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Olefin Epoxidation with molybdenum-based catalysts in ionic liquids

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„Irgendwann kommt der Zeitpunkt,
an dem Du vom
Wissenskonsument zum Wissensproduzent wirst“
B. Graser

Für meine Eltern.

Abstract

More than 40 years ago the first complex of the general formula η^5-$CpMoO_2X$ has been synthesized by Cousins and Green, and it seems that this field of chemistry is still in its adolescence. This work aims at giving the reader a deeper insight into the area of molybdenum-catalysed epoxidation of olefins and represents the latest results that have been discovered within almost three years of research.

The thesis is divided into 6 chapters of which the first one comprises a general introduction into the field of ionic liquids and epoxidation chemistry. Here not only applications and historical developments are described, also issues of toxicity and mechanistic discussions are depicted and highlighted.

The second chapter points out the objectives of the presented studies. An explanation of why the studies were necessary and a short introduction into the chapters that follow thereafter are given.

Chapter three contains the results of the studies in a summary fashion. All articles that have been published throughout the studies are summarizes and the key points are highlighted. The complete studies and articles can be found in the appendix or viewed online in the respective journals. The chapter begins with studies on transition-metal complexes bound to 1,2,3-triazolylidene ligands and their application in homogeneous catalysis. The second publication is represented in the form of a manuscript and deals with a comparison of a benzyl-substituted MoCp-compound and its fluorinated congener. In the following article, an investigation is reported of the epoxidation of olefins with *in situ* formed polyoxomolybdates. Publication number four deals with the synthesis and characterisation of two novel imidazo-[1,5-a]-pyridyl-3-pyridyl-3-ylidene MoCp complexes and their utilization as pre-catalyst in the epoxidation of olefins is described.

These descriptions are followed by two review articles which were prepared in side projects undertaken during the course of this dissertation. Subchapter number 7 deals with an excursion into the rhenium chemistry and biomass valorisation.

Chapter four contains a summary and concludes the thesis. A brief discussion of the results is provided.

Chapter five contains the appendix, where all publications are given either as a link the do online document or a publication and manuscript basis.

Chapter six provides the author’s information.

List of Abbreviations

Bz - Benzyl
Bu_4P - Tetrabutylphosphate
DCM - Dichloromethane
DMSO - Dimethylsulfoxid
GC - Gas Chromatography
IFP - French Petroleum Institute
IL - Ionic Liquid
m.p. - melting point
MS - mass spectroscopy
NHC - *N*-heterocyclic carbene
PE - Polyethylene
POM - Polyoxometalate
RTIL - Room Temperature Ionic Liquid
r.t. - room temperature
SILP - Supported Ionic Liquid
TBHP - Tert-butylhyrodperoxide
THF - Tetrahydrofuran
TOF - Turn Over Frequency
TON - Turn Over Number

1. Introduction

1.1. Ionic Liquids

One of the dominating trends in modern research is the task specific design of chemicals to create a new generation of chemical procedures. Several breakthrough technologies are being already applied due to the rapid progress which has been made in the field: solid state[1] and solvent-free[2] syntheses, smart functional materials[3], ultrasound[4]- and microwave[5] promoted processes, reactions in water[6], supercritical fluids[7] as well as micro[8]- and nanoreactors. An extraordinary task-specific optimization has been achieved by altering anionic and cationic parameters of ionic liquids (ILs) to meet the request of target properties. ILs have been designed as non-volatile, non-explosive and non-flammable reaction media with high thermal stability.[9] They were able to contribute to the replacement of standard volatile and flammable organic solvents with environmental benign materials. Today the scope of applications involving ILs ranges far beyond the boundaries of being just a convenient “alternative” solvent. Their essential role in controlling both the direction and the selectivity of chemical reactions as well as their important function in catalytic activity have been demonstrated in numerous important reactions as well as industrially important processes. An increase in interest and publication activity reflects the tremendous progress which has been made in diverse areas[10].

Ethylammoniumnitrate $[EtNH_3][NO]_3$ (m.p. 12°C) the first compound which matches todays definition of a room temperature ionic liquid (RTIL), was synthesized by P. Walden in 1914[11]. The U.S. Air Force Academy intensified the research on ionic liquids in the following years with the target of finding capable electrolytes for thermal batteries. The development of chloroaluminates derived from mixing aluminium chloride with alkali halides can be ascribed to this research period[12]. A big part of the scientific community took notice of these new solvents when 1-butylpyridinium tetrachloroaluminate was first synthesized[13,14]. With the substitution of the water-sensitive tetrachloroaluminate with stable hexafluorophosphate and tetrafluoroborate anions by Zaworotko *et al.* in 1992 the next step towards industrial applications of dialkylimidazolium salts was taken[15].

Meanwhile a plethora of ILs has been synthesized for different applications in academia as well as in industry. Figure 1 shows typical cations and anions, which can be combined with ionic liquids.

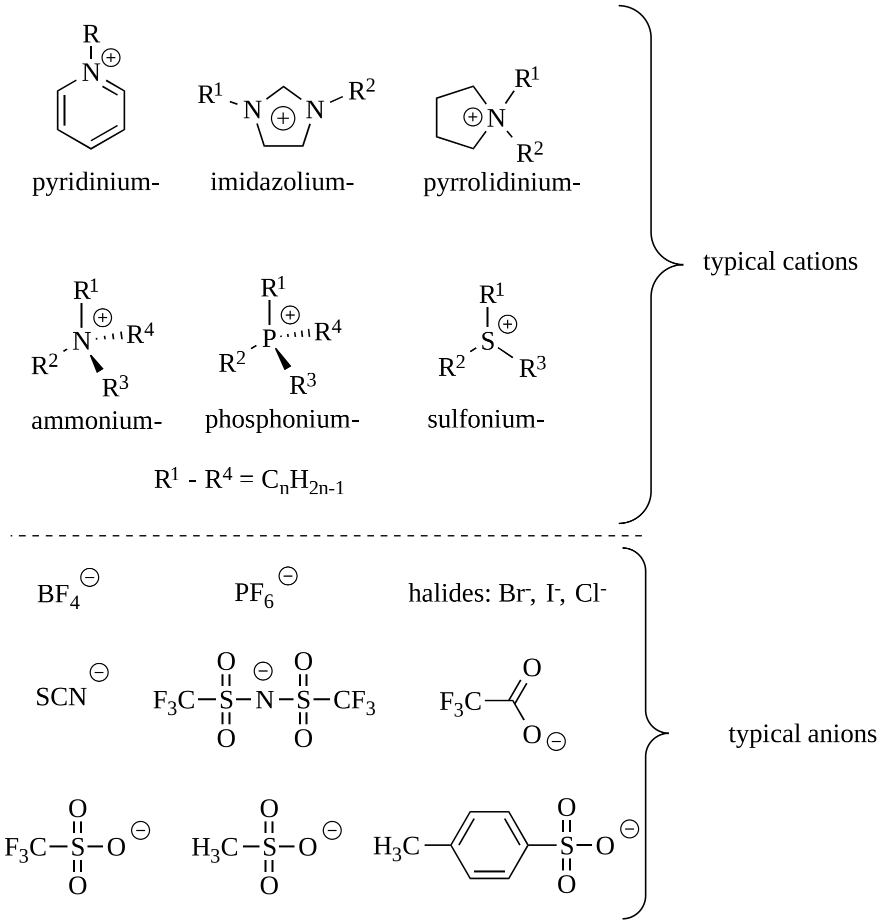
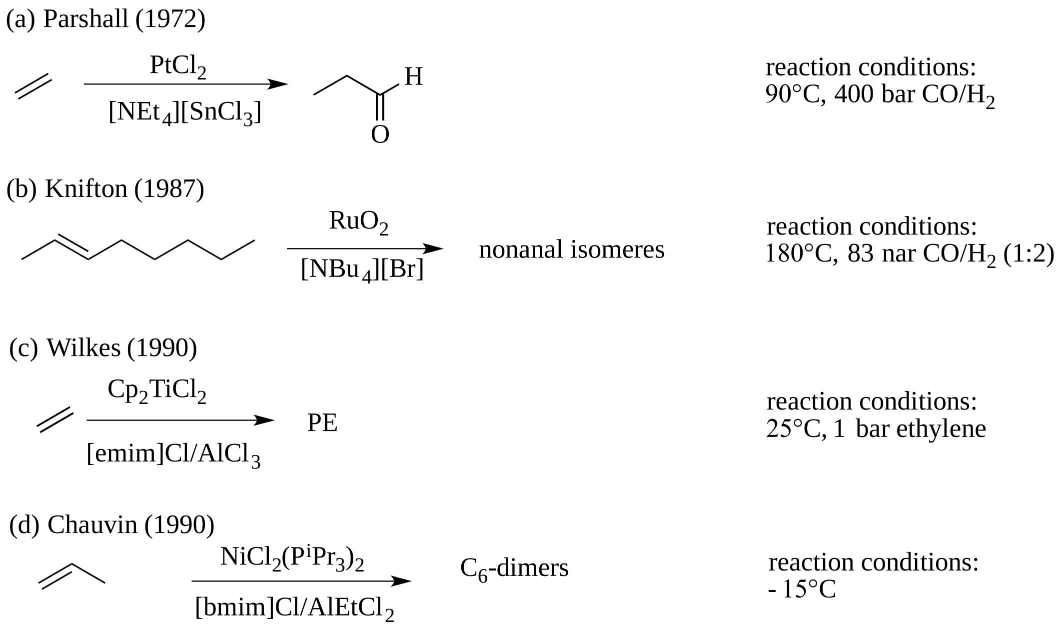


Figure 1: Typical anions and cations in ionic liquids.

Collated with other “green” solvents, e.g. supercritical fluids or perfluorinated compounds, ILs are able to dissolve many organometallic complexes while being generally immiscible with common organic solvents. Furthermore the possibility of varying the composition of anion and cation, resulting in different physico-chemical properties, opens up a broad scope of applications.

The requirement of a homogenous solution is a nontrivial but essential part of homogenous catalysis. The Pt-catalyzed hydroformylation of ethane[16] was the first described homogenous transition-metal catalysis using an ionic liquid as the solvent (Scheme 1, a). In 1987 Knifton *et al.*[17] used [Bu_4P]Br as solvent for the ruthenium- and cobalt catalysed hydroformylation of different olefins (Scheme 1, b). Further examples[1819] for the first assignments of ionic liquids in homogenous catalysis are given in scheme 1.



Scheme 1. First examples of homogenous catalysis in ILs.

1.1.1 Toxicity of ionic liquids

As already mentioned do ionic liquid system show promising opportunities in the development of sustainable and therefore greener technologies. However, the chemical nature of ionic liquids is not intrinsically green. Even if they do not evaporate and thus do not contribute to air pollution many of them are water soluble and thereby able to enter the environment via this pathway. In 2000 Jastroff *et al.*[20] were the first to study the toxic nature of different ILs. The study is strictly based on theoretical estimations. It claims that the length of the alkyl chain of the imidazolium cation corresponds to the bioaccumulation due to its molecular similarity of imidazolium cation. They were able to prove their estimations in 2007 in a more a detailed study on the (eco)toxicological behaviour of 1-alkyl-3-methylimidazolium ILs[21]. Recently, an extensive revision of publication dealing with the toxicity of ionic liquids was published by Ananikov *et al*[22]. It concludes that an ionic liquid may be non-toxic for particular cells or organisms, but may demonstrate high toxicity towards another target present in the environment.

1.1.2 Immobilization in ionic liquids

These days almost all types of homogeneous catalytic reactions have been performed in ionic liquids. One of the most interesting features for a convenient product work-up is the negligible vapour pressure of ILs. Due to this physical property, volatile products can be easily distilled out of the reaction mixture while the catalyst is dissolved in the ionic liquid phase and can be recycled. A tremendous advantage to low boiling solvents. One of the most important advantages homogenous catalysis offers is the fact that all metal centres are active during the catalysis. Furthermore reaction conditions (temperature and pressure) are usually far more benign than in analogues heterogeneous systems. Moreover selectivities are usually superior to heterogeneous systems.

