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Adding Value to Double Bonds: Epoxidation Reactions Catalyzed by Iron *N*-Heterocyclic Carbene Complexes

Jens Wilhelm Kück

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“For one voyage to begin, another voyage must come to an end, sort of.”

David Mitchell – The Bone Clocks

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Zusammenfassung

In dieser Arbeit wurden die Synthese, Eigenschaften und Reaktivität in der Epoxidierungskatalyse von Eisenkomplexen, die von mehrzähligen N-heterozyklischen Carbenliganden komplexiert werden, untersucht. Die verwendeten Katalysatoren ähneln bereits bekannten polydentaten N-Donorligandsystemen, wie substituierten Pyridinen und Piperidinen. Wie bei allen Eisensystemen gibt es große Übereinstimmungen in der Struktur und Reaktivität der Verbindungen mit aktiven Zentren in Enzymen wie den Cytochromen P450 oder der löslichen Methanmonooxygenase (sMMO).

Ein Eisen(bis-carben-bis-pyridin)komplex (FeNCCN) wurde dazu als homogener Epoxidierungskatalysator untersucht. Die Bedingungen für optimale Umsätze sind dann erreicht, wenn sowohl eine hohe Stabilität der Komplexe als auch eine hohe Aktivität erreicht ist. Die besten Umsatzfrequenzen dieses Systems sind vergleichbar mit den besten Aminopyridin-ligierten Eisenkatalysatoren. Durch eine Änderung des Ligandensystems hin zu einem Tetracaben kann die Aktivität noch bedeutend gesteigert werden. Mit diesem Liganden wurden zwei strukturell vergleichbare Eisen(II)- und Eisen(III)katalysatoren untersucht. Ihre Umsatzfrequenzen sind deutlich höher als die des FeNCCN-Systems und überragen sogar jene der besten homogenen Katalysatoren, die bisher bekannt sind. Ebenfalls ist es möglich, mechanistische Aussagen zu treffen. Die Kinetikdaten deuten darauf hin, dass eine Ein-Elektronenoxidation hin zum Eisen(III)komplex stattfindet bevor die Epoxidierungskatalyse beginnt.

Der Eisen-NCCN Komplex wurde bezüglich Austauschreaktionen der axialen Liganden untersucht. Die resultierenden Komplexe wurden cyclovoltammetrisch vermessen und die Ergebnisse mit DFT Ergebnissen verglichen. Es wurde eine starke Übereinstimmung der Werte festgestellt, die eine Vorhersage der Oxidationspotentiale der mono- und di-substituierten Komplexe ermöglicht.

Zur genaueren Untersuchung der Stabilität und Reaktivität des Eisen-NCCN-Komplexes unter oxidativen Bedingungen wurde dieser mit einem Ein-Elektronen-Oxidationsmittel umgesetzt. Interessanterweise konnte der Eisen(III)komplex nicht isoliert werden, sondern lediglich ein organisches Bisimidazoliumsalz. Diese Bisimidazoliumsalze konnten hinsichtlich ihrer Reaktivität und strukturellen Eigenschaften untersucht werden. Insbesondere ihr Reduktionsverhalten und die Synthese von NHC-Komplexen ausgehend von diesen Salzen zeigen das Potenzial dieser neuen Stoffklasse.

Abstract

The synthesis, properties, and catalytic reactivity in epoxidation of alkenes of iron complexes bearing multidentate N-heterocyclic carbenes is investigated. Similar systems based on N-donor ligands such as pyridines and piperidines are analogs of enzymes found in nature and have proven to be interesting compounds in oxidation catalysis.

In depth investigations of the catalytic properties of an iron(II) bis-carbene bis-pyridine complex (FeNCCN) give insight into favorable conditions for epoxidation catalysis. A delicate balance of conditions favoring high activity or high stability has to be maintained for optimal epoxide yield. The turnover frequencies obtained are comparable to the best amino-pyridine iron(II) complexes. A second class of iron NHCs is even more promising. A set of corresponding iron(II) and iron(III) tetra-NHC complexes are investigated as epoxidation catalysts. Their activity is significantly higher than all previously known iron catalysts and they even outperform the most active known homogeneous epoxidation catalysts to date. Mechanistic insight is given by the kinetic reaction behavior, showing that a peroxidation step takes place before epoxidation occurs.

The iron NCCN complex is further investigated to elucidate ligand exchange behavior in axial positions. Of the synthesized complexes cyclic voltametric (CV) data is obtained and compared to theoretical predictions via density functional theory (DFT). Overall for mono- and di-substituted complexes theoretical predictions of oxidation potentials is feasible.

In order to assess stability and reactivity under oxidizing conditions the iron NCCN complex is subjected to one-electron oxidation. A defined organic decomposition product is identified and its structure and reactivity investigated. The resulting organic decomposition product, a 2,2'-biimidazolium salt, can be used in the synthesis of other complexes or studied in its reduction behavior.

List of Abbreviations

bpmen	N,N'-dimethyl-N,N'-bis-(pyridin-2-ylmethyl)-1,2-diaminoethane
bpmpn	N,N'-bis(2-pyridylmethyl)-1,3-diaminopropane
BTSA	bis(trimethylsilyl)amide
cod	1,5-cyclooctadiene
CV	cyclic voltammetry
cyclam	1,4,8,11-tetraazacyclotetradecane
CYP	cytochrome P450 oxidases
DFT	density functional theory
DMAP	4-dimethylaminopyridine
equiv.	equivalents
Fc	ferrocene
Fc ⁺	ferrocenium
FCC	fluid catalytic cracking
GC	gas chromatography
HFIP	hexafluoroisopropanol
HOMO	highest occupied molecular orbital
mCPBA	meta-chloroperbenzoic acid
Me ⁱ nico	methyl isonicotinate
MMO	methane monooxygenase
MO	molecular orbital
MTO	methylrhenium trioxide
NCCN	bis(o-imidazol-2-ylidene)pyridine-methane
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance
OTf	triflate
pMMO	particulate methane monooxygenase
py	pyridine
pyBP	N,N'-bis-2-pyridylmethyl-bispiperidine
sMMO	soluble methane monooxygenase

TBHP	tert-butyl hydroperoxide
Th ^{•+}	thianthrene radical cation
TOF	turnover frequency
TUM	Technische Universität München
XRD	X-ray diffraction

