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Development, Optimization and Application of Catalysts in Cyclic Carbonate Synthesis and Olefin Epoxidation

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Denken ist die schwerste Arbeit, die es gibt.

Das ist wahrscheinlich auch der Grund,

warum sich so wenig Leute damit beschäftigen.

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Deutsches Abstract

Imidazoliumsalze mit nukleophilen Anionen werden in einer Vielzahl verschiedener Reaktionen als Katalysatoren eingesetzt. Das Ziel der vorliegenden Arbeit ist die Untersuchung von Einflüssen auf die Stärke der Ionenpaarung, bzw. auf den Grad der Nukleophilie des Anions, die sich direkt auf die katalytische Aktivität auswirkt. Am Imidazoliumring können organische Substituenten eingeführt werden, die erheblichen Einfluss auf die Verteilung der Ladungsdichte, sowie Sterik und Acidität ausüben, welche allesamt entscheidend für die Wechselwirkung mit dem Anion sind. Ferner beeinflusst die Wahl der Substituenten am Kation den Schmelzpunkt und die Löslichkeit der Verbindungen in organischen Lösungsmitteln, bzw. Wasser.

Der Hauptfokus dieser Arbeit lag auf der katalytischen Umsetzung von Epoxiden und Kohlenstoffdioxid (CO_2) zu zyklischen Carbonaten. Dabei kommen Imidazoliumhalogenide als bifunktionelle Katalysatoren zum Einsatz, die ohne Verlust der Aktivität wiedergewonnen und recycelt werden können. Zudem kann durch Optimierung der Kationenstruktur ihre Aktivität erhöht werden. Im weiteren Verlauf wird der Einfluss des Substitutionsmusters des Imidazoliumringes (sterische und elektronische Einflüsse, Löslichkeit im Epoxid) in Gegenwart einer Lewis Säure untersucht. Alternativ werden Alkohole verwendet, die durch Wasserstoffbrücken die Ringöffnung des Epoxids erleichtern.

Die industriell wichtige Epoxidation von Propen wurde mit homogenen Übergangsmetallkatalysatoren durchgeführt. Zusätzlich wurden supramolekulare Ionenpaare (SIPs), bestehend aus Ammoniumamidkationen und Perrhenat ($[ReO_4]^-$) als Anion, synthetisiert. Hierbei wird $[ReO_4]^-$ durch Wasserstoffbrücken des protonierten Rezeptors eingeschlossen und von der Wasserphase in die organische Phase transferiert. Durch diesen Transfer wird ein aktiver Epoxidationskatalysator erhalten, der in Gegenwart von Wasserstoffperoxid gute Umsätze zeigt und im Gegensatz zu anderen molekularen Katalysatoren vom Produkt leicht abgetrennt und wiederverwendet werden kann.

English Abstract

Imidazolium salts with nucleophilic anions are applied as versatile catalysts in a variety of different reactions. This work mainly focuses on the effects of ion pairing and thus, nucleophilicity of the anion, on the catalytic activity. Introducing organic substituents at the imidazolium ring can have a significant impact on the charge distribution, steric conformation and arrangement as well as acidity of the imidazolium C2 proton. These properties are decisive for the interaction with the anion. Additionally, the substitution pattern of the imidazolium moiety influences the melting point and the solubility in organic solvents or water.

The work's major focus is the catalytic conversion of epoxides and carbon dioxide (CO_2) to cyclic carbonates. In this context, imidazolium halides act as bifunctional organocatalysts, which can be easily recycled without loss of activity. Through optimization of the cation structure, higher activities can be achieved. Furthermore, the impact of different substitution patterns at the imidazolium ring (steric and electronic changes, solubility in the epoxide) on the catalytic activity, in presence of a Lewis acid, was investigated. Alternatively, alcohols are used to facilitate the ring opening of the epoxide through hydrogen bonding.

The epoxidation of propylene with different homogeneous molecular catalysts is performed. Furthermore, supramolecular ion pair (SIP) host-guest assemblies of perrhenate ($[ReO_4]^-$) anions with ammoniumamide receptor cations are reported. Within this compounds $[ReO_4]^-$ is encapsulated by the protonated receptor via N–H and C–H hydrogen bonds and transferred from the aqueous into an organic phase. By this transfer, an active epoxidation catalysts was obtained, which shows good conversion using aqueous hydrogen peroxide as oxidant. In contrast to molecular catalysts, the SIP catalysts can be reused several times with no loss in activity.

List of Abbreviations

APT	azaphosphatrane
BTPPI	butyltriphenylphosphonium iodide
COE	*cis*-cyclooctene oxide
COO	*cis*-cyclooctene
CO_2	carbon dioxide
CTP	cyclotriphosphazane
DBU	1,8-diazabicyclo[5.4.0]unde-7-ene
DMAP	4-*N,N*-dimethylaminopyridine
EC	ethylene carbonate
EO	ethylene oxide
FTIR	fourier transform infrared spectrscopy
HPPO	Hydrogen-peroxide-propylene-oxide
IL	ionic liquid
MTO	Methyltrioxorhenium
NMR	nuclear magnetic resonance
PC	propylene carbonate
PO	propylene oxide
SC	styrene carbonate
SILP	supported ionic liquid phase
SO	styrene oxide
TBAB	tetrabutylammonium bromide
TBAI	tetrabutylammonium iodide
TBD	1,5,7-triazabicyclo[4.4.0]dec-5-ene
TBHP	*tert.*-butylhydroperoxide
TBPB	tetrabutylphosphonium bromide
THAB	tetrahexylammonium bromide
UHP	urea hydrogen peroxide

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1.   Introduction

1.1.   Organocatalytic Conversion of Epoxides and CO$_2$ to Cyclic Carbonates

1.1.1.   Carbon Dioxide – A promising C1 feedstock

Due to the foreseeable shortage of fossil fuels for the synthesis of chemical products,[1] the use of renewable carbon sources as feedstock is a promising alternative.[1b, 2] For instance, the valorization of the greenhouse gas carbon dioxide (CO$_2$), as most abundant renewable carbon source, is of great interest in both industry and academia.[3] Additionally, CO$_2$ is ubiquitous, non-toxic and cheap, thus representing a possible and interesting C1-feedstock for industrial application.[3a] However, the carbon atom is present in its most oxidized form and therefore CO$_2$ is very stable and shows low reactivity.[4] For this reason, a high energy input is needed for the conversion of CO$_2$ to valuable products.[5] This finding results in high costs and emissions of greenhouse gas, which hinder the application of CO$_2$ as C1-feedstock in chemical industry.[6] Thus, the development of high performance catalysts for an efficient and sustainable fixation of CO$_2$ is one of the key technologies.[7] Therefore, the carbon footprint of the reaction can be minimized, leading to the possible usage of CO$_2$ as reactant, while additional emission of the greenhouse gas is simultaneously avoided.[8] In terms of industrial CO$_2$ usage, the synthesis of methanol or the production of polycarbonates through copolymerization of CO$_2$ and epoxides is of great interest.[9] Furthermore, the cycloaddition of epoxides and CO$_2$ to the respective cyclic carbonates (Scheme 1.1) is a promising, environmentally benign reaction due to the reaction being 100 % atom economical.[10]
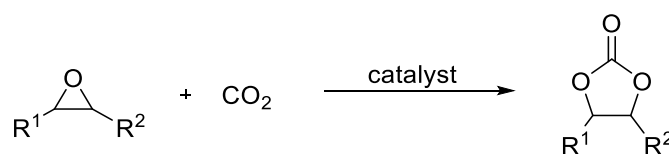
Scheme 1.1 Catalytic conversion of epoxides and CO$_2$ to yield cyclic carbonates.

The resulting cyclic carbonates, mainly ethylene carbonate (EC) and propylene carbonate (PC), are produced in industrial scale.[11] They are used as high boiling polar aprotic solvents, as electrolytes in batteries and as raw material.[12] Nevertheless, high temperatures and pressures are needed to reach satisfactory yields.[10] In order to op-

timize the harsh reaction conditions, which are undesirable from an economic and environmental point-of-view, a plethora of metal catalysts have been developed so far.[13] The use of metal halides like zinc(II)bromide ($ZnBr_2$),[14] niobium(V)chloride (($NbCl_5)_2$)[15] or cobalt(II)chloride ($CoCl_2$)[16] as well as metal oxides,[17] modified silica[18] and zeolites[19] as Lewis acids for epoxide activation are known. In combination with suitable nucleophiles like imidazolium halides, 4-*N,N*-dimethylaminopyridine (DMAP) or tetraalkylammonium halides (e.g. tetrabutylammonium bromide = TBAB or tetrabutylammonium iodide = TBAI) cyclic carbonates can be obtained with good yields under mild conditions (down to room temperature and atmospheric CO_2 pressure).[15b] In addition, a large range of molecular metal complexes is described in literature.[13] Besides Al,[20] Cr[21] and Co[22] porphyrin complexes, mono- and bimetallic Al,[23] Co[24] and Cr[25] salen complexes have emerged as highly active catalytic systems in combination with nucleophilic cocatalysts.[13]

Metal-porphyrin-complexes
M = Al, Cr, Co

Metal-salen-complexes
M = Al, Cr, Co
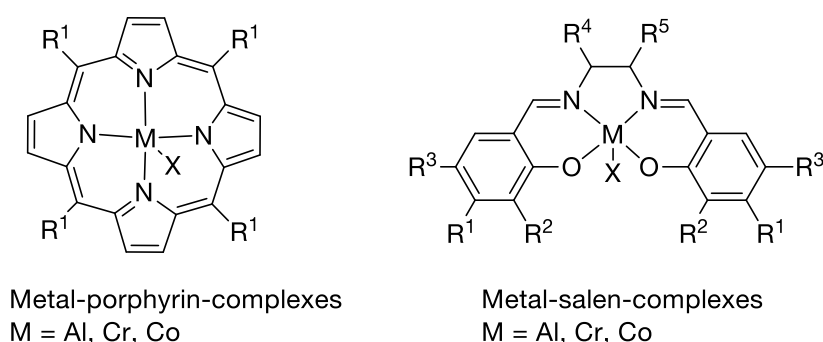
Fig 1.1 Metal-porphyrin and –salen complexes as catalyst for the cycloaddition of epoxides and CO_2.

In contrast to the use of metal containing catalysts, the organocatalytic valorization of CO_2 with epoxides represents a promising alternative. This approach is very attractive and environmental friendly because any metal waste is avoided. In particular, there are two main ways to design metal-free catalysts.[26] For instance, it is possible to use ionic compounds for the catalytic cycloaddition of epoxides and CO_2. In this case very often the cation activates the epoxide or CO_2 or both and the anion acts as nucleophile. In addition, also binary systems are described in literature. As mentioned for the combination of e.g. metal halides with nucleophiles, one molecule activates the epoxide (mainly through hydrogen bonding), whereas another compound is needed for the ring opening of the epoxide. Further, metal-free catalysts in general have the advantage of an air and moisture insensitivity, which enable their use in simple and safe manner.[27] Additionally, the preparation of organocatalysts is easy and economical and therefore

can contribute to improvements in terms of costs and sustainability (energy input, process design).[27-28]

Conclusively, the efficiency of organocatalysts regarding the carbon footprint and sustainability of the cycloaddition reaction of CO_2 with epoxides to cyclic carbonates has to be optimized. So far, the applied reaction conditions are too harsh which is undesirable from an environmental and economic point-of-view. Further reducing the temperature and CO_2 pressure would offer the opportunity to use CO_2 as reactant in industrial application.

1.1.2. Bifunctional Organocatalytic Systems – Important Aspects in Molecular Catalyst Design

Initial work in the field of metal-free synthesis of cyclic carbonates was conducted by Nishikubo et al. in 1993.[29] Afterwards, Calo et al. published the efficient cycloaddition of styrene oxide (SO) and CO_2 to styrene carbonate (SC) catalyzed by a molten mixture of TBAB and TBAI.[30] Further, a possible mechanism for the catalytic formation of cyclic carbonates was postulated (Scheme 1.2). First, the halide anion performs a nucleophilic attack to the epoxide and the ring was opened to form an oxy-anion species. Subsequently, the negatively charged oxygen atom reacts with the electrophilic carbon atom of CO_2. The resulting open chain carbonate undergoes an intramolecular nucleophilic attack ('Back-biting'). After eliminating the catalytically active halide, the cyclic carbonate product is formed. This mechanism was further confirmed by experimental and theoretical studies.[31]
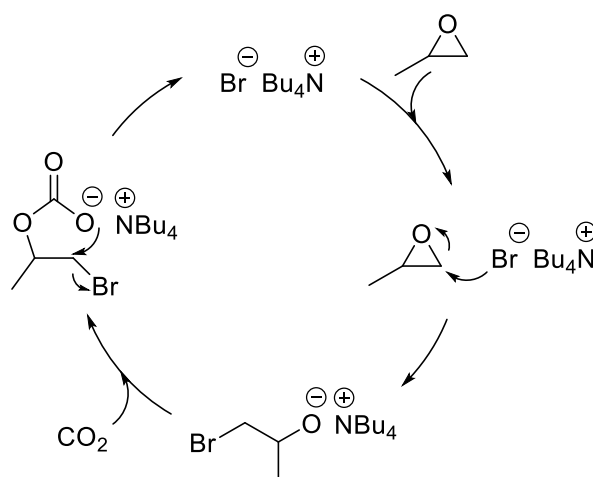
Scheme 1.2 Postulated catalytic cycle for the formation of PC with TBAB as catalyst.[30]

In accordance to the mechanism, the cation has not a direct influence in the performance of the catalyst. The bulky *n*-butyl chains of the ammonium ion lead to weak cation-anion interactions making the halide more nucleophilic compared to methyl groups at the ammonium cation.[32] To continue the improvement of the catalytic performance, functional groups at the cation structure were introduced. The functionality works as activator for the epoxide, for CO_2 or for both. For this reason, hydroxyl functionalized ammonium salts were introduced as catalyst for the cycloaddition of propylene oxide (PO) and CO_2.[33] Through hydrogen bonding of the hydroxyl group to the oxygen of the epoxide, the C-O bond is weakened and therefore the nucleophilic attack of the halide is facilitated. Besides hydroxyethylammonium halides,[33-34] also choline-based[35] and amino acid derived bifunctional catalytic systems[36] can activate the epoxide efficiently. By comparison of ammonium based catalysts, it can be stated that a hydroxyl functionality is crucial for efficient epoxide activation. In addition to that, plenty of ammonium salts were supported on different carrier materials like polystyrene,[29, 35, 37] poly(ethyleneglycols),[38] biopolymers[39] or silica.[32, 40] It was shown that by the choice of the right support, the activity of the catalyst could be further improved compared to their molecular analogous. In case of silica as support, this mainly derives from hydroxyl groups on the surface, thus, activating the epoxide. Furthermore, recyclability of the systems was facilitated through immobilization of the catalysts. Because of the simplicity of the ammonium based systems, the range of possible improvements is limited. For this reason, another structural motif, which can be tailored in an easier way, is necessary for the efficient conversion of epoxides and CO_2.