Despite these advantages most industrial processes are performed using heterogeneous systems. The most abundant reasons for that are problems of separating the dissolved catalyst from products when using conventional organic solvents. This is the idea of combining the advantages of both systems (heterogeneous and homogeneous) by forming a biphasic system using ionic liquids to immobilize the catalyst is an important approach towards the development of green and sustainable technologies.

The principle of biphasic catalysis using ILs is shown in figure 2.

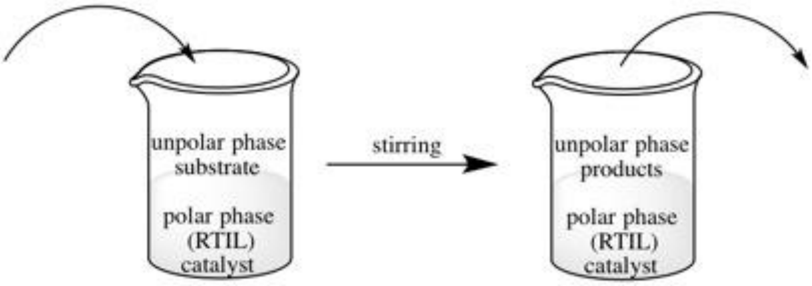


Figure 2: Principle of biphasic catalysis in ILs.

Ideally the organometallic complex used as catalyst is immobilised in the ionic liquid phase, while substrates and products are dissolved in the organic phase. After the reaction, product separation can be easily achieved by decantation or *via* a cannula. Preferably the catalyst can be recycled and reused without further treatment.

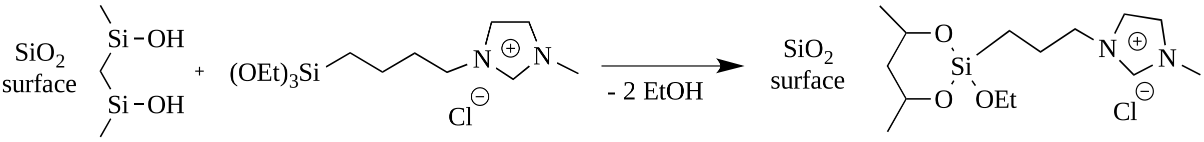
Task-specific optimisation by fine-tuning of the structure of the ionic liquid results in efficiency at the molecular level. Catalytic activity can be optimized by an in situ extraction of reaction intermediates or catalyst poison from the catalytic layer. To achieve this it is required that the solvent possesses a very low solubility for the substances which have to be extracted from the ionic liquid phase under reaction conditions.

Lately, the concept of mutually immiscible ionic liquids has attracted more and more attention. Mixtures of some hydrophilic and some specific hydrophobic ILs rise to two phases, in particular when there are large structural differences in either the cation or the anion[23,24]. These systems are already being applied to the separation of rare earth metals. Such separation processes are relevant for the recycling of valuable metals from batteries.

Mehnert and Wasserscheid introduced another interesting concept for the immobilisation of homogeneous catalysts - SILP (supported ionic liquid phase).

In the novel supported ionic liquid phase a homogeneous catalyst is dissolved in an IL which itself is highly dispersed on the internal surface of a porous material. The resulting ionic liquid catalyst film is only a few nanometers thick and allows complete utilization of ionic liquid and catalyst since the mass transport resistance from gas into the liquid phase is minimized.[25–27]

A representative route for the synthesis of a supported ionic liquid phase is shown in scheme 2.

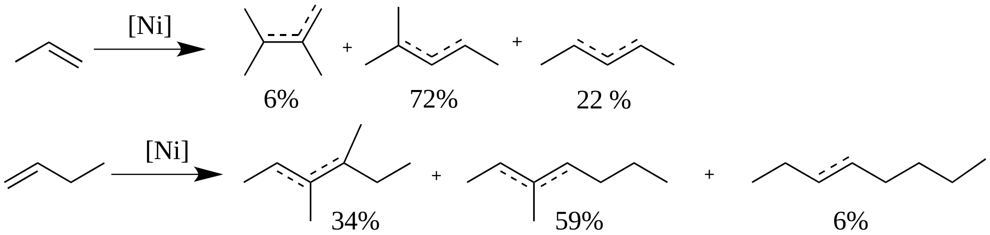


Scheme 2. Synthesis of a supported ionic liquid phase.

1.1.3 Important industrial applications

1.1.3.1 Difasol/Dimerisol process

In 1998 the French Petroleum Institute (IFP) launched the so called DIFASOL process. Herein ionic liquids are used for the production of isooctenes from butenes (scheme 3).



Scheme 3. DIFASOL process.

These isooctenes are hydroformylated in industry to produce alcohols such as isononanols. The esterification of these alcohols yields dialkyl phthalates, which can be applied as plasticizers in polyvinylchloride. The process employs a nickel based catalyst, which is dissolved in a chloroaluminate ionic liquid. The ionic liquid activates the nickel salt and the resulting catalyst is the same as the one which is used in the well known DIMERISOL process (Figure 3)[28].

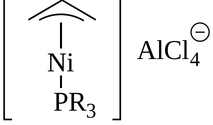


Figure 3. Structure of the utilized cationic Ni(II) catalyst.

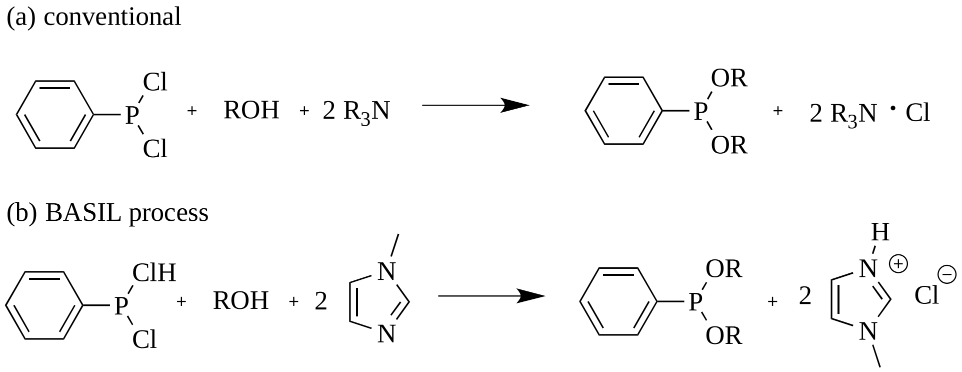
The immobilisation of the Ni(II) complexes in the ionic liquid provides significant benefits in catalyst activity, catalyst stability and the recyclability of the catalyst. Furthermore the selectivity of the reaction is increased.

1.1.3.2 BASIL process

The best-known application of ionic liquids in industry is probably the BASIL process (biphasic acid scavenging utilizing ionic liquids) which was established by BASF in 2002 and awarded with the “innovation for growth award” in 2004 of ECN[29,30]. Hydrochloric acid (HCl) is formed as a by-product in many chemical processes. If the reaction product has to be protected from side reactions or acid decomposition the acid needs to be scavenged which is usually done by the addition of triethylamine. The generated ammonium-salt can be removed by an aqueous extraction in many cases. Things get complicated if the reaction products or the utilized catalyst is water sensitive. Furthermore the formation of ammonium salt leads to several disadvantages:

- Highly viscous solutions
- Limited heat transfer
- salt has to be separated by filtration

BASF faced these problems in the production of diethoxyphenylphosphine (scheme 4). After the addition of equimolar quantities of triethylamine a thick nearly non-stirrable slurry was observed. They avoided the problem by using 1-methylimidazole instead of triethylamine as acid scavenger. The resulting methylimidazolium chloride has a melting point of below 80°C and is therefor liquid and stirrable at the reaction temperature of approximately 80°C. When the reaction is done, 2 clear phases are observed – the upper phase containing the product, the lower phase consisting of the pure ionic liquid 1-methylimidazolium chloride. The IL can subsequently be deprotonated with sodium hydroxide and the methylimidazol is regenerated.



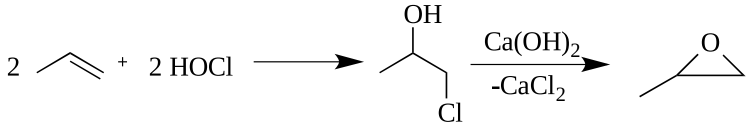
Scheme 4. Conventional – vs. BASIL process.

1.2 Epoxidation of olefins

Alkene epoxidation is one of the main routes for the production of epoxides, which are of high importance in both synthetic organic chemistry and chemical technology. The epoxides are important intermediates as they undergo ring-opening reactions with a variety of reagents. These reactions yield mono- or bifunctional products. Therefore they can be seen as key raw material for a wide variety of chemicals such as alkanolamines, gycols and glycol ethers[31,32]. Epoxides can be prepared in general by the reaction of different alkyl hydroperoxides, peracids or hydrogen peroxide with olefins. The reaction is mostly catalysed by transition metal complexes.[33–36]

1.2.1 Industrial processes

Speaking of industrial oxidation of olefins with a production of 5.3 Mt and 1.8 Mt respectively the two main product targets are ethylene oxide and propylene oxide[37]. Ethylene oxide is mostly produced by a silver catalysed vapour-phase oxidation of ethylene using air or oxygen as an oxidant. 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-Al_2O_3.[38] A huge drawback of this reaction is the fact that it is sensitive towards allylic C-H-bonds. The oxidation of the compounds that contain an allylic double bond result in low yields due to numerous by-products. For this purpose the chlorohydrine process is still used for the oxidation of higher olefins. Propene is reacted at 35°C at 2-3 bar in reaction columns with an aqueous chlorine solution in which HCl and HOCl are in equilibrium. The resulting 4-6 % mixture of α- and β-chlorohydrin is dehydrochlorinated – without intermediate separation – at 25°C with an excess of alkali solution (scheme 5).



Scheme 5. Chlorohydrine process.

The propylene oxide is then rapidly driven out of the reaction mixture to avoid hydration. Due to the massive amounts of by-product (e.g. $CaCl_2$), a direct oxidation route was independently developed by Halcon and Atlantic Richfield (ARCO) in 1967.

In 1983 Enichem introduced a titanium-substituted silcalite (TS-1) catalyst. Due to its hydrophobic surface it proved to be effective in a variety of liquid-phase oxidations using hydrogen peroxide as oxidant.[39] BASF, Dow and Solvay developed the so called HPPO process (hydrogen peroxide to propylene oxide) on the basis of the Enichem process.[40] Propene is oxidised in a slurry containing hydrogen peroxide and the catalyst. The preferred solvent is methanol. Propylene oxide can be separated and purified by distillation after the reaction.

1.2.2 Asymmetric epoxidation

Enantiopure epoxides as important intermediates are of high interest in the pharmaceutical and chemical industry for the synthesis of mainly pharmaceuticals, but also flavour and aroma chemicals, agricultural chemicals and speciality materials. Especially concerning pharmaceuticals, enantiopurity is highly important as enantiomers of a chiral compound can have dramatically different biological activities. In 1979 the first catalysed asymmetric epoxidation of olefins was achieved by Sharpless and Katsuki in 1979. The catalytic system consists of diethyl tartrate (DET), $Ti(O^iPr)_4$ and TBHP as oxidizing agent. The enantionmeric excess of epoxide from an allylic alcohol was very effective with an ee of >90%.[41–43] This achievement was honoured with the Nobel Prize in Chemistry in 2001 and is nowadays well known as the “Sharpless Epoxidation”. It has to be mentioned that the catalytic system is limited to laboratory scale and has no industrial application. In 1990 Katsuki and Jacobsen introduced another highly important catalyst system for asymmetric olefin epoxidation.[4445] Figure 4 shows the cationic Mn(III) salen complex. For the asymmetric epoxidation of *cis*-olefins excellent enantioselectivities of >95% ee are achieved.

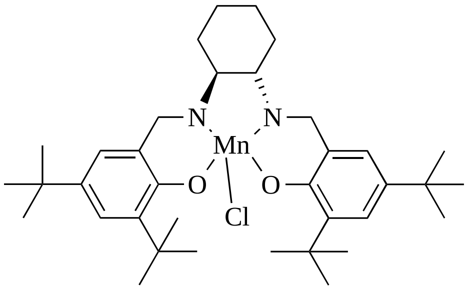


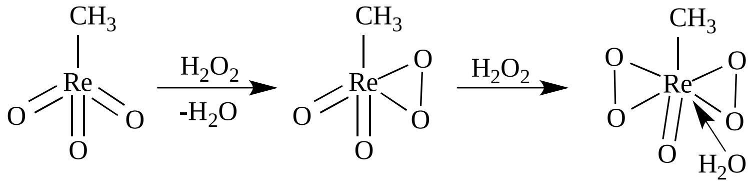
Figure 4. Jacobsen Catalyst.