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1 INTRODUCTION

1.1 Fossil Carbon Feedstocks in the Chemical Industry

The rise of the chemical industry was only made possible by the availability of cheap, exploitable, and reliable carbon feedstocks.^[1] By and large, the highest margin for value addition of chemical products is a direct result of manipulations of carbon bonds and the construction of complex organic molecules.^[1] To this end, tar residues of coal-gas production were initially used as an abundant and versatile carbon source, supplying aromatics for the use in dyes and other organic chemicals.^[2] In the mid-nineteenth century this key resource was the basis for what would become modern organic chemistry.^[3] The dependence of the fast growing chemical industry on coal was so pronounced that IG Farben in Germany, DSM in the Netherlands and other major chemical companies owned coal mines well into the second half of the 20th century in order to obtain a steady and reliable supply of aromatics and other carbon based molecules. However, many downsides to this resource began to emerge rendering the coal paradigm in organic chemistry less favorable. Among these are the disposal of toxic wastes such as heavy metals, heavy emissions of nitrous and sulfuric gases, unsafe working conditions, a larger demand for high automatization and low overall yield.

Nearly a century after the inception of industrial organic chemistry, a shift in chemical carbon resources took hold. Contemporaneously to the development of individual mobility through the automobile, the chemical industry took advantage of the emergence of oil refinement, making use of liquid mineral oil fractions for their endeavors. In turn the catalytic cracking of refinement products of mineral oil fractions such as naphtha became the basis for the large majority of organic chemicals produced in Europe. Key technologies in the chemical utilization of petroleum are the catalytic cracker as well the steam cracker with subsequent product separation by distillation.

Fluid catalytic cracking (FCC) is implemented in order to facilitate the utilization of longer chain mineral oil fractions.^[1] High boiling fractions of mineral oil distillation are split in the presence of a powdered catalyst comprised of amorphous or crystallized alumino-silicates (zeolites). The product stream contains only a small fraction of unsaturated hydrocarbons usable for further functionalization. However, the lighter saturated hydrocarbons are usable either as gasoline fuel or as a feedstock for steam cracking, thus indirectly providing a valuable fuel for the chemical industry.

Naphtha and lower boiling alkanes are subjected to steam or thermal cracking. In this process steam, high pressures, and heat are applied to alkanes leading to bond breaking and dehydrogenation. The product distribution highly depends on the severity of conditions applied, favoring shorter length products at highly severe conditions.^[1] These severe conditions cause carbon hydrogen bond hemolysis which in turn start radical elimination reactions. Due to the radical mechanism of this

process the major products are light alkenes such as ethylene and propylene, as well C4 olefins. These products are immensely important for the synthesis of a wide array of petrochemicals, aromatics, and polymers.

These technologies enable the conversion of most hydrocarbons comprising at least one C2 unit. However, one of the largest resources of hydrocarbons, natural gas, cannot be utilized in this way. It rather has to be converted to synthesis gas, a mixture of carbon monoxide and hydrogen, through partial oxidation and can then be converted to higher alkanes and alkenes through the Fischer-Tropsch-process. Some of the products yielded in this way are in turn used as raw materials for in cracking processes, showing the large disadvantage and energetic folly of this chemical detour. A direct conversion of methane to methanol or ethylene, would be of great economic impact and could transform the chemical valorization chain altogether, considering the vast natural gas resources that are currently mainly used energetically. Synthesis gas, still is a valuable resource for the production of waxes (Fischer-Tropsch), methanol and acetic acid (Monsanto process) and aldehydes through addition of a C1 unit (oxo synthesis). As a basis for the majority of base chemicals synthesis gas or methane are not yet feasible alternatives to petroleum or heavier gas fractions (Figure 1).

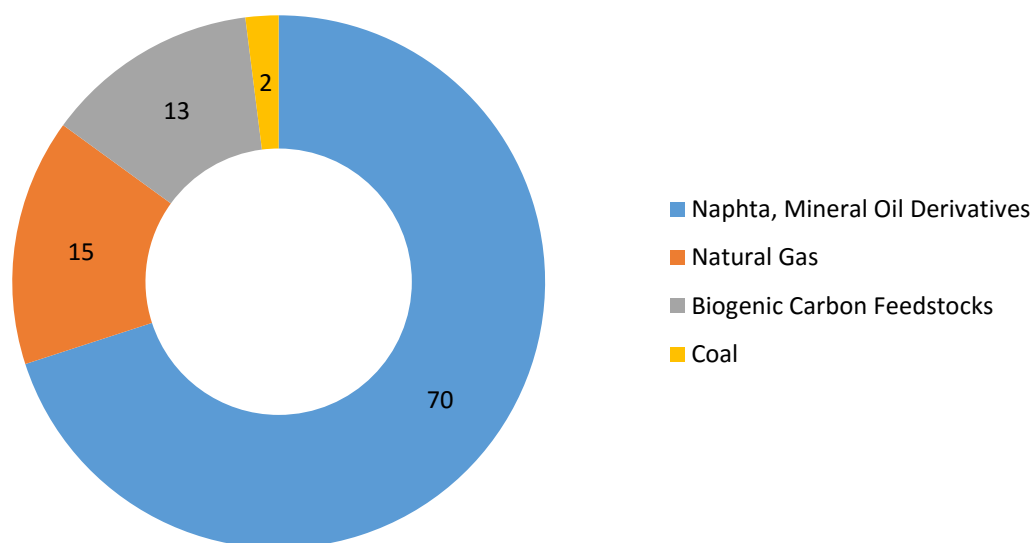


Figure 1: Percentage of carbon feedstocks of the chemical industry in Germany 2011.^[4]

Alternatives for the current systems of mineral oil based carbon feedstocks are strongly sought after. The reason for this is rooted in the finite nature of oil resources. In the last two decades the average oil price has increased steadily with a strong downturn only in the recent two years. This development is caused by an influx of mineral oil from non-conventional sources such as tar sands and shale oils.