Through protonation of nitrogen bases like 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) with the corresponding acid, new catalysts were synthesized and applied for cyclic carbonate synthesis. The protonated form of DBU stabilizes the oxy-anion intermediate in a high extent due to a high positive charge density in the delocalized cationic structure. So far, this system represents one of the most efficient organocatalysts for the cycloaddition of epoxides and CO_2.[41] Further experimental and theoretical investigations in this field were carried out with protonated TBD. Tassaing et al. point out the significant decrease in the energy barrier for the ring opening caused by the activation of the epoxide through hydrogen bonding.[42] As an open-chain alternative to known nitrogen bases, amidinium halides were also used as catalysts.[43] In presence of a hexylamine-CO_2 adduct, cyclic carbonates were obtained in quantitative yields under mild conditions. Moreover, the amine is capable

to store and release CO_2 at ambient pressure. Hence, this adduct represents an activated form of CO_2 and opens the possibility to work as reactant for CO_2 valorization. Additionally, catalysts based on protonated amines,[44] pyridine,[45] pyrrolidine[45] and guanidine[46] are efficient cycloaddition catalysts. All of them are based on a relatively high Lewis acidic cation for epoxide activation combined with a halide as nucleophile. Nevertheless, none of them exhibits activities in the range of protonated DBU.[41] In addition, the separation of the catalyst from the product is a high energy process due to the need of distilling the cyclic carbonate. If this challenge can be solved, e.g. by precipitation, the respective nitrogen base derived catalysts will be suitable candidates for sustainable conversion of CO_2 and epoxides.

As an alternative, phosphonium halides were also introduced as catalysts for the cycloaddition of epoxides and CO_2. In spite of the fact that phosphonium salts exhibit nearly the same catalytic activity like ammonium salts, the use as molecular catalyst for cyclic carbonate synthesis is relatively rare. In the first literature known example for this kind of catalysts, only moderate yields could be achieved by the use of tetrabutylphosphonium bromide (TBPB), an analog to TBAB.[29] In 2009 Zhang et al. showed a significant improvement of the catalytic activity of butyltriphenylphosphonium iodide (BTPPI) in the presence of water as solvent.[47] As mentioned, this improvement is explained by the hydrogen bonding capability of water leading to an acceleration of the epoxide ring opening. Interestingly, also alcohols, like *iso*-propanol, can function as both solvent and activator in the presence of a phosphonium salt.[48] Further, triphenylphosphine was derivatized with different functionalities. According to the expected hydrogen bond strength, the carboxyl functionality performs slightly better than their hydroxyl or amine analogues.[49] Very recently, simple hydroxyl functionalized phosphonium salts were introduced as catalysts. They can be used in multigram scale due to the easy separation procedure and the reusability of the catalyst up to five cycles.[50] Besides common phosphonium salts, new structural motifs like cyclotriphosphazane[51] (CTP) and azaphosphatrane[52] (APT) (Fig 1.2) were used in the catalytic synthesis of cyclic carbonates.

Whereas the catalytic activity of CTP derives from multiple ion-pair motifs, the structure of APT opens the possibility for efficient cyclic carbonates synthesis due to activation of the epoxide and CO_2. Through hydrogen bonding of the partially protonated nitrogen atom, the epoxide is activated. During the catalytic cycle it is proposed that a phos-

phoryl carbamate species is formed by insertion of CO_2 into the P-N bond. Neverthe-less, this species can only be stabilized by sterically demanding substituents in the nearer surrounding.[52a] Therefore, the catalytic performance can be optimized by in-troducing new substituents. As a first approach, a molecular cavity around the active site of the APT was created, yielding a supramolecular catalyst.[52b] In this case, the catalyst was more active and stable than previous reported APT compounds. However, still rather high temperature (100 °C) and long reaction time (24 h) are required to efficiently synthesize SC. Due to the many possibilities of further substituting APT, this system has high potential for further optimization to reduce the applied temperature and reaction time. Similar to ammonium halides, a broad range of supported phospho-nium catalysts is known. In addition to silica,[53] also polystyrene,[29, 54] poly(ethylenegly-col),[55] cross-linked polymeric nanoparticles[56] or fluorous polymer[57] can function as carrier material. Through fluorination of the polymer, an increase of the solubility of CO_2 is supposed and the reaction was accelerated. Furthermore, the use of a suitable support facilitates the separation of the catalyst from the reaction mixture. The variety of different support materials opens the possibility for efficient immobilization and therefore a remarkable improvement of molecular catalysts in terms of recycling and sustainability.

Fig 1.2 Novel structural motifs for phosphonium based catalyst.

Bifunctional imidazolium based systems are the best studied organocatalysts for the cycloaddition of epoxides and CO_2, so far. The substitution pattern of the imidazolium moiety can easily modified to tailor the properties towards the actual desired applica-tion (Fig 1.3).

First mentioned in 2002 by Peng and Deng, quantitative conversion of PO and CO_2 to the corresponding PC was obtained with 1-butyl-3-methylimidazolium (BMIm) tetra-fluoroborate (BF_4^-) or a halide as anion.[14c, 58] This investigations were supported by studies of the CO_2 solubility in a variety of imidazolium based systems.[59] It could be shown that the solubility of CO_2 rather depends on the anion than on the cation.[60]

Nevertheless, fluorination of the cation moiety also leads to an increased content of dissolved CO_2 in the ionic liquid (IL).[61] In addition, longer alkyl side chains enhance solubility of CO_2. Based on these results, it can be stated that an increase of dissolved CO_2 in an imidazolium based IL might be achieved by varying both, the cation and the anion. However, the role of the cation is still not fully understand and under current research in academia.[62] Hence, for a rational design of catalysts, the role of the cation in catalysis has to be examined in more detail.
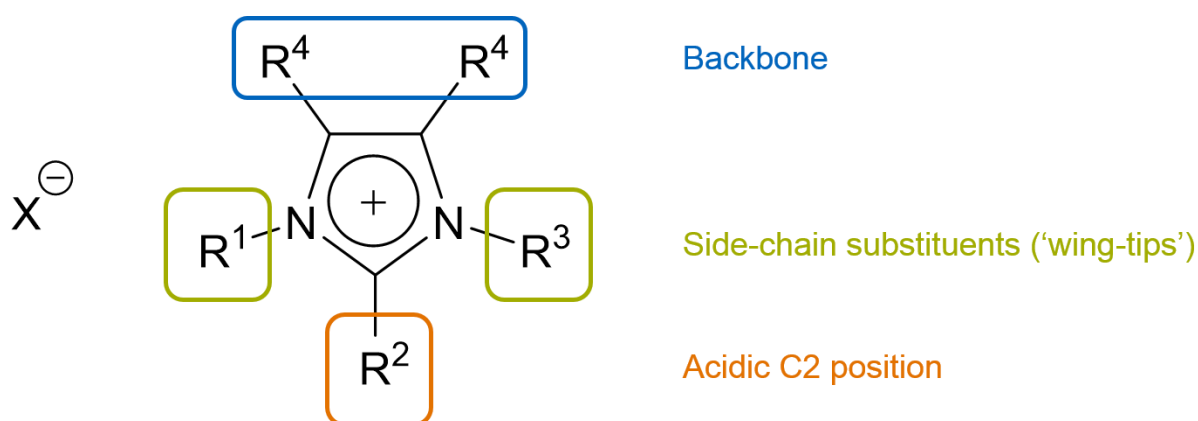
Fig 1.3 Possible optimization sites of the imidazolium moiety for functionalization and tailoring for certain applications (e.g. X = Cl, Br, I, NTf_2, PF_6, NO_3)

In the first instance, the side chains (R^1 and R^3 in Fig 1.3) were functionalized by introducing hydroxyl and carboxyl groups.[33, 63] Hydroxyl functionalized imidazolium catalysts exhibit good activity and selectivity for cyclic carbonate formation. Nevertheless, the separation of the product from the catalyst was only possible by distillation due to the good solubility of the catalyst in PC. Therefore, the separation process is energy-intensive and highly undesirable from an environmental point-of view. The functionalization of the side chain with a carboxyl group, as a supposedly better hydrogen bond donor, results in a higher activity of the applied catalyst.[63a, 64] Interestingly, the Brønsted acidity of the imidazolium moiety has a crucial impact on the catalytic performance.[63d] A series of imidazolium halides was investigated and evaluated in dependence of the activity on the substitution pattern. If the catalyst is too acidic the hydrogen bond between the catalyst and the epoxide will be strong. Thus, the insertion of CO_2 is hindered and a decrease in the catalytic performance is obtained.[63d] For this reason, the acidity of the applied hydrogen bond donor for the activation of the epoxide can be optimized through the choice of the right substituents.

This enables the possibility for further tailoring the structure of the imidazolium catalyst. In particular, the imidazolium moiety has an acidic proton in C2 position (R^2 in Fig 1.3) which is influenced by the electronic and steric properties of R^1, R^3 and R^4. In a series of ten imidazolium bromides the influence of the substitution pattern of R^1, R^2 and R^3 on the catalytic performance was investigated.[65] It was found that by replacing the acidic C2 proton with alkyl groups the activity of the catalysts drops down. Nevertheless, no indications for the formation of a carbene, which is known as active catalysts,[66] was observed under the applied conditions. Thus, it was stated that the C2 proton is crucial for an efficient activation of the epoxide. This was corroborated by FTIR studies which indicate a strong interaction of the whole imidazolium ring with the epoxide. However, the strongest interaction was detected for the C2 proton with the epoxide. As a result, the C-O bond is weakened and the ring-opening of the epoxide is facilitated. By introducing a fluorinated benzyl side chain, the acidity of the C2 proton was further increased. Besides the efficient activation of the epoxide also a good solubility of the catalyst in the epoxide and cyclic carbonate is necessary. For this reason, a long aliphatic alkyl chain was introduced to solve this problem. Through systematic tailoring of the catalyst structure the conversion of epoxides and CO_2 to the corresponding cyclic carbonates was achieved under very mild conditions (70 °C, 4 bar CO_2). Similar studies were carried out by Dupont et al. who evaluated the catalytic performance of 21 different imidazolium based catalysts at low CO_2 pressures (5 – 8 bar) and 150 °C.[67] The obtained results indicate a synergism between basic and acidic sites of the imidazolium ring. Nevertheless, a certain hydrogen bond strength is considered to be crucial for efficient activation of the epoxide. Through the higher reaction temperature the reaction time was also slightly decreased compared to previous study.[65] Hence, it can be argued that the most favorable scenario is higher reaction temperature and thus, shorter reaction time. This has to be evaluated in detail for every catalyst to rate the sustainability of the system. Very recently, a hydroxyl functionalized bisimidazolium bromide was used as catalyst for the cycloaddition of epoxides and CO_2.[68] Through three neighboring hydrogen bond donors, the epoxide is efficiently activated and possible transition states were stabilized. This was confirmed with DFT calculations and is in accordance to previous published results concerning binary catalyst systems.[69]
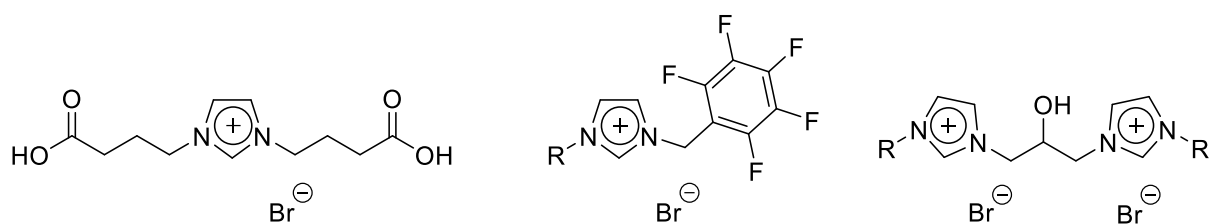
Fig 1.4 Examples of active imidazolium based organocatalysts for the conversion of epoxides and CO_2 to form cyclic carbonates (R = *n*-octyl).

The introduction of a second imidazolium moiety enables further modification possibilities in terms of side chain and backbone substituents, as well as the used bridging reagent. Additionally, the backbone of the imidazolium ring (R^4 in Fig 1.3) was not substituted and its influence on the catalytic performance was not investigated, so far. For this reason, functional groups in the backbone with high hydrogen bonding capability, like hydroxyl groups, can possibly further increase the activity of imidazolium based catalysts. In addition, the use of supported imidazolium catalyst for the cycloaddition of epoxides and CO_2 was investigated in detail by using polymeric materials,[56c, 70] silica[71] or biopolymers.[72] Nevertheless, the applied conditions are very harsh and no environmental and economic advantages compared to molecular imidazolium catalysts were obtained except for the work of Kleij et al.[72d] In this case, a highly active molecular activator for epoxides was supported on polystyrene using "click-chemistry". The obtained catalyst shows high conversion and selectivity under mild conditions. Unfortunately, reactivation with methyl iodide is necessary after at least five runs so that the process cannot be considered as 'green'.

Conclusively, imidazolium halides can be exactly adjusted to the desired application. The acidic C2 proton was shown to be crucial for the activation of the epoxide. Further, through varying the substitution pattern of the imidazolium moiety the nucleophilicity of the halide can be tailored by adapting the cation anion interaction. In addition, the solubility can be tuned by modifying the side chain substituents. In contrast to the organocatalytic conversion of epoxides and CO_2, the requirements of the imidazolium halide change as soon as a strong Lewis acid like $(NbCl_5)_2$ is present.[15b] $(NbCl_5)_2$ activates the epoxides more efficiently than any single imidazolium halide. Therefore, the imidazolium halide only functions as nucleophile in the catalytic cycle. As a result, weak cation anion interactions are desirable for increasing the nucleophilicity of the halide. This can be easily achieved by substituting the proton of R^2 with bulky alkyl groups. Besides a high nucleophilicity, the solubility of the imidazolium halide in the substrate is relevant for an efficient catalytic system. As mentioned previously, with long alkyl

side chains in R^1 and/or R^3, the solubility of the imidazolium halide can be adjusted to the desired substrate. This study demonstrates the diversity of the imidazolium moiety with regard to different applications.

1.1.3. Binary Catalytic Systems – Simple and Sustainable?

In addition to bifunctional catalysts, a wide range of binary catalytic systems is known in literature. Binary systems consist of two single components which show a synergistic effect leading to excellent epoxide conversion and selectivity towards the cyclic carbonate. The single component itself is not catalytically active, but in presence of the synergistic partner molecule, high reaction rates and mild reaction conditions can be achieved.

One molecule activates the epoxide or CO_2 or both, whereas the other molecule is able to act as nucleophile to promote the ring opening of the epoxide. Based on this mode of action, a wide range of tuning possibilities for binary systems is feasible. Nevertheless, the optimization of especially the activator can become very complicated due to the associated synthetic procedure. Therefore, the principles for a sustainable use of binary systems should include easy accessibility of the desired single components, low applied reaction temperature and CO_2 pressure and easy recyclability. It has turned out that in particular the recycling of the single components represents the major problem of these systems. For example amino acids[73], phenol derivatives[11b, 69, 74] or glycerin[75] as activator for epoxides were not recyclable, presumably due to the possible consumption of the catalyst during the reaction. The use of L-tryptophan for the activation of the epoxide is an exception in this row.[76] In combination with potassium iodide as nucleophile, the binary system could be recycled without any loss in activity. Only the applied harsh reaction conditions (120 °C, 20 bar CO_2) hinder this system to be considered sustainable.