1.2.3 Methyltrioxorhenium(VII) in olefin epoxidation

Methyltrioxorhenium (MTO) is a thermally stable compound decomposing above 300°C. It is highly volatile and soluble in all common solvents from pentane to water. Furthermore it is an extremely efficient catalyst precursor for all kinds of organic reactions.[31]

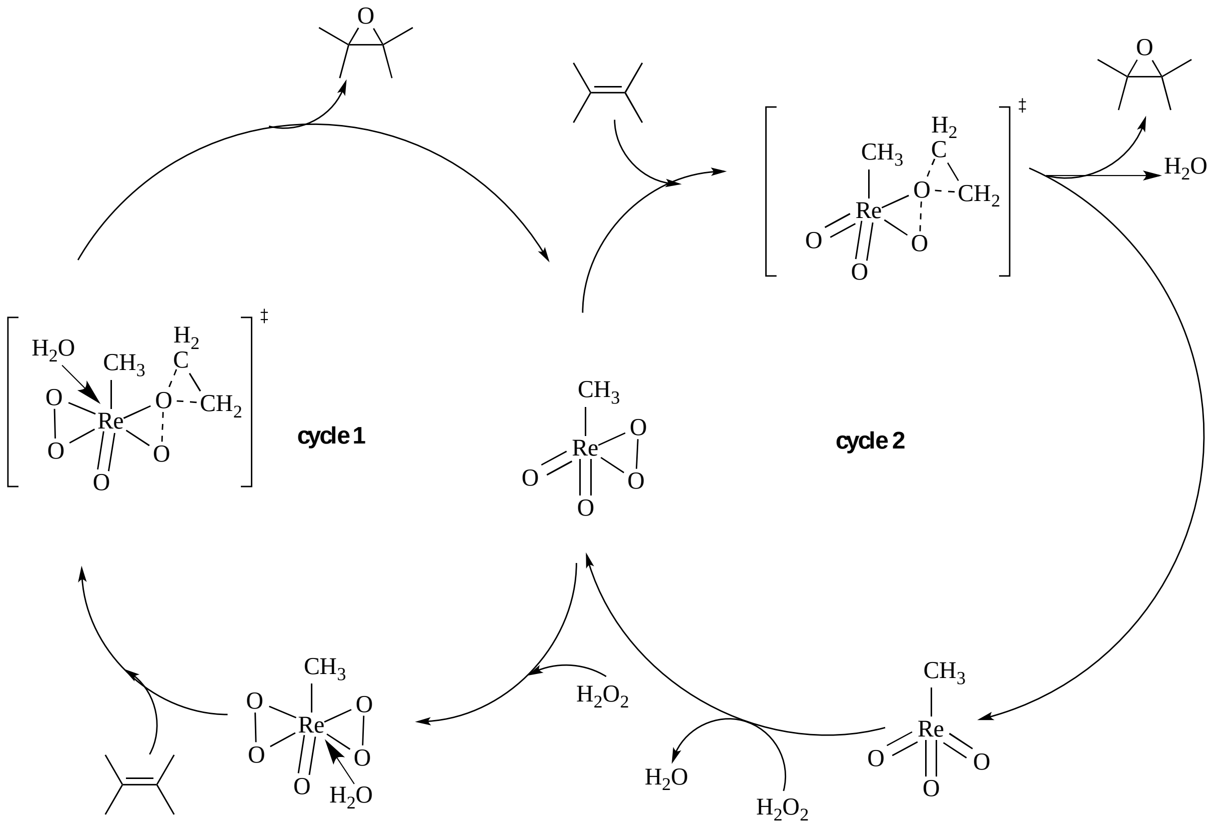
The epoxidation of olefins without a doubt is the most thoroughly studied application of MTO. There are several studies concerning the reaction mechanism – both from theoretical and kinetic points of view.[46–51]

The formation of the mono- and bisperoxo species is shown in scheme 6.



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

Hermann *et al*. were able to structurally characterise the active bisperoxo species in 1993.[52] Although the monoperoxo species has never been isolated, the mechanism for the epoxidation of olefins using MTO/H_2O_2, which is shown in Scheme 7, is mostly agreed.



Scheme 7. Mechanism of the epoxidation of olefins with MTO and H_2O_2.

A concerted mechanism is suggested for both cycles (1 and 2) where the peroxidic oxygen of the so called "butterfly complex" $[CH_3(Re(O_2)_2O$□$H_2O]$ is attacked by the double bond of the olefin.[53–55]□

1.2.4 Molybdenum complexes in olefin epoxidation

Olefin epoxidation catalysed by molybdenum complexes and peroxides as oxidants has been extensively studied in the last decade.[56] With some degree of success, dioxomolybdenum(VI)complexes of the type $MoO_2X_2L_2$ (X = Cl, Br, Me, Et; L = Lewis base ligand) have been utilized in the oxidation of alkenes with peroxides. They have been examined and reviewed in homogeneous[57–59] as well as in heterogeneous[60,61] phase. There have also been thorough investigations on stereoselective epoxidations with such catalysts[62,63].

In the last ten years the investigation of complexes where a cyclopentadienyl ring is coordinated directly to molybdenum has received more attention from the research community. The organometallic compounds have been synthesized and examined with respect towards their catalytic activity in alkene epoxidation with several oxidants such as alkyl peroxides or hydrogen peroxide. What makes the cyclopentadienyl (Cp) ligand and its derivatives such a useful part in the design of a catalytic system is its ability to undergo haptotropic shifts in the transitions state. This might result in a coordinatively unsaturated metal centre, which in turn assists insertion or coordination and therefore subsequent transformation of substrate. Another feature is the inert behaviour of the Cp moiety towards oxidation during epoxidation reactions and furthermore towards attack of electrophilic or nucleophilic reagents.[64–66]

In 2010 Kühn et al. reported about a molybdenum-cyclopentadienyl system applied in ionic liquid that was able to outperform the well-known CH_3ReO_3/H_2O_2 system[67]. The utilized complexes are shown in figure 5.

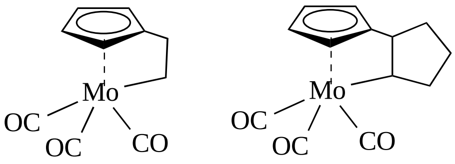


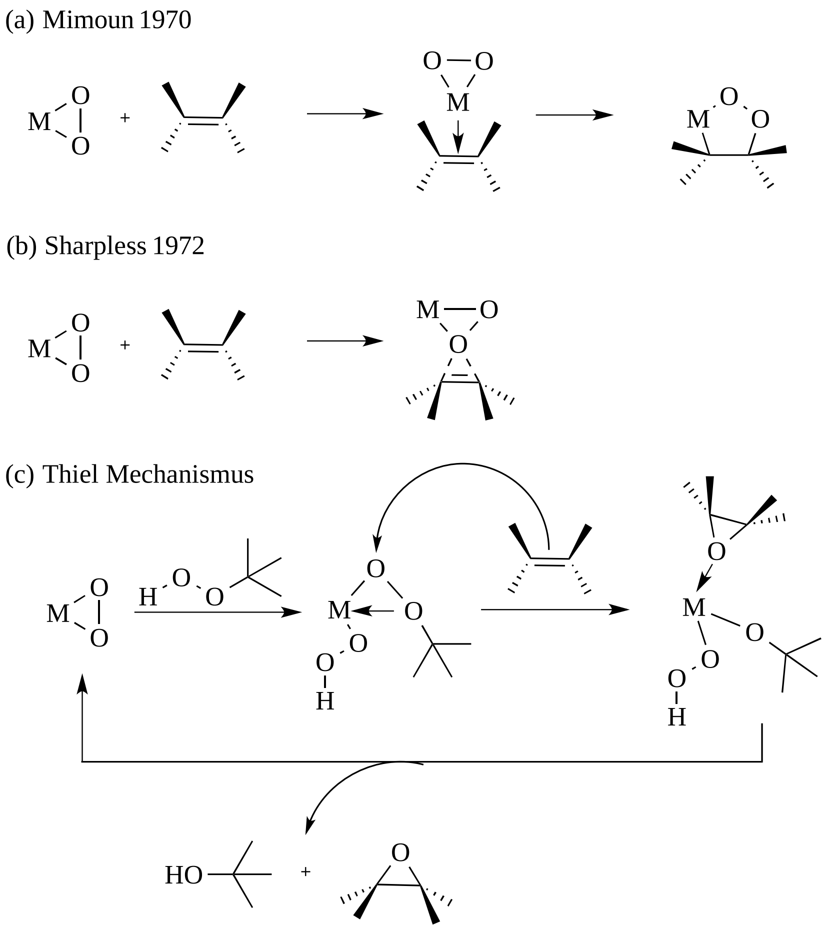
Figure 5. Ansa complexes.

Quantitative yields without formation of diols and TOFs up to 44.000 h^{-1} were reported for biphasic epoxidation of selected olefins. The represented system can be seen as a benchmark for the catalytic epoxidation of olefins utilizing $MoCp(CO)_3X$ compounds.

The mechanism for olefin epoxidation using dioxomolybdenum(VI) compounds[68] MoO_2X_2L X = halide, CH_3; L = bidentate ligand) and molybdenum oxo bisperoxo complexes[55] has been studied intensively.

By contrast the exact nature of the active species formed when $MoCp(CO)_3X$ compounds are applied in catalysis is still an issue of current research. Illustrated below are the widely accepted models for oxygen transfer with Mo-oxo(Fig. 7) and Mo-peroxo species (Fig. 6).

The oxo and the peroxo ligand act as a temporary repository of the proton when TBHP is used as an oxidant. Thus the oxidant is activated by the coordination to Mo and therefore becomes susceptible to a nucleophilic attack of the olefin. The Thiel mechanism is reasoned for TBHP but can also be operative for H_2O_2. The principle of the mechanism is identical to the one of Sharpless but in this case the exogenous attack of the olefin takes place at the electrophilic oxygen atom without coordination at the metal centre[69,70].



(a) Mimoun 1970

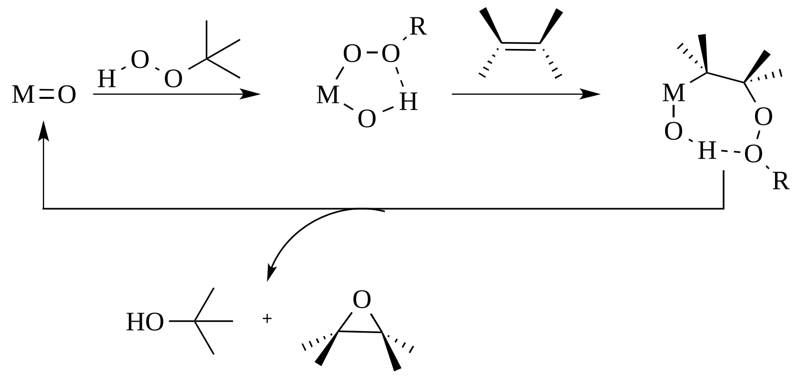
(b) Sharpless 1972

(c) Thiel Mechanismus

Figure 6. Proposed mechanism for olefin epoxidation with Mo-peroxo species.

Calhorda et al proposed a mechanism where the oxido ligand is the hydrogen depository and the alkylperoxido moiety bonds with Mo to form an intermediate. The H-bonding between the hydroxide proton and the O^{β} of the alkyl peroxido group stabilizes the intermediate. Subsequent olefin insertion similar to Mimoun has been proposed[70].

(a) Calhorda et al 2010



(b) Poli et al 2010

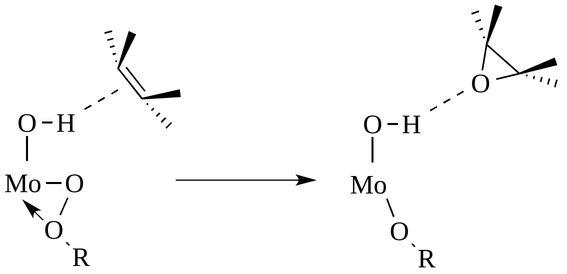


Figure 7. Proposed mechanism for olefin epoxidation with Mo-oxo species.