These resources are highly controversial due to their significant impact on the environment, destroying important natural habitats, and having negative impacts on ground water purity. However, the fact remains that of all fossil resources, oil is the scarcest and by far most expensive. Moreover, even optimistic forecasts predict a depletion of oil resources within this century. Considering that of all the oil products produced in western Europe in 2010 only 8% were consumed by the chemical industry, a reduction in the energetic use of oil seems to provide part of the answer to this pressing issue (Figure 2).^[5] However, other more sustainable carbon feedstocks for the chemical industry can provide a more sustainable alternative altogether. While carbon dioxide recycling seems like an attractive alternative, the energetic demand is so high that it is not economical or sustainable yet with the current energy production system. The most promising alternative in the short term is the use of biogenic molecules such as lignin, cellulose, sugars, fatty acids and waxes. This growing carbon feedstock contributed to 13% of organic chemicals produced in Germany in 2013 and is expected to be even more important in the future.^[4]

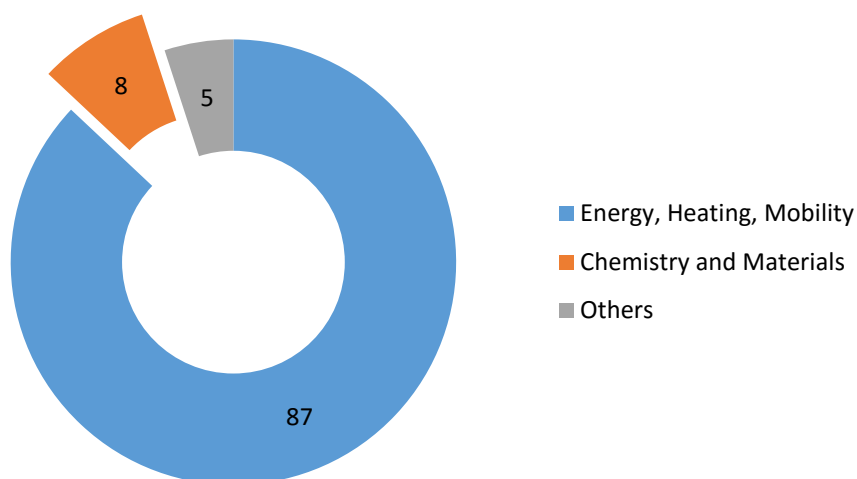


Figure 2: Percent usage of mineral oil in different economic sectors in Western Europe 2010.^[5]

One fact remains true throughout the history of industrial organic chemistry: As in the past century, the efficient, economical, and sustainable use of carbon feedstocks is the absolute basis for the chemical industry as we know it and the economic health of our globalized societies.

1.2 The C=C Double Bond: Important Synthons and Versatile Motif

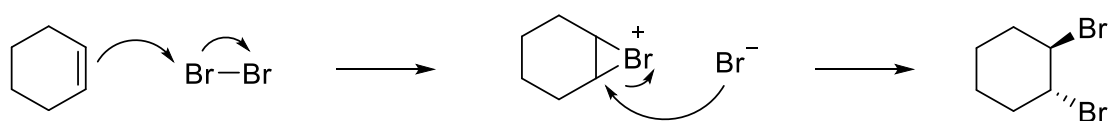
The use of every synthon in industrial organic chemistry is highly dependent on the resource availability as well as chemical reactivity. In coal-based chemistry up to the 1950s most reactions were based on aromatic systems as well as alkynes.^[1] This was a direct consequence of the binding motifs of carbon atoms in coal and the possibility to form inorganic reaction products. An important step in the chemical valorization of coal was the synthesis of calcium carbide used as a resource for acetylene and other alkynes which in turn were used for various organic compounds^[6]. Through the change in carbon feedstocks to mineral oil, alkyne synthons became less important in industrial organic chemistry. Chemical valorization of coal today is based either on aromatics, as it was in the past, or through the gasification to synthesis gas from which most major modern intermediates can be synthesized.^[7]

The transition from coal to oil also brought about changes in the availability and use of basic chemical resources derived from the carbon feedstocks. One of the main reasons for the increase of crude oil production was the advent of the automobile. The increased demand of gasoline and diesel fuel for automobiles left a need to valorize other fractions of crude oil distillation leading to the development of aforementioned cracking methods for a higher gasoline yield.^[8] In these processes as well as in the distillation of crude oil olefins are yielded in significant quantities. In addition to the increase in production, alkenes have many favorable qualities which render them ideal as a basis for many organic transformations. In combination these two facts led to a consequential and almost complete transformation of industrial organic chemistry.

Chemically, alkenes are more versatile than any other carbon-carbon binding motif. By default olefins are electron rich and prone to nucleophilic reactions.^[9-10] However, the nature of the substituents on the carbon atoms has a significant influence on the reactivity of the double bond, tuning it either in the direction of very high nucleophilicity or even rendering it a superb electron acceptor. The latter case can be achieved for instance by conjugation to a carbonyl moiety, so called Michael systems, which in turn makes the β -position a very good electron acceptor.^[11] Conjugation to hetero-atoms such as oxygen (allyl-ethers) or nitrogen (ene-amines) has a converse effect.^[10] To add to this versatility, asymmetrically substituted olefins are prochiral which is especially important in the synthesis of biologically active molecules. The intermediate oxidation state of the carbon atoms in alkenes allow for the oxidation as well as the reduction of this motif, while the planarity of the system allows for an easy attack of reaction partners.^[10]

These qualities combined allow for a plethora of organic manipulations that can be carried out with alkenes. A selection of these reactions is presented in the following paragraphs in order to showcase the versatility of the olefin synthon. In virtually all alkene reactions an addition to the three coordinate carbon atoms is the first step which can then lead to isomerizations and eliminations in order to form the desired products.

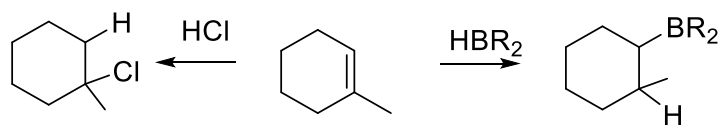
Addition of symmetric molecules



Scheme 1: Bromination of cyclohexene as an example of the predominant electrophile addition reaction of an unpolarized symmetric molecule to an alkene.

Halogens, hydrogen and other reactive dimeric unpolarized molecules can react with alkenes to form addition products (Scheme 1).^[9, 12] The addition can follow two distinct reaction mechanisms. The first comprises a X-X bond heterolysis and which is initiated by an attack of the nucleophilic C-C double bond. The resulting carbocation is then prone to a nucleophilic attack of the X⁻ anion. In the presence of a radical starter or induced by light of a specific wavelength a bond homolysis of the X-X bond can lead to a radical addition to the C-C double bond which in turn can recombine with another X radical. One significant downside of radical additions is however their lower selectivity.^[13] For several alkenes oligomers or even polymers can form, diminishing yields and posing purification problems. The radical reaction mechanism is energetically less favored than the heterolytic mechanism for most heavy halogens, because their polarizability suffices for a heterolysis upon nucleophilic attack and the presence of a good anionic leaving group.