Furthermore, readily available bio macromolecules like β-cyclodextrine,[77] cellulose[78] and lignin[79] are used as binary catalytic system in the presence of a nucleophile. Those molecules have hydroxyl groups on the surface which are proposed to activate the epoxide. In contrast to previous mentioned examples, these systems can be easily recycled by precipitation due to the insolubility of the catalysts in organic solvents. Unfortunately, the activity is not comparable to, e.g. a phenol derivative[69] (45 °C, 10 bar), so that, high temperatures and CO_2 pressures are required (≥ 120 °C, 20 bar). Besides

bio macromolecules, the exploration of pentaerythritol (PETT) as epoxide activator and active catalyst in combination with TBAI, is an interesting example for sustainable CO_2 conversion.[80] This system shows excellent yields of PC under very mild reaction conditions. Furthermore, the single components can be recycled by precipitation with diethyl ether. Thus, PETT and TBAI is a non-toxic, cost-efficient and readily available approach for the efficient synthesis of cyclic carbonates with a high level of sustainability. For the use of electrophilic bromine (originated from Br_2 or N-bromosuccinimide) in dimethylformamide (DMF) as solvent, the simultaneous activation of the epoxide and CO_2 is proposed.[81] Further, the catalytic experiments were performed in a continuous flow process. In addition to the cheap catalysts and the relative mild conditions, this system represents a promising and sustainable candidate for future application. Very recently, the screening of a series of different hydrogen bond donors resulted in a new and very active binary system.[82] This consists of a silane-diol hydrogen bond donor for activation of the epoxide and TBAI as nucleophile. The silane-diol holds a special position in the catalytic cycle, since the recognition of both the epoxide and the iodide by the silane-diol were demonstrated through ^{1}H NMR studies. This provides an example for increasing the nucleophilicity of an anion through hydrogen bonding, paired with simultaneous activation of the epoxide. For this reason, quantitative epoxide conversion was observed at room temperature and atmospheric CO_2 pressure. To the best of my knowledge, this is the first organocatalytic binary system which operates at such mild reaction condition. However, a possible way to recycle the system is missing in this study. If this problem can be solved, the silane-diol/TBAI system will be the most promising candidate for future application in terms of the carbon footprint of the reaction and sustainability.
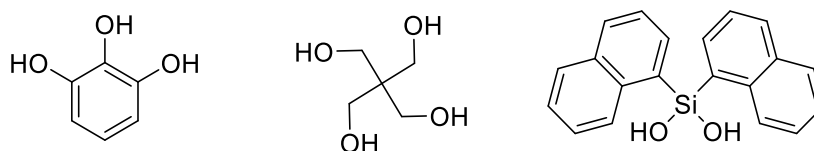
Fig 1.5 Most active hydrogen bond donors used for the binary catalyzed cycloaddition of epoxides and CO_2 in the presence of TBAI.

1.2. Epoxidation of Olefins

1.2.1. Industrial Important Epoxides

The epoxidation of olefins is of high interest in academia as well as in the chemical industry.[83] Epoxides are important intermediates for the synthesis of fine chemicals, such as pharmaceuticals, food additives and flavor/fragrance compounds.[84] Even more important is the use of epoxides as monomers in polymerization processes, like the large scale productions of polyglycols, polyamides and polyurethanes in the chemical industry.[85] The applied catalytic process strongly depends on the structure and the complexity of the desired product. For this reason, the market for different kinds of epoxides ranges from millions of tons per year to a few grams per year.
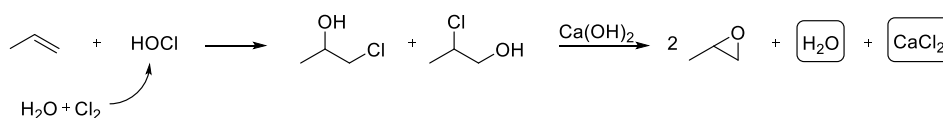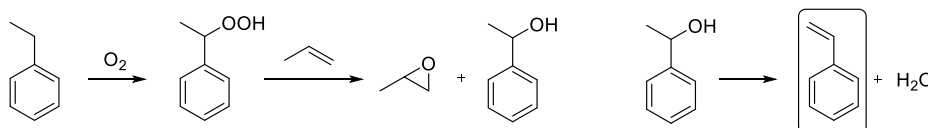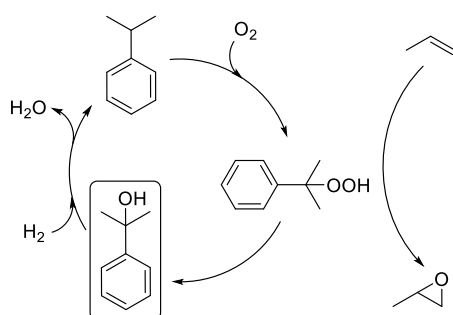
Scheme 1.3 Pathways for PO synthesis using different mediators and the resulting waste per produced ton of PO.[86]

Besides ethylene oxide (EO), propylene oxide (PO) is the most important epoxide for industrially large scale production.[87] In 2013, approximately 8 million tons PO are produced per year with an expected yearly increase of 4 %.[88] Whereas ethylene can be

directly oxidized with molecular oxygen to EO in presence of Ag/Al_2O_3 as catalyst,[89] mediators have to be used for economic PO synthesis in industry. First, chlorine and water (chlorohydrin process), followed by ethylbenzene or isobutane (Halcon/Arco) and cumene (Sumitomo) were applied in industry (Scheme 1.3).[86] These processes deal with a low overall efficiency and also cause a high amount of waste side products. Thus, further research focused on catalysts for either direct propylene epoxidation using oxygen or hydrogen peroxide (H_2O_2) as oxidant, or the development of processes with water as only side product.

As a result, the **H**ydrogen-**P**eroxide-**P**ropylene-**O**xide (HPPO) process was developed by EniChem, Evonik, Dow and BASF, representing the nowadays state-of-the-art.[86, 90] In this process the epoxidation of propylene is carried out in a tubular reactor with a titania-doped zeolite TS-1 catalyst and water is created as the only side-product. Therefore, the environmental benefits versus conventional processes are significant. This mainly results from the nature of the used oxidant. Through in-situ synthesis of H_2O_2 from molecular hydrogen and oxygen at least 0.3 tons of waste water per ton PO was produced which is considerably better than any previously applied process.[86]
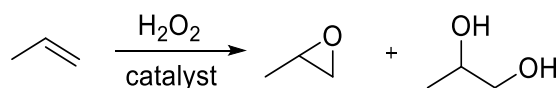

Scheme 1.4 Epoxidation of propylene using H_2O_2 as oxidant.

Besides waste products, the recycling, conversion and selectivity of the process are aspects to be considered for the evaluation of the efficiency. In the presence of water, PO is known to easily undergo ring opening to form the corresponding 1,2-propanediol (Scheme 1.4). Since heterogeneous catalysis is applied for the industrial synthesis of PO, problems of recycling the catalyst do not occur. Nevertheless, through the need of doping the catalyst with titanium and the necessary regeneration, the process is still expensive. However, the conversion of H_2O_2 can exceed 99 % with a selectivity of above 95 %, which is the best result obtained for the synthesis of PO, so far. In addition, a variety of highly active organometallic transition metal catalyst in homogeneous phase have been developed in the past 40 years.[91] However, they were mainly applied for the proof of principle and for general comparison of the activities of the catalytic systems.[92]

1.2.2.   Molecular Molybdenum and Rhenium Epoxidation Catalysts

Only a few reports deal with the epoxidation of propylene with molecular catalysts.[93] Molecular molybdenum catalysts are well known and very efficient in the epoxidation of olefins. Nevertheless, the use of H_2O_2 as oxidant is not possible because of instant decomposition of H_2O_2 and to some extent degradation of the catalyst in presence of water. Therefore, hydroperoxides, like *tert.*-butylhydroperoxide (TBHP), ethylbenzene hydroperoxide or cumene hydroperoxide, were the most efficient oxidizing agents. For this reason, molybdenum catalyst were applied in the Halcon/Arco process for the synthesis of PO.[94] Mo complexes were also shown to catalyze the formation of PO at room temperature with TBHP as oxidant. Unfortunately, the catalytic active species decomposes and no conversion above 35 % was observed. However, the selectivity for PO formation is ≥ 99 % due to absence of any water.[95]

Methyltrioxorhenium (MTO) is one of the best studied molecular catalysts in literature. Firstly discovered in 1979 by oxidation of trimethyldioxorhenium in air,[96] Herrmann et al. developed an efficient synthesis route using tetramethyltin ($Sn(CH_3)_4$) and Re_2O_7 as precursors.[97] To avoid toxic starting materials like $Sn(CH_3)_4$, a cheap, environmental benign high-yield synthetic way for MTO was presented by Herrmann and coworkers.[98] In the first step, e.g. silver perrhenate ($AgReO_4$) reacts with acetyl chloride to the corresponding perrhenyl acetate. This is very advantageous for large-scale synthesis of MTO because there is no need of moisture sensitive Re_2O_7. After methylation with methylzinc acetate, MTO can be obtained in high yields and quantities. To date, MTO is one of the most versatile and widely applicable catalyst in numerous catalytic reactions like olefin metathesis,[99] aldehyde olefination,[100] dehydration of alcohols,[101] deoxydehydration[102] of diols and C-O cleavage in lignin model compounds.[103]

The mechanism of MTO catalyzed epoxidation of olefins is presented in Scheme 1.5. Initially, MTO reacts with one equivalent H_2O_2 to the monoperoxo complex $[(CH_3)Re(\eta^2\text{-}O_2)O_2]$ as active species. Further, the monoperoxo complex is transferred to the bisperoxo complex $[(CH_3)Re(\eta^2\text{-}O_2)_2O] \cdot H_2O$ by another equivalent of H_2O_2. Both species can take part in the catalytic cycle as displayed in Scheme 1.5. Finally, a concerted mechanism is suggested in which the electron rich double bond of the olefin attacks a peroxidic oxygen.[104]
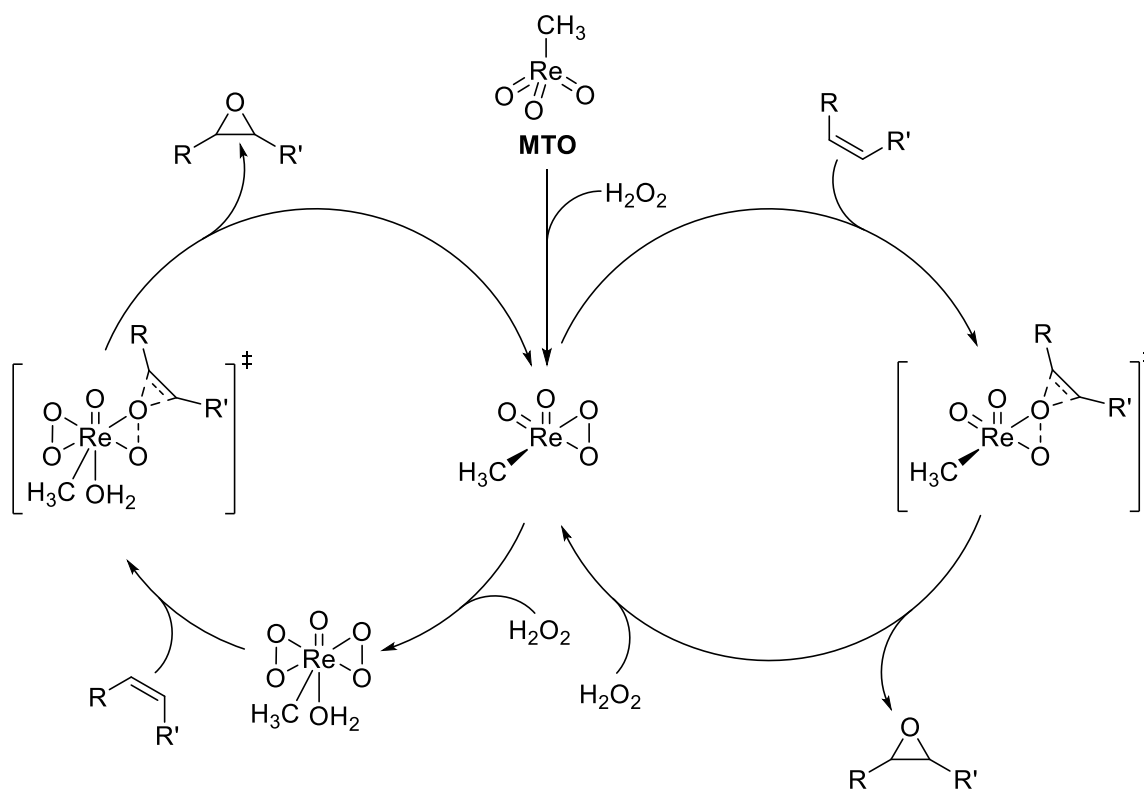
Scheme 1.5 Catalytic cycle for MTO catalyzed epoxidation of olefins with aqueous hydrogen peroxide.

In regard to industrial application, there are only two reports dealing with the epoxidation of propylene with MTO. The first report was published in 1997, showing moderate conversion and poor selectivity for PO formation, suggesting ring opening of PO to the diol by reaction with water (H_2O).[93a] Further research was carried out by Subramaniam and Busch et al. where a two-phase system (liquid/gas), consisting of MTO as catalyst, H_2O_2 as oxidant and methanol as solvent, is presented.[93b] Pyridine-N-oxide was used to stabilize MTO and it is proposed that PO is obtained in 98 % yield at ambient temperature under 20 bar N_2. It is known that the MTO/H_2O_2 catalytic system for epoxidation of olefins tends to cause ring opening of sensitive epoxides, like PO, to the corresponding diols (Scheme 1.4).[105] This is mainly attributed to the Lewis-acidity of the Re center. For suppressing the formation of diols, the addition of a base like pyrazole or pyridine and its derivatives is necessary.[106] Typically, those additives are used in a five- to tenfold excess related to MTO, as the Re-N bond is rather weak. Very recently, Cokoja, Kühn, Fehrmann and coworkers have shown the efficient formation of PO with a MTO/H_2O_2 system in acetonitrile as solvent.[95] Through the addition of a pyridine functionalized imidazolium salt, a conversion of 96 % with a selectivity of at least 90 % was achieved at 40 °C and 3 bar propylene. However, a recycling of the system was not possible. It is proposed that MTO slowly degrades to perrhenate

([ReO$_4$]$^-$) during catalysis. With perspective to industrial application, the loss of expensive rhenium (approx. 3000 $/kg) hinders the use of MTO as catalyst. In addition, the resulting [ReO$_4$]$^-$ was considered to be inactive in epoxidation catalysis. However, it was shown that the chemical environment around the inactive [ReO$_4$]$^-$ can be tuned and therefore, [ReO$_4$]$^-$ itself is capable to promote the epoxidation of olefins.[107] The implementation of [ReO$_4$]$^-$ in an ionic liquid (IL) is a possible route to create a suitable surrounding for the [ReO$_4$]$^-$ anion. There is indeed a literature known example, which deals with a certain activity of perrhenic acid as epoxidation catalyst but the origin of the activity is not fully understood.[108]

1.2.3. Perrhenate – Containing Ionic Liquids

The unique chemical and physical properties, such as low volatility, low flash point, high thermal stability and polarity or low miscibility with organic solvents render ILs as attractive alternative to conventional solvents.[109] Based on works of Rogers,[110] Wasserscheid,[111] Seddon,[112] Welton,[113] Dupont[114] and many others,[115] the application of Ils and SILPs[116] (supported ionic liquid phase) as reaction media for catalytic reactions is of high interest.[117] Industrially, Ils are applied e.g. in the BASF-BASIL process where 1-methylimidazol is used to trap hydrochloric acid to form methylimidazolium chloride (MImCl).[118] After completion of the reaction, the product can be obtained by easy phase separation.