However Poli et al have proposed an asymmetrical η^2-coordination of the alkylperoxido intermediate[71]. An intrinsic interaction between Mo and O^β takes place. This interaction is the crucial point for the activation of the O^α towards an exogenous attack of the olefin substrate – activation barriers for the oxygen transfer to the olefin are significantly lower compared to the Calhorda mechanism[72].

1.2.5 Polyoxometalates in olefin epoxidation

Polyoxometalates (POM) are an architecturally and structurally diverse and fascinating class of redox active anionic transition metal–oxygen-based materials [73–75]. Numerous organic transformations can be catalysed by POMs due to their controllable redox and acidic properties. It is also well-known that POM catalysts are widely used for organic oxidations, with the Venturello-Ishii complex $\{PO_4[WO(O_2)_2]_4\}^{3-}$ utilized in the alkene epoxidation with H_2O_2 as an outstanding example.[76–78] Owing to the good solubility of POMs in polar reaction media, heterogenization of homogeneous POM catalysts is very attractive to overcome the difficulty of catalyst isolation.

In recent times the concept of combining POM anions with “weakly coordination cations”, such as those typically used for ionic liquids (e.g. phosphonium, imidazolium, pyridinium, tetralkylammonium), has gained more and more interest in the scientific community as it is regarded as a feasible way to increase the reactivity of POMs in ionic liquids.

However most of these “hybrid materials”, for example $[Bmim]_4[SiM_{12}O_{40}]$, $[Bmim]_4[S_2M_{18}O_{62}]$ (M = Mo, W) and $[(n\text{-}C_4H_9)N]_4[Mo_8O_{26}]$ have been characterized and mainly used as electrochemicals[79–82].Therefore only few POM salts have been examined as catalysts. For example the compound $[(n\text{-}C_4H_9)N]_2[W_6O_{19}]$ was investigated by Davoodna et al as a catalyst for the synthesis of biscoumarins[83]. The Keggin-type POM anion $[PW_{12}O_{40}]^{3-}$ can be used as a catalyst for esterification[84] and for epoxidation reactions in ionic liquids[85]. That being so, their molybdenum based congeners, such as the Lindqvist-type POM containing an $[Mo_6O_{19}]^{2-}$ anion are rather rare and have not often been used in oxidation catalysis so far. In 2013 our group reported about the use of such molybdenum-based polyoxometalate salts in the epoxidation of olefins and the oxidation of sulphides to sulphoxides.

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2. Objectives

As maybe concluded from the state of the art literature Cp ligated molybdenumdioxo(VI)-complexes are in general more active than their MoO_2X_2L congeners and are even able to rival the MTO/H_2O_2 system in the epoxidation of certain olefins.

However has it to mentioned that these systems still suffer from some crucial disadvantages. They are generally less active towards un-functionalized olefins and asymmetric epoxidation is not yet achieved to a satisfactory extent. Their biggest drawback is certainly the fact that efficient catalysis with them is largely dependent on the use of TBHP as oxidant instead of the more environmental benign H_2O_2.

The aim of this thesis is to gain a better understanding of molybdenum based pre-catalysts for the epoxidation of olefins.

Besides steric influences the electronic properties of the complex can mainly be hold responsible for the catalytic performance.

Therefor studies on the influence of electron-donating and electron-withdrawing ligand systems on cyclopentadienyl-substituted molybdenum complexes have been done.

Complementary to this study on molecular MoCp compounds and their recyclability in ionic liquid, the development of an environmental benign, cheap and reusable metal containing ionic liquid was an objective of this work. Therefore a functional IL containing an imidazolium cation was *in situ* combined with a polyoxomolybdate anion.

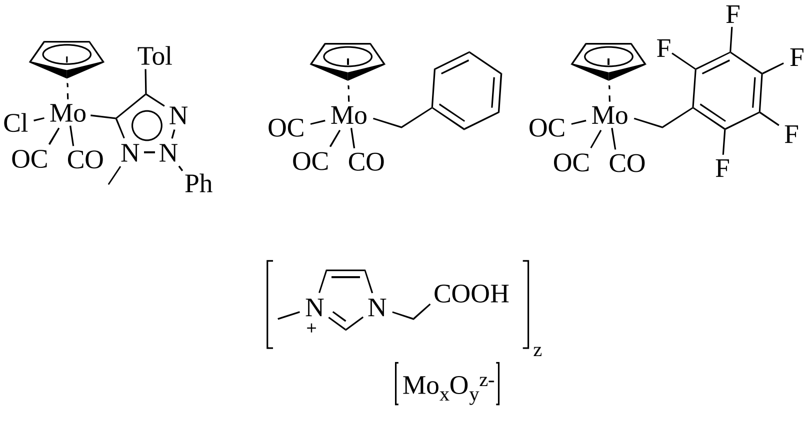


Figure 8. Structures of the during this thesis investigated pre-catalysts for the epoxidation of olefins.

3. Results

This chapter contains published and unpublished results of the research work that have been carried out in the laboratories of the Lehrstuhl für Anorganische Chemie at Technische Universität München.

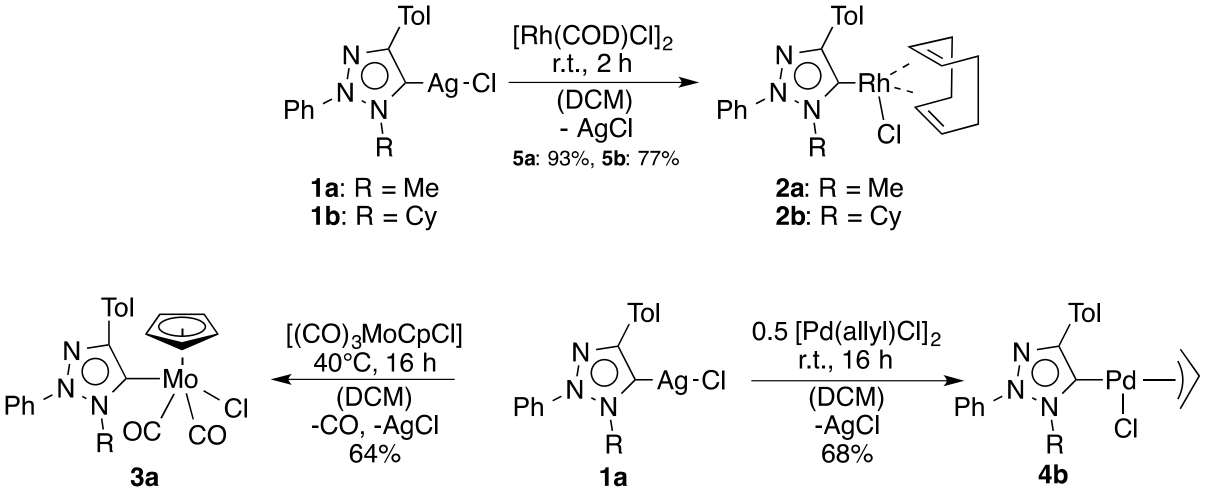
3.1 Exploring the Scope of a Novel Ligand Class: Synthesis and Catalytic Examination of Metal Complexes with 'Normal' 1,2,3- Triazolylidene Ligands

This chapter originates from the following publication:

Lars-Arne Schaper*, **Lilian Graser***, Xuhui Wei, Rui Zhong, Karl Öfele, Alexander Pöthig, Mirza Cokoja, Bettina Bechlars, Wolfgang A. Herrmann und Fritz E. Kühn (* equally contributing co-authors),
"Exploring the Scope of a novel ligand class: Synthesis and catalytic examination of metal complexes with 'normal' 1,2,3-triazolylidene ligands"
Inorg. Chem., doi: /10.1021/ic400533u
(refer to 5.1.1)

Mesoionic 1,2,3-triazolylidenes provide strong donor properties and have therefor received expanded interest of the scientific community over the last few years[1].
Our group was able to show that compared to their mesoionic relatives, 1,2,3-triazolylidenes with 'normal' 1,2,4-substitution pattern retain marginal stronger electron donor power[2]. To be able to compare the sterical and electronical influence of these special NHCs the amount of characterized transition metal complexes needs to be amplified and their activity in homogenous catalysis tested.
The preparation of the carbene precursor salts followed a ring closing protocol that Moderhack and co-workers described in 2003[3]. The silver complexes shown in scheme 8 were prepared from these precursor salts via the route of Wang and Lin[4]. Yields were moderate to good and notable variation of this protocol was required to isolate **1b** (see Appendix for experimental details). To determine the feasibility of these silver complexes as carbene transfer reagents they were allowed to react with $[Rh(COD)Cl]_2$ to form the Rh complexes **2a** and **2b** in good yields. Both compounds were successfully isolated and characterized. The syntheses protocol proceeds under mild reaction conditions within 2 hours reaction time (scheme 8). Both, the Mo complex **3a** and the Pd complex **4a** were synthesized by applying only slight modified reaction conditions (see appendix for details).

These compounds were also isolated and fully characterized.



Scheme 8. Synthesis of new transition metal complexes with normal 1,2,3-triazolylidene ligands using silver complexes **1a** and **1b** as precursor.

As already mentioned compounds of the general formula $[MoCp(CO)_3X]$ have been extensively studied as pre-catalyst for the epoxidation of olefins. When **3a** was applied in the epoxidation of cyclooctene using *tert*-butyl hydroperoxide as oxidant full conversion was observed within 24 hours at 55°C. The utilization of the room temperature ionic liquid $[C_8mim]^+[NTf_2]^-$ as reaction medium allowed 6 consecutive catalyst cycles without considerable loss of activity. Nevertheless it has to be stated that the catalytic activity is best case modest when compared to benchmark systems[5]. Aside catalyst deactivation together with precipitation of a decomposition product is observed when common organic solvents are used as reaction media.

Likewise pre-catalyst **4a** was tested in the Suzuki-Miyaura coupling catalysis. The catalytic activity is comparable to other triazolylidene based systems for arylbromide substrates[6]. Mediocre performance was observed in the reaction of arylboronic acids and the more challenging arylchloride substrates. It is likely that under catalytic conditions catalytically active nanoparticles are formed. This assumption is underpinned by reduced yields in mercury poisoning experiments.

Insufficient ligand stability is revealed in catalytic examinations. It is also noteworthy that the sterically shielded Rh cyclohexyl substituted triazolylidene complexe **2b** is even less stable than its methyl substituted analogue **2a**. Hence a triaryl-substituted triazolylidene ligand design might enhance stability and therefor improve the catalytic performance of compounds utilizing this new ligand class.

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

This chapter originates from the following publication:

Lilian Graser, Andrea Schmidt, Alexander Pöthig, Mirza Cokoja, Fritz E. Kühn
“ CompaAryl-substituted organomolybdenum (II) complexes as olefin epoxidation catalysts”
Catalysis Science &Technology, **2015**, *accepted*
(refer to 5.1.2)

In 2013 our group was able to compare the activity of the fluorinated organomolybdenum complex [MoCp(CO)$_3$CF$_3$] with its non fluorinated counterpart [MoCp(CO)$_3$CH$_3$][1]. Although both complexes are sterically very similar great difference in their catalytic activity was observed. This behaviour was reduced to disparities in the Lewis acidity of the metal centre. Based on the on going dearth of information with regard to electron-withdrawing groups located at the metal centre, we further widened the scope of available molybdenum compounds.
Compounds **5** and **6** were generated by the reaction of Na[MoCp(CO)$_3$] with benzylbromid and pentafluorobenzylbromide respectively (see appendix for experimental details). Both complexes were isolated and fully characterized.
IR spectroscopic examinations were performed with both complexes, since the vibrational bands of the carbonyl ligand represent a sensitive tool for electronic properties at the metal centre[2-4]. The frequency of the symmetric stretching of the CO ligand is 20 wavenumbers higher for compound **6** than for compound **5**. These findings lead to the assumption that the electron density at the molybdenum centre is lower in compound **6** resulting in an increased Lewis acidity.
For both compounds single crystals suitable for X-ray diffraction spectroscopy could be grown (Figure 9). A resemblance of selected bond lengths also reflects the electronic differences at the metal centre. The Mo-R bond length in compound **6** is decisively shorter than in compound **5**.

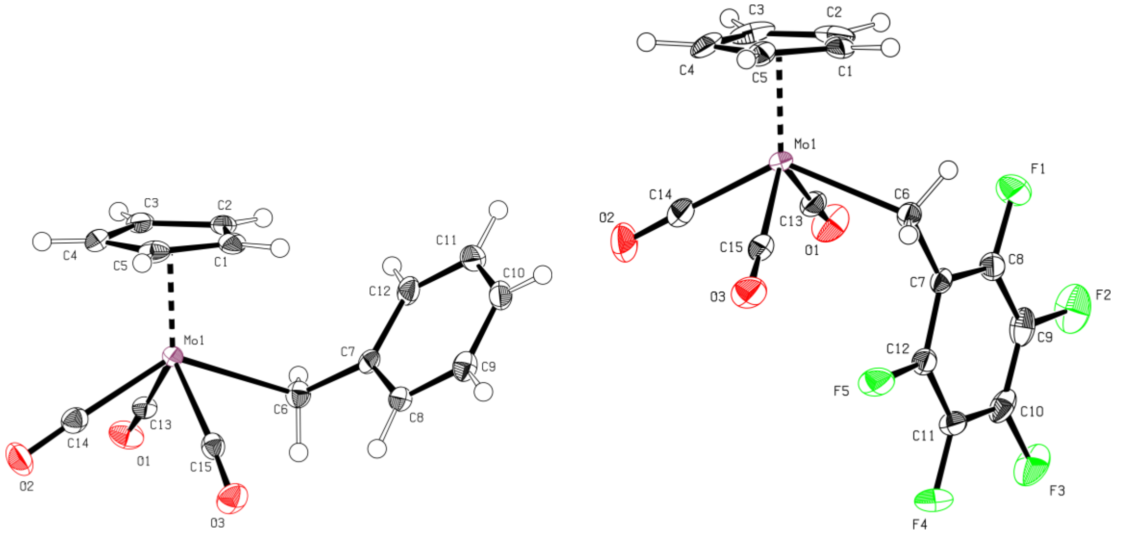

Figure 9. ORTEP drawing of compound **5** and **6**.

Since both compounds showed good stability towards air and moisture they were tested as pre-catalyst in the epoxidation of olefins using *tert*-butyl hydroperoxide as oxidant. Both compounds showed excellent results in hexafluorobenzene. This behaviour is in accord with recent observations for related systems[5,6]. Hexaflourinated solvents gained more interest in recent times in oxidation catalysis as they are able to activate the oxidant.

Table 1 gives an overview on the extent of difference in the catalytic activity of compound **5** and **6**.

Table 1. Activity of the pre-catalyst in dependence of the catalyst load.

Entry	catalyst	catalyst loading [mol %]	benzene TOF [h^{-1}]	hexafluorobenzene TOF [h^{-1}]
1	**1**	1	2.960	4.250
2	**1**	0.1	6.820	8.330
3	**1**	0.05	10.430	11.580
4	**2**	1	4.300	6.370
5	**2**	0.1	12.220	13.470
6	**2**	0.05	15.540	17.820

Reaction conditions: 55 °C, 0.5 mL solvent, ratio cyclooctene : TBHP = 1 : 2.

As can be seen from table 1 compound **6** is roughly 50% more active than compound **5**.

Both complexes also showed good results when utilized for the epoxidation of more demanding substrates, e.g. 1-octene, styrene and stilbene.

To scrutinize the stability of the catalytically active species and to test the recyclability of the system recycling experiments for both compounds were undertaken in [C_8mim][NTf_2]. We were able to implement 8 consecutive runs without a significant loss in activity.

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[1] S.A. Hauser, M. Cokoja, F. E. Kühn, *J. Mol. Cat. A.*, **2012**, *363-364*, 237-244.
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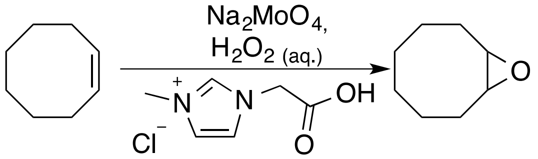
3.3 Epoxidation of Olefins Catalyzed by Polyoxomolybdates Formed in-situ in Ionic Liquids

This chapter originates from the following publication:

Lilian R. Graser, Sophie Jürgens, Michael E. Wilhelm, Mirza Cokoja,
Wolfgang A. Herrmann, and Fritz E. Kühn
"Epoxidation of Olefins Catalyzed by Polyoxomolybdates formed in-situ in ionic liquids"
Z. Naturforsch. **2013**, 68b, 1-5; DOI: 10.5560/ZNB.2013-3139
(refer to 5.1.3)

Polyoxometalate based ionic liquids have been developed lately by exchanging the usually monocharged anions of ionic liquids with the multicharged polyoxometalate anions as counterions. There are some reports about the catalytic activity of these systems[1-4]. A prototype system was cultivated by Wang et al. in 2012[5]. They synthesized several imidazolium polyoxometalate salts using Keggin-type polyoxometalate anions and varied the length of the carbon chain on the imidazolium based cations. In their work they focused on the oxidation of sulfides utilizing H_2O_2 as oxidant and were able to achieve good conversions. Based on the on going dearth for efficient systems we used an acid functionalized ionic liquid instead of an organic acid to lower the pH value of the reaction mixture and were therefor able to form *in situ* an active catalytic system. The system was utilized in the epoxidation of *cis*-cyclooctene (scheme 9).

In a typical reaction a biphasic system composed of a yellow ionic liquid and molybdate containing phase and the colorless organic substrate phase formed.



Scheme 9. Epoxidation of *cis*-cyclooctene using *in situ* generated polyoxometalates.

As can be seen in table 2 the yield of epoxide is strongly contingent on the amount of [camim]Cl in the reaction mixture. This can be ascribed to the determination of the pH value by the acid functionalized ionic liquid and the relative formation of the polyoxomolybdate species.

Table 2. Epoxidation of *cis*-cyclooctene using different amounts of [camim]Cl.

Entry	mmol (camim)Cl	pH	Conv. (%)[b]	Yield (%)[b]	Conv. (%)[b]	Yield (%)[b]
			after 4h		after 24 h	
1	0,1	7,0	14	14	21	21
2	0,5	5,5	18	18	26	26
3	0,75	4,0	28	28	37	37
4	1	3,5	39	39	68	68
5	1,5	2,5	34	34	62	62
6	2	2,0	33	33	56	56

(a) Reaction conditions: 2.00 mmol *cis*-cyclooctene, 3.00 mmol H_2O_2, 20,5 mg (0.1 mmol) Na_2MoO_4, 3 mL deionized water, 60 °C . (b) Determined by GC-MS analysis.

The best catalytic activity was achieved when a pH value of ca. 3.5 was generated by the addition of 1.00 mmol [camim]Cl to the system. It is most likely that under these conditions $[Mo_xO_y]^{2-}$ clusters are formed.

Furthermore the catalytic system is sensitive towards the applied amount of sodiummolybdate. A blind experiment showed that molybdate serves as precursor as there was negligible conversion without the addition of Na_2MoO_4. It was found that under the deployed reaction conditions the ideal molybdenum to ionic liquid ratio is 1 to 10.

Also a strong temperature dependence of the catalytic activity was investigated. This fact is ascribed to solubility issues between the substrate in the reaction mixture on the one hand and the formed polyoxometalate in water/IL phase.

A further point of scrutiny was catalyst recycling and reusability. The system was used for six consecutive runs without a significant loss of activity.

Recapitulating it can be stated that the activity of the catalytic system is inferior to its molecular congeners but the active species is formed *in situ* from a cheap and readily available precursor. Furthermore it can be used for several times without a significant loss in activity.

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[1] C. L. Hill, C. M. Prosser-McCartha, *Coord. Chem.* **1995**, *143*, 407-455.
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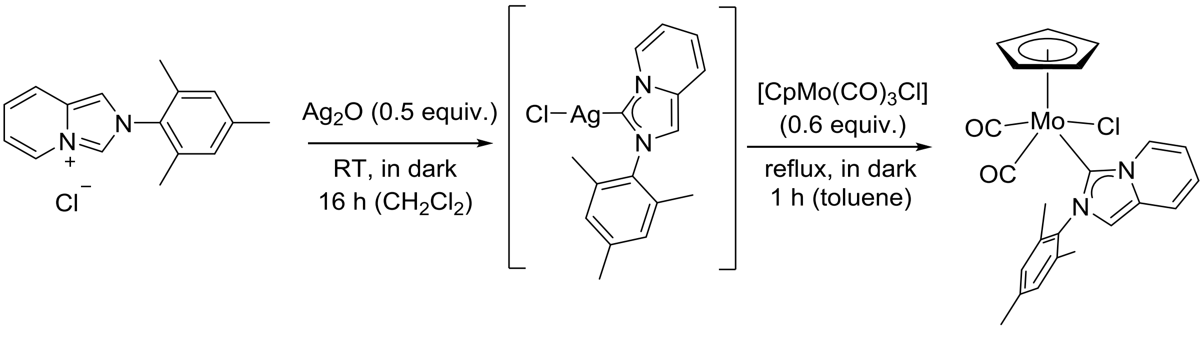
3.4 Synthesis and Characterization of Novel Cyclopentadienyl Molybdenum Imidazo[1,5-a]pyridine-3-ylidene Complexes and their Application in Olefin Epoxidation Catalysis

This chapter contains unpublished results:

Andrea Schmidt,[a] Nidhi Grover,[a] Teresa Zimmermann,[a] **Lilian Graser**, Alexander Pöthig, and Fritz E. Kühn* [a] equally contributing co-authors
"Synthesis and Characterization of novel cyclopentadienyl molybdenum imidazo[1,5-a]pyridine-3-ylidene complexes and their application in olefin epoxidation catalysis"
(refer to 5.1.4)

In 2010 Hor and Zaho et al. reported the synthesis of a series of cyclopentadienyl imidazolylidene molybdenum complexes.[1] The neutral complexes of the general formula [CpMo(CO)$_2$(NHC)X] (X = halide) show poor activities in epoxidation reaction, whereas their ionic counterpart containing a BF$_4$ anion results in TOFs higher than 3400h^{-1}. Imidazo[1,5]pyridine-3-ylidenes (ImPy) are among the strongest heteroaromatic σ-donors. Furthermore they are sterically more demanding than 1,3-disubstituted imidazolylidenes. Consequently by varying the substituents o the NHC ligand, the stereoelectronic environment at the metal centre may be manipulated easily.[2,3]

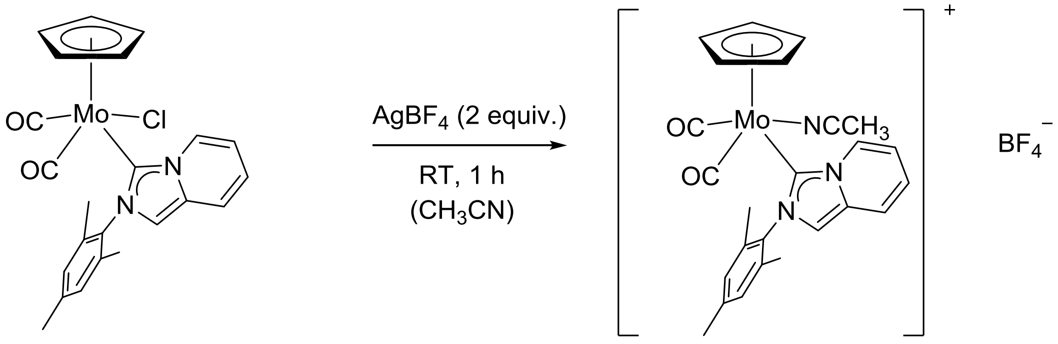
In this study, the synthesis and characterisation of two novel NHC molybdenum complexes - [CpMo(CO)$_2$(ImPyMes)Cl] (ImPyMes = 2-mesitylimidazol[1,5-a]pyridine-3-ylidene) **1** and [CpMo(CO)$_2$(ImPyMes)(NCCH$_3$)]BF$_4$ **2** – and their utilization as pre-catalysts in the epoxidation of olefins have been investigated.



1, 90 %

Scheme 10. Synthesis of complex **1** *via* a silver carbene of 2-mesitylimidazo[1,5-a]pyridinium chloride.

The synthesis of complex **1** is shown in scheme 10. It was synthesized by the transmetallation route via the silver carbene of 2-mesitylimidazo[1,5-a]pyridinium chloride (for experimental details see Appendix). By treating complex **1** with AgBF$_4$ in acetonitrile the synthesis of the ionic complex **2** was conducted in good yields (scheme 11).[1]



1 **2**, 87 %

Scheme 11. Synthesis of the ionic complex **2**.

To determine the effect of the ImPyMes ligand on the catalytically activity of these Mo NHC complexes they were applied in the epoxidation of several olefins such as *cis*-cyclooctene, 1-octen and *cis*-stilbene. *Tert*-butylhydroperoxid was used as oxidant under various reaction conditions. Both catalysts outperform known molybdenum epoxidation catalysts in terms of catalytic activity. Extraordinarily high TOFs up to 40900 h^{-1} (**1**) and up to 53100 h^{-1} (**2**) are observed. It is noteworthy that the more challenging substrates can be epoxidized in good yields with high selectivities.

In addition, catalyst **1** can be reused for at least 10 consecutive runs without loss of activity when utilised in RTIL $[C_8mim][NTf_2]$. This indicates a extraordinary stability of the catalyst.

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3.5 Ionic Liquids as Solvents for Ionic Transition-Metal Catalysts

This chapter originates from the following publication:

Lilian Graser, Daniel Betz, Mirza Cokoja and Fritz E. Kühn
"Ionic liquids as solvents for ionic transition-metal catalysts"
Curr. Inorg. Chem., **2011**, *1*, 166-181.
(refer to 5.1.5)

This review deals with the catalytic application of ionic transition-metal complexes using different ionic liquids as solvents. Additionally, so-called organometallic ionic liquids have been described with regard to their activity in several types of reaction.

First an overview over recent examples of catalysis with ionic compounds in ionic liquids was given[4-6]. In 2008 Noland and Maudit synthesized and characterized a ruthenium complex containing an unsaturated *N*-heterocyclic carbene (1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene) and an ionic alkylidene moiety which is shown in figure 10.[1] They investigated the catalytic activity in the cross metathesis of methyl acrylate and a more reactive olefin.

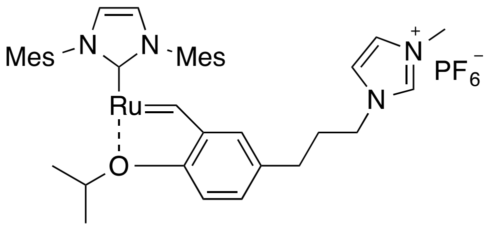

Figure 10. Ruthenium pre-catalyst utilized by Noland et al.

Reactions were performed in a 4/1 [Bmim][PF_6]/co-solvent biphasic mixture. The authors stated that the use of aromatic solvents as co-solvents led to the formation of a clathrate phase due to pi-stacking interactions between the organic solvent and the imidazolium moiety. Better pre-catalyst solubility was achieved because of the lower viscosity of ionic liquid medium. Singh et al. described the synthesis of an ammonium tagged palladacycle for Mizoroki-Heck and Sonogashira reactions (figure 11).[2] The group reported that palladium leaching was dramatically reduced by the ionic tag.

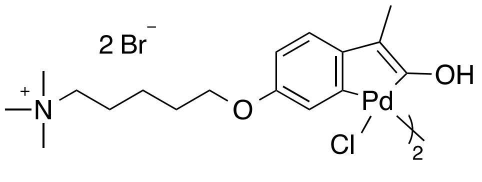

Figure 11. Ammonium tagged oxime carbapalladacycle.

They ascribe this to the increased solubility of the palladacyle compound in the ionic liquid media. By the intercalation of the palladacycle into a Na-montmorillonite by ion-exchange the authors were able to create a homogeneous supported catalytic system. [Tmba][NTf$_2$] was used as solvent for both systems. A remarkable detail is the fact, that there is no need to add copper(I) salts as co-catalyst in the Sonogashira coupling. The recycling studies showed little loss of activity even after seven cycles and no precipitation of palladium black.

Another growing field of interest which was reviewed in this article is catalysis using metal-containing ionic liquids. Hou and co-workers synthesized and characterized four polyoxometalate anion functionalized catalysts.[3] As a model reaction the epoxidation of *cis*-cyclooctene was chosen. They could show that the length of the alkyl chain in the imidazolium cation has a crucial effect of catalytic activity. [Hdmim]$_2$[W$_2$O$_{11}$] proved to be the most active catalyst and can be regarded as a reaction-induced phase-separation catalyst. A remarkable fact is that the catalytic system switched the reaction mixture from tri-phase to emulsion, then to a biphasic system and finally to all the catalyst self-precipitating from the reaction mixture after the reaction. Catalyst recycling via decantation is easily possible.

The utilization of ionic liquids as a reaction media is more and more common in different fields of catalytic applications. In many cases they are able to improve the performance of the catalytic reaction. Unfortunately, the interaction between the different ions (ionic liquid and ionic catalyst) and the correlating influence on the catalytic activity are not sufficiently described.

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3.6 Epoxidation of Olefins with Molecular Catalysts in Ionic Liquids

This chapter originates from the following publication:

Christian J. Münchmeyer*, **Lilian R. Graser***, Iulius I.E. Markovits*, Mirza Cokoja and Fritz E. Kühn (equally contributing co-authors),

"Epoxidation of Olefins with molecular catalysts in Ionic Liquids"
Top. Organomet. Chem., Springer Berlin Heidelberg, 2012
(refer to 5.1.6)

This book chapter gives a summary of the epoxidation of various olefins catalyzed by different transition metal complexes, as well as by metal-fee compounds in ionic liquid media.

The epoxidation of olefins catalyzed by molecular transition metal compounds is a research field, which has been extensively studied over the past forty years. To date, numerous types of complexes have been presented as widely applicable and highly efficient. They are utilized in organic solvents as well as in ionic liquids. A broad scope of different transitions metals, among which are Ti-, Cr-, Mo-, W-, Re-, Fe-, V- and Ru-catalysts, using quiet a wide range of different oxidants have found application as homogeneous catalyst. They are usually capable of forming stable epoxides in good to excellent yields without diol-formation – the most likely side reaction. Furthermore a broad scope of substrates from cyclic to acyclic/terminal olefins has been tested. Also a good range of epoxidation reaction of pro-chiral olefins have been reported with catalysts carrying chiral information, giving good enantiomeric excess.

Homogenous catalysis finds rare application in chemical industry. This is largely caused by the high costs of the catalyst and the oxidant agent needed. Reusability of the systems for several times is one of the main reasons that mages homogenous catalysis in ionic liquid promising candidate for sustainable processes. Another striking effect is that most of these systems work at low pressures and at temperatures below 60°C. However it has to be mentioned that "long term recycling" experiments in which the catalyst would be recycled for thousands of times (as required for most industrial applications) are yet not available. Meanwhile the epoxidation of bulk chemicals such as ethylene or propylene is not yet revised in a satisfying way. Heterogeneous catalyst such as Ag@Al_2O_3 and titania doped zeolite type silicates developed by EniChem, Evonik, Dow and BASF are the state of the art process.

Very few reports deal with the exact role of the ionic liquid and its influence during the catalytic process. A detailed understanding of these interdependencies should help making it possible to "tailor-make" ionic liquids for different reactions/reaction paths. The next step in improvement of epoxidation catalysis of olefins with homogenous catalyst will most likely be the search for molecular catalyst that match or even surpass the reusability, stability and activity of the currently utilized heterogeneous systems which suffer from catalytic decomposition of the oxidant, hydrogen peroxide.

The ideal epoxidation catalyst for industry should provide the following features:

- air and moisture stable
- high turn over numbers
- active at temperatures around 25°C

- cooperating with a cheap and environmental friendly oxidant (cumene hydroperoxide, H_2O_2 or O_2)

3.7 Excursus: Rhenium heptoxid as highly active Lewis acidic catalyst in the C–O bond cleavage of β-hydroxy aryl ether

This chapter contains unpublished results.

R. G. Harms,[†a] **L. Graser**,[†a] S. Schwaminger,[b] W. A. Herrmann,[a] M. Cokoja*[a] and
F. E. Kühn*[a] ([†] equally contributing co-authors)

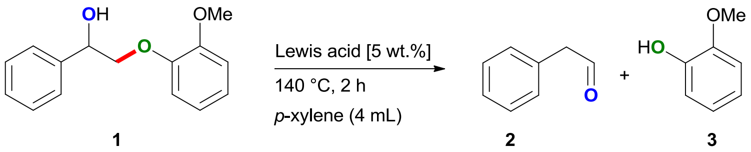
" Rhenium heptoxid as highly active Lewis acidic catalyst in the C-O bond cleavage of
β–hydroxy aryl ether"
(refer to 5.1.7)

With the increasing importance of research into biomass as a feedstock for the chemical industry, new methods to reduce the oxygen content of biomass are required. Biomass can provide sufficient carbon-based material o a yearly basis to supply the current chemical industry with feedstock for production.[1,2]
For the renewable fuel production the pyrolysis or hydrodeoxygenation of lignin into bio-oils are promising candidates. Lignin is a very complex phenolate based heterogeneous polymer, which inhibits its efficient degradation and application as chemical feedstock so far. The predominant intermonomer linkage between aromatic units in natural lignin is the β-O-4 bond – simply described as a β-hydroxy aryl ether bond.[3-5]
Hence that linkage represents a promising target in fundamental C-O bond cleavage studies.
Lewis acids have been proven to catalyse the degradation of lignin model compounds and even several technical lignins.[6-8]

In this work the application of Lewis acidic rhenium heptoxid catalyst for the efficient C-O bond cleavage of exceedingly stable 2-(2-methoxyphenoxy)phenylethanol (**1**) lignin model dimer to phenylacetaldehyd (**2**) and guiacol (**3**) is reported.

In a screening of various Lewis acids in *p*-xylene under aerobic conditions Re_2O_7 catalyst yields in quantitative conversions and almost complete mass balance (entry 5).

Table 3. Screening of various Lewis acids in the catalytic C–O bond cleavage of β-hydroxy aryl ether **1**.



Entry	Lewis acid catalyst	Conv. [%][a]	Yield **2** [%][a]	Yield **3** [%][a]
1	$AlCl_3$	16	0	4
2	$Al_2(SO_4)_3*18H_2O$	21	0	0
3	BF_3*Et_2O	70	0	36
4	$FeCl_3$	72	2	46
5	$\mathbf{Re_2O_7}$	**100**	**86**	**93**
6	$Sc(OTf)_3$	100	7	71
7	$SnCl_4$	100	0	36
8	$TiCl_4$	100	0	47

Reaction conditions: 100 mg 2-(2-methoxyphenoxy)phenylethanol (**1**); [a] conversions and yields were determined by GC FID.

Re_2O_7 seems to provide the best properties for the reaction meaning sufficient strong acidic to obtain substrate conversion, but also not to exceedingly strong to catalyse product decomposition.

The optimal reaction conditions were found at a low catalyst loading of 0.1 mol% - under those conditions the catalyst reaches a remarkable TOF of 1500 h^{-1}.

To elucidate if the C-O cleavage reaction is catalysed due to the Lewis acidity of Re_2O_7 or due to the formation of a metallic or oxidic rhenium compound, commercially available rhenium compounds in several oxidation states were utilised in the reaction. Re_2O_7 outperforms all other rhenium compounds in both activity and product yield.

Despite the marginal solubility in *p*-xylene rhenium heptoxid is reported to be active in the dehydration of benzylic alcohols in both homogeneous and heterogeneous phase.[7,9]

The formation of a black precipitate alludes to the generation of the active catalyst species as either soluble particles or insoluble matter. To undeceive whether the reaction is catalysed by a homogeneous or heterogeneous catalyst filtration experiments were performed.

The formation of this black solid renders the reusability of the catalyst. The deactivation was studied in detail and revealed two probably independent pathways.

Rhenium heptoxid undergoes complete reduction from Re(VII) to Re(0) which is catalytically inactive. This has been shown by XPS (see figure 12). Additionally, Raman spectroscopy revealed the formation of disordered graphite. Furthermore, the formation of catalytically inactive nanoparticles is observed on homogeneous phase.

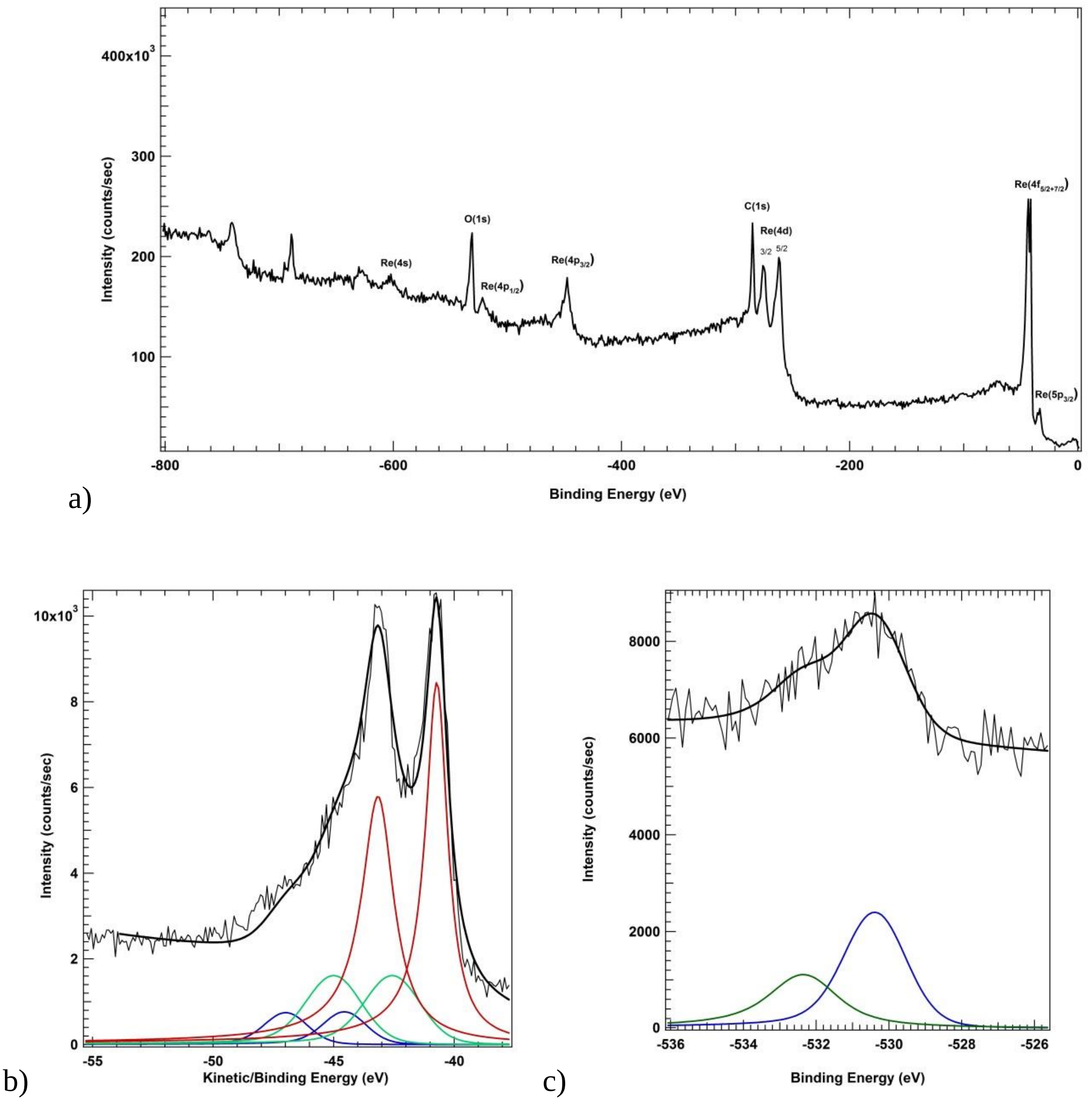


Figure 12. X-ray photoelectron spectra of the black precipitate: a) survey scan (b.e. –800 to 0 eV) with annotation of the corresponding orbital signal; b) narrow scan over the Re4f energy window (b.e. –58 to –38 eV) and deconvolution of the overlapped proportion; c) narrow scan over the O1s energy window (b.e. –537 to –526 eV) and deconvolution of two overlapped proportions.

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4. Summary and Conclusion

4.1 Zusammenfassung

Um ein besseres Verständnis des Zusammenhanges von katalytischer Aktivität und spektroskopischen bzw. strukturellen Merkmalen cylopentadienyl-substituierter Molybdänkomplexe zu erhalten, wurden in dieser Arbeit mehrere solcher Verbindungen isoliert und charakterisiert. Das bereits weitgehende akzeptierte Konzept der Korrelation von Elektrophilie und Lewis-acidität am Molybdän Zentralatom wurde überprüft. Die Fragestellung der Verfahrensentwicklung und der Katalysatorstabilität wurde bearbeitet durch Studien zum Recycling in ionischen Flüssigkeiten.

In Kapitel 3.1 wird die Synthese und Charakterisierung von neuen 1,2,3-Triazolyliden-Übergangsmetallkomplexen beschrieben. Durch die Nutzung der entsprechenden Silbercarbene als Carbentransferreagentien ließen sich erhöhte Ausbeuten erzielen. Der Pd-Komplex zeigte nur durchschnittliche Aktivität als Präkatalysator in der Suzuki-Miyaura Reaktion. Es konnte nachgewiesen werden, dass die Stabilität des neuartigen Ligandensystems unter katalytischen Bedingungen limitiert ist. Es wird angenommen, dass ein Triaryl-substitutionsmuster den Liganden in seiner Stabilität verbessern könnte. Die Verwendung des Molybdänkomplexes als Präkatalysator in der Epoxidation von Olefinen mit *tert*-butyl hydroperoxid zeigte die besten Ergebnisse wenn die ionische Flüssigkeit $[C_8mim]^+[NTf_2]^-$ als Lösungsmittel diente. Bei einer Reaktionstemperatur von 55°C wurden nach 4 Stunden 74% des Substrates umgesetzt. Desweiteren kann der Katalysator sechs mal ohne nennenswerten Aktivitätsverlust rezyklisiert werden.

Die Synthese und Charakterisierung eines neuartigen benzyl-substituierten MoCp Komplex und seines pentafluorobenzyl-substituierten Gegenstückes sind in Kapitel 3.2 beschrieben. Beide Verbindungen wurden als Präkatalysator in der Epoxidierung von Olefinen getestet. In Benzol oder Hexafluorobenzol wurden TOFs von bis zu 18.000 h^{-1} erreicht. Auch die Umsetzung von anspruchsvolleren Substraten wie Styrol oder Stilben gelang in guten Ausbeuten mit einer vergleichsweise geringen Beladung von 0.5 mol%. Beide Verbindungen können in ionischen Flüssigkeiten immobilisiert werden wodurch Produktseparation durch Dekantieren möglich wird. Überdies wurden beide Systeme acht mal rezyklisiert ohne einen Aktivitätsverlust zu beobachten.

Ein einfaches, günstiges und umweltfreundliches Katalysatorsystem für die Epoxidierung von *cis*-cycloocten wird in Kapitel 3.3 vorgestellt. Durch die Zugabe einer säurefunktionalisierten ionischen Flüssigkeit zu einer wässrigen Lösung von Natriummolybdat werden Polyoxomolybdate generiert. Die Epoxidausbeute steht hierbei in direkter Korrelation zur zugegeben Menge an säurefunktionalisierter ionischer Flüssigkeit. Dies ist darauf zurückzuführen, dass der pH-Wert der Lösung durch die Konzentration der IL bestimmt wird was wiederum die Bildung der entsprechenden Polyoxomolybdatspezies determiniert. Auch der Natriummolybdatgehalt der Reaktionslösung hat einen entscheidenden Einfluss auf den Erfolg der Katalyse. Basierend auf den erhalten Daten wurde ein Molybdän zu IL Verhältnis von 1:10 als ideal unter den verwendeten Reaktionsbedingungen herausgearbeitet. Das

Katalysatorsystem zeigt gute Ausbeuten für die Epoxidierung von *cis*-cycloocten und kann mehrere male ohne Aktivitätsverlust wiederverwendet werden.

Kapitel 3.4 handelt von der Synthese und Charakterisierung neuartiger Imidazo[1,5-a]pyridin-3-yliden substituierten MoCp Komplexe und ihrer Verwendung in der katalytischen Epoxidierung von Olefinen. Beide Katalysatoren übertreffen alle bisher bekannten molybdän-basierten Katalysatorsysteme in ihrer Aktivität. Sogar mit einer geringen Katalysatorbeladung von nur 0.005 mol% werden quantitative Umsätze nach 24 Stunden Reaktionszeit erreicht. Desweiteren spricht die Wiederverwendbarkeit der Verbindungen für 10 Katalysezyklen ohne nennenswerten Aktivitätsverlust für eine hohe Stabilität der Komplexe.

Ein Übersichtsartikel und ein Buchbeitrag sind die Grundlage für die Kapitel 3.5 und 3.6. Die Berichte beschäftigen sich mit Verwendung von ionischen Flüssigkeiten als Lösungsmittel und als Katalysator in der homogenen Katalyse.

Thematisch handelt es sich bei Kapitel 3.7 um einen Exkurs. Eine Studie zur Lewis aciden Spaltung eines Lignin-model-substrates wurde durchgeführt. Hierbei zeigte sich das Rheniumheptoxid unter den getesteten Reaktionsbedingungen alle anderen geläufigen Lewissäuren in Aktivität und Selektivität übertrifft. Während der Reaktion in *p*-Xylol bildet sich ein schwarzer Feststoff der katalytisch nicht mehr aktiv ist. Dieser wurde mittels Raman Spektroskopie und XPS analysiert. Auf Grund dieser Analysemethoden kann der Feststoff als ein Agglomerat aus Kohlenstoff und Rhenium(0) partikeln identifiziert werden.

4.2 Summary

In this thesis isolation and complete characterization of several different types of molybdenum complexes is described. These complexes have been utilized as pre-catalyst for the epoxidation of olefins. With the broader objective to gain an insight on the correlation between catalytic activity and either spectroscopic or structural parameters a venture to framework design principles of these molecular catalysts has been made. The accepted concept of the linkage between electrophilicity and Lewis acidity of Mo is challenged using several examples. Issues of process development and catalyst robustness have been also addressed by studying recyclability in ionic liquids.

In Chapter 3.1 synthesis and characterization of several transition metal complexes with new 1,2,3-triazolylidene ligands has been described. Using the ’normal’ substituted 1,2,3-triazolylidene silver compounds as starting material allowed for preparation of a series of ruthenium, rhodium, palladium and molybdenum transition metal complexes bound to the new 1,2,3-triazolylidene ligand system. Application of the molybdenum and the palladium compounds in catalysis were examined. In the case of the Pd-promoted Suzuki-Miyaura CC-coupling only moderate conversions were achieved for arylchloride substrates. This is ascribed to stability issues. It is highly likely that a triaryl-substitution pattern will help to improve ligand stability of ‘normal’ 1,2,3-triazolylidenes as it is described for abnormal triazolylidenes in the literature. When the Mo complexes is used as pre-catalyst for the epoxidation of olefins with *tert*-butyl hydroperoxide as oxidant, the room temperature ionic liquid $[C_8mim]^+[NTf_2]^-$ excelled as the best solvent. At a reaction temperature of 55°C 74% conversion were observed after 4 hours and the catalyst could be recycled for six times without considerable loss of activity.

In Chapter 3.2, a novel benzyl-substituted MoCp complex and its pentafluorobenzyl substituted congener were synthesized and utilized as pre-catalyst in the epoxidation of olefins. Using benzene and hexafluorobenzene as solvent TOFs up to 18.000 h^{-1} were achieved. The scope of the catalytic system was tested by applying more demanding substrates such as styrene and stilbene – they are epoxidized in moderate to good yields with a catalyst loading of 0.5 mol%. Again recycling issues were addressed by immobilization of the catalyst in a room temperature ionic liquid. This manoeuvre lead to the possibility of an easy product separation by decantation and the system can be reused for at least eight consecutive runs with only minor loss in activity.

An easy, cheap and environmental friendly catalytic system for the epoxidation of *cis*-cyclooctene is presented in chapter 3.3. Polyoxomolybdates are formed in situ by the addition of an acid-functionalized ionic liquid to an aqueous solution of sodium molybdate. The yield of epoxide is strongly dependent on the amount of acid functionalized ionic liquid as it determines the pH value of the reaction solution and therefor the formed polyoxomolybdate species. Furthermore it is shown that the amount of sodiummolybdate is a crucial parameter for the catalytic performance. Based on the gained data a molybdenum to ionic liquid ratio of 1 to 10 occurred to be ideal under the applied reaction conditions.

The system showed good conversions for the epoxidation and can be reused for several times without a significant loss in activity.

Chapter 3.4 deals with the synthesis and characterisation of a novel MoCp complexes with a imidazo[1,5-a]pyridine-3-ylidene ligand and its utilization as pre-catalyst in the epoxidation of olefins. The complex and its ionic counterpart outperform all known MoCp-based catalyst systems in their activity. Even at a low catalyst concentration of 0.005 mol% full conversion is observed after 24 hours reaction time. Furthermore it is noteworthy that the catalyst can be reused for 10 consecutive runs without any loss in activity.

A Review and a bookchapter are the fundament for chapter 3.5 and 3.6. Both deal with the utilization of ionic liquids as solvents in homogeneous catalysis.

As regards subject matter, chapter 3.7 can be seen as an excursus. A studie on the lewis acidic cleavage of a lignin-model compound is presented. It is shown that rheniumheptoxid outperforms all other commercially available Lewis acids under the applied reaction conditions in terms of activity and selectivity. During the reaction in *p*-xylene a black precipitate forms which is shown to be catalytically inactive. It was characterised by Raman spectroscopy and XPS and revealed to be an agglomerate of carbon and Re(0) particles.

5. Bibliographic Data of complete publications

This chapter intended to provide the reader with bibliographic details of the publications summarized in chapter 3 of this dissertation to allow for retrieval of the complete manuscripts and supporting information.

5.1. Exploring the Scope of a Novel Ligand Class: Synthesis and Catalytic Examination of Metal Complexes with 'Normal' 1,2,3-Triazolylidene Ligands

Lars-Arne Schaper[‡], Lilian Graser[‡], Xuhui Wei, Rui Zhong, Karl Öfele, Alexander Pöthig, Mirza Cokoja, Bettina Bechlars, Wolfgang A. Herrmann* and Fritz E. Kühn*
Chair of Inorganic Chemistry/Molecular Catalysis, Catalysis Research Center, Technische Universität München, Ernst-Otto-Fischer-Str. 1, D-85747 Garching bei München (Germany).

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[‡] Equally contributing co-authors.

5.2. Comparison of the catalytic performance of a fluorinated organomolybdenum complexe and its non fluorinated congener in the epoxidation of olefins

Lilian Graser, Mirza Cokoja, Alexander Pöthig, Fritz E. Kühn*

Chair of Inorganic Chemistry // Molecular Catalysis, Catalysis Research Center
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5.3 Epoxidation of Olefins Catalyzed by Polyoxomolybdates Formed *in-situ* in Ionic Liquids

Lilian R. Graser, Sophie Jürgens, Michael E. Wilhelm, Mirza Cokoja,
Wolfgang A. Herrmann and Fritz E. Kühn

Chair of Inorganic Chemistry/Molecular Catalysis, Catalysis Research Center, Technische Universität München, Ernst-Otto-Fischer-Straβe 1, D-85747 Garching bei München, Germany
Reprint requests to Prof. F. E. Kühn. Tel: +49 89 289 13081. Fax: +49 89 289 13473. E-mail: fritz.kuehn@ch.tum.de

5.4 Synthesis and Characterization of Novel Cyclopentadienyl Molybdenum Imidazo[1,5-a]pyridine-3-ylidene Complexes and their Application in Olefin Epoxidation Catalysis

Andrea Schmidt,[a] Nidhi Grover,[a] Teresa Zimmermann,[a] Lilian Graser, Alexander Pöthig, and Fritz E. Kühn*
Chair of Inorganic Chemistry/Molecular Catalysis, Catalysis Research Center, Technische Universität München, Ernst-Otto-Fischer-Str. 1, D-85747 Garching bei München, Germany
[*] Corresponding author, E-Mail address: fritz.kuehn@ch.tum.de
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5.5 Ionic Liquids as Solvents for Ionic Transition-Metal Catalysts

Lilian Graser[a], Daniel Betz[a], Mirza Cokoja[a] and Fritz E. Kühn[a,b*]

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[b] Molecular Catalysis, Catalysis Research Center, Technische Universität München, Lichtenbergstraße 4, 85747 Garching

5.6 Epoxidation of Olefins with Molecular Catalysts in Ionic Liquids

Christian J. Münchmeyer,† Lilian R. Graser,† Iulius I.E. Markovits,† Mirza Cokoja and Fritz E. Kühn

Chair of Inorganic Chemistry/Molecular Catalysis, Catalysis Research Center, Technische Universität München, Ernst-Otto-Fischer-Straße 1, D-85747 Garching bei München. E-Mail: fritz.kuehn@ch.tum.de

† These authors have equally contributed to the manuscript.

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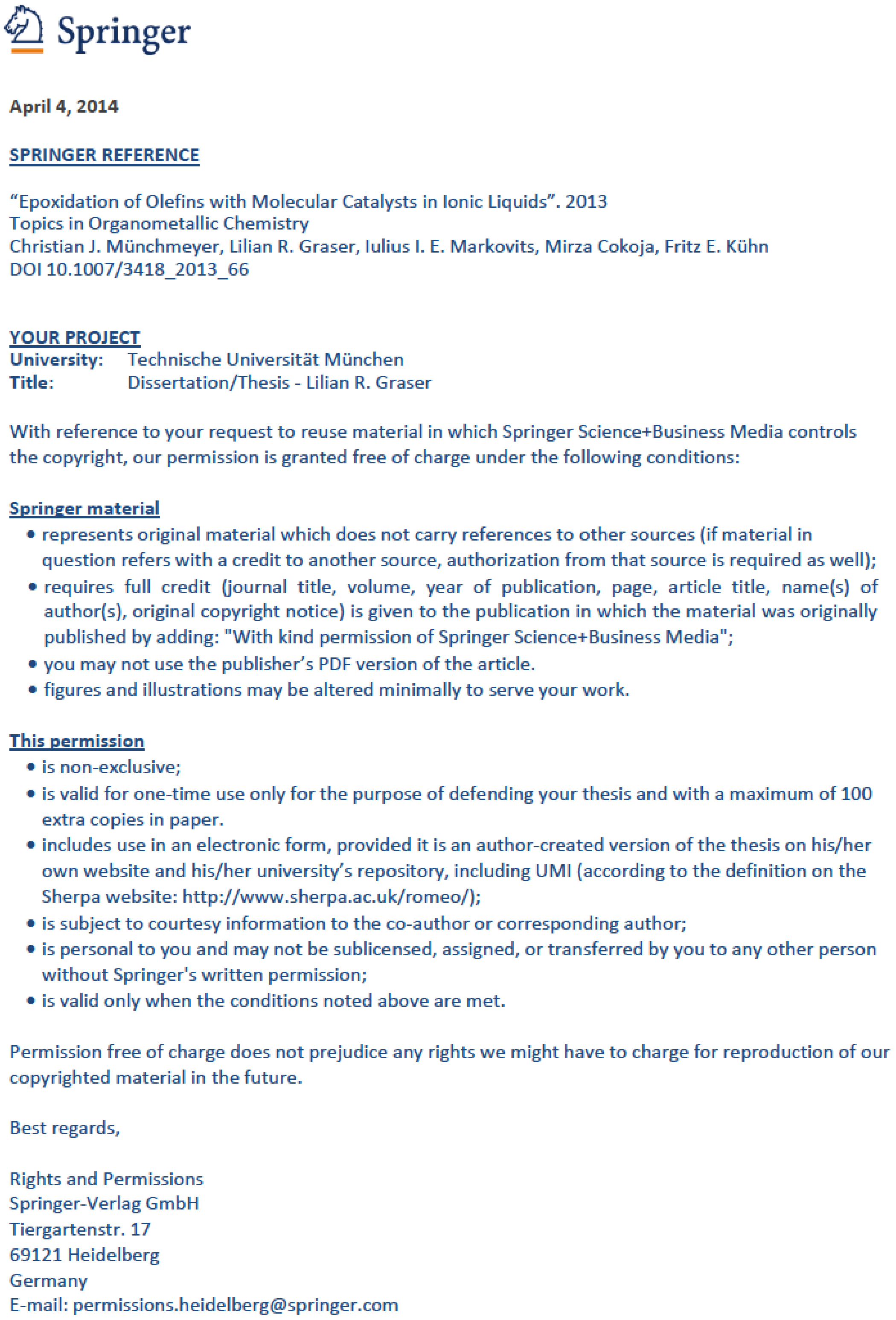

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Author: Lars-Arne Schaper, Lilian Graser, Xuhui Wei, Rui Zhong, Karl Öfele, Alexander Pöthig, Mirza Cokoja, Bettina Bechlars, Wolfgang A. Herrmann, and Fritz E. Kühn
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1) L. Graser, L.-A. Schaper, X. Wei, R. Zhong, K. Öfele, A. Pöthig, M. Cokoja, B. Bechlars, W. A. Herrmann und F. E. Kühn, “Exploring the scope of a novel ligand class: Synthesis and Catalytic Examination of metal complexes with ‘normal’ 1,2,3-triazolylidene ligands”, *Inorg. Chem*, **2013**, **DOI**: 10.1021/ic400533u.

2) L. Graser, A. Pöthig, M. Cokoja, F. E. Kühn, “Aryl-substituted organomolybdenum (II) complexes as olefin epoxidation catalysts, *Catalysis Science & Technology,* **2015**, *accepted.*

3) L. Graser, S. Jürgens, M. Wilhelm, M. Cokoja, W. A. Herrmann, F. E. Kühn, “Epoxidation of olefins catalyzes by polyoxomolybdates formed in situ in ionic liquids”, *Z. Naturforsch.,* **2013**, **DOI**: 10.5560/ZNB.2013-3139.

4) A. Schmidt, N. Grover, T. Zimmermann, L. Graser, A. Pöthig, F. E. Kühn, “Synthesis and Characterization of novel cyclopentadienyl molybdenum imidazo[1,5-a]pyridine-3-ylidene complexes and their application in olefin epoxidation catalysis”, *submitted.*

5) L. Graser, D. Betz, M. Cokoja, F. E. Kühn, “Ionic Liquids as solvents for transition-metal catalysis”, *Curr. Inorg. Chem.,* **2011**, *1,* 166-181.

6) Book Contribution in: “*Topics in Organometallic Chemistry*”, **2012**, Springer Berlin Heidelberg

7) R. G. Harms, L. Graser, S. Schwaminger, W. A. Herrmann, M. Cokoja, F. E. Kühn, “Rhenium heptoxid as highly active Lewis acidic catalyst in the C-O bond cleavage of β-hydroxy aryl ether”, *in preparation.*

7. Curriculum Vitae

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September 2009 –	**Master of Science in Chemistry**

October 2011	*Technische Universität München (Germany)* Thesis: Chair of Inorganic Chemistry Prof. Dr. Dr. h. c. mult. Wolfgang A. Herrmann Prof. Dr. Fritz E. Kühn Molybdenum-based ionic liquids for catalytic epoxidation of olefins: Synthesis and characterisation
October 2006 – July 2009	**Bachelor of Science in Chemistry** *Technische Universität München (Germany)* Thesis: Chair of Inorganic Chemistry Prof. Dr. Dr. h. c. mult. Wolfgang A. Herrmann Prof. Dr. Peter Härter Thesis Title: Cu(I)-NHC complexes for Hydrosilylation – synthesis and characterisation
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