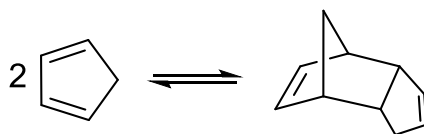
Addition of Brønsted acids and polarized H-R molecules



Scheme 2: Examples of Markovnikov (left) and anti-Markovnikov (right) additions to methyl-cyclohexene using H-X reagents with opposite polarizations.

Acidic protons are easily added to nucleophilic olefins forming a carbenium ion. The addition takes place under thermodynamic control, favoring the more stable i.e. most highly conjugated or hyperconjugated carbenium ion.^[9] This preference has chemical implications for the addition of the corresponding base. The base forms a bond to the carbenium ion and consequently the nucleophile is located at the more highly substituted site of the final molecule (Scheme 2). This addition behavior has been named Markovnikov's addition rule.^[14-15] It also holds true for the addition of polarized molecules, albeit steric hindrance can cause a product mixture or even a complete reverse of the stereoselectivity. In case of a negative polarization, as it can be observed for instance in reducing agents such as boro-hydrides, the bulky substituent is positively polarized and consequently added to the site with lower substitution. Due to the reverse location of the bulky substituent the rule governing hydridic additions such as hydroboration is called Anti-Markovnikov addition.

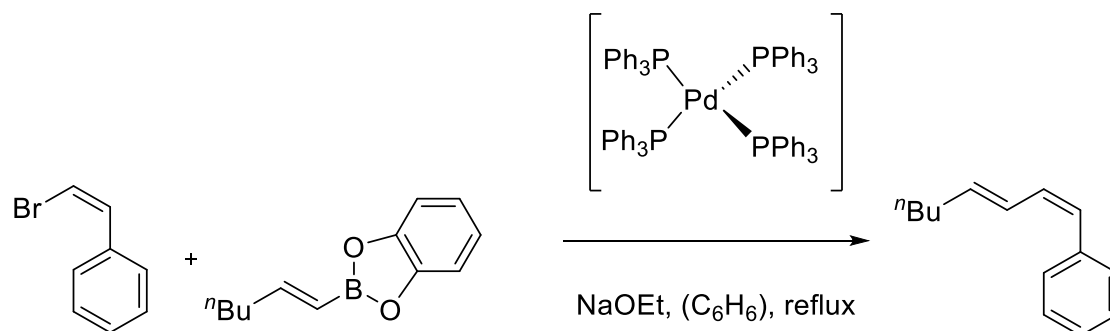
Cycloadditions



Scheme 3: Diels-Alder equilibrium of cyclopentadiene, a typical [4+2] cycloaddition reaction.

Additions to olefins are often used to build up ring structures and even heterocycles. This is especially possible due to their ability to be added to other double bond systems.^[9, 16] A typical reaction of this nature is the Diels-Alder reaction which is an addition of an alkene to a 1,3-diene system. This so called [4+2] cycloaddition forms a product with a six membered ring and one double bond (Scheme 3). [2+2] cycloadditions are forbidden due to orbital geometries.^[17] A possibility to overcome this is irradiation with UV light in order to excite electrons into orbitals with a matching geometry. Cycloadditions are also applicable in the formations of heterocycles by using for instance sulfur dioxide, diazo compounds or organic azides.^[18]

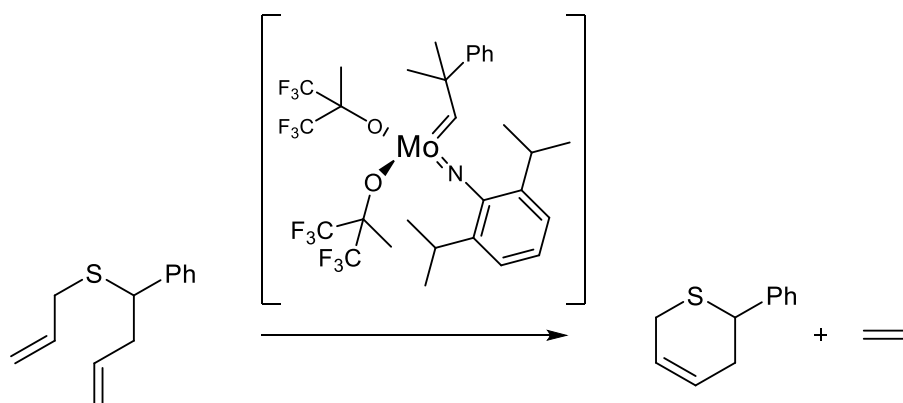
Cross-Coupling reactions



Scheme 4: Example of a vinylic palladium catalyzed cross-coupling reaction.^[19]

Cross-coupling reactions are C-C bond forming reactions between a metallated nucleophile, an organic electrophile (typically vinylic), a base, and a late transition metal catalyst (often palladium, platinum or nickel) with strongly donating ligands such as phosphines or carbenes (Scheme 4).^[20-21] Cross-coupling reactions can be applied to a variety of organic substrates; however it has proven especially useful for alkenes substituted with a potent leaving group. In contrast to common reaction mechanisms involving alkenes, cross-coupling reactions involve an insertion of the electron-rich late transition metal, typically palladium or nickel, into the alkene-leaving group bond. This complex then reacts with organotin,^[22] organoboron,^[23] organosilicon,^[24] organozinc^[25] or other metallated compounds^[26] to form carbon-carbon bonds.^[21] This type of reaction has gained significant traction in the last decades culminating in the Nobel Prize in 2010 for Richard F. Heck,^[27] Ei-ichi Negishi^[27] and Akira Suzuki.^[28-29] Since its inception the reaction has become highly significant in the synthesis of many complex bioactive molecules and pharmaceuticals.

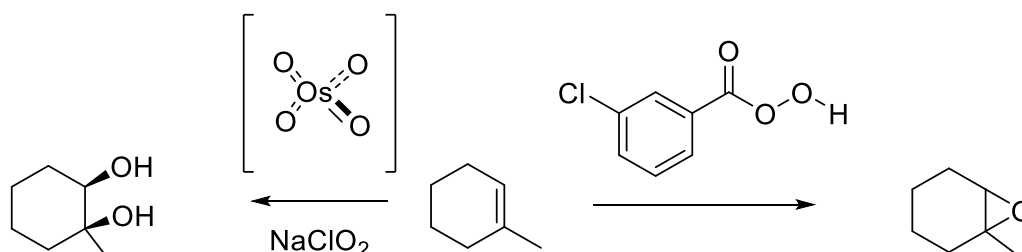
Olefin metathesis



Scheme 5: Ring closing metathesis reaction catalyzed by a Schrock alkylidene.^[30]

Olefin metathesis reactions are also catalyzed C-C bond formation reaction, however with a distinctly different mechanism and different reagents. Olefin metathesis is a reaction between two alkene moieties resulting in two olefins with mixed substituents from both reagents, analogously to salt metathesis in inorganic chemistry (Scheme 5).^[31] Suitable catalysts are typically Schrock type molybdenum alkylidene or Herrmann-Grubbs Ruthenium NHC alkylidene complexes. The mechanism proposed by Harrison and Chauvin involves a metalacyclobutane step which allows for a variety of different ring opening and addition reactions. This in principle unselective reaction step causes a scrambling of different products in a statistic distribution. Taking advantage of symmetric reagents, intramolecular reactions or volatile products can however lead to the selective formation of only one product. This reaction has been applied for the synthesis of a vast amount of different molecules such as polymers, macrocycles, and to fuse large fragments in the synthesis of natural products. In 2005 the Nobel Prize was awarded to Yves Chauvin,^[32] Robert H. Grubbs,^[33] and Richard R. Schrock^[34] for their contributions in this field, showing the growing relevance of this reaction.

Epoxidation/Dihydroxylation reactions



Scheme 6: Example of epoxidation and cis-dihydroxylation using osmium tetroxide and meta-chloroperbenzoic acid.

Similarly to the reduction of alkenes, the oxidation is in itself just an addition reaction as described in the first two examples listed in this chapter. However, epoxidations and dihydroxylations demand specific oxidation agents in order to selectively form the desired products. Analogously to nucleophilicity, the oxidation potential of olefins can be tuned by suitable substituents, making highly substituted olefins more prone to oxidation. For dihydroxylation reactions early transition metals in high oxidation states are employed as oxidation agents.^[9] Typical examples are potassium permanganate and osmium tetroxide. In case of osmium a co-oxidation agent, such as sodium chlorite, can be used to reoxidize osmium in situ, making it effectively a catalyst (Scheme 6).^[35] In case of epoxidation peroxy acids are typically used as the oxidation agent. Suitable reagents are mCPBA

(meta-chloroperoxybenzoic acid) and peroxyacetic acid.^[9] In these compounds the terminal oxygen has a partially positive polarization, making it prone to an attack of the π -bond. The formed intermediate then eliminates the carboxylic acid in a ring closing reaction to form the epoxide. Catalyzed versions of this have been applied in the organic syntheses using other oxidation agents such as TBHP (tert-butylhydroperoxide) and hydrogenperoxide. Of special significance is Sharpless' catalyst consisting of a titanium tartrate complex which has been employed in several syntheses of natural products. Further epoxidation catalysts will be presented in the following chapters.

1.3 Industrial Epoxidations of Commodity Olefins

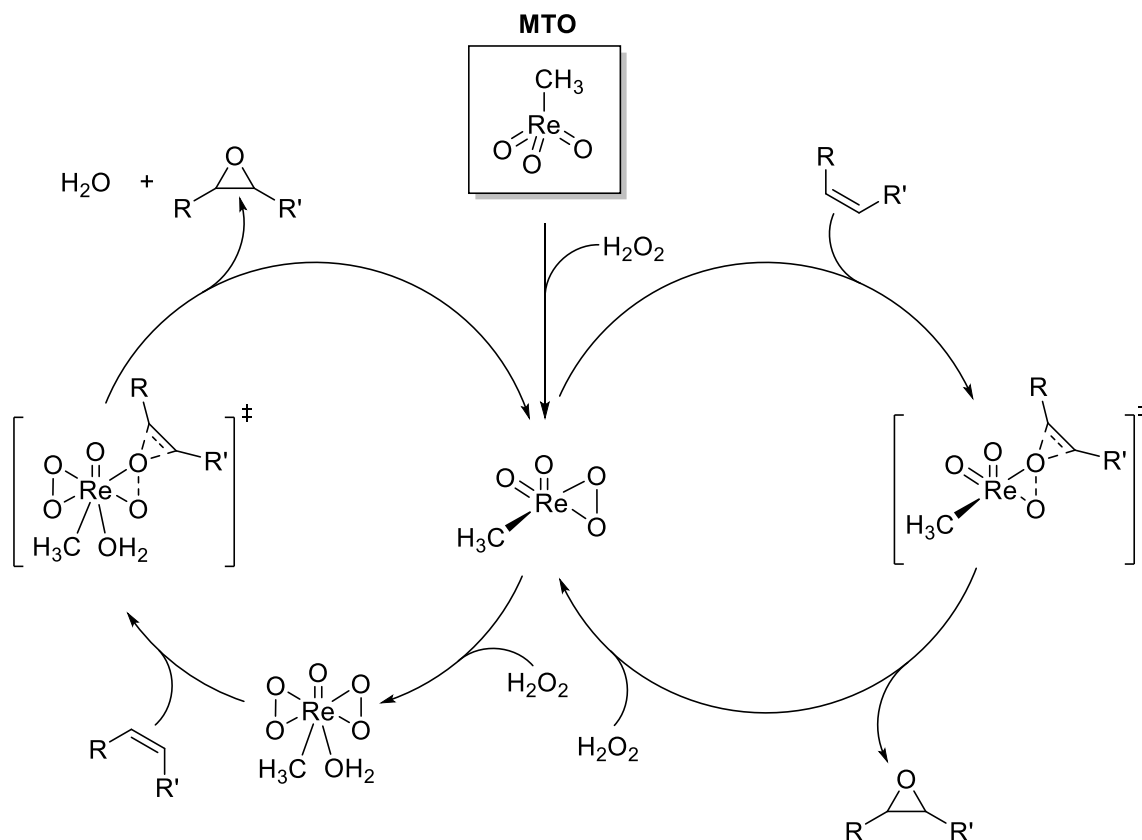
Among the many epoxides that are used as intermediates in industrial organic processes, propylene oxide and ethylene oxide are of special significance due to their large production volumes and importance in polymer and material chemistry.^[1] Polyglycols, polyurethanes, epoxy resins, polyamides, organic carbonates and surfactants are common applications for these products, which can be considered important commodities in the chemical industry. The large volumes which are produced of these epoxides mandate a continuous and catalyzed process in order to be cost effective. A second aspect which is highly important for an economical epoxidation is the choice of oxidant. In case of ethylene a heterogeneous catalyst comprised of silver alumina is commonly used.^[1, 36] This catalyst enables the use of air as a cheap oxidant. For propylene oxide synthesis the use of air as the oxidant remains a challenge.^[1] While several catalytic methods for the epoxidation of propylene are known, all of them require a stoichiometric oxidant such as organic peroxides or hydrogen peroxide instead of molecular oxygen.^[37] In several processes the organic peroxides are formed in situ through oxidation of a precursor with oxygen, but the fact remains that a stoichiometric byproduct is formed. Two main catalytic systems have been established. The first, known as the Shell catalyst, is a heterogeneous catalyst based on titania and silica; the second known as the Halcon/Arco catalyst is a homogeneous molybdenum(VI) naphthenate complex that can be used at higher temperatures and pressures.^[1, 38] As an alternative to the catalyzed processes the uncatalyzed chlorohydrin route is still used, albeit with decreasing relevance to the overall production volumes.

1.4 Homogeneous Olefin Epoxidation

Epoxidation reactions have been performed for decades without catalytic methods.^[9] Peroxo carbonic acids are known to epoxidize alkenes without the need of a catalyst. However, this method has the disadvantage that it is very unselective, i.e. that it does not discriminate between different alkene moieties in one molecule and that peracids are very aggressive oxidants that can oxidize other functional groups as well.^[9] Several transition metal catalyzed epoxidation reactions are known, typically involving early transition metals.^[37] In the Kühn and Herrmann groups especially rhenium and molybdenum based epoxidation catalysts have been studied in recent years.^[37, 39]

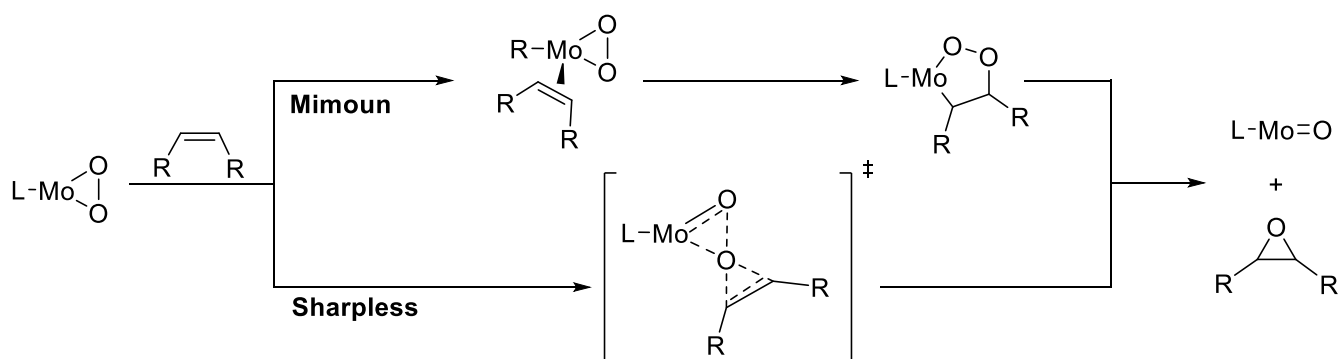
Methyltrioxorhenium (MTO) has been known since the late 1970s,^[40] but its application in oxidation chemistry was only discovered a decade later in the group of Herrmann at TUM.^[41] The main challenge at first was to find a synthetic route to access MTO in high yields and purity.^[42-44] In its application in oxidation catalysis, MTO proved to be a versatile catalyst that is active in the oxidation of a variety of substrates such as alkenes, alkynes, sulfides, halides and phosphines.^[45-49] Due to their significance MTO was especially investigated as an epoxidation catalyst under mild conditions.^[37, 39] Kinetic and stoichiometric investigations using hydrogen peroxide yielded a detailed mechanism.^[45, 50] Two key reactive intermediates were determined using different relative amounts of oxidant. The bis-peroxo complex $[(\text{Me})\text{Re}(\eta^2\text{-O}_2)_2\text{O}]$ was first identified spectroscopically and could later be investigated by single crystal X-ray diffraction, while the mono-peroxo complex $[(\text{Me})\text{Re}(\eta^2\text{-O}_2)\text{O}_2]$ is more elusive and could only be studied spectroscopically. The currently accepted mechanism invokes both species as active species in epoxidation of alkenes (Scheme 7).

MTO proved to be extraordinarily active in the epoxidation of *cis*-cyclooctene with turnover frequencies (TOF) of up to $40,000 \text{ h}^{-1}$.^[51] In order to reach such high activities *N*-donor additives are used in fluorinated solvents, such as hexafluoroisopropanol (HFIP). Also, MTO is able to convert a variety of substrates like cyclic, terminal and aromatic olefins but also terpenes.^[52-54] However, no other stable MTO analogs could be synthesized so far, making it the exception rather than the rule in rhenium-catalyzed epoxidation chemistry.^[37]



Scheme 7: Mechanism of MTO catalyzed epoxidation reactions. Two active species (mono-peroxo/ bis-peroxo) convert olefins to epoxides concomitantly.

In order to overcome the lack of modifiability that MTO poses and in order to mediate rhenium's high price, molybdenum catalysts have been investigated in depth in the Kühn group.^[39] This research has been strongly inspired by the Halcon/ARCO process which uses molybdenum hexacarbonyl as a precatalyst. Molybdenum in low oxidation states acts only as a precatalyst in these reactions and needs to be oxidized in a first step in order to be active as epoxidation catalyst.^[55] After oxidative decarbonylation two pathways are possible and have been proposed by Sharpless^[56] and Mimoun^[57-58] (Scheme 8).



Scheme 8: Proposed mechanisms for molybdenum catalyzed epoxidation reactions.

Sharpless' proposed mechanism involves a direct oxygen transfer from the peroxy molybdenum complex to the alkene. DFT studies suggest this mechanism to be plausible for certain molybdenum motifs. Mimoun proposed a metal centered mechanism involving a pre-coordination of the alkene to the molybdenum atom. The subsequent insertion of the alkene into the molybdenum oxygen bond yields a metallacycle which is in turn cleaved to form the epoxide.

Typical design motifs for molybdenum epoxidation catalysts are half sandwich complexes bearing one cyclopentadienyl ligand, three carbonyl ligands and alkyl or carbene ligands.^[59-62] Some catalysts comprise a combined chelating alkyl and cyclopentadienyl ligand and form an *ansa*-complex (Figure 3).^[63]

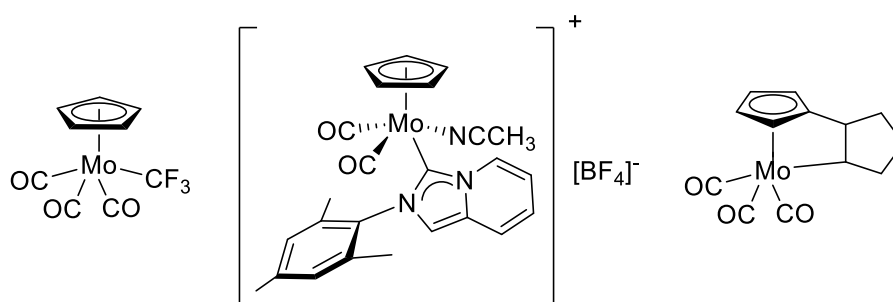


Figure 3: Examples of molybdenum epoxidation catalysts bearing fluorinated, NHC or *ansa*-ligands.

While these types of complexes are in general very active towards epoxidation of alkenes, some challenges remain. Molybdenum complexes bearing the aforementioned ligands are generally very sensitive towards moisture. This requires a change of oxidant from hydrogen peroxide to *tert*-butyl hydroperoxide which does not contain any water.^[37, 39] Also the induction period for many molybdenum precatalysts is very long which reduces the apparent activity, while the active species are not isolable or difficult to study in situ due to their short lifespan. Nonetheless, high activities and selectivities are observed in the epoxidation of the model substrate *cis*-cyclooctene with TOFs of up to 53000 h^{-1} .^[64] Their scope is generally more limited than for MTO. However, studies on sophisticated substrates, such as terpenes, are in many cases yet to be published. Overall, molybdenum catalysts mediate some of the shortfalls of MTO such as rhenium's high price and its lack of synthetic modifiability while in turn introducing other shortcomings such as sensitivity to water and a limited scope of oxidants.

1.5 Iron Oxidation Catalysts

With the emergence of more accurate knowledge of the role of iron as a cofactor in biological catalysis, synthetic iron complexes have been investigated in more and more detail within the last decades. Important enzymes that inspired this increase in interest in iron oxidation catalysis are methane monooxygenases (MMO)^[65-67] and cytochrome P450 oxidases (CYP)^[68-69]. These enzymes are potent oxidation catalysts that are able to oxidize several substrates like alkenes, alkanes and even methane. Furthermore, they use molecular oxygen as an oxidant to oxidize these challenging substrates. MMO and CYP are structurally very different, yet both are based on iron(II) centers.

While different methane monooxygenases are known, mainly two types have been studied in depth, namely the particulate methane monooxygenase (pMMO)^[70] and the soluble methane monooxygenase (sMMO).^[65-67, 71-72] Of these two, only sMMO contains iron cofactors. The substructure of soluble methane monooxygenase responsible for hydroxylating methane contains a diferric cofactor in which the iron(III) atoms are bridged by a hydroxide and two carboxylates (acetate and glutamate). The remaining coordination sites are occupied by histidine or glutamate ligands (Figure 4).^[73]

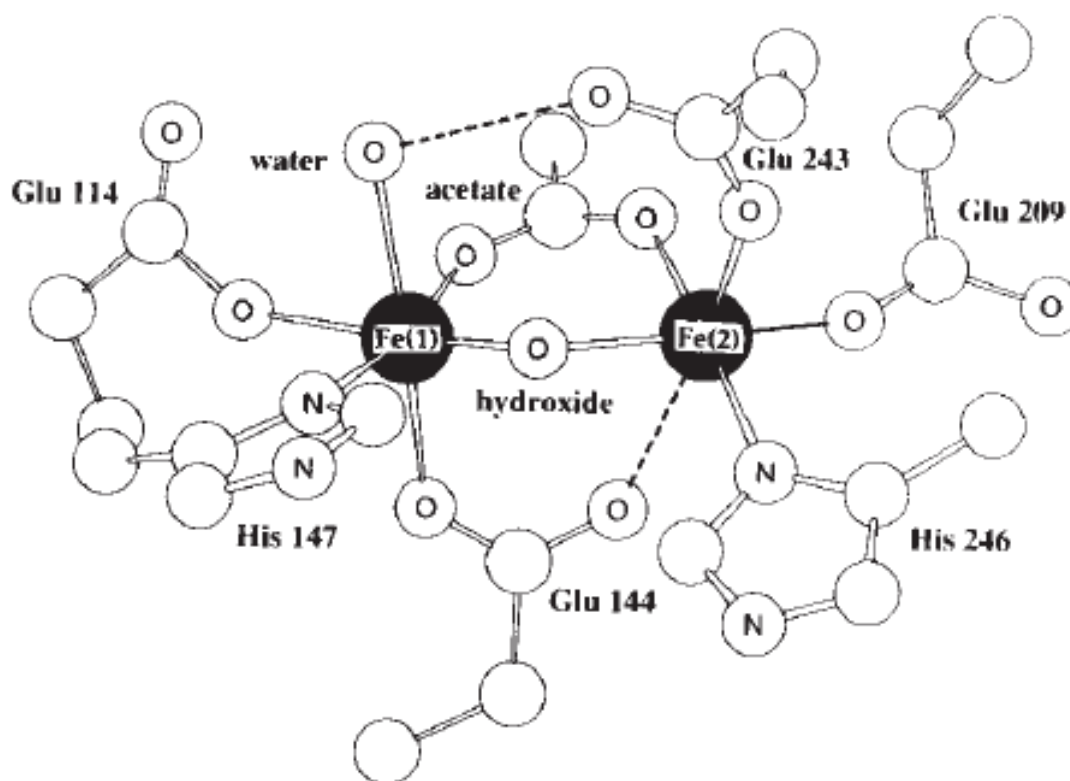


Figure 4: Active site of the hydroxylase subunit in sMMO. Reprinted with permission from Macmillan Publishers Ltd: *Nature* 1993, 366, 537-543, copyright 1993.^[73]

In contrast to this, monooxygenases of the CYP family only contain a single atom iron cofactor.^[68-69, 74] CYPs are hemoproteins in which a heme ligand coordinates the iron(III) center equatorially and in one apical position the iron is ligated by a cysteine group of the protein (Figure 5). This anchors the heme group to the protein and has a significant trans-effect noticeable in the coordination and reduction of molecular oxygen.^[75] CYPs are comparably versatile enzymes that have been linked to the oxidation of a wide variety of substrates including aromatics and olefins.

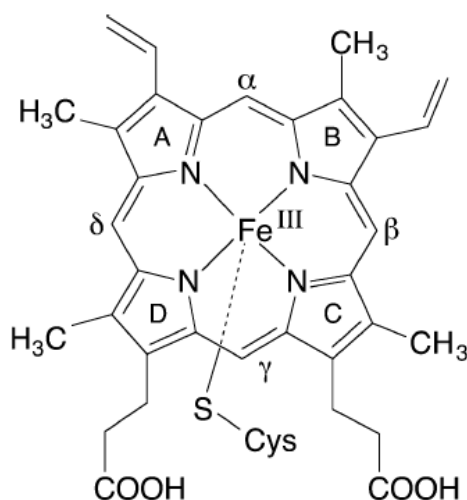
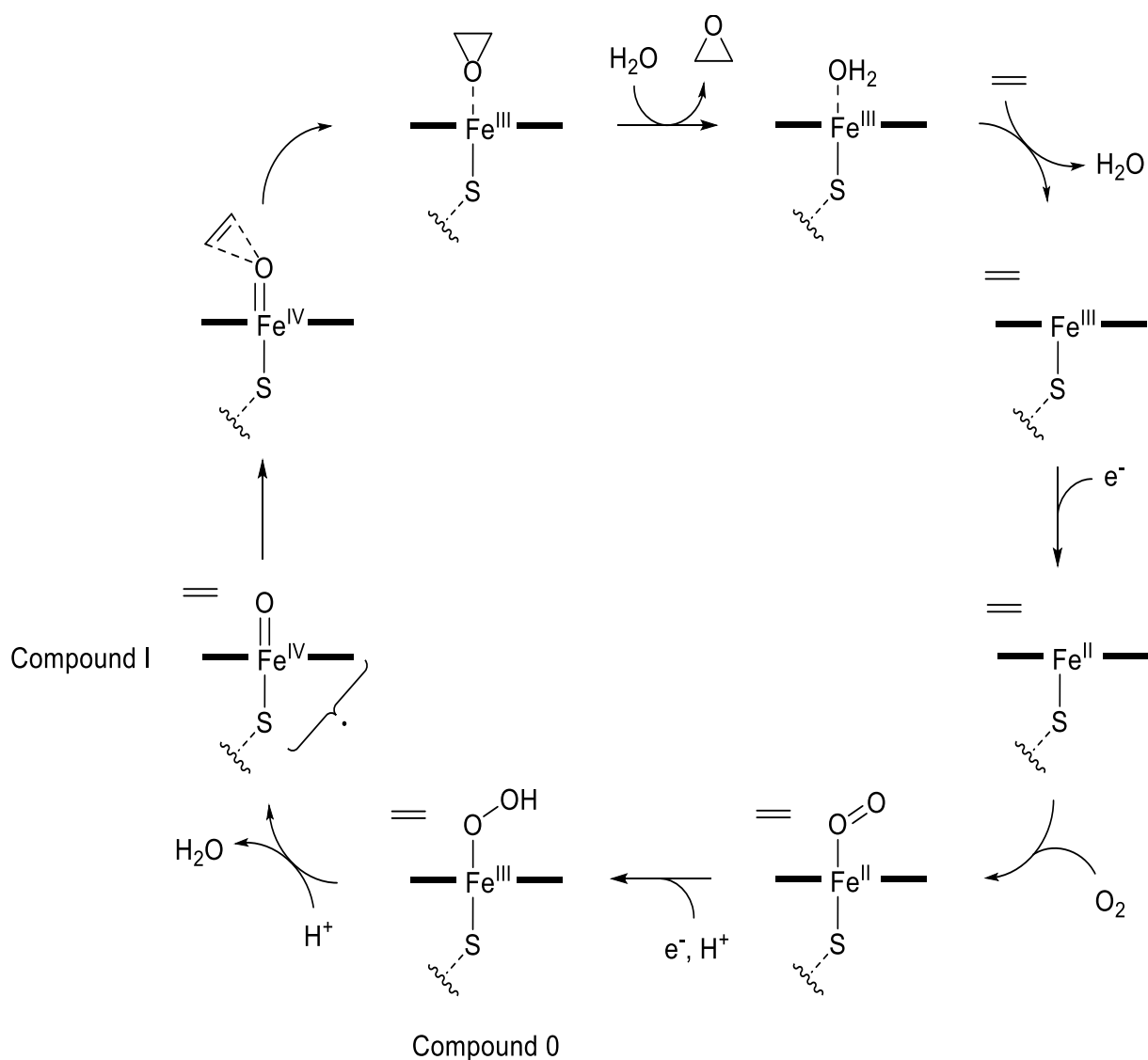


Figure 5: Active iron(III) heme cofactor in Cytochrome p450 oxidases.^[68] Reprinted with permission from B. Meunier, S. P. de Visser, S. Shaik, *Chemical Reviews* **2004**, *104*, 3947. Copyright 2004 American Chemical Society.

Since the 1970s the mechanism of CYP enzymes has been studied extensively.^[68-69] Groves first invoked the key species involved in CYP oxidation catalysis. The by now commonly accepted mechanism developed by Groves et al. is mainly founded on three isolable intermediates, aptly named compounds 0, I and II (Scheme 9).^[76-78] Compound I is the product of end-on dioxygen coordination and a subsequent one-electron ligand centered reduction. The so formed hydroperoxo iron(III) complex can then undergo a two electron oxidation step to form the nominally iron(V) oxo complex (compound I).^[79-80] However, the true nature of the resulting intermediate was found to be an iron(IV) center ligated by singly oxidized heme ligand. The redox non-innocent nature of the ligand apparently supports and facilitates substrate oxidation significantly. For the two