Besides, a variety of different catalytic processes in ILs as reaction media, also epoxidation catalysis, is mentioned in several reports.[119] Originally, ILs were applied to facilitate the product/catalyst separation. However, this purpose could be realized in only a few cases compared to the original process. But there is a positive effect of the IL on the catalytic performance. Through the application of ILs in the epoxidation of olefins, several very active systems were created.[94b, 120] Surprisingly, the previous mentioned inactive [ReO$_4$]$^-$ showed high activity in epoxidation of olefins when applied as anion in an IL.[107] Cyclooctene (COO) was efficiently converted to the corresponding cyclooctene oxide (COE) in excellent yields using H$_2$O$_2$ as oxidant (Scheme 1.6).
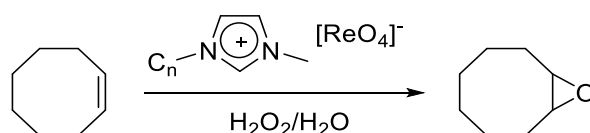
Scheme 1.6 Epoxidation of cyclooctene with [ReO$_4$]$^-$ containing ILs (n = 4, 8, 12) and H$_2$O$_2$ as oxidant.

In comparison to MTO catalyzed epoxidation reactions, the reaction time (4 h) and the applied reaction temperature (70 °C) are significantly higher for [ReO$_4$]$^-$ based ILs. But these ILs can be easily recycled over ten runs without any loss of activity. This is their main advantage over MTO, which is mainly attributed to a thermodynamically stable cation and anion. Interestingly, in presence of other oxidants like urea hydrogen peroxide (UHP) or TBHP, a remarkable decrease of the catalytic activity was observed. Consequently, H$_2$O$_2$ was proposed to play an important role in the catalytic cycle for [ReO$_4$]$^-$ based ILs. Previously, Welton et al. described a strong interaction of ILs with water molecules through hydrogen bonding.[121] For this reason, the formation of an outer-sphere complex between H$_2$O$_2$ and [ReO$_4$]$^-$ via hydrogen bonding is proposed as possible active species.[107] Nevertheless, this contradicts to the transfer of the oxygen to the olefin by (hydro)peroxo ligands.[122]
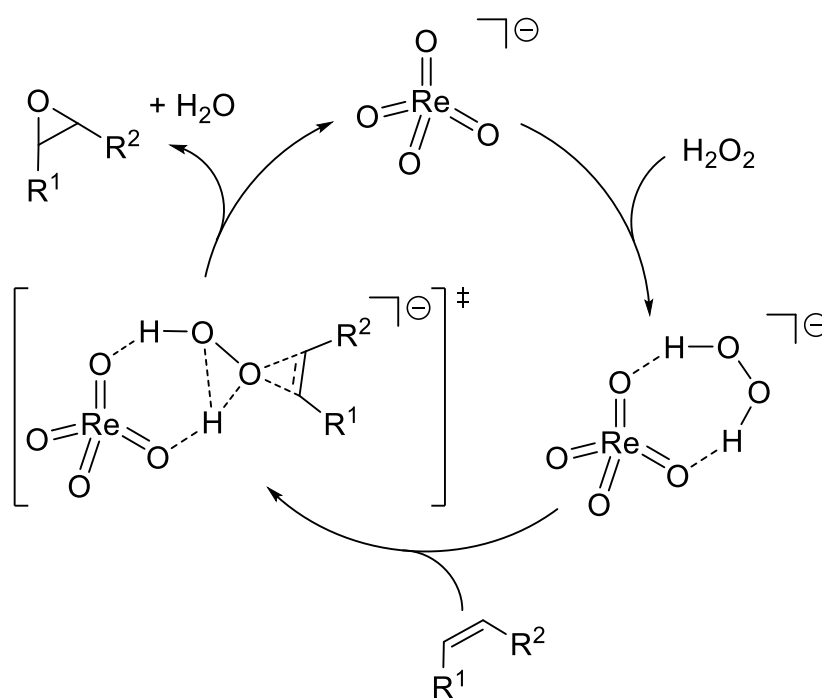
Scheme 1.7 Proposed catalytic cycle for the epoxidation of olefins with [ReO$_4$]$^-$ containing ILs and H$_2$O$_2$ as oxidant.

The catalytic cycle presented in Scheme 1.7 is the most feasible scenario according to DFT studies carried out by Kühn et al.[107] This mechanism was proven by means of IR, RAMAN and NMR spectroscopy. In the first step, an outer-sphere complex with [ReO$_4$]$^-$ was formed through the addition of H$_2$O$_2$. Afterwards, the olefin is introduced and an oxygen atom from the pre-coordinated H$_2$O$_2$ is transferred to the olefin. The desired epoxide was obtained with water as side product during the catalytic cycle. At

the end of the reaction, the product can be easily separated from the IL by extraction with *n*-hexane and thus, the next catalytic can be started. Nevertheless, an equimolar mixture of IL and cyclooctene was applied. For this reason, further optimization of the $[ReO_4]^-$ containing IL has to be carried out. There are several possibilities which can be addressed in order to improve this system. Because the cation obviously influences the activity of $[ReO_4]^-$, the focus will be on the tailoring of the cation comparable to the way mentioned in chapter 1.1.2. Therefore, the introduction of substituents in C2 position of the imidazolium ring reveals a possibility. In this way, the solubility in H_2O_2 or the epoxide can be increased and weaker cation anion interactions, meaning weaker ion pairing, can be achieved. This should facilitate the formation of the outer-sphere complex of H_2O_2 and $[ReO_4]^-$.

1.3. Organic Receptors for Metal Extraction

1.3.1. Amidopyridine and –Ammonium Receptors

Organic receptors can be used for the extraction of metal anions from aqueous phase into an organic environment. For this purpose, supramolecular strategies are often applied in regard to their efficiency and selectivity. As an example, tetrachlorozincate and –cobaltate can be effectively transferred from a hydrochloric acid solution into an organic phase (e.g. toluene). This transfer is highly selective over the extraction of chloride and other metalates (e.g. tetrachloroferrate) using amidopyridine and –amine receptors (Fig 1.6).[123]
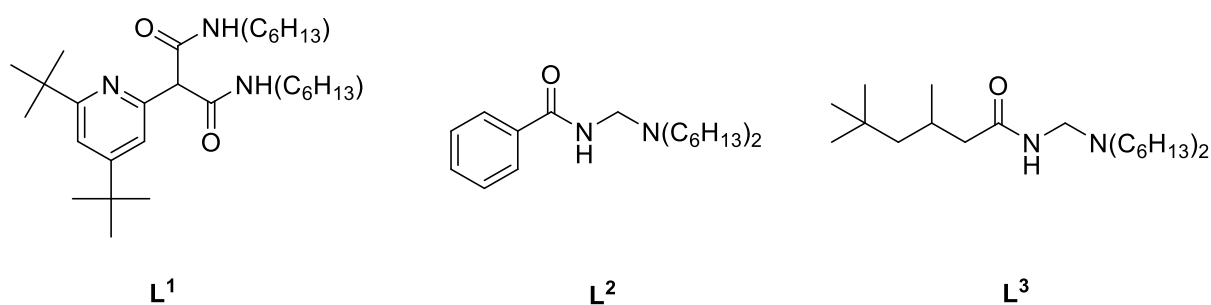
Fig 1.6 Amidopyridine and –amine receptors (**L^1** – **L^3**) used for the extraction of metalates from acidic solution into organic solvents.

The functional principle of all receptors is identical. Through protonation of a nitrogen atom and the hydrophobic environment of the receptors, the toluene soluble complexes [HL^n]$_2$[MCl$_4$] (n = 1 – 3, M = Co, Zn) are formed. Among those examples, complexes of protonated **L^1** are the best studied and understood. [HL^1]$_2$[MCl$_4$] (M = Co, Zn) was examined by single crystal X-ray diffraction, DFT calculations and ^{1}H NMR spectroscopy. It could be shown that the pyridine nitrogen atom is protonated and forms a six-membered "proton-chelate ring" with the carbonyls of both amide functionalities. Furthermore, through the bulky *tert.*-butyl substituents the proton is sterically shielded and the solubility in organic solvents is increased. Therefore, the pyridinium proton is not involved in the coordination of the metalanions. In fact, the coordination originates from an array of 'soft' N-H and C-H hydrogen bonds which pre-organize and recognize the large and charge diffuse metalates. The selectivity for metalates over chloride anions is based on the "hard and soft acids and bases" (HSAB) concept. Chloride is a

very hard anion and the interaction via hydrogen bonding of the soft and charge diffuse metal anions is preferred. So far, the receptors were only applied to extract twice negatively charged metalates. However, based on their structural motif, they might be also considered for the extraction of simple negatively charged metal anions, e.g. $[ReO_4]^-$.

1.3.2. Aqueous Rhenium Extraction and Supramolecular Catalysis

Compounds containing [186]Re, [188]Re or ^{99m}Tc are of great interest for diagnostics in nuclear medicine. Due to the hazards deriving from their long half-life, environmental mobility and the high metal costs, the extraction of those 'soft' Lewis acids from aqueous solutions is burgeoning and highlighted in a review.[124] Therein, different approaches for the successful synthesis of organic perrhenate ($[ReO_4]^-$) and pertechnetate ($[TcO_4]^-$) receptors are summarized and evaluated. Those receptors range from discrete polycationic systems to newer systems based on hydrogen bonding interaction. In conclusion, supramolecular receptors for anion recognition have to be optimized in terms of cavity size, basicity, level of protonation and lipophilicity. So far, $[TcO_4]^-$ was proven to be extracted more effectively than $[ReO_4]^-$.[125] Nevertheless, there is an example where $[ReO_4]^-$ is transferred very efficiently from aqueous phase into an organic solvent through hydrogen bonding. 2,2′-(imino)bis(N,N′-dioctylacetamide) (IDOA) and 2,2'-(methylimino)bis(N,N-dioctylacetamide) (MIDOA) were used to transfer $[ReO_4]^-$ from acidic aqueous solution into a hydrophobic organic solvent.[126] The formation of the H^+MIDOA ion was further supported with EXAFS and IR investigations as well as DFT calculations. It was demonstrated that the interaction between $[ReO_4]^-$ and the H^+MIDOA ion takes place through multiple hydrogen bonds. Although the phase transfer of the anion is scarcely explored, the hydrophobic environment in the organic phase should promote supramolecular interactions between receptor, complex and reagents.[127]

Interestingly, supramolecular concepts become more and more prevalent in catalysis due to secondary interactions, host-guest interactions and encapsulation of catalysts and reagents. In addition, self-assembly processes might be able to overcome major synthetic and technical challenges.[128] Imitating nature in catalysis with molecular model compounds is of current interest in chemical research especially for the activation of nitrogen[129] or methane.[130] Fundamental work in this field was done by van

Leeuwen,[131] Reek,[132] Breit[133] and others.[128, 134] However, the application of supramolecular concepts in transition metal catalyzed reactions is still limited. This finding is an interesting aspect and a good link for the exploration of supramolecular $[ReO_4]^-$ for the epoxidation of olefins based on the results of Kühn et al.[107]

1.3.3. Aspects of Phase-Transfer in Oxidation Catalysis

Due to the superior use of aqueous H_2O_2 as oxidant instead of TBHP (usually in *n*-decane) in epoxidation catalysis, a two-phase catalytic process is usually obtained. In regards of activity, the phase transfer of the oxidant or the catalyst or both is considered to be crucial for an efficient catalytic system.

In 1979, Dehmlow et al. presented the transfer of H_2O_2 into non-polar solvents by simple ammonium halides, thereby leading to a significant increase of its oxidative power. As a possible mechanism for the phase transfer of molecular H_2O_2 into the organic phase, interactions via hydrogen bonding to the halide are proposed (Scheme 1.8). Further screening of the anions showed the best results for tetrahexylammonium bromide (THAB) which was able to transfer 1.0 equiv. H_2O_2 into dichloromethane.[135]

Organic phase

$$[R_4N][X] \text{---} H_2O \quad\longleftarrow\quad [R_4N][X] \text{---} H_2O_2$$

$S_{ox} \quad S_{red}$

$$[R_4N][X] \text{---} H_2O \quad\longrightarrow\quad [R_4N][X] \text{---} H_2O_2$$

$H_2O_2 \quad H_2O$
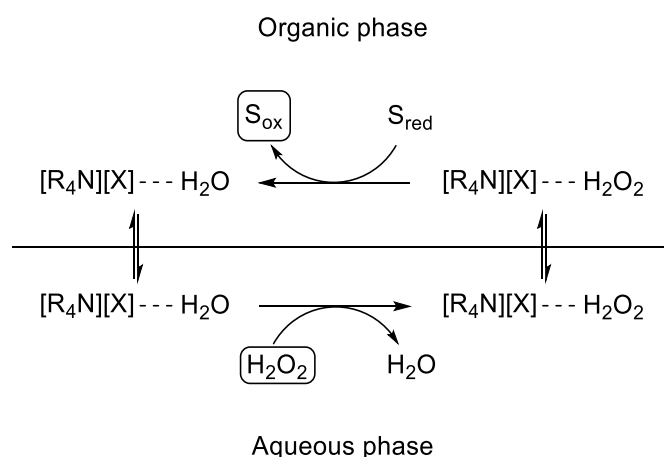
Aqueous phase

Scheme 1.8 Transfer of molecular H_2O_2 from aqueous phase into organic phase with ammonium halides as phase-transfer catalyst.

In contrast, the transfer of the catalyst from the aqueous phase into organic solvents is a possible way to enhance the catalytic performance. Macrocyclic polyethers (crown ethers) were known to encage alkali metals (Li+, Na+, K+) leading to reduced ion pairing of alkali metal salts.[136] This behavior was e.g. successfully applied in the catalytic cycloaddition of CO_2 and epoxides to cyclic carbonates.[137] Additionally, complexation of the metal cation increased the solubility of the respective alkali salts in non-polar

solvents significantly. Thus, higher activities in e.g. nucleophilic substitutions were observed through transfer of anions in non-polar solvents.[138] In general, "hard" anions like F^- or SO_4^{2-} are rather difficult to transfer, whereas "soft" anions (e.g. I^-, SCN^-) can be transferred comparatively easy due to their charge diffuseness. Furthermore, crown ethers were often used in solid-liquid phase-transfer catalysis.[139]

In respect to oxidation chemistry, Simmons et al. reported the transfer of potassium permanganate ($KMnO_4$) into benzene through the addition of catalytically amounts of dicyclohexyl-18-crown-6.[140] The resulting complex was able to oxidize trans-stilbene to benzoic acid in quantitative yields at room temperature. Without the addition of the crown ether, no reaction takes place at all. This indicates the need of the crown ether as phase transfer reagent for $KMnO_4$. Nevertheless, this is the only example for the application of a phase-transfer reagent in oxidation catalysis so far. For this reason, the room of improvement is huge as different anions can be considered for different catalytic transformations. However, a detailed understanding of the respective mechanism of the catalytic processes is necessary for tailoring the phase-transfer reagent. Based on this, crown ethers display a basic model which can be modified according to the desired application.

2. Objective

Given the high potential for sustainable CO_2 fixation as cyclic carbonates, the aim of the thesis was the development of bifunctional organocatalysts and binary systems operating at mild conditions (see Chapter 1.1). Many reports describe the use of imidazolium halides as catalysts in the cycloaddition of epoxides and CO_2. However, harsh reaction conditions are often applied (T > 100 °C, $p(CO_2)$ > 20 bar) and the role of the cation on the catalytic performance is not fully understood. In order to gain a detailed understanding of the role of the imidazolium cation, mechanistic investigations are one objective of this dissertation. Therefore, it is important to systematically vary the cation structure and correlate the structure with the catalytic performance of the respective imidazolium halide. Through optimization of the imidazolium moiety, the decrease of the applied reaction temperature (room temperature) and CO_2 pressure (ambient pressure) was of special interest in this study.
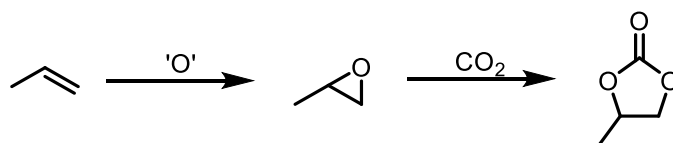
Scheme 2.1 Two-step catalytic synthesis of propylene carbonate through epoxidation of propylene and subsequent cycloaddition of propylene oxide with CO_2.

The second part of the thesis focuses on the epoxidation of industrial important substrates, e.g. propylene (see Chapter 1.2). Thus, a database of molecular transition-metal catalysts can be applied for the epoxidation of propylene. So far, there are only few reports dealing with catalytic formation of PO in homogeneous phase. Therefore, a detailed screening of known epoxidation catalysts is still missing. These investigations should focus on the activity and selectivity of the reaction, as well as, the recycling of the catalyst. Additionally, novel recycling procedures, like the metal extraction from aqueous into an organic phase, are needed (see Chapter 1.3) to achieve an alternative to industrially applied heterogeneous catalysts. The direct syntheses of propylene carbonate in an 'one-pot-reaction' starting from propylene represents the long-term objective of this thesis by combination of all findings.
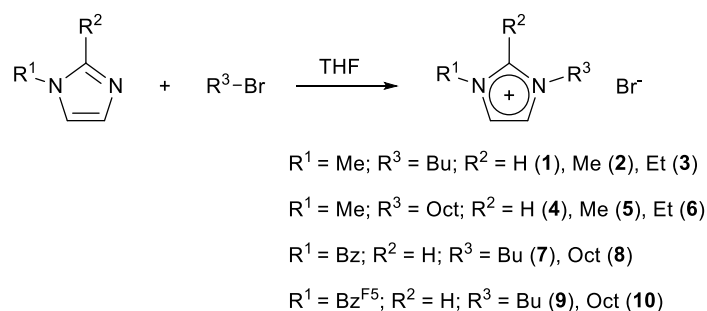
3. Results – Publication Summaries

In this chapter, short summaries of the publications prepared during the course of this dissertation are presented. The full manuscripts can be found in the appendix of this thesis.

3.1. Cycloaddition of CO$_2$ and Epoxides Catalyzed by Imidazolium Bromides under Mild Conditions: Influence of the Cation on Catalyst Activity

A series of imidazolium bromides with varying alkyl group lengths as well as fluorinated substituents were synthesized and characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis (Scheme 3.1). Additionally, the structure of **10** was confirmed by single crystal X-ray crystallography (Fig 3.1). It is notable that all investigated compounds are liquid under applied conditions (70 °C).

R^1 = Me; R^3 = Bu; R^2 = H (**1**), Me (**2**), Et (**3**)

R^1 = Me; R^3 = Oct; R^2 = H (**4**), Me (**5**), Et (**6**)

R^1 = Bz; R^2 = H; R^3 = Bu (**7**), Oct (**8**)

R^1 = Bz^{F5}; R^2 = H; R^3 = Bu (**9**), Oct (**10**)

Scheme 3.1 Synthesis of imidazolium bromides **1 – 10** (Me = methyl; Bu = *n*-butyl; Oct = *n*-octyl; Bz = benzyl; Bz^{F5} = 1-(2,3,4,5,6-pentafluoro)benzyl).

The catalytic activity of the synthesized imidazolium bromides **1 – 10** was tested for the cycloaddition of CO$_2$ and PO to PC under mild reaction conditions (70 °C, 4 bar CO$_2$ pressure, 22 h). Regarding the conversion of PO for **1 – 3**, it was shown that substitution of the C2 proton of the imidazolium moiety reduces the catalytic activity. For this reason, a proton in C2 position is crucial for the efficient activation of the epoxide via hydrogen bonding. Besides, the formation of free carbenes as catalysts can be excluded in agreement with the observed PO conversion for catalysts **1 – 3**. In addition, fluorination of the benzyl side chain enhances the catalytic activity. Through the electron withdrawing effect of the substituent, the proton gets more acidic, so that the activation of PO by hydrogen bonding is more efficient. Based on these findings, **10** was the most active catalyst with PC yields of 91 %. Moreover, the solubility of CO$_2$ in ILs

4, **5**, **6**, **8**, **10** was determined to examine the impact on the catalytic performance. As no significant difference in CO_2 solubility was observed, this can be neglected. For getting a detail insight into the activation of PO through hydrogen bonding of **10**, FTIR studies were carried out. The IR spectrum of **10** exhibits a distinct vibration band for the C2-proton at 3064 cm^{-1} which becomes broader and shifts to 3040 cm^{-1} after addition of an excess of PO at room temperature. This shift was assigned to intermolecular interactions caused by hydrogen bonding. Furthermore, several other imidazolium ring vibrations are shifted which could be responsible for the interaction with PO. This makes it difficult to exactly pinpoint which part or fragment of the imidazolium moiety is relevant for hydrogen bonding to PO. Nevertheless, the main interaction was found to take place between the acidic C2-proton and the oxygen atom of PO, thereby leading to a facilitated ring opening of PO by the bromide. Additionally, **10** was tested under harsher conditions to compare the activity with protonated DBU chloride[41] as state-of-the-art catalyst. As a result comparable catalytic activity of **10** was observed. For this reason, variations of reaction time, temperature and catalyst loading were performed with catalyst **10**. Based on these results, nearly quantitative conversion of PO with a selectivity of ≥ 99 % was obtained with 10 mol % of catalyst **10** at 70 °C and 4 bar CO_2 pressure after 22 h. In addition, the catalytic system could be recycled be simple precipitation and was reused for at least ten times without any loss in activity (Fig 3.1). Further, **10** was shown to be an efficient catalyst for the conversion of a broad scope of epoxides to yield the corresponding cyclic carbonates. Conclusively, **10** demonstrates an efficient and sustainable organocatalytic system for the fixation of CO_2.

a)   b)
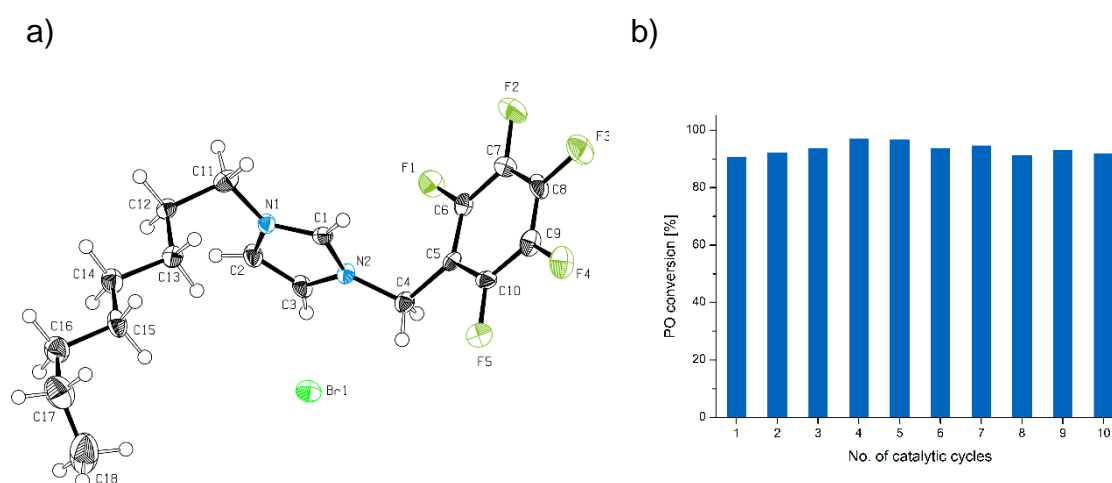
Fig 3.1 a) ORTEP view of the structure of compound **10**; b) Studies on the influence of catalyst recycling on the activity and PO conversion (reaction conditions: 10 mmol PO, 1 mmol **10**, 4 bar CO_2, 70 °C, 22 h. Conversions are based on GC analysis. PC selectivity ≥ 99 %).

3.2. Hydroxy-functionalized Imidazolium Bromides as Catalysts for the Cycloaddition of CO_2 and Epoxides to Cyclic Carbonates

It is reported that acidic C2 protons of the imidazolium ring activate the epoxide via hydrogen bonding (Chapter 1.1).[65] Furthermore, it was shown that three hydroxyl groups in spatial proximity show superior activity compared to one or two.[69, 72d] In general, hydrogen bond donors are proposed to stabilize intermediates and transition states by intra- and intermolecular interactions during the catalytic cycle. For this reason, a series of imidazolium bromides with three (**11 – 13**) and two (**14 – 16**) neighboring hydrogen bond donors were synthesized and fully characterized by means of IR, mass, ^{1}H and ^{13}C NMR spectroscopy as well as by elemental analysis.

11: R^1 = methyl   **14**: R^2 = methyl
12: R^1 = benzyl   **15**: R^2 = n-octyl
13: R^1 = n-octyl

16   **17**
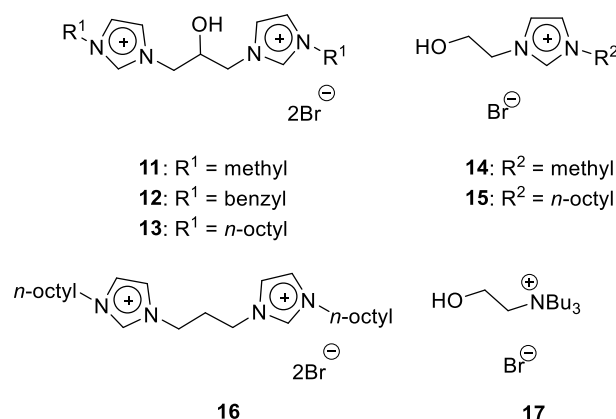
Fig 3.2 Investigated catalysts 11 – 17 for the synthesis of PC from PO and CO_2.

The compounds **11 – 17** were used as catalysts for the cycloaddition of PO and CO_2. **17** was chosen as benchmark to evaluate the activity of the newly introduced catalysts **11 – 16**. For a proper evaluation, previous reported reaction conditions were applied.[80] It was shown that within the order methyl < benzyl < n-octyl (**11 – 13**) the conversion of PO rises which is attributed to a better solubility of **13** in PC. Therefore, 95 % conversion of PO is achieved after 16 h with catalyst **13** leading to a decrease in reaction time compared to catalyst **10**. The high activity of **13** is mainly attributed to the three neighboring hydrogen bond donors, being capable to activate the epoxide and to stabilize intermediates and transition states. By comparing the activity of catalysts **14 – 16**, a maximum conversion of 79 % PO was obtained for **15**. Overall, it can be stated that three neighboring hydrogen bond donors as well as at least one hydroxyl functionality is crucial for an efficient organocatalyst. The catalytic activity of **13** is slightly higher than for **17** (92 %). Furthermore, variations of reaction time, temperature and catalyst

loading were performed applying **13** as catalyst. It was found that a reaction time of 16 h is necessary to quantitatively yield PC. Lowering the temperature leads to a decrease in PO conversion with a minimum reaction temperature of 50 °C. The reduction of the catalyst loading to 1 mol % does not lead to a distinct decrease in activity (60 % PO conversion) compared to previous reported catalysts. Moreover, the recyclability of **13** was investigated as important aspect in terms of sustainability and further large-scale application. **13** can be easily separated from the product with addition of diethyl ether and reused for at least ten runs with constant conversion of PO. Further, no leaching of the catalyst was observed. This is the major advantage of **13** compared to **17**. Additionally, catalyst **13** is applicable to a broad range of different epoxides and converts them to the corresponding cyclic carbonates in very good yields. For getting a detailed insight into the mechanism, DFT calculations were carried out. The results lead to the proposed mechanism shown in Scheme 3.2. Thus, the activation of the epoxide and the stabilization of ring open intermediates could be confirmed.

The hydroxyl-functionalized bisimidazolium bromide **13** is a very efficient catalyst for the conversion of epoxides and CO_2 to cyclic carbonates. Because of mild reaction conditions and easy recyclability, **13** is a promising candidate for sustainable CO_2 fixation and minimizes the gap of activity between bifunctional and binary organocatalytic systems.
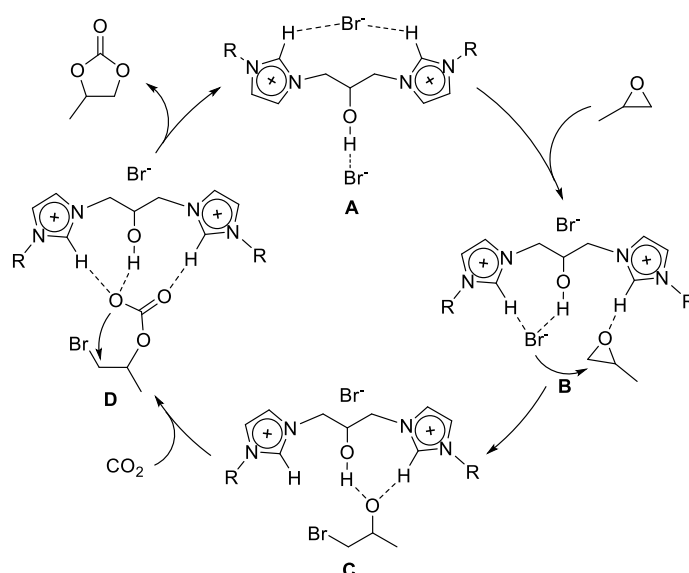
Scheme 3.2 Proposed mechanism for the cycloaddition of CO2 and PO using **13** as catalysts.

3.3. Niobium(V)chloride and Imidazolium Bromides as Efficient Dual Catalyst System for the Cycloaddition of Carbon Dioxide and Propylene Oxide

In this study, the combination of niobium(V)chloride $((NbCl_5)_2)$ and a series of imidazolium bromides as catalytic active system for the cycloaddition of CO_2 and PO to PC is presented. $(NbCl_5)_2$ acts as Lewis acid and activates PO through coordination to the oxygen and thus, weakening the C-O bond of PO. In presence of a nucleophile, e.g. TBAB, this allows the quantitative conversion of PO and CO_2 to PC at room temperature and 4 bar CO_2 pressure in 2 h. As an alternative to common TBAB, imidazolium bromides were investigated as nucleophiles. Particular emphasis was given on the impact of the cation structure on the catalytic activity through comparison of different substitution patterns at the imidazolium moiety. A database of 31 different imidazolium bromides with varying substituents was synthesized and investigated on their catalytic performance. First, imidazolium bromides bearing only aliphatic side chain substituents were applied in the catalytic formation of PC. It was shown that all imidazolium bromides with aliphatic substituents are very active. However, imidazolium cations bearing a proton in C2 position show lower yields compared to their substituted analogous. This was ascribed to the stronger hydrogen bonding of the cation to the bromide and hene varying nucleophilicity of the anion. For instance, the nucleophilicity of the bromide anion increases in the order H < methyl < ethyl for substitution of the C2 position, leading to slightly higher PC yields.

Besides the nucleophilicity of the anion, the solubility of the imidazolium bromide in PO is an additional important aspect. In case of aliphatic substituents the catalysts were readily soluble in PO, leading to an efficient conversion of PO. Additional variation of the ratio $(NbCl_5)_2$/nucleophile showed a superior performance of 0.1 mmol $(NbCl_5)_2$ and 0.2 mmol nucleophile in relation to 10.0 mmol PO. For getting a detailed insight into the kinetics of the reaction, *in situ* IR measurements were carried out and all results were compared to the common $(NbCl_5)_2$/TBAB system. It was shown that the use of imidazolium bromides as nucleophiles leads to higher turnover frequencies in the beginning of the reaction but then the activity decreases rapidly. In contrast, TBAB as nucleophile results in a lower reaction rate but the following decrease is less strong. This is attributed to the change of the chemical environment from slightly polar (PO) to polar (PC) during catalysis.

Furthermore, imidazolium bromides with aliphatic and an aromatic side chains were investigated as nucleophiles for PC synthesis. It is notable that the obtained PC yields are generally lower compared to imidazolium bromides with aliphatic substituents only, which is a result of their poor solubility in PO. Nevertheless, increasing the steric hindrance in C2 position leads to an increase of PC yield due to weaker ion pairing. By fluorination of the aromatic ring, slightly higher solubilities and yields were achieved than for the non-fluorinated analogues. For completion, imidazolium bromides exclusively substituted with aromatic side chains were also applied as nucleophiles in combination with $(NbCl_5)_2$. However, those nucleophiles show poor conversion which can be attributed to a) poor solubility in PO and b) strong ion pairing through π-stacking of the aromatic rings. Previous described trends on the catalytic performance by substituting the C2 position of the imidazolium ring were confirmed. Therefore, it can be stated that substituting the C2 position influences the nucleophilicity of the anion whereas the side-chains mainly influence the solubility of the nucleophile in this system. Likewise in the work of D'Elia and Cokoja et al., the application of $(NbCl_5)_2$/imidazolium bromide as catalysts for the valorization of various epoxides was examined. For efficient conversion 40 °C and 8 h reaction were needed. The conversion of epichlorohydrin displays an exception. This is mainly ascribed to an interaction of the chloro substituent with $(NbCl_5)_2$, thus competing with the epoxide.

Conclusively, this report showed the efficient conversion of PO and CO_2 to PC under very mild conditions (r.t., 4 bar CO_2, 2 h) in a tandem catalytic process. $(NbCl_5)_2$ activates the epoxide effectively whereas the imidazolium bromides act as nucleophile to promote the ring opening of the epoxide. Through a detailed screening of a plethora of imidazolium bromides as nucleophiles, this work helped to understand the role of the cation in the catalytic cycle.
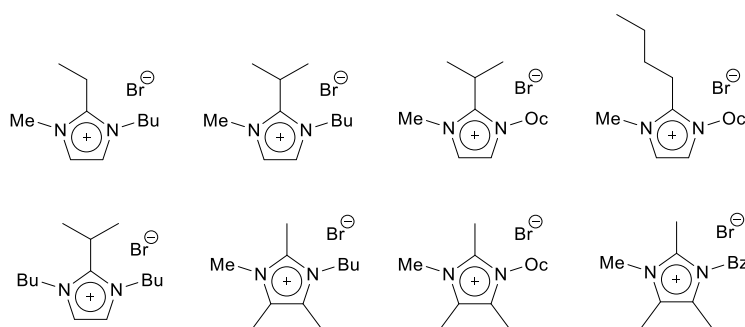
Fig 3.3 Most promising alternative nucleophiles to TBAB in tandem catalysis with $(NbCl_5)_2$ for the cycloaddition of epoxides and CO_2.

3.4. Cycloaddition of Carbon Dioxide and Epoxides Using Pentaerythritol and Halides as Dual Catalyst System

The application of pentaerythritol (PETT) and TBAI as binary catalytic system for the cycloaddition of CO_2 and epoxides is described within this report (Scheme 3.3).
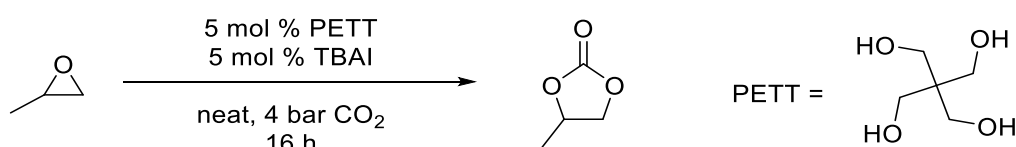

Scheme 3.3 PETT/TBAI catalyzed cycloaddition of PO and CO_2.

It was shown that the activity originates from a synergistic effect between both catalysts. This was manifested as no or very little conversion of PO was obtained when using only PETT or TBAI. Through hydrogen bonding of PETT, the C-O bond is weakened and the nucleophilic attack is facilitated. In addition, possible intermediates and transition states are stabilized by PETT, which decreases relative energies compared to the use of TBAI as single component catalyst. Due to the synergistic effect, the system converts PO to PC under very mild reaction conditions. Previous studies already showed the catalytic activity of PETT and KI under harsh reaction conditions.[141] Applying mild conditions, a PO conversion of only 6 % was achieved, which is mainly attributed to the strong cation anion interactions of KI in comparison to TBAI. In fact, the degree of electrostatic interaction between the ions can be correlated to the nucleophilicity of the anion, e.g. weaker-interactions lead to higher nucleophilicity. The role of the cation was further investigated by the use of imidazolium halides as co-catalysts in presence of PETT. Nevertheless, the best results were obtained with TBAI as nucleophile. Interestingly, the substituition of the proton in C2 position of the imidazolium ring leads to an increase of PO conversion. This observation can be attributed to weaker cation anion interactions of C2 substituted imidazolium halides, due to the prevention of strong hydrogen bonding of the C2 proton to the epoxide/halide. Furthermore, the PC yield of PETT with TBAI or TBAB as binary systems were investigated in dependence of the reaction time. A slightly better catalytic performance for TBAI instead of TBAB was observed. This is explained by a stronger hydrogen bond acceptor capability of bromide in contrast to iodide. Thus, the bromides interacts with PETT to a stronger extent than iodide, thereby hindering the activation of PO through hydrogen bonding. The variation of reaction times and catalyst loadings lead to the optimized

reaction conditions of 70 °C, 4 bar CO_2 pressure with 5 mol % PETT and TBAI. After a reaction time of 16 h, in absence of any solvent, 96 % PC was obtained. This represents a reduction of 6 h reaction time compared to previous reported imidazolium based systems.[65]

For potential industrial application, the recyclability of PETT/TBAI is of particular importance. Previous efficient binary systems, like pyragallol/TBAI, cannot be reused because of consumption or decomposition of the catalyst during the reaction. In case of PETT/TBAI, PC can be easily extracted by addition of diethyl ether, while both catalysts precipitate. No leaching or deactivation of the catalyst was monitored and no decrease in activity was observed over 8 consecutive catalytic cycles (Fig 3.4). Finally, the dual catalyst system was applied for the conversion of a variety of different epoxides. As a result, a broad scope of epoxides was converted to the corresponding cyclic carbonates in very good yields.

In conclusion, PETT/TBAI is a very efficient binary system for the catalytic conversion of epoxides and CO_2. Moreover, the system consists of commercially available, readily available and non-toxic catalysts which can be easily recycled by the addition of diethyl ether. Therefore, PETT/TBAI is a cost-efficient, 'green' and sustainable approach for the fixation of CO_2 in cyclic carbonates.
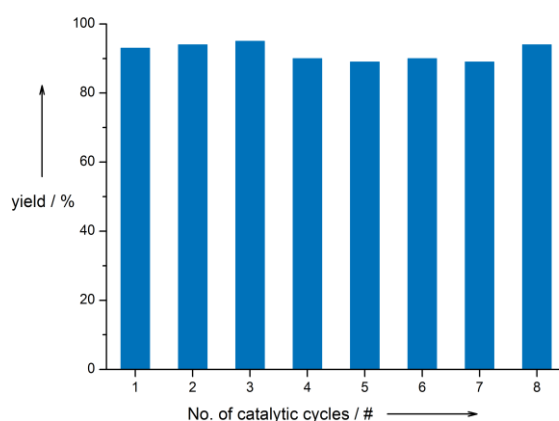
Fig 3.4 Influence of the catalyst recycling on the yield of PC; Reaction conditions: 10.0 mmol PO, 0.5 mmol PETT, 0.5 mmol TBAI, p(CO2) = 4 bar, 70 °C, 16 h.

3.5. Efficient Epoxidation of Propene Using Molecular Catalysts

The epoxidation of propylene to industrially important PO, mediated by molecular homogeneous catalysts, is presented in this report (Fig 3.5).
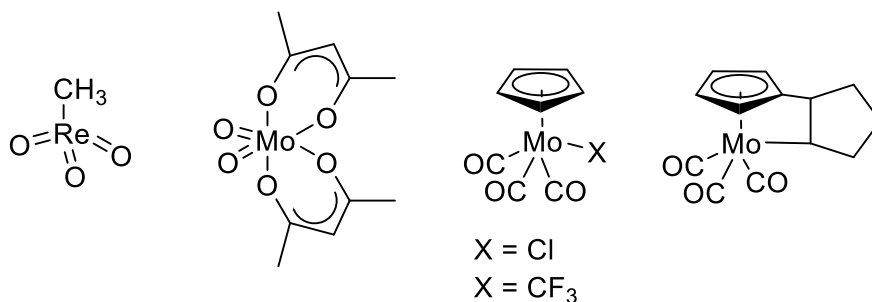
Fig 3.5 Investigated molecular epoxidation catalysts within this study.

Well-known and very efficient Mo catalysts were used with TBHP as oxidant. Depending on the solvent, no yields above 35 % could be achieved and even the addition of an IL was not successful to increase the activity. However, excellent selectivities of ≥ 99 % were obtained due to the absence of any water in the systems. This prevents the formation of the undesired diol. Nevertheless, discoloration of the reaction solution indicates the decomposition of the catalytic active species.

Further, the application of MTO as epoxidation catalyst for PO formation was carried out. Besides the huge versatility of MTO, the use of H_2O_2 as oxidant instead of TBHP is another big advantage of this system. In case of applying H_2O_2 as oxidant, only water is generated from the oxidant during the course of the reaction, whereas the use of TBHP results in *tert.*-butanol. Additionally, TBHP is explosive and expensive. The reaction with MTO and H_2O_2 was carried out in acetonitrile (MeCN) as solvent and functionalized ILs with at least one pyridine substituent as additive. The use of N-donor bases suppresses the formation of diol and allows high selectivity to the epoxide. Moreover, pyridine functionalized imidazolium salts exhibit the possibility to bind the Re species and thus, allow the separation of the catalysts from the product and solvent. This could lead to a proper recycling procedure for the MTO/H_2O_2 system. Under applied reaction conditions (25 °C, MTO:propylene:H_2O_2 1:100:250), the absence of an additive leads to 75 % conversion with a selectivity of 80 %. Additionally, pyridine as N-donor base was investigated to compare the results with pyridine functionalized ILs. Therefore, the conversion drops to 42 % but the selectivity increases significantly to 98 %. At room temperature, no positive influence of pyridine functionalized ILs was

observed, but the increase of the temperature to 40 °C revealed that **A1** is superior to all other additives (Fig 3.6).

a)   b)
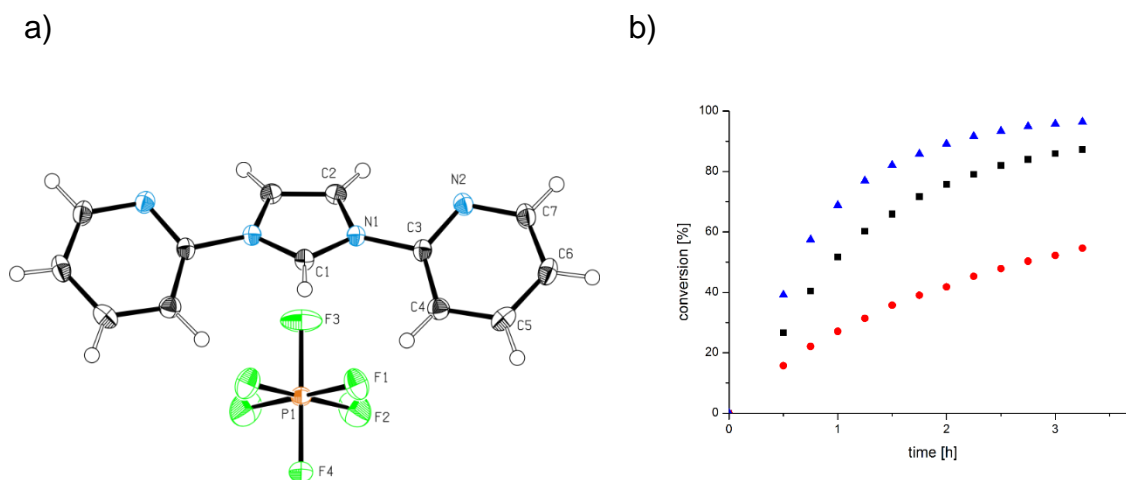
Fig 3.6 a) ORTEP view of compound **A1**; b) Propene conversion using MTO/H_2O_2 with **A1** (blue), no additive (black) and pyridine (red); Reaction conditions: 40 °C, MTO:propylene:H_2O_2 1:100:250, MeCN.

Interestingly, the selectivity for **A1** as additive remains constant at 93 % but the reaction time was shortened to 3 h instead of 18 h at room temperature. When compared to the additive-free reaction (82 %) and pyridine as additive (52 %) significant lower propylene conversion could be obtained. However, the highest selectivities were observed for pyridine as additive, which suggests a very active and selective catalytic system by combining **A1** and pyridine. Instead of an enhanced activity, the solution turned colorless and gas evolution was observed indicating the decomposition of MTO. Furthermore, the recyclability of the system was tested and a loss in conversion and selectivity of about 30 % and 20 % was detected after each run. Therefore, the active species decomposes during catalysis. However, the recycling experiments could only be performed with **A1**. With all other additives no further conversion of propylene was possible.

In conclusion, MTO/H_2O_2 is a very efficient system to epoxidize propylene to PO under mild conditions. All examined Mo catalysts exhibit lower activity. The addition of **A1** leads to nearly quantitative conversion of propylene with a high selectivity (93 %). Further development and optimization of a recycling process would enable the way for industrial application of the system.

3.6. Catalytic Epoxidation by Perrhenate Through the Formation of Organic Phase Supramolecular Ion Pairs

Due to the slow decomposition of MTO to $[ReO_4]^-$ during the catalytic epoxidation of olefins, a possible way to extract $[ReO_4]^-$ from aqueous phase is of high interest to recycle expensive rhenium metal. Literature known organic receptors **L^1** – **L^3** (see Chapter 1.3.1) were applied to extract $[ReO_4]^-$ from an acidic aqueous phase in a model reaction. The receptor was dissolved in toluene and perrhenic acid was added to the solution. After stirring at room temperature for 16 h, toluene soluble $[HL^n][ReO_4]$ (n = 1, 2, 3) were synthesized (Scheme 3.4).
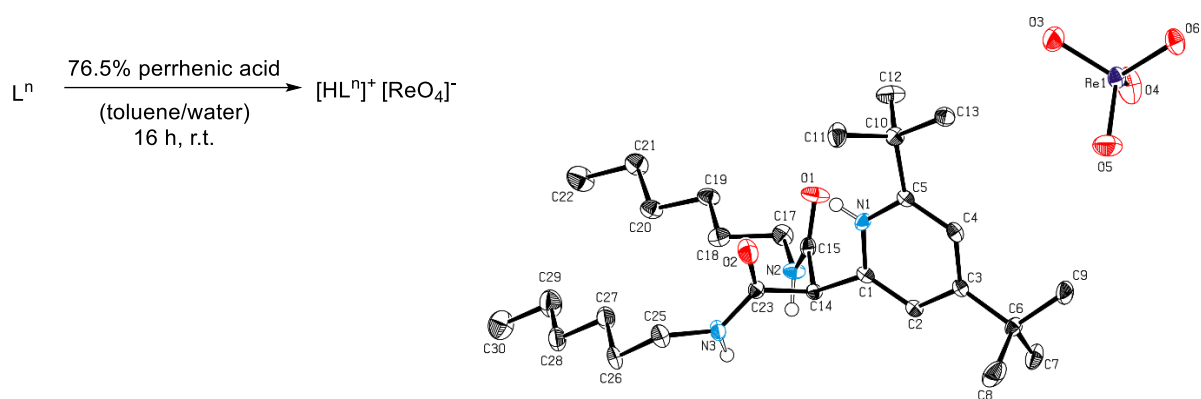
Scheme 3.4 Model reaction for the synthesis of toluene soluble $[HL^n][ReO_4]^-$ (n = 1, 2, 3) and crystal structure of $[HL^1][ReO_4]^-$.

All compounds were analyzed by ^{1}H-, ^{13}C-NMR and IR spectroscopy as well as elemental analysis. In addition, the solid-state structure of $[HL^1][ReO_4]$ was determined by single-crystal X-ray diffraction. It was found that the proton is stabilized through a six-membered 'proton-chelate-ring' according to a previous report.[123a] By expansion of the structure, a dimeric motif was detected where two protonated receptors interact with two $[ReO_4]^-$ anions. Through hydrogen bonding of the protonated receptor to the $[ReO_4]^-$ anion, the optimal tetrahedral structure was distorted. This was corroborated by FTIR studies proposing a C_{2v} symmetry of the $[ReO_4]^-$ anion. For getting a more detailed insight into the solution structure of $[HL^1][ReO_4]$, ESI-MS was carried out. However, no ions, which correlate to the X-ray structure, were detected. However it is assumed that host-guest assemblies are formed in solution. ESI-MS of $[HL^n][ReO_4]$ (n = 2, 3) show facile fragmentation of the methylene bridge of the receptors, resulting in more complex spectra. Also ^{1}H-NMR spectra of $[HL^n][ReO_4]$ (n = 2, 3) indicate fragmentation of the receptors with broad signals which can be assigned to separate amide and ammonium constituents of the receptor. $[HL^1][ReO_4]$ was also analyzed with

DOSY NMR spectroscopy leading to a single species with a hydrodynamic radius of 6.3 Å. This is larger than the free receptor and consistent with a degree of aggregation in solution. Similar results were obtained for $[HL^n][ReO_4]$ (n = 2, 3) with a hydrodynamic radius of 6.6 Å and 6.7 Å, respectively.

Interestingly, the extraction of $[ReO_4]^-$ from aqueous into the organic phase exhibit a change in activity. Through the transfer, $[HL^n][ReO_4]$ (n = 1, 2, 3) can be applied in the catalytic epoxidation of cyclooctene. It has to be stated that $[HL^1][ReO_4]$ is the only SIP being stable under oxidative conditions, whereas $[HL^n][ReO_4]$ (n = 2, 3) show fragmentation of the receptors. Besides its stability, $[HL^1][ReO_4]$ is also the most active catalyst, leading to quantitative conversion of cyclooctene within 6 h using H_2O_2 as oxidant under applied conditions (catalyst:substrate:oxidant 5:100:250; 70 °C). For this reason, all further variations of the reaction parameters were carried out with $[HL^1][ReO_4]$. The influence of the reaction temperature, catalyst loading, substrate to oxidant ratio and solvent was evaluated. Additionally, mechanistic aspects were investigated by ^{17}O-NMR spectroscopy, suggesting a similar mechanism to previous work and DFT calculations (see Chapter 1.2.3).[107] This corroborate an oxygen transfer to the olefin from an outer-sphere activation of H_2O_2 (Scheme 1.7).

Note that the biphasic system also facilitates the catalyst-product separation. After extraction with toluene and subsequent distillation of the solvent and product, $[HL^1][ReO_4]$ was recovered. This procedure allows the reuse of the catalyst, rendering the system suitable and potentially applicable for further large-scale reaction. Finally, $[HL^1][ReO_4]$ could be recycled over 5 consecutive runs without any loss in activity. To demonstrate the efficiency of the catalyst, the epoxidation of other olefins was performed leading to good conversion in nearly every case. It is noteworthy that $[HL^1][ReO_4]$ also catalyzes the formation of PO with comparable activity to the performance of molecular catalysts (see Chapter 1.2.2). Only MTO shows high conversion and selectivity for PO formation but cannot be recycled without loss of catalyst. For this reason combining both principles is an attractive alternative to known established molecular catalysts.

Conclusively, the epoxidation of olefins by $[ReO_4]^-$, which is mainly extracted from aqueous into organic phase, is described. In addition, the concept of transferring catalytically inactive compounds into an organic phase to initiate a catalytic activity is highlighted. The facile back-transfer of the anion through pH regulation should facilitate the separation and recovery process of the catalyst. This opens several possibilities for a simple and sustainable use of rhenium.

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4. Bibliographic Data of Complete Publications

This chapter intended to provide the reader with bibliographic details of the publications summarized in chapter 1 of this dissertation to allow for retrieval of the complete manuscripts and supporting information.

4.1. Cycloaddition of CO₂ and Epoxides Catalyzed by Imidazolium Bromides under Mild Conditions: Influence of the Cation on Catalyst Activity

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4.2. Hydroxy-functionalized Imidazolium Bromides as Catalysts for the Cycloaddition of CO₂ and Epoxides to Cyclic Carbonates

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4.3. Niobium(V)chloride and Imidazolium Bromides as Efficient Dual Catalyst System for the Cycloaddition of Carbon Dioxide and Propylene Oxide

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4.4. Cycloaddition of Carbon Dioxide and Epoxides Using Pentaerythritol and Halides as Dual Catalyst System

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4.5.   Efficient Epoxidation of Propene Using Molecular Catalysts

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4.6.   Catalytic Epoxidation by Perrhenate Through the Formation of Organic Phase Supramolecular Ion Pairs

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5.   Summary and Outlook

In order to improve the sustainable usage of CO_2 as possible C1 feedstock, the cycloaddition of epoxides and CO_2 was investigated in the first part of the thesis. So far, this reaction requires high temperatures and high pressures and therefore, more CO_2 is emitted than consumed. For this reason, new catalysts have to be developed which operate at milder reaction conditions, thus minimizing the carbon footprint of the reaction. In addition, the use of metal free catalysts is desirable in terms of toxicity, reusability and sustainability, although organocatalysts are generally not as active as metal based catalysts. The significant reduction of the activity gap between organocatalysts and transition metal catalysts is a long-term goal and under current research in academia and industry.

It is known that imidazolium halides catalyze the valorization of CO_2 with epoxides to cyclic carbonates. However, the role of the cation was not fully understood. To get a more detailed insight, the first manuscript describes the synthesis and catalytic application of 10 different imidazolium bromides with different substitution patterns at the imidazolium ring.
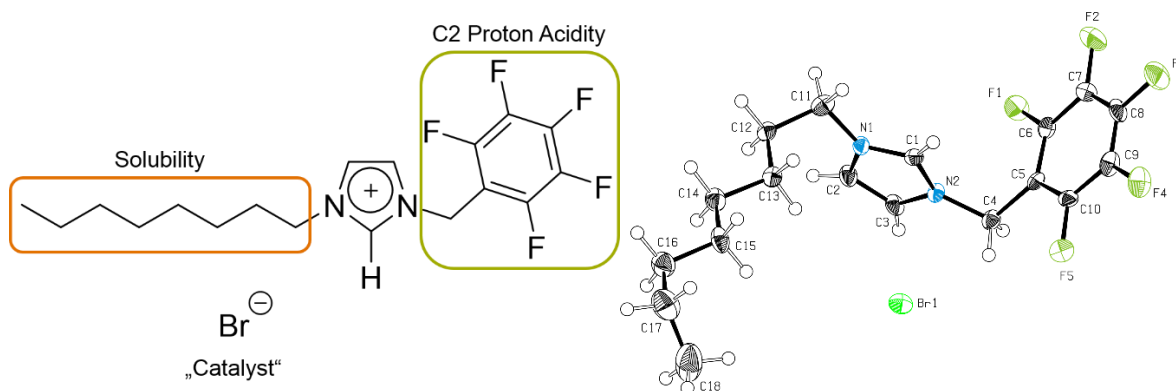
Fig 5.1 Tuning the catalytic performance of imidazolium bromides for the cycloaddition of CO_2 and epoxides by variation of the substitution pattern of the imidazolium moiety.

It was found that an acidic C2 proton at imidazolium moiety is crucial for an efficient organocatalyst for the cycloaddition of epoxides and CO_2. This is mainly ascribed to hydrogen bonding of the C2 proton to the oxygen of the epoxide and thus, facilitating the nucleophilic attack. The conducted FTIR studies supported this finding. Moreover, substitution of the C2 proton with alkyl groups was carried out to investigate a possible formation of a free carbene. This would be able to catalyze the formation of cyclic

carbonates as well. Although reduced carbonate yields are obtained, the catalyst is still active so that a free carbene as catalyst can be excluded. Additionally, through the right choice of side chains substituents, the acidity of the C2 position can be tuned, thereby enhancing the activation of the epoxide through hydrogen bonding. Also the solubility of the imidazolium bromide in the epoxide influences the activity, which can be improved by introducing long alkyl side chains. Tailoring the cation structure leads to 1-(2,3,4,5,6-pentafluorobenzyl)-3-octylimidazolium bromide (**10**) as most active catalyst in this study (Fig 5.1). This ionic liquid catalyzes the transformation of CO_2 to cyclic carbonates under mild reaction conditions (70 °C, 4 bar CO_2 pressure). Due to absence of any metal or solvent and the easy recyclability of the catalyst, this system demonstrates a particularly 'green' approach. Finally, these findings result in an example for useful CO_2 fixation in respect to an energy and CO_2-emmission point-of-view.

Three neighboring hydrogen bond donors:
- Efficient activation of the epoxide
- Stabilization of intermediates and transtition states

High solubility through long alkyl side chains
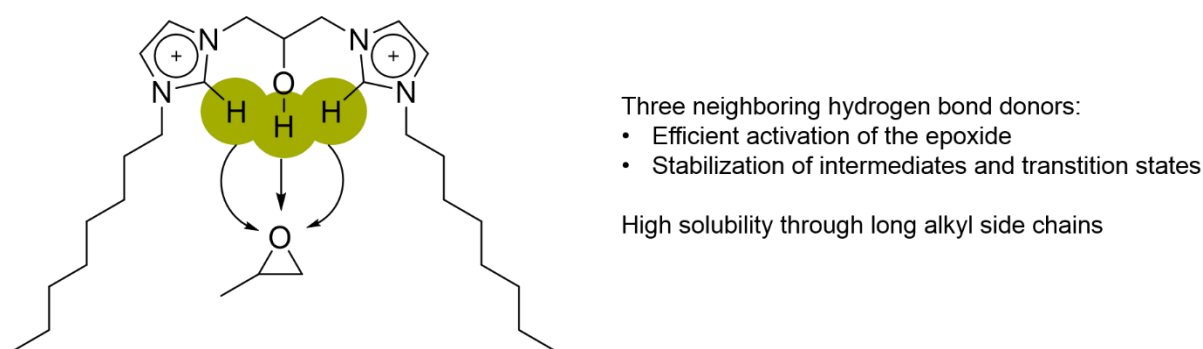
Fig 5.2 Efficient activation of PO using **13** as catalyst for the cycloaddition of PO and CO_2.
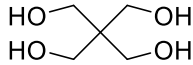
Based on these results and the gained understanding of the role of the cation in the catalytic cycle, new imidazolium based catalysts were developed in the second report of this dissertation. The imidazolium salts were functionalized with a hydroxyl group since those were shown to efficiently activate the epoxide through hydrogen bonding. Enhanced catalytic performance was also observed when three neighboring hydroxyl groups were involved in the formation of cyclic carbonates. Therefore, two imidazolium units were connected with a hydroxyl-functionalized propylene bridge, leading to bisimidazolium bromide catalyst **13**. Through the coexistence of three neighboring hydrogen bond donors, **13** is able to catalyze the cycloaddition of various epoxides and CO_2 under mild conditions. DFT calculations show the importance and synergism of the three neighboring hydrogen bond donors in the activation of the epoxides, which opens new possibilities for the development of more efficient catalysts. Conclusively, **13** is superior to **10** and reduces the gap of activity between bifunctional imidazolium

halide catalysts and binary, phenol-based catalytic systems, which challenge in activity with metal containing catalysts.

The combination of niobium(V)-chloride $(NbCl_5)_2$ for Lewis acidic epoxide activation with DMAP or TBAB as nucleophilic co-catalysts is well established for the coupling of epoxides and CO_2. This tandem catalytic systems enables the reaction to proceed at room temperature and atmospheric CO_2 pressure. By changing the nucleophile from TBAB to imidazolium halides, the activity is proposed to be increased. Therefore, different imidazolium bromides bearing aliphatic, aliphatic/aromatic, and aromatic side chain substituents were synthesized and characterized. They were shown to be active towards the formation of cyclic carbonates in presence of $(NbCl_5)_2$ as activator. However, the solubility and the degree of ion pairing of the respective imidazolium bromide is important for the performance of the catalyst. In absence of a Lewis acid like $(NbCl_5)_2$, the C2 proton of the imidazolium moiety is crucial for epoxide activation and high catalytic activity. As soon as $(NbCl_5)_2$ is present, this changes significantly and C2 substituted imidazolium bromides become superior. Due to their weaker cation anion interactions, the nucleophilicity of the bromide is increased and the formation of cyclic carbonates is accelerated. Imidazolium bromides were shown to be promising alternatives to commercially available TBAB. A major drawback of the tandem catalytic system consisting of $(NbCl_5)_2$ and TBAB or imidazolium bromide is that they cannot be recycled. Further research could focus on possibilities to allow the recyclability of the system by suitable functionalization of the imidazolium ring. For instance, introducing DMAP derivatives at the side chain of the imidazolium ring might allow the reusability of $(NbCl_5)_2$ through coordination. This would lead to a very effective and cost-efficient way for the sustainable valorization of CO_2.

Following the work on binary catalytic systems, pentaerythritol (PETT) was used as metal free alternative to $(NbCl_5)_2$. PETT consists of four neighboring hydroxyl groups which can activate the epoxide efficiently. In combination with TBAI as nucleophile, various cyclic carbonates are obtained in very good yields under mild conditions (70 °C, $p(CO_2) = 4$ bar, 5 mol % catalyst concentration). The binary system PETT/TBAI is cost-efficient (commercially available and non-toxic compounds), metal free, easily recyclable and can be reused for at least eight times without loss of activity. Additionally, no solvent is needed, rendering this system sustainable and economic. Table 5.1 summarizes the most important aspects which have to be considered for comparison of metal-free systems with metal containing catalysts.

Table 5.1 Comparison of $(NbCl_5)_2$ and the metal free alternative PETT for the activation of epoxides.

	$(NbCl_5)_2$	HO⟍⟋OH HO⟍⟋OH
Reaction temperature	25 °C	70 °C
Reaction time	2 h	16 h
CO_2 pressure	4 bar	4 bar
Catalyst concentration[a]	2 mol % (5.40 g)	5 mol % (6.81 g)
Price per catalytic run[b]	13.82 €	7.01 €
Reusability	✘	✓
Air stability	✘	✓
Metal free	✘	✓

[a] Catalyst amount in brackets correlated to 1.0 mol PO; [b] Prices for a 50 g package at Sigma Aldrich (purity of the compound ≥ 99%).

Metal free catalysts, like PETT, operate at higher temperatures and catalyst concentrations and require longer reaction time to obtain quantitative carbonate yields. Nevertheless, in comparison to $(NbCl_5)_2$ the catalyst price per run and the reusability are major advantages of PETT. In addition, PETT is metal free and can be handled under air without decomposition. These criteria illustrate the great potential of PETT for sustainable valorization of CO_2. Future investigations should focus on alternatives to PETT which even allow the conversion of epoxides and CO_2 to cyclic carbonates at room temperature in short time. This research could be facilitated by DFT calculations to screen and evaluate potential candidates before applying them in catalytic reactions. In a side project, well-known molybdenum and rhenium based epoxidation catalysts were examined for the epoxidation of propylene. It was found that molybdenum catalyst show high selectivity towards the epoxide but do not exceed conversions of 35 % due to decomposition of the catalytic active species. Nevertheless, MTO is superior to hitherto known molybdenum catalysts, leading to quantitative conversion of propylene with a selectivity of at least 93 %. This results were obtained at mild conditions (40 °C, 3 bar propylene), in the presence of a pyridyl-functionalized imidazolium salt as additive and H_2O_2 as oxidant. Unfortunately, the system could not be reused without the loss of catalyst and therefore activity. Besides optimization of the additive in terms of recycling, the comparison with other molecular transition metal catalysts should be the focus of future research in this area.

Since MTO slowly decomposes to perrhenate ($[ReO_4]^-$) during the catalytic epoxidation of olefins, new concepts to extract rhenium metal from the aqueous phase are explored. For this purpose the organic receptors L^1 – L^3 (Fig 1.6), which are known to extract metals like cobalt, zinc and iron from acidic aqueous phase, have great potential. The extraction of rhenium from aqueous perrhenic acid into an organic solvent (e.g. toluene) by the respective receptors, was investigated as model system. As a result, toluene soluble perrhenate salts were obtained and characterized with the use of ^1H, ^{13}C-NMR and IR spectroscopy as well as elemental analysis. Through slow evaporation of diethylether/n-hexane (50/50), crystals of $[HL^1][ReO_4]$ were obtained and analyzed by single-crystal X-ray diffraction. The solid-state structure of $[HL^1][ReO_4]$ shows the encapsulation of two $[ReO_4]^-$ anions by two protonated receptors (Fig 5.3).
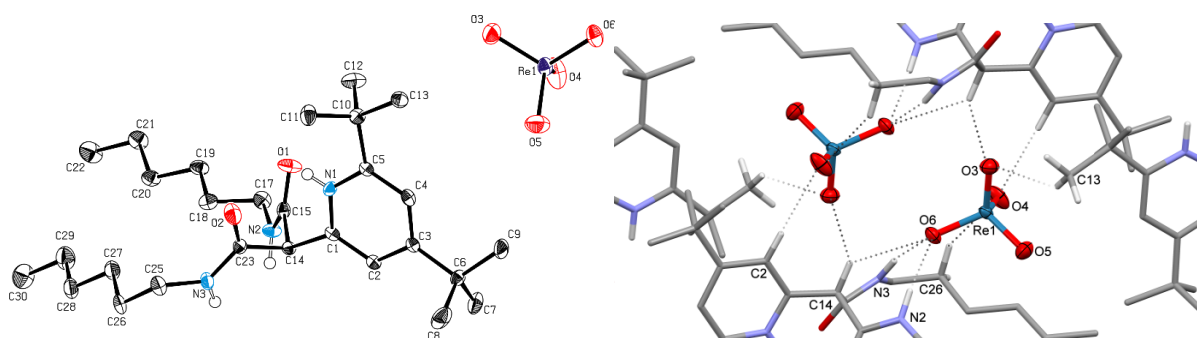
Fig 5.3 The solid-state structure of $[HL^1][ReO_4]$ and visualization of encapsulation of the $[ReO_4]^-$ anion by intermolecular N–H and C–H contacts (displacement ellipsoids drawn at 50% probability).

Moreover, ESI-MS and DOSY-NMR experiments were carried out to analyze the supramolecular structure in solution. These results corroborate the solid-state structure in non-polar solvents, like toluene. Besides structural investigations, the phase transfer of perrhenate into a hydrophobic medium switches on its reactivity towards alkene epoxidation. This is mainly based on an enhancement of supramolecular interactions, resulting in very robust and active catalysts. Furthermore, this is the first report on the epoxidation of alkenes catalyzed by perrhenate in organic solvents. What is even more important is that it describes the concept of transferring compounds, regarded as notoriously inactive in catalysis, into an organic phase to switch on catalytic performance. This finding opens the possibility to various new applications. For instance, notoriously inactive anions, being structurally similar to $[ReO_4]^-$, can be extracted and applied in epoxidation catalysis. As possible candidates nitrate (NO_3^-), acetate (Ac^-), sulphate

(SO_4^{2-}) and phosphate (PO_4^{3-}) are imaginable to activate H_2O_2 via outer-sphere coordination comparable to $[ReO_4]^-$. Initial experiments show activity of those anions for the epoxidation of cis-cyclooctene with H_2O_2 as oxidant in some extent. However, the stability of the catalysts as well as mechanistic aspects have to be investigated in more detail to manifest and understand the obtained results. Besides the 'switch on' of activity by the extraction of $[ReO_4]^-$ from aqueous phase, the back-transfer of the anion through pH regulation should allow for straightforward separation and recovery of the catalyst. Thus, $[HL^1][ReO_4]$ clearly outperforms other immobilized molecular catalysts, thereby offering a simple, sustainable alternative to established molecular catalysts.

Since imidazolium $[ReO_4]^-$ are not applied catalytically, so far, this could also be performed to increase the efficiency and consequently reduce the costs caused by the high amounts of applied rhenium. Taking into account the observations for imidazolium bromides as catalysts for the cycloaddition of epoxides and CO_2, the cation structure is expected to strongly influence the activity. Hence, a detailed investigation by varying the substitution pattern of the imidazolium $[ReO_4]^-$ is of great interest to improve the performance in the epoxidation of olefins. In respect to the increased activity by the extraction of $[ReO_4]^-$ from aqueous phase, the solubilities of imidazolium $[ReO_4]^-$ may play an important role. For this reason, the exact role of the imidazolium cation in catalysis has to be clarified. After solving this problem, the application of metal free imidazolium salts as epoxidation catalysts can be considered in an analogous way like mentioned previously.

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7.   List of Publications and Curriculum Vitae

7.1.   Journal or Book Chapter Contributions

1)   *"Catalytic Epoxidation by Perrhenate Through the Formation of Organic-phase Supra-molecular Ion Pairs"*
Mirza Cokoja, Iulius I. E. Markovits*, **Michael H. Anthofer***, Saner Poplata, Alexander Pöthig, Danny S. Morris, Peter A. Tasker, Wolfgang A. Herrmann, Fritz E. Kühn, Jason B. Love, *Chem. Commun.*, **2015**, *51*, 3399 – 3402.

2)   *"Hydroxy-functionalized Imidazolium Bromides as Catalysts for the Cycloaddition of CO_2 and Epoxides to Cyclic Carbonates"*
Michael H. Anthofer, Michael E. Wilhelm, Mirza Cokoja, Markus Drees, Wolfgang A. Herrmann, Fritz E. Kühn, *ChemCatChem* **2015**, *7*, 94 – 98.

3)   *"Efficient Epoxidation of Propene Using Molecular Catalysts"*
Iulius I. E. Markovits, **Michael H. Anthofer**, Helene Kolding, Mirza Cokoja, Alexander Pöthig, Andreas Raba, Wolfgang A. Herrmann, Rasmus Fehrmann, Fritz E. Kühn, *Catal. Sci. Technol.*, **2014**, *4*, 3845 – 3849.

4)   *"Cycloaddition of Carbon Dioxide and Epoxides Using Pentaerythritol and Halides as Dual Catalyst System"*
Michael E. Wilhelm, **Michael H. Anthofer**, Mirza Cokoja, Iulius I. E. Markovits, Wolfgang A. Herrmann, Fritz E. Kühn, *ChemSusChem* **2014**, *7*, 1357 – 1360.

5)   *"Cycloaddition of CO_2 and Epoxides Catalyzed by Imidazolium Bromides at Mild Conditions: Influence of the Cation on Catalyst Activity"*
Michael H. Anthofer, Michael E. Wilhelm, Mirza Cokoja, Iulius I. E. Markovits, Alexander Pöthig, János Mink, Wolfgang A. Herrmann, Fritz E. Kühn, *Catal. Sci. Technol.* **2014**, *4*, 1749 – 1758.

6)   *"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, Wolfgang A. Herrmann, Mirza Cokoja, Fritz E. Kühn, *Catal. Sci. Technol.* **2014**, *4*, 1638 – 1643.

7)   *"Valorization of Carbon Dioxide to Organic Products with Organocatalysts"*
Michael H. Anthofer, Michael E. Wilhelm, Mirza Cokoja, Fritz E. Kühn, in *Transformation and Utilization of Carbon Dioxide* (Eds.: B.M. Bhanage, M. Arai), Springer Berlin Heidelberg **2014,** 3 – 37.

7.2. Talks and Poster Presentations

10/2014   7th Green Solvents Conference
Dresden, Deutschland
Posterbeitrag *"Hydroxy-Functionalized Imidazolium Bromides for Propylene Carbonate Synthesis"*

08/2014   248th ACS National Meeting & Exposition
San Francisco, United States of America
Vortrag *"Reusability of Molecular Catalysts for the Efficient Epoxidation of Propylene"*

03/2013   46. Jahrestreffen Deutscher Katalytiker
Weimar, Deutschland
Posterbeitrag *"Organocatalytic Conversion of CO_2 with Propylene Oxide Under Mild Reaction Conditions"*

7.3. Curriculum Vitae

Surname	Anthofer
First name	Michael
Nationality	German
Date of birth	10/02/1987
Place of birth	Kösching, Germany
Phone	☎ +49 (0)176 - 56290455
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Education

01/2012 – today Technical University Munich (TUM)
Chair of Inorganic Chemistry/Molecular Catalysis
Catalysis Research Center (CRC)
PhD in Chemistry (Dr. rer. nat.)
Supervisor: Prof. Dr. Dr. h.c. mult. W.A. Herrmann
Dissertation *"Development, Optimization and Application of Catalysts for Cyclic Carbonate Synthesis and Olefin Epoxidation"*
- Synthesis and characterization of novel catalysts
- Evaluation and interpretation of results
- Mechanistic investigations
- Writing of 10 publications/presentations
- Assistant for the course *„Chemisches Praktikum für Geologen und Geowissenschaftler"*

10/2009 – 09/2011 Technical University Munich (TUM)
Master of Science Chemistry
Major subject: Organic chemistry
Minor subject: Construction chemicals
MA-Thesis *"Mechanistic Investigations of Copolymerization of Epoxides and CO_2"*

10/2006 – 09/2009 Technical University Munich (TUM)
Bachelor of Science Chemistry
BA-Thesis: *„Transport of Hydrocarbon Mixtures Followed by Infrared Spectroscopy in Molecular Sieves"*

09/1997 – 06/2006 Christoph-Scheiner-Gymnasium, Ingolstadt, Germany
Abitur

International experience

03/2014 – 04/2014 Singapore Polytechnic, TUM Asia, Singapore
Assistant for the course *"Advanced Inorganic Chemistry and Analytical Chemistry"*

08/2010 – 12/2010 Uppsala University, Sweden
Exchange semester

Work experience

02/2011 – 08/2011	Bayer Technology Services (BTS), Leverkusen, Germany **Internship**

- Polymerization in lab-scale pressure vessels
- Evaluation and interpretation of results
- Mechanistic investigations
- Creation of a structured reaction model
- Clarification of the reaction mechanism

11/2009 – 02/2010	Technical University Munich (TUM) **Research assistant** (part-time) at the WACKER-Chair of Macromolecular Chemistry
04/2009 – 07/2009	Technical University Munich (TUM) **Student employee** (part-time) at the Chair of Organic Chemistry

Skills

Language	German (native), English (business fluent), French (school knowledge), Swedish (basic)
Analytical methods	NMR, IR, FAB-MS, ESI-MS, GC, GPC, MALDI-TOF
Computer	MS Office, Origin, Grams AI, SciFinder, ChemDraw, MestreNova, EndNote, Diamond, Crystal Explorer
Student supervision	One MA-Thesis, one BA-Thesis, 5 research internships
Courses	TUM Graduate School/Carl-von-Linde Akademie *"Führungserfahrung entwickeln und Leitung von Teams"* (2 days) *"Presenting Convincingly and Self-Confidently"* (2 days) *"Erfolgreiche Zusammenarbeit in internationalen Teams"* (2 days) Agilent Technologies *"Einführung in die Flüssigkeitschromatographie"* (2 days)

Interests

Soccer (active member since 1993; Championship A-Klasse Süd)
Tennis (active membership since 2002; Double champion 2013)
Running (10 km in 50 min)
Cooking (Mediterranean)
Round trips (Ireland, USA)