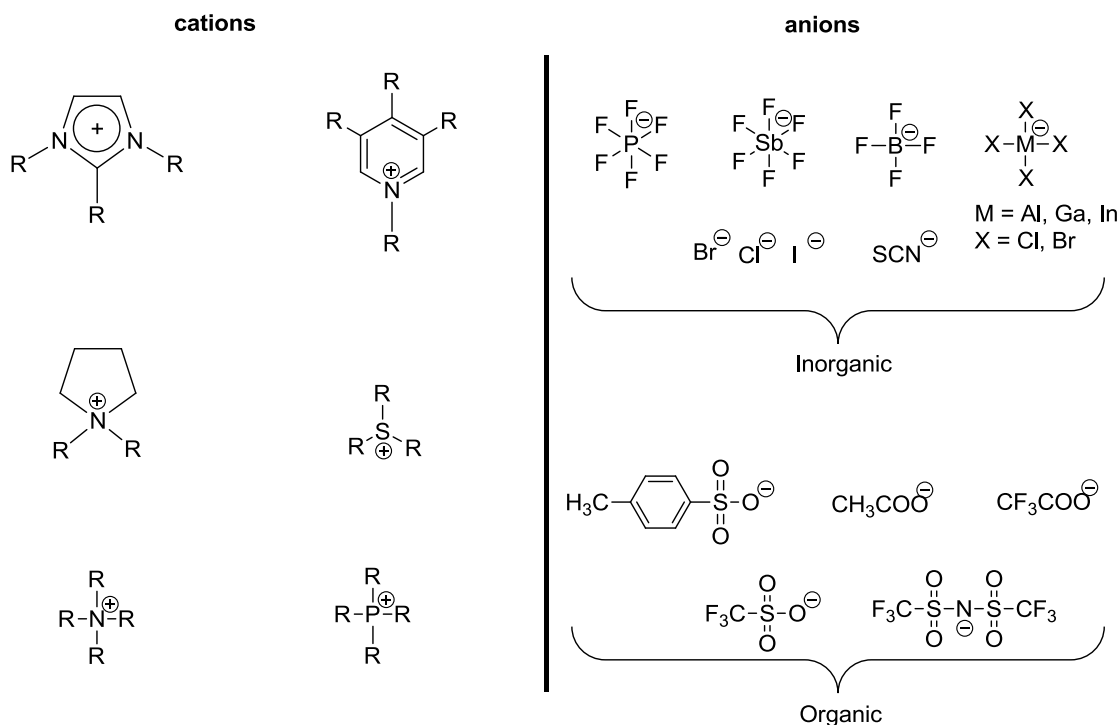


Figure 1.5.2 Commonly used cations and anions which can be combined to ionic liquids (R = alkyl).

The potential of ILs lead to various industrial applications since the late 1980s, of which the most important are summarized in the following. Several companies contributed to the application of ILs including BASF, Evonik Degussa, Eastman Chemical Company, IFP (Institute France petrole) – Axens, Central Glass company, SASOL, Exxon Mobile, BP, Petro China to name the most important. Already in 1996, Eastman Chemical Company established the first industrial RTIL process: the isomerization of 3,4-epoxybut-1-ene to 2,3-dihydrofuran.¹²⁵ Hereby, a *Lewis* basic phosphonium based IL was used in combination with a *Lewis* acid based catalyst.

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The BASIL™ (**B**iphasic **A**cid **S**cavenging utilizing **I**onic **L**iquids) process is one of the most prominent examples for the use of ionic liquids in an industrial process, which has been introduced in 2002.^{114, 126} In the course of the reaction alkoxyphenyl-phosphines are produced, which are commonly used as photoinitiator precursor. In the former process trimethylamine was used to scavenge the acid formed during the reaction. This had several disadvantages in handling and product separation. 1-Methylimidazole was used as replacement, leading to significant improvements as the IL 1-methylimidazolium chloride is formed, which is self-separating and can be easily handled (Figure 1.5.3).

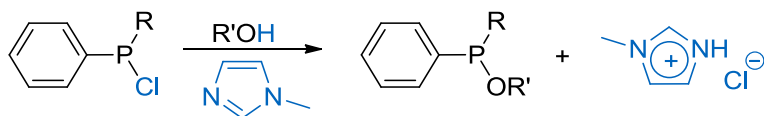


Figure I.5.3 BASIL™ process, introduced by BASF in 2002.

IFP launched the first ionic liquid pilot plant for the dimerization of short chain alkenes to more valuable alkenes (Dimersol process), which is usually performed without solvent.^{104, 127-130} Chloro-aluminate(III) ILs were introduced as suitable solvents for the catalytic active nickel complex with the general formula $[(PR_3)NiCH_2R'] [AlCl_4]$. As a result, the overall activity and selectivity as well as the olefin scope of the catalytic process were improved (patented as DIFASOL process).

The following examples of industrial applications are presented to highlight the influence of the cation moiety. Especially the acidic C2 proton (in the imidazolium cation) or long alkyl wing tips can influence the performance of any catalytic reaction dramatically. This thesis mainly dealt with these influences and the industrial applied examples illustrate the relevance of these factors apart from academia.

The metathesis of olefins is an industrial relevant field, awarded with the Nobel Prize in chemistry in 2005.¹³¹ SASOL used ILs in metathesis (first described in 2003)¹³² and olefin trimerisation reactions with Grubbs catalysts of the first, second and third generation (Grubbs-Hoveyda).¹⁰² While no improvement was observed for the first generation, a remarkable positive change concerning activity and selectivity was found for the second generation. The Grubbs-Hoveyda catalysts were even more active, outperforming the results of the reaction without ILs as solvent. The company also studied the influence of the chain length of the imidazolium wing tips on the catalytic activity. The shorter the alkyl

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chain, the faster is the catalytic reaction. With the IL 1,2-dimethyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide, it was possible to conduct the reaction at mild temperatures, thereby expanding the life time (TON) of the catalysts.

The Sonogashira coupling, a palladium-copper catalyzed reaction of terminal alkyl-, or aryl-alkynes with aryl halides, was carried out by the Central Glass Company in ionic liquids.^{133, 134} It was also described earlier that it is possible to use 1-butyl-3-methylimidazolium hexafluorophosphate as solvent. However, the anion hydrolyzed and generated HF under the applied conditions.¹³⁵ Therefore, different anions (and cations) were studied. 1,3-Dialkylimidazolium cations proved to be less efficient than the standard organic solvents (such as toluene or tetrahydrofuran), probably due to the formation of carbenes. This demonstrates the strong influence of the acidic C2 proton. A tetraalkylphosphonium triflate salt of the general formula $[P(C_nH_{2n+1})_3R][OTf]$ ($R = (CH_2)_2C_8F_{17}$) with a fluorinated “wing tip” was also found as a suitable IL. Thus, high yields and an easy product separation were achieved, which enables the recycling of the IL and palladium catalyst without distinct loss in activity for several cycles (Figure 1.5.4).¹³⁶

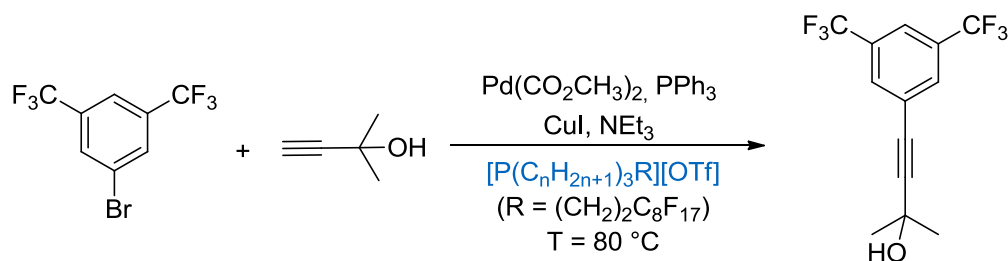


Figure 1.5.4 Industrial applied Sonogashira coupling with phosphonium based IL by the Central Glass Company.

Evonik (previously Degussa) has used ILs for the dissolution of ionic ($H_2[PtCl_6]$) and molecular ($[\mu-Cl]_2[PtCl-(cyclohexene)]_2$) catalysts for the hydrosilylation of polydimethylsiloxanes. No leaching effects occurred, and the products (polyethersiloxanes) were insoluble in the used imidazolium based ILs.¹³⁷⁻¹³⁹ 1,3-Dialkylimidazolium cations did not yield the desired polyethersiloxanes and caused side reactions due to the very reactive C2 proton. The more hydrophilic the applied IL was, the more suitable it was for the reaction. This applies in particular for the ionic catalyst, as the ionic liquid phase could be separated more easily from the (hydrophobic) organosilicon products. The hydrophilicity was controlled via the wing tips on the nitrogen atoms of the

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imidazolium based ILs. In the course of the reaction, the ionic catalyst, which did not suffer from leaching effects compared to the molecular catalyst, is strongly “bound” in the IL (similar to chemically bonded catalysts attached to polymers).

The observed relevant structural features of imidazolium and phosphonium based cations with a distinct impact on catalyst activity are summarized in Figure I.5.5 for the metathesis reaction, Sonogashira coupling and Hydrosilylation. So far, mainly the influence of the anion, the wing tips and the influence of the acidic C2 proton of the cationic moiety are well examined in industrial processes.

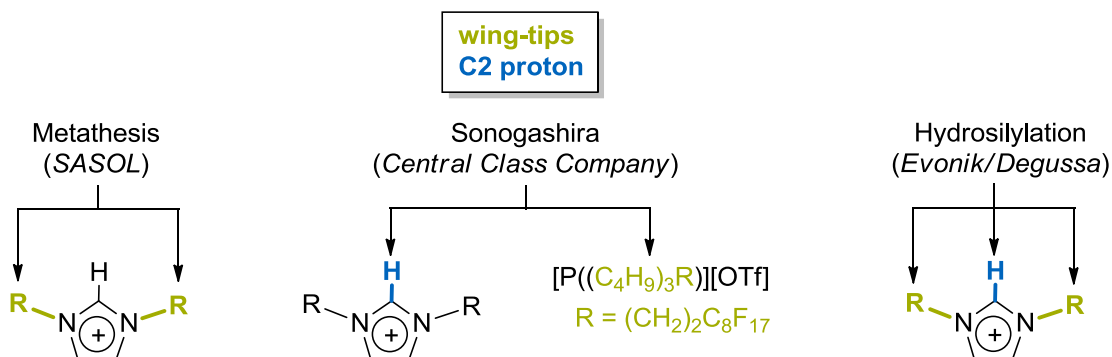
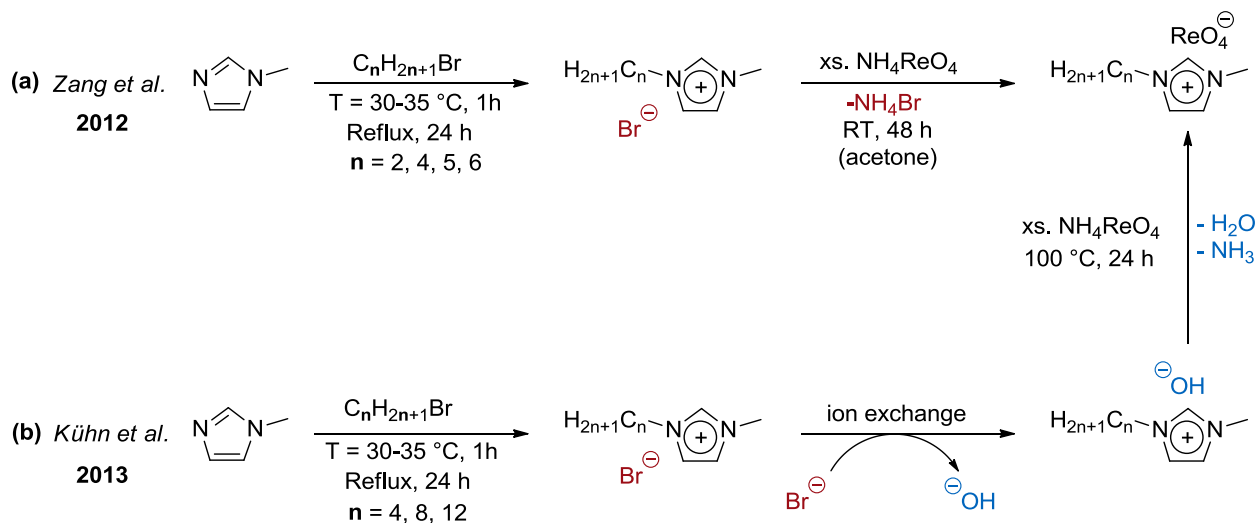


Figure I.5.4 Relevant interaction sites of imidazolium and phosphonium cations important for industrial applied processes using ILs.

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I.6 Perrhenate based ionic liquids as active compounds in the stoichiometric and catalytic epoxidation of olefins

Typically ILs are used as solvents in catalytic oxidation to perform a two-phase reaction with homogeneous catalysts or to enhance selectivity and activities.^{140, 141} Besides, it was demonstrated that perrhenate based imidazolium ionic liquids are able to act as active compounds in the epoxidation of olefins.¹⁴² The perrhenate anion was often regarded as inactive decomposition product of methyltrioxorhenium or other organorhenium(VII) oxides.^{22, 143-146} The imidazolium perrhenates were also synthesized earlier, however with rather low purities by dissolving the respective imidazolium bromides in acetone and subsequent addition of NH_4ReO_4 .¹⁴⁷ This procedure has been improved by first converting the bromide anion to the hydroxide anion followed by the addition of NH_4ReO_4 . No bromide remains in the reaction mixture and the only by-products are water and ammonia, which can be removed by evaporation. The product was diluted in dichloromethane and filtered from excess of NH_4ReO_4 (Scheme I.6.1).



Scheme I.6.1 Synthesis of imidazolium perrhenates using NH_4ReO_4 as perrhenate source by the route of (a) Zang and (b) Kühn *et al.*

ILs with different chain lengths (**I.6.a-I.6.c**, see Figure I.6.1) were applied in a stoichiometric reaction with *cis*-cyclooctene and different oxidation agents at 70 °C for 4 h. At least two main conclusions can be drawn:

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1. The activity is higher, the less bulky the oxidation agents are and
2. the longer the alkyl side chain, the more active is the imidazolium perrhenate.

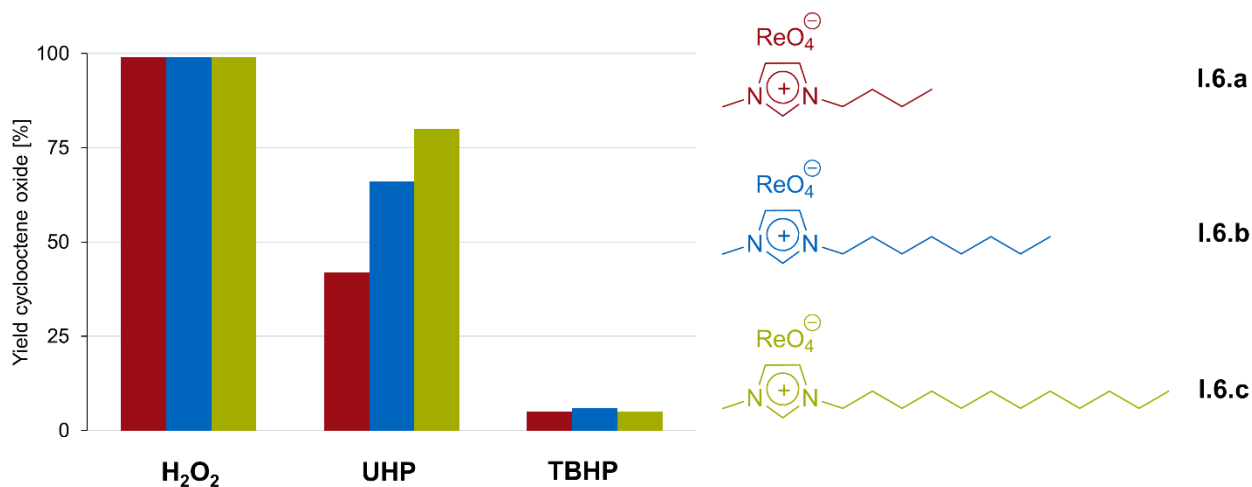
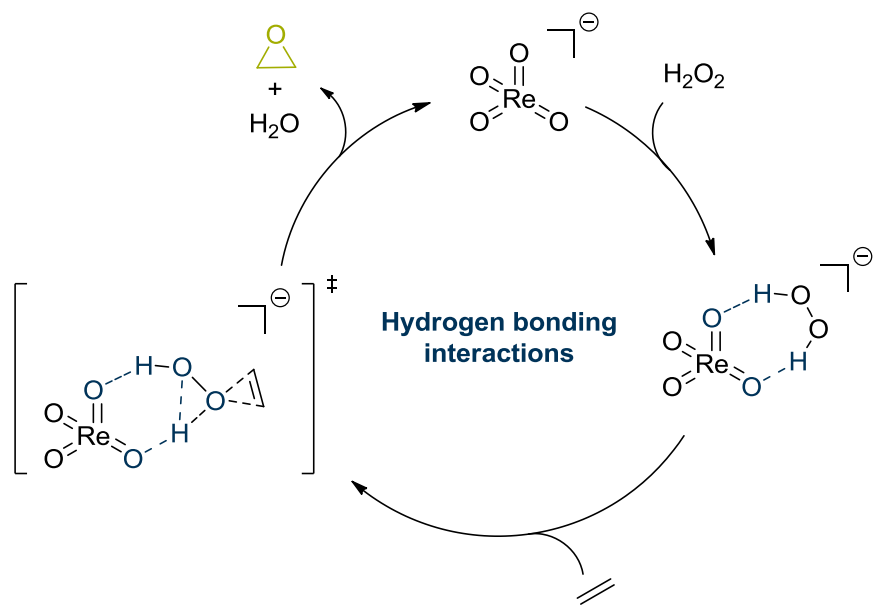


Figure I.6.1 Influence of different oxidation agents and the chain length on the imidazolium moiety on the activity in the epoxidation of *cis*-cyclooctene.

The imidazolium perrhenates are much more active compared to strong coordinating cations, e.g. NH₄⁺ and K⁺. This is an additional hint for a mechanism where the interaction between the anion and cation is crucial. The formation of Re-peroxo or even dioxo species (see MTO in chapter I.2) is excluded by IR spectroscopy (as the local symmetry of the Re center does not change after addition of hydrogen peroxide) and ¹⁷O labelled NMR experiments. The symmetry of the perrhenate anion changes from T_d to C_{2v} after addition of hydrogen peroxide. In combination with these *in-situ* IR and Raman spectroscopic evidence, DFT calculations proposed an outer sphere mechanism where the anion activates the oxidant via hydrogen bonds. Subsequently, the oxygen atom is transferred to the olefin (see Scheme I.6.2). The catalytic results in combination with DFT calculations and spectroscopy imply that the interaction of the anion and cation is an important factor for the perrhenate reactivity. However, it has to be mentioned that solubility effects (instead of steric effects) are also a relevant factor for these observations.

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Scheme I.6.2 Proposed outer sphere mechanism of the activation of hydrogen peroxide with perrhenate.

As it can be seen from many academic examples (and ILs applied in industry - see chapter I.5), small variations result in a significant change of the physicochemical behavior of ILs.¹⁴⁸⁻¹⁵² The understanding of the influence of different substitution patterns on these properties are essential to develop rational design TAILs. Several experimental and theoretical studies described the influence of the substitution on the imidazolium moiety, especially concerning the alkylation of the C2 position^{122, 153-156} and wing tips.^{122, 157-162} DFT calculations of Strassner et al. showed that different substitution patterns lead to a changed distribution of the electron density on the cation. This provides insight in preferred interactions sites of the anion with the cation.^{163, 164} The C2 position is the preferred interaction site on the imidazolium moiety as it possesses a strong partial charge which can be significantly decreased by methylation.^{147, 153} Taking these considerations into account, it is possible to further “tune” the imidazolium cation as counter ion for the perrhenate anion. Figure I.6.2 shows the possible interaction sites of the imidazolium cation. Especially the investigation of the influence of the C2 position of the imidazolium moiety and the effect of the wing tips on ion pairing and catalytic activity are part of this thesis. The great variety of studies concerning the influence of the C2 position and the wing tips (and partially of the backbone protons) show that the imidazolium cation is well examined in academia. However, as shown before a variety of different cations exist and

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the general mechanism of the epoxidation of olefins with perrhenate indicates that further candidates could be suitable counter cations.

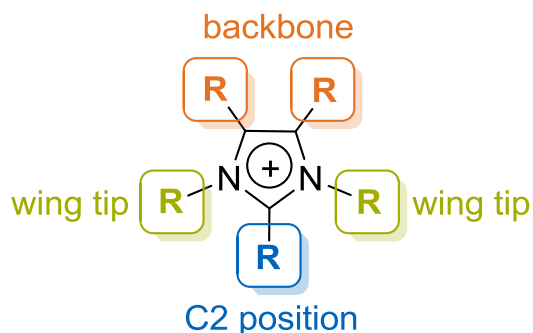
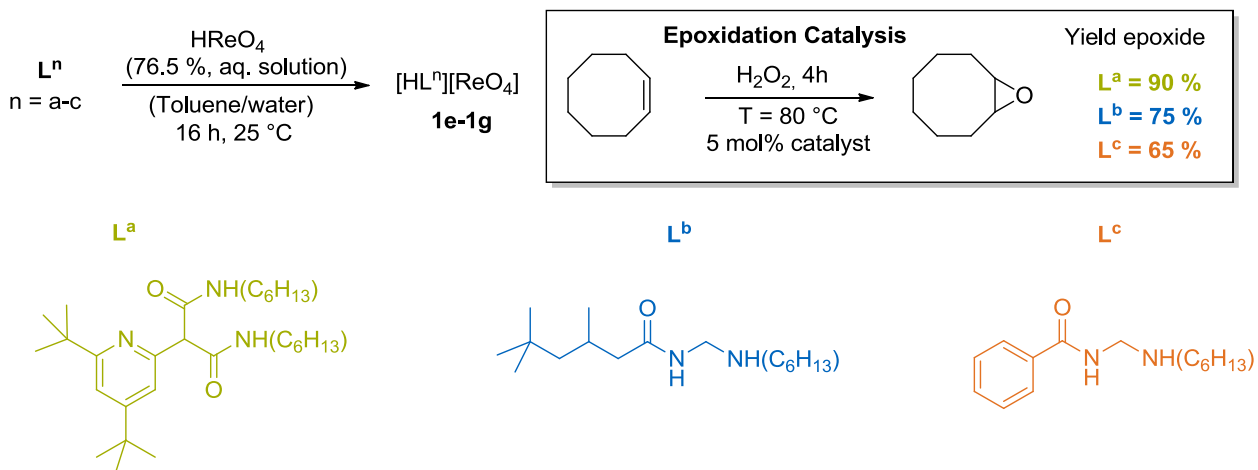


Figure I.6.2 Possible interactions sites of the imidazolium cation with the perrhenate anion.

This was recently demonstrated by Cokoja et al. with the use amido-ammonium and pyridinium receptors forming supramolecular ion pairs (SIPs) with the perrhenate anion (Scheme I.6.3).¹²³ This is the first example using perrhenate based ionic compounds in catalytic amounts as active epoxidation catalysts with hydrogen peroxide as oxidant.



Scheme I.6.3 Synthesis of different perrhenate SIPs and application in the oxidation of *cis*-cyclooctene.

II. Objective

II. Objective

The first part of this work is focused on the development of active cyclopentadienyl molybdenum tricarbonyl complexes as precursor for the homogeneous oxidation of olefins. Varying fluorinated and non-fluorinated ligands were used and their potential for the industrial highly desired epoxidation of olefins was investigated. The influence of the ligands on the *Lewis* acidity of the metal center and the velocity of the decarbonylation and formation of the active species is studied. For this purpose various analytical and theoretical methods like NMR, IR spectroscopy, X-Ray diffraction crystallography and DFT calculations were used. Another key point of this thesis is the analysis of the course of the reaction via *in-situ* spectroscopy to shed some light on the mechanism of the epoxidation of olefins with molybdenum catalysts. Additionally, the application of ionic liquids as solvents for a two-phase reaction is evaluated, which is supposed to enable the recycling of the active catalytic species.

The second part of this thesis deals with the influence of different substituents on the imidazolium cation moiety on ion-pairing and catalyst activity. On the one hand, this was examined anion, in the catalytic cycloaddition of propylene oxide to propylene carbonate with carbon dioxide using imidazolium bromides. On the other hand, the epoxidation of olefins with hydrogen peroxide is investigated with imidazolium perrhenates. It is intended to synthesize a set of different imidazolium cations to find the most suitable cation for the desired catalytic process. In this context the (eco)toxicological effects and biodegradation of different imidazolium (and ammonium) perrhenates are under investigation to find suitable catalysts for a sustainable and “green” epoxidation of olefins.

III. Results – Publication Summaries

In this chapter the publications are summarized which originated from the dissertation. The original manuscripts are attached to this thesis and can be found in its appendix.

III.1 Influence of structural and electronic properties of organomolybdenum(II) complexes of the type $[\text{CpMo}(\text{CO})_3\text{R}]$ and $[\text{CpMo}(\text{O}_2)\text{OR}]$ ($\text{R} = \text{Cl}, \text{CH}_3, \text{CF}_3$) on the catalytic epoxidation of olefins

This publication deals with the synthesis and catalytic investigation of various molybdenum tricarbonyl and oxo-peroxo complexes with different ligands. All complexes were characterized and applied in the oxidation of *cis*-cyclooctene. The focus was to evaluate the influence of the ligand on the decarbonylation for the tricarbonyl complexes and to analyze the impact on the activity in oxidation catalysis (Figure III.1.1). The influence of the ligands was examined by means of IR-spectroscopy, X-ray crystallography and DFT calculations. In order to explain the different catalytic activities the results were compared with literature known compounds.

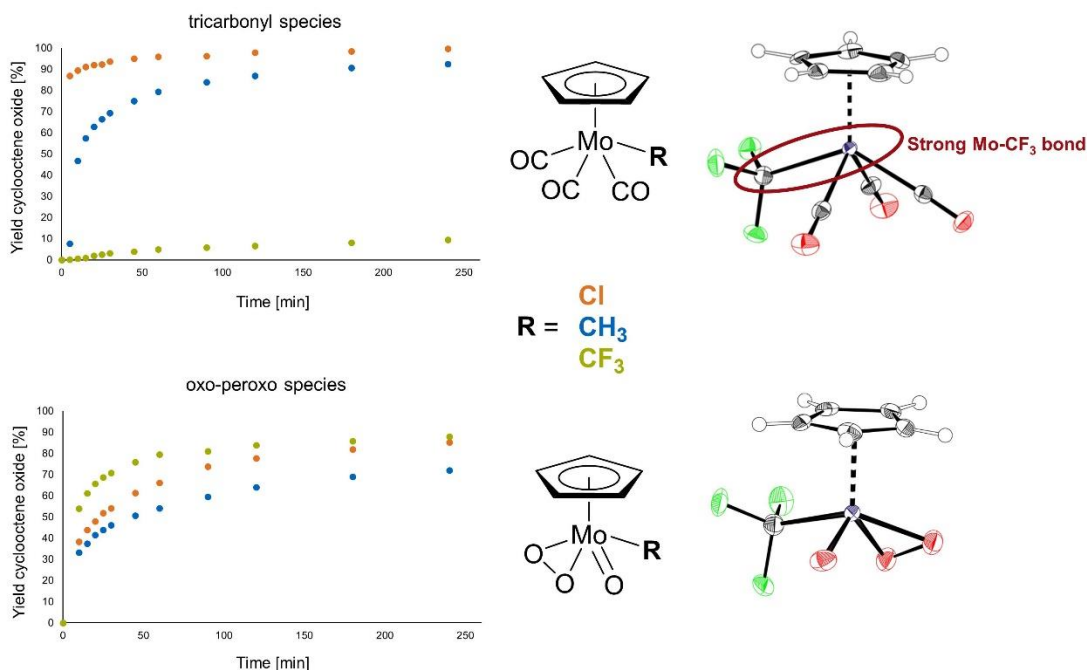


Figure III.1.1 Kinetic plots of tricarbonyl and oxo-peroxo species with different ligands in the epoxidation of *cis*-cyclooctene. Reaction conditions - catalyst:*cis*-cyclooctene:TBHP; ratio: (0.0025:1:1.2); T = 25 °C.

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It has been shown that *Lewis* acidic substituents in molybdenum cyclopentadienyl tricarbonyl complexes do not necessarily enhance the overall catalytic activity. Based on the analytic data (especially IR and X-ray crystallography) a strong bond between the ligand and the molybdenum center is formed for *Lewis* acidic ligands (e.g. CF₃). This might be an important factor for the observed slow decarbonylation, leading to low activity and long induction periods (Figure III.1.1). The oxo-peroxo complexes do not show any induction periods although it could be shown that these species are also only catalyst precursor. In these cases, the most *Lewis* acidic ligand results in the highest activity in epoxidation catalysis. This study has the potential to form the basis for a future design of active molybdenum cyclopentadienyl tricarbonyl and oxo-peroxo complexes.

III.2 Aryl-substituted organomolybdenum(II) complexes as olefin epoxidation catalysts

This work deals with the synthesis and application of a benzyl-substituted molybdenum cyclopentadienyl tricarbonyl complex and its fluorinated derivative in epoxidation catalysis. The complexes were characterized by X-Ray-, NMR- and IR-spectroscopy. Additionally, DFT calculations were performed to determine the influence of fluorination on the Lewis acidity and activity in catalysis. It was demonstrated that both complexes are active in epoxidation catalysis with TOFs > **15 500 h⁻¹** for several olefins using TBHP as oxidant and hexafluorobenzene (HFB) as solvent of choice. The recycling of the active species was also possible in a two-phase reaction performed in ionic liquids (Figure III.2.1).

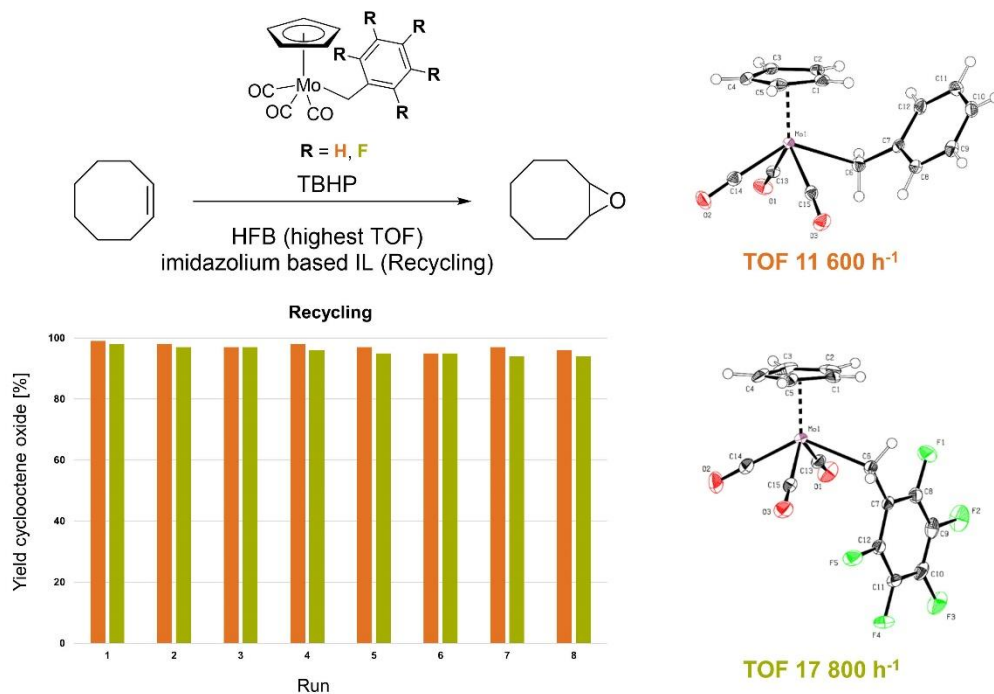


Figure III.2.1 Recycling of the active species of the arylated tricarbonyl complex and its fluorinated derivative with an imidazolium based ionic liquid (left) and highest obtained TOFs in hexafluorobenzene (HFB) next to the molecular structures (right). Reaction conditions - catalyst:*cis*-cyclooctene:TBHP; ratio: (0.005:1:2); T = 55 °C, 0.5 ml solvent.

III. Results – Publication Summaries

To compare the complexes in terms of the formation of the active pre-catalysts after decarbonylation, X-Ray crystallography in combination with DFT calculations have been used. It was shown that the arylated complexes ($[\text{CpMo}(\text{CO})_3\text{Bz}]$ and $[\text{CpMo}(\text{CO})_3\text{Bz}^{\text{F}5}]$) behave more similarly than the alkylated derivatives $[\text{CpMo}(\text{CO})_3\text{CH}_3]$ and $[\text{CpMo}(\text{CO})_3\text{CF}_3]$. Therefore, the decarbonylation prior to the formation of active species is comparable. In case of the alkylated complexes, however, the fluorination led to an increased induction period. In the arylated complexes the activity is mainly controlled by the *Lewis* acidity of the ligand, explaining the high activity of the fluorinated compound $[\text{CpMo}(\text{CO})_3\text{Bz}^{\text{F}5}]$ compared to $[\text{CpMo}(\text{CO})_3\text{Bz}]$. The methylene bridge apparently prevents the formation of a strong bond between the *Lewis* acidic ligand and the molybdenum metal center. This study is an example for the successful combination of analytical (X-Ray crystallography, IR spectroscopy) and theoretical (DFT calculations) methods. Therefore, the prediction of the velocity of the decarbonylation and catalytic activities and thus also the rational design of active epoxidation catalysts is enabled.

III.3 Kinetic studies of fluorinated aryl molybdenum(II) tricarbonyl precursor in epoxidation catalysis

This study deals with the influence of the position and amount of trifluoromethyl groups within the benzyl moiety of such complexes on the activity in homogeneous epoxidation catalysis. Various substrates as well as the formation of possible intermediates and active species were investigated. Four molybdenum cyclopentadienyl tricarbonyl complexes bearing CF₃ groups were synthesized, characterized by X-ray diffraction crystallography, NMR- (¹H, ¹³C, ¹⁹F and ⁹⁵Mo) as well as IR-spectroscopy and applied in the epoxidation of *cis*-cyclooctene.

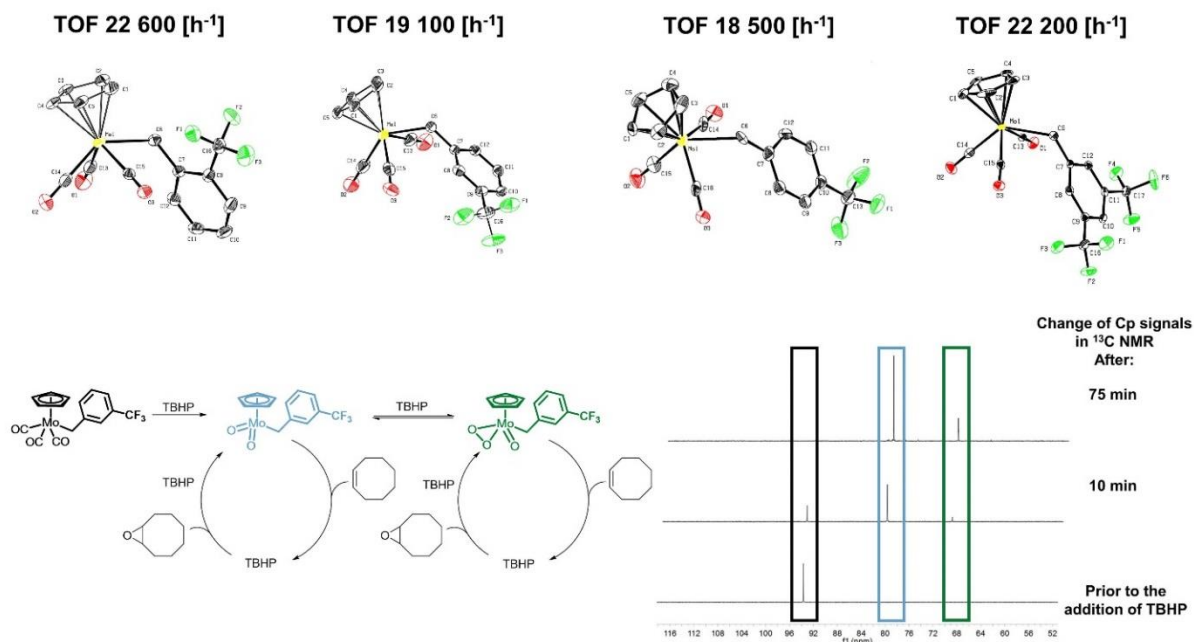


Figure III.3.1 Highest achieved TOFs and crystal structures of the synthesized compounds (up). Reaction conditions – pre-catalyst:*cis*-cyclooctene:TBHP; ratio: (0.05:100:200); T = 55 °C, 0.5 ml HFIP (hexafluoroisopropanol). Mechanistic investigations (bottom): Change of the cyclopentadienyl shift over the time in ¹³C NMR spectroscopy with excess TBHP (ratio pre-catalyst:TBHP; 1:20, 55 °C in C₆D₆).

High TOFs of up to **22 000 h⁻¹** could be achieved using hexafluoroisopropanol (HFIP) as solvent and TBHP as oxidant of choice. It was shown that the closer the CF₃ group is located to the molybdenum center, the more active is the catalyst. ⁹⁵Mo NMR spectroscopy and DFT calculations showed that the activity correlates with the electron density on the metal center and the respective calculated *Lewis* acidities. The CF₃ group does not only enhance the *Lewis* acidity of the metal complexes compared to a benzyl

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moiety without trifluoromethyl groups, but also enables the possibility to use ^{19}F *in-situ* NMR spectroscopy. In combination with ^1H and ^{13}C NMR spectroscopy this was helpful to determine different pre-catalysts (oxo-peroxo and dioxo species) formed during the reaction with oxidant and substrate. Here, the substrate has a major influence on the formation of the pre-catalysts, as it favors one species. It was also possible to recycle one complex for at least 10 times in a two-phase reaction applying ionic liquids. Furthermore, it was demonstrated that it is feasible to oxidize a variety of different substrates with two of these catalysts. This underlines the effect of an additional CF_3 group on the aryl moiety. In the study certain possibilities to analyze the course of the reaction were revealed and several ways to influence the formation of different pre-catalysts have been shown. This might enable a future X-ray crystallographic characterization of molybdenum cyclopentadienyl dioxo and oxo-peroxo species with an aromatic ligand.

III.4 Niobium(V) chloride and imidazolium bromides as efficient dual catalyst system for the cycloaddition of carbon dioxide and propylene oxide

In this publication, varying imidazolium bromides, were synthesized, characterized and catalytically applied in combination with niobium(V) chloride for the cycloaddition of propylene to propylene carbonate (PC) with carbon dioxide. An optimized imidazolium co-catalyst allowed the valorization of carbon dioxide under mild conditions (room temperature, 4 bar CO₂ pressure) with high yields and selectivities for PC and other substrates (Figure III.4.1).

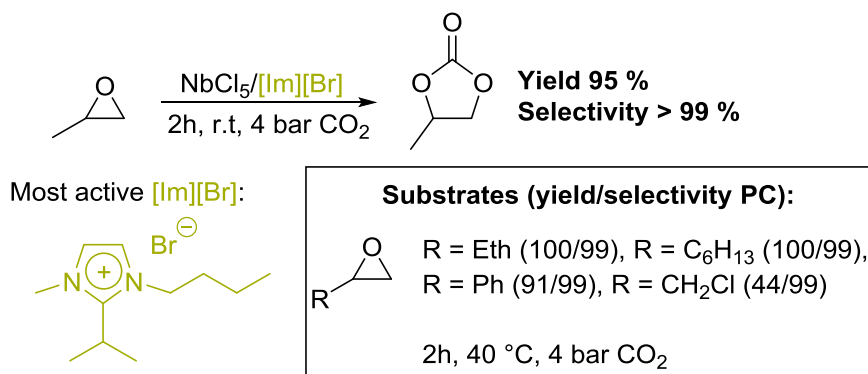


Figure III.4.1 Conversion of propylene oxide to propylene carbonate and other substrates with NbCl₅ and the most active imidazolium bromide under mild conditions.

In the catalytic dual system the niobium salt activates the epoxide, while the imidazolium salt serves as nucleophile for the ring opening of the pre-coordinated epoxide. The moieties of the examined imidazolium cations were either aliphatic, aromatic or aliphatic and aromatic. It was shown that aliphatic wingtips are favorable for the catalytic cycloaddition. Furthermore, a positive influence was revealed for substituting the C2 proton with a methyl group in the imidazolium cation. The vast set of imidazolium bromides allowed a comprehensive insight on the influence of substituents on the steric and electronic environment of the cation as well as the solubility. Especially the influences on the steric and electronic environment are of general importance in the field of ionic liquids in catalysis and the results are not restricted on the cycloaddition. Therefore, this study helps to develop future task-specific imidazolium based ionic liquids for different catalytic applications as solvent and/or catalyst

III.5 Influence of substituents on cation-anion contacts in imidazolium perrhenates

In this work a series of imidazolium perrhenates with different residues on the imidazolium moiety was synthesized and characterized by ^1H , ^{13}C and ^{19}F NMR spectroscopy as well as X-ray diffraction crystallography. The focus of this study was to identify the effects of the substitution pattern on

- a) the aggregation state,
- b) charge delocalization (investigated by DFT calculations) and
- c) anion-cation interaction via hydrogen bonds.

The interaction was studied in the solid state via Hirshfeld surface analysis, in the liquid state by ^1H NMR spectroscopy and in the gas phase by DFT calculations. The comparison of DFT and Hirshfeld surface analysis between the 1-benzyl-3-methylimidazolium cation and perrhenate salt and the 1-benzyl-2,3-dimethylimidazolium cation and perrhenate salt is exemplarily shown in figure III.5.1.

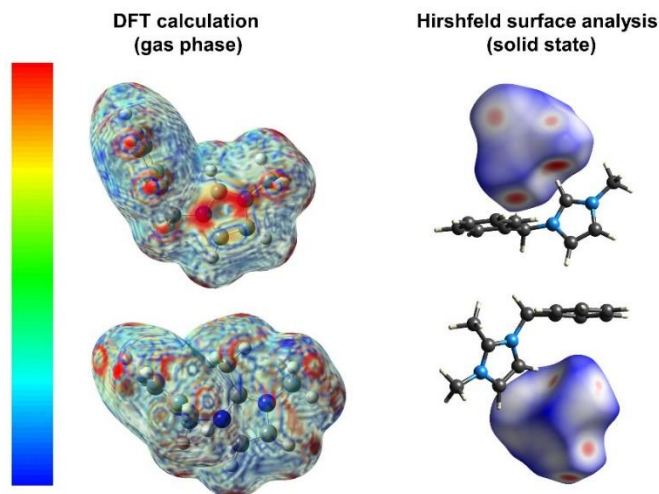


Figure III.5.1 Influence of alkylation of the C2 position in the imidazolium cation determined with DFT calculations in gas phase (left - (B3LYP/6-311++G(d,p) level of theory. The range of the scale lasts from 3.770e^{-4} red, less electron density to 3.990e^{-4} blue, more electron density. The numbers represent energy per charge in units of Hartree per elemental charge), and in the solid state with Hirshfeld surface analysis (right - red: distances between anion and cation are shorter than the ideal calculated van-der Waals radius; blue: distances between cation and anion are longer than the ideal calculated van-der-Waals radius).

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Especially the C2 proton on the imidazolium cation is the preferred binding site of the perrhenate anion. By methylation the cation-anion interactions are decreased, leading to an elongation of the shortest donor-acceptor contacts. Further, alkylation of the C2 position with a steric demanding substituent like an isopropyl group seems to lead to a relocation of the anion towards the imidazolium backbone protons. This results in decreased interionic attractions and reduction of the contacts. Pentafluoro benzyl groups led to enhanced O–F and O–C interactions between anion and cation leading to high melting points. In these cases the methylene bridge to the imidazolium nitrogen atom provides a second important binding site with the anion. This is in accordance with DFT calculations and the distinct downfield shift of the methylene bridge observed in ^1H NMR spectroscopy. In this study, the most important binding sites of the imidazolium cation with the perrhenate anion were examined. The results assisted to create a set of imidazolium perrhenates as active catalysts in the epoxidation of olefins, where the anion-cation interaction is a key factor. These results are summarized in chapter III.8 in this thesis. .

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III.6 Catalytically active perrhenate based ionic liquids: a preliminary ecotoxicity and biodegradability assessment

In this publication the (eco)toxicological and biodegradation behavior of a set of ammonium and imidazolium based perrhenate ionic liquids has been investigated. The investigated compounds, which were also synthesized and characterized in this work, are shown in Figure III.6.1).

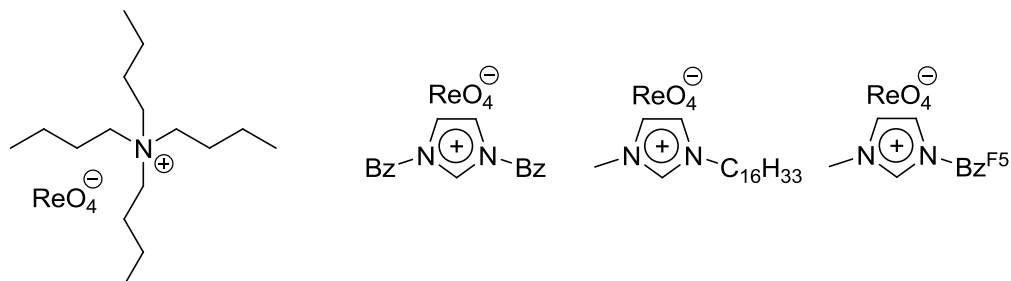


Figure III.6.1 Ammonium- and imidazolium perrhenates synthesized and used in the (eco)toxicological and biodegradation study: (From left to right) tetrabutyl ammonium perrhenate, 1,3-dibenzylimidazolium perrhenate, 1-hexadecyl-3-methylimidazolium perrhenate, 1-methyl-3-(2', 3', 4', 5', 6'-pentafluorobenzyl)-imidazolium perrhenate.

It is interesting to note that the hazard potential of the ILs are mainly caused by the cations while the perrhenate anion has no mentionable effect on the toxicity. In fact, the perrhenate anion is even much lower toxic than well examined and applied anions such as $[\text{N}(\text{CF}_3\text{SO}_2)_2]^-$ or $[(\text{C}_2\text{F}_5)_3\text{PF}_3]^-$ in combination with non-toxic cations. Therefore, it is also not surprising that the perrhenate anion is far more non-toxic than methyltrioxorhenium, its equivalent in homogeneous epoxidation catalysis. Unfortunately, the most active imidazolium perrhenates in heterogeneous epoxidation of olefins are the most toxic. ILs with a long hydrophobic side chain such as 1-hexadecyl-3-methylimidazolium had a low EC_{50} value towards daphnids as model aquatic organism. Although other short alkyl side chained cations exhibit low toxic effects, none of the investigated imidazolium based ILs is biodegradable. As it is known that the perrhenate anion is the active part in the epoxidation of olefins, a vast number of cations are possible candidates as counter ions. The future focus should therefore be the examination of cations exhibiting a less toxic potential. In the course of this ammonium, pyridinium, piperidinium, pyrrolidinium or morpholinium cations with small or hydrophilic side chains

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could be used, which are all well examined in literature. Although these compounds might also exhibit toxic potential with long alkyl side chains, at least some of them, e.g. the pyridinium cation show higher biodegradability than the imidazolium moiety. In general this study could help to design more task-specific and “green” ILs for the epoxidation of olefins or other catalytic processes.

III.7 Molecular Epoxidation Reactions Catalyzed by Rhenium, Molybdenum and Iron Complexes

This study deals with the advances in epoxidation reactions catalyzed by rhenium, molybdenum and iron complexes in the last 25 years by the groups of Herrmann and Kühn. The focus of this chapter is the progress in the research field of rhenium and molybdenum complexes as homogeneous and heterogeneous oxidation catalysts. A brief overview is given of the most active systems developed so far. Although cheaper complexes with other metals than rhenium are able to achieve high turnover frequencies (TOFs) with *cis*-cyclooctene and other simple olefins, methyltrioxorhenium (MTO) remains the benchmark catalyst (Figure III.7.1).

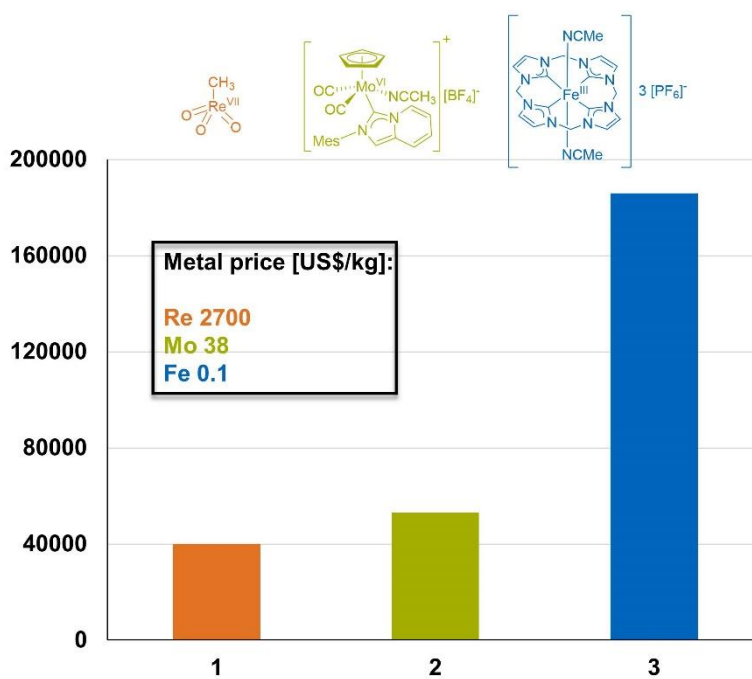


Figure III.7.1 TOFs of the most active rhenium, molybdenum and iron based catalysts for the epoxidation of *cis*-cyclooctene and metal prices of rhenium, molybdenum and iron (in US\$/kg): rhenium (orange, 99.9% purity), molybdenum (green, scrap molybdenum pure) and iron (blue, iron ore fines 65% Fe metal content). Data from: metalprices.com (May 2014).

There are mainly two reasons for this:

1. MTO is still the most active system for more sophisticated olefins like (+)-limonene, α -pinene or pseudocumene in homogeneous epoxidation catalysis with hydrogen peroxide as rather green oxidant and

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2. the epoxidation mechanism is very well investigated in contrast to molecular molybdenum and iron complexes.

A lot of studies were carried out to get insights in the mechanism of molybdenum based and partly iron based epoxidation reactions and the formation of possible active species. In future, these studies might lead to a deeper understanding of the ways to influence critical features in catalysis such as activity (TOF), catalyst life time (TON) and selectivity. The way for a sustainable and cost-efficient epoxidation of olefins with molybdenum and iron based catalysts under mild conditions using green oxidants has been paved in the last decade.

III.8 Olefin Epoxidation in Aqueous Phase Using Ionic-Liquid Catalysts

This publication deals with the synthesis and characterization of a set of imidazolium perrhenates and its application in the catalytic epoxidation of olefins. Solubility measurements of the respective catalysts in substrate, water and oxidant, performed by the group of Andreas Jess, shed more light on the mechanism of the epoxidation process. The focus of this work was the variation of the C2 position of the imidazolium cation as it had a vast impact on the catalytic activity (Figure III.8.1).

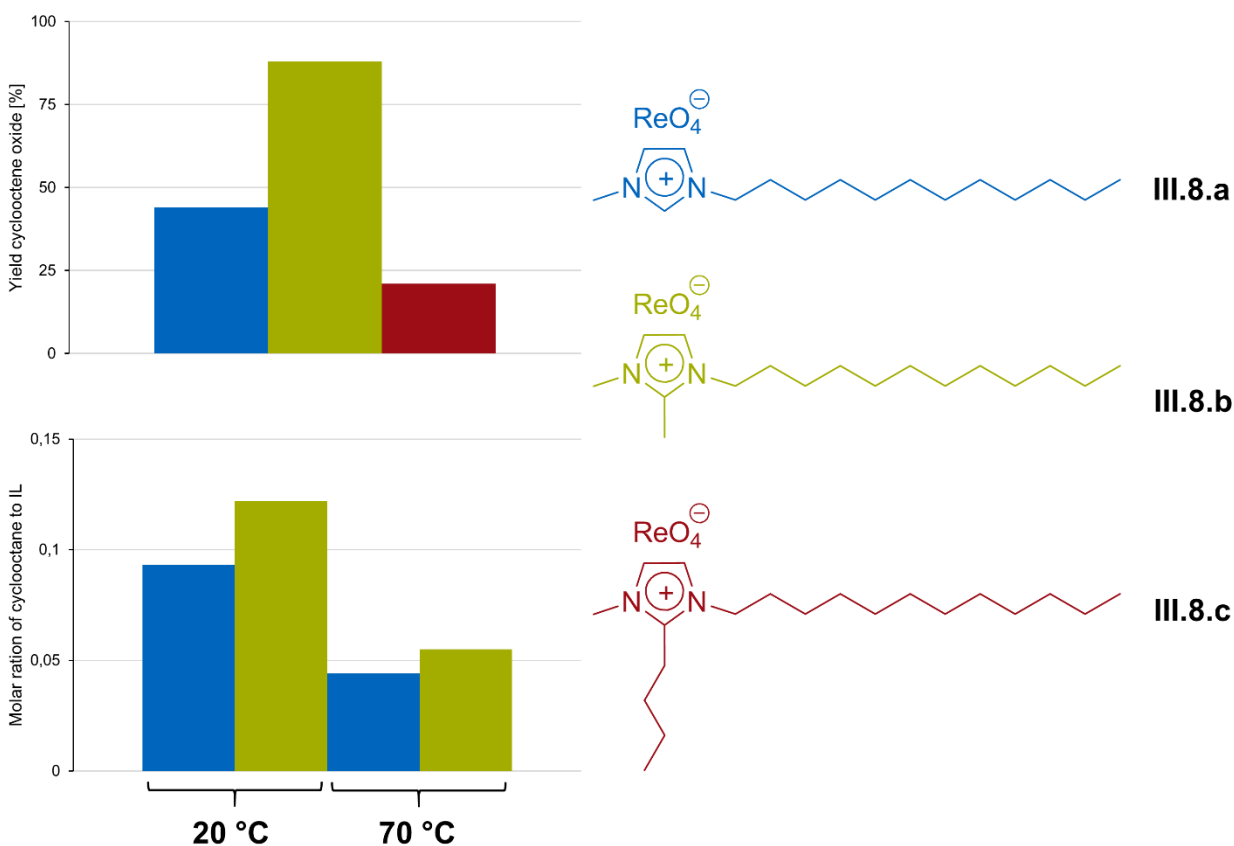


Figure III.8.1 Comparison of catalytic activity of imidazolium perrhenates **III.8.a-III.8.c** (up left) in the epoxidation of *cis*-cyclooctene (Reaction conditions: 10 mmol cyclooctene, 0.5 mmol catalyst (5 mol %), 25 mmol oxidant, T = 70 °C, after 4 h) and a comparison of the molar ratio of cyclooctane to IL **III.8.a** and **III.8.b** in aqueous hydrogen peroxide (50 wt.%) at different temperatures (bottom left).

Solubility measurements of the ILs **III.8.a-III.8.c** show that these compounds are less than 2 wt.% (weight percent) soluble in water. However catalysts **III.8.a** and **III.8.b** are completely miscible or 25 wt.% soluble (**III.8.b**) in aqueous hydrogen peroxide solution (50 wt.%) while the hydrophobic catalyst **III.8.c** is completely insoluble. All ILs are very

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sparingly soluble in *cis*-cyclooctene 100 ppm, indicating that the epoxidation reaction takes place in the aqueous phase. The decrease of the amount of oxidant during the reaction leads to the observation that **III.8.b** is no longer soluble in the aqueous phase, thereby reducing its activity. This fact shows that a usual phase transfer mechanism is not responsible for the observed activities. However, this does not explain the observed differences in catalytic activity for ILs **III.8.a** and **III.8.b**. An important point might be the solubilization of substrate into the aqueous phase induced by the ionic liquid. The content of *cis*-cyclooctene in the aqueous hydrogen peroxide solution (catalyst:oxidant ration of 5:250) was determined by extraction of the substrate from the aqueous phase with *n*-heptane. Catalysts **III.8.a** and **III.8.b** positively affect the solubility in the aqueous phase with **III.8.b** being the most efficient solubility enhancer. Experiments with cyclooctane were performed to show that this trend is also apparent at reaction temperature (Figure III.8.1 bottom left) to explain the observed differences in activity. A possible mechanism, which is currently under investigation, might also include the formation of micelles. Furthermore, it was possible to oxidize several olefins and to recycle the imidazolium perrhenates **III.8.a** and **III.8.b** for at least 9 times. This study shows that it is possible to change the activity drastically by small variations of the cationic structure. It also provides a future design for task-specific ILs for the two-phase epoxidation of olefins. A structure of the cation with one long alkyl side chain, which allows micelle formation, seems to be favorable. Moreover, the IL induced solubility of substrate in oxidant seems to be crucial. Further systematic investigations with different cations including solubility measurements might enable the epoxidation of more industrial relevant olefins like 1-propene.

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III.9 Reprint Permissions

III.9.1 RSC publications

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III.9.2 Wiley publications

Jens W. Kück, **Robert M. Reich**, Fritz E. Kühn, “Molecular Epoxidation Reactions Catalyzed by Rhenium, Molybdenum and Iron Complexes” *Chem. Rec.*, **2016**, 16, 349 – 364.

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Pages	16
Type of use	Dissertation/Thesis
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Format	Print and electronic
Portion	Full article
Will you be translating?	No
Title of your thesis / dissertation	Application of imidazolium based ionic liquids as solvents and catalysts in the epoxidation of olefins - Influence of the substitution pattern of the imidazolium cation on ion-pairing and catalytic activity
Expected completion date	Jun 2016
Expected size (number of pages)	200
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Mirza Cokoja, Robert M. Reich, Michael E. Wilhelm, Marlene Kaposi, Johannes Schäffer, Danny S. Morris, Christian J. Münchmeyer, Michael H. Anthofer, Iulius I. E. Markovits, Fritz E. Kühn, Wolfgang A. Herrmann, Andreas Jess and Jason B. Love, "Olefin Epoxidation in Aqueous Phase Using Ionic-Liquid Catalysts" ChemSusChem, 2016 (accepted manuscript, DOI: 10.1002/cssc.201600373).*

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In this chapter the bibliographic details of the publications summarized in chapter III of this thesis are presented to facilitate the retrieval of the complete manuscripts and supporting information.

IV.1 Influence of structural and electronic properties of organomolybdenum(II) complexes of the type $[\text{CpMo}(\text{CO})_3\text{R}]$ and $[\text{CpMo}(\text{O}_2)\text{OR}]$ ($\text{R} = \text{Cl}, \text{CH}_3, \text{CF}_3$) on the catalytic epoxidation of olefins

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IV.2 Aryl-substituted organomolybdenum(II) complexes as olefin epoxidation catalysts

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IV.3 Kinetic studies of fluorinated aryl molybdenum(II) tricarbonyl precursor in epoxidation catalysis

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IV.4 Niobium(V) chloride and imidazolium bromides as efficient dual catalyst system for the cycloaddition of carbon dioxide and propylene oxide

*Michael E. Wilhelm,^{‡a} Michael H. Anthofer,^{‡a} Robert M. Reich,^a Valerio D'Elia,^b
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IV.5 Influence of substituents on cation-anion contacts in imidazolium perrhenates

Robert M. Reich,[‡] Mirza Cokoja,^{} Iulius I. E. Markovits,[‡] Christian J. Münchmeyer,[‡]
Marlene Kaposi, Alexander Pöthig, Wolfgang A. Herrmann and Fritz E. Kühn^{*}*

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IV.6 Catalytically active perrhenate based ionic liquids: a preliminary ecotoxicity and biodegradability assessment

*Ha Bui Thi Thu,^a Marta Markiewicz,^a Jorg Thöming,^a Robert M. Reich,^b
Valentina Korinth,^b Mirza Cokoja,^b Fritz E. Kühn^{*b} and Stefan Stolte^{*ac}*

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IV.7 Molecular Epoxidation Reactions Catalyzed by Rhenium, Molybdenum and Iron Complexes

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IV.8 Olefin Epoxidation in Aqueous Phase Using Ionic-Liquid Catalysts

*Mirza Cokoja,^{*a} Robert M. Reich,^{a‡} Michael E. Wilhelm,^{a‡} Marlene Kaposi,^{a‡} Johannes Schäffer,^{b‡} Danny S. Morris,^c Christian J. Münchmeyer,^{a‡} Michael H. Anthofer,^a Iulius I. E. Markovits,^a Fritz E. Kühn,^a Wolfgang A. Herrmann,^a Andreas Jess^b and Jason B. Love^c*

^a Dr. M. Cokoja,* M. Sc. R. M. Reich, Dr. M. E. Wilhelm, Dr. M. Kaposi, Dr. C. J. Münchmeyer, Dr. M. H. Anthofer, Dr. I. I. E. Markovits, Prof. Dr. F. E. Kühn, Prof. Dr. W. A. Herrmann
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V. Summary and Outlook

The epoxidation of olefins is an industrial key process, as many epoxides are precursors for industrial relevant products in food chemistry, pharmaceuticals, polymer chemistry and other fields. For simple olefins like *cis*-cyclooctene, rather high activities and selectivities can already be obtained. Benchmark catalysts in homogeneous epoxidation catalysis, which are reviewed in the course of this thesis, are methyltrioxorhenium (MTO), and molybdenum or iron based metal complexes. All of these systems have several advantages and disadvantages. While MTO and iron catalysts exhibit high activities/TOFs with the simple and rather green oxidant hydrogen peroxide, their lifetime/TONs are rather limited. Although *tert*-butylhydroperoxide as oxidant is needed for molybdenum based tricarbonyl cyclopentadienyl molybdenum precursors, they possess distinct advantages. Not only high TOFs similar to MTO are reached but also high TONs are possible by applying ionic liquids as solvents. In contrast to MTO, a broader variety of different ligands can be introduced to the molybdenum center. This allows the adjustment of its electronic environment, so that different activities and selectivities in epoxidation catalysis can be reached. Hence, it is possible to use more *Lewis* acidic ligands, which is a broadly accepted concept to increase the activity of the metal complexes. For that purpose, fluorinated moieties can be introduced and the properties of the complex can be compared with their non-fluorinated derivatives. This is not possible with MTO, as a fluorinated MTO – CF_3ReO_3 could, hitherto, not be synthesized.

Therefore, the first part of this work focuses on the influence of ionic liquids as solvents, as well as different fluorinated and non-fluorinated ligands in cyclopentadienyl tricarbonyl molybdenum complexes.

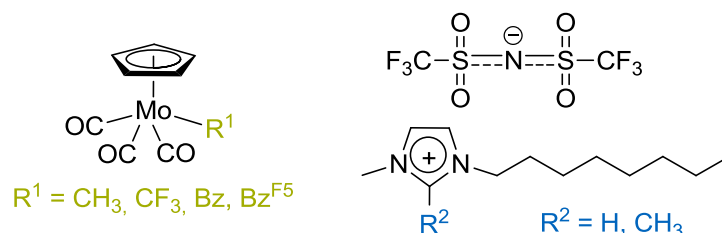


Figure V.1 Overview of synthesized molybdenum metal complexes as pre-catalysts and ionic liquids as solvents in homogeneous and two-phase epoxidation catalysis.

V. Summary and Outlook

The comparison of the methylated complex $[\text{CpMo}(\text{CO})_3\text{CH}_3]$ and its fluorinated counterpart $[\text{CpMo}(\text{CO})_3\text{CF}_3]$ showed that a simple correlation of *Lewis* acidity and activity is not always possible. The velocity of the decarbonylation of the latter complex is decreased, leading to a slow formation of the oxo-peroxo and dioxo species. These are known to act as intermediates in the formation of the active species. The comparison of the oxo-peroxo complexes ($[\text{CpMo}(\text{O}_2)(\text{O})\text{CH}_3]$ and $[\text{CpMo}(\text{O}_2)(\text{O})\text{CF}_3]$) show the expected catalytic superiority of the fluorinated complex due to increased *Lewis* acidity on the metal center. DFT calculations propose that one possible reason for the increased stability and therefore long induction period of the fluorinated tricarbonyl complex might be a strong Mo–CF₃ bond. The problem of a slow decarbonylation process could be solved by using activating solvents like HFIP or by introducing benzyl moieties as ligands ($[\text{CpMo}(\text{CO})_3\text{Bz}]$ and $[\text{CpMo}(\text{CO})_3\text{Bz}^{\text{F5}}]$). With these ligands, it was possible to increase the TOFs in fluorinated solvents like hexafluorobenzene. In addition it was possible to recycle the active species for at least 8 times in two different ionic liquids (see Figure V.1. left). Higher yields were obtained with an imidazolium based IL with a methyl residue in C2 position, presumably due to a higher solubility of the catalyst precursor. Because of its increased *Lewis* acidity at the metal center, the fluorinated compound $[\text{CpMo}(\text{CO})_3\text{Bz}^{\text{F5}}]$ is much more active in epoxidation catalysis. A further, more systematic, study revealed the influence of the position of trifluoromethyl groups on the benzyl moiety (figure V.2).

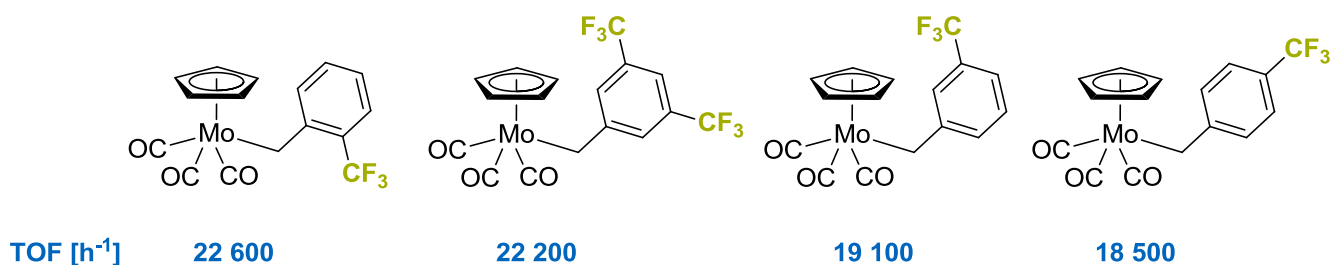


Figure V.2 Different arylated molybdenum cyclopentadienyl tricarbonyl complexes with different position and amount of trifluoromethyl groups and their activity in the epoxidation of *cis*-cyclooctene (Reaction conditions: Ratio pre-catalyst:*cis*-cyclooctene:TBHP; 0.05:100:200; in 0.5 ml HFIP, internal standard: mesitylene T = 55 °C, after 5 min. Determination via ¹H NMR spectroscopy)

The closer the CF₃ group is located to the metal center, the more active is the complex. Moreover, the more CF₃ groups are present, the more active is the complex (figure V.2, complex 2 and 3). These results are in accordance with calculated *Lewis* acidities on the

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metal center and the determined ^{95}Mo NMR shifts. These are well-studied indicators for the electronic environment on the molybdenum metal center. NMR spectroscopy further revealed that mainly the dioxo and oxo-peroxo species form during the reaction with TBHP. The addition of substrate shows that one species is favored. Future studies should focus on the formation of different species in different substrates to enable the crystallization and characterization of one desired species. In general, one great challenge in epoxidation catalysis with molybdenum based catalysts in homogeneous phase remains: the stereoselective epoxidation of sophisticated olefins. Therefore, the introduction of stereoselective groups close to the metal center is a desired goal, which might achieve these types of epoxidation reactions. Even though these complexes might not be as active or selective, they might enable NMR or IR spectroscopy to get more insight into the mechanism of the epoxidation. This is under review for a long time, without considerable advance since the proposals of Mimoun and Sharpless in the early 1970ies. Further studies might also include a systematic evaluation of several ILs as solvents for the two-phase olefin epoxidation, to improve activities and the recycling of the active species. In the course of this the focus should not only be the investigation of suitable imidazolium based ILs. Especially anion-cation combinations towards rather “green” and well examined ILs in terms of biodegradation and (eco)toxicology should be a desirable goal in terms of sustainability

The second part mainly dealt with the influence of the imidazolium cation structure on ion-pairing with the perrhenate anion and its effect on the catalytic epoxidation of olefins. Previous studies and the proposed mechanism of the catalytic process implied that the reduction of the perrhenate-cation interaction should lead to highly active epoxidation catalysts. The drastic influence of the interaction between the imidazolium cation and the anion was already described for the cycloaddition of propylene oxide with carbon dioxide using bromide as anion. The same effects reported there, were also apparent for the interaction of the imidazolium cation with the perrhenate anion. In general, the alkylation of the C2 position reduces the anion-cation interaction. However, further substitution with a bulky isopropyl group leads to a relocation of the anion towards the backbone protons of the cation. A X-Ray diffraction crystallographic study in combination with DFT calculations implied that also the wing-tips have a great influence on ion-pairing.

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Fluorinated substituents on the wing-tips increase the possible interaction sites with the perrhenate anion. The comparison of 1,2-dimethylimidazolium perrhenate and 1,2,4,5-tetramethylimidazolium perrhenate revealed that not only the interaction of the anion with the cation is a relevant factor in epoxidation catalysis. One might assume that the latter compound is more active in epoxidation catalysis as the anion-cation interactions are decreased because of the methylation of the backbone protons. However, the opposite is observed, which also the case for the comparison of the highly active 1-methyl-3-octylimidazolium perrhenate with the clearly less active 1-methyl-2-butyl-3-octylimidazolium perrhenate. This clearly shows that the anion-cation interaction is not the dominant factor in the epoxidation of olefins with hydrogen peroxide. Therefore, a systematic investigation of the solubility of several imidazolium perrhenates with a different cationic structure in *cis*-cyclooctene and aqueous hydrogen peroxide was conducted. Special attention was paid to a set of imidazolium perrhenates with identical wing-tips but different C2 residues as its alkylation had a vast impact on the activity (figure V.3).

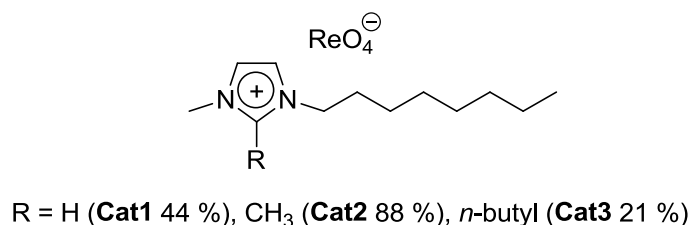


Figure V.3 Imidazolium perrhenates with different substitution on the C2 position. The activity in the epoxidation of *cis*-cyclooctene is given in brackets. Reaction conditions: 10 mmol cyclooctene, 0.5 mmol catalyst (5 mol %), 25 mmol oxidant, T = 70 °C (after 4 h).

No drastic decomposition of hydrogen peroxide occurs without substrate for all compounds (**Cat1-Cat3**). They are also similarly soluble in water and substrate, however compound **Cat1** and **Cat2** are very good soluble in aqueous hydrogen peroxide. This suggests that the epoxidation reaction takes place in the aqueous phase. As a consequence of the decreasing hydrogen peroxide concentration in the course of the reaction **Cat2** is no longer completely soluble which results in a reduced activity. This does not occur with **Cat1** which stays soluble in the water phase even with reduced amounts of hydrogen peroxide. Therefore, a classical phase transfer mechanism is not present in this

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case. Hence, the ability of the compounds to transfer the substrate *cis*-cyclooctene into the aqueous hydrogen peroxide phase was examined. While the solubility changes by a factor of 50 for **Cat1** and **Cat2** compared to blank experiments without catalyst, no change is observed for **Cat3**. This transfer causes the observed differences in activity, as the effect is around 30 % more pronounced for **Cat2** than for **Cat1**. One possible explanation for the substrate transfer might be the formation of micelles in the course of the reaction. Future studies should examine the detailed mechanism of this transfer, especially for industrial relevant substrates like propene. If the formation of micelles is responsible for the activity of this system, it is only limited to simple olefins as enantioselective epoxidation is not possible with undefined micelle formation. However, two aspects of this system make further academic research highly desirable:

1. Is it possible to add stereochemical information on the anion, which contains the catalytically active center for the epoxidation, and
2. as the mechanism of the epoxidation does not include the direct interaction with the metal center, it is feasible to exchange the (costly) perrhenate anion with simple and cost-efficient anions, such as sulfates, phosphates or carbonates.

In terms of the cation, the focus should shift from toxic compounds like the applied imidazolium structures to more sustainable moieties, which allow micelle formation (e.g. ammonium cations, with one longer alkyl side chain). This might enable higher activities and a more sustainable epoxidation catalysis.

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VII. List of Publications and Curriculum Vitae

VII.1 Journal Contributions

- 1) *“Influence of structural and electronic properties of organomolybdenum(II) complexes of the type $[CpMo(CO)_3R]$ and $[CpMo(O_2)OR]$ ($R = Cl, CH_3, CF_3$) on the catalytic epoxidation of olefins”*
Simone A. Hauser, **Robert M. Reich**, János Mink, Alexander Pöthig, Mirza Cokoja and Fritz E. Kühn*, *Catal. Sci. Technol.*, **2015**, 5, 2282 – 2289.
- 2) *“Aryl-substituted organomolybdenum(II) complexes as olefin epoxidation catalysts”*
Lilian Graser, **Robert M. Reich**, Mirza Cokoja, Alexander Pöthig and Fritz E. Kühn*, *Catal. Sci. Technol.*, **2015**, 5, 4772 – 4777.
- 3) *“Kinetic studies of fluorinated aryl molybdenum(II) tricarbonyl precursor in epoxidation catalysis”*
Robert M. Reich, Marlene Kaposi, Alexander Pöthig and Fritz E. Kühn*, *Catal. Sci. Technol.*, **2016** (accepted manuscript: DOI: 10.1039/c5cy02220g)
- 4) *“Niobium(V) chloride and imidazolium bromides as efficient dual catalyst system for the cycloaddition of carbon dioxide and propylene oxide”*
Michael E. Wilhelm, Michael H. Anthofer, **Robert M. Reich**, Valerio D’Elia, Jean-Marie Basset, Mirza Cokoja,* and Fritz E. Kühn*, *Catal. Sci. Technol.*, **2014**, 4, 1638 – 1643.
- 5) *“Influence of substituents on cation-anion contacts in imidazolium perchlorates”*
Robert M. Reich, Mirza Cokoja,* Iulius I. E. Markovits, Christian J. Münchmeyer, Marlene Kaposi, Alexander Pöthig, Wolfgang A. Herrmann and Fritz E. Kühn*, *Dalton Trans.*, **2015**, 44, 8669 – 8677.

VII. List of Publications and Curriculum Vitae

- 6) *“Catalytically active perrhenate based ionic liquids: a preliminary ecotoxicity and biodegradability assessment”*
Ha Bui Thi Thu, Marta Markiewicz, Jorg Thöming, **Robert M. Reich**, Valentina Korinth, Mirza Cokoja, Fritz E. Kühn* and Stefan Stolte*, *New J. Chem.*, **2015**, 39, 5431 – 5436.
- 7) *“Molecular Epoxidation Reactions Catalyzed by Rhenium, Molybdenum and Iron Complexes”*
Jens W. Kück, **Robert M. Reich** and Fritz E. Kühn*, *Chem. Rec.*, **2016**, 16, 349 – 364.
- 8) *“Olefin Epoxidation in Aqueous Phase Using Ionic-Liquid Catalysts”*
Mirza Cokoja,* **Robert M. Reich**, Michael E. Wilhelm, Marlene Kaposi, Johannes Schäffer, Danny S. Morris, Christian J. Münchmeyer, Michael H. Anthofer, Iulius I. E. Markovits, Fritz E. Kühn, Wolfgang A. Herrmann, Andreas Jess and Jason B. Love, *ChemSusChem*, **2016** (*accepted manuscript*, DOI: 10.1002/cssc.201600373).

VII.2 Poster Presentations

- 03/2016 49. Jahrestreffen Deutscher Katalytiker Weimar, Germany
Posterbeitrag *“Fluorinated Molybdenum(VI) Complexes as precursor in Epoxidation Catalysis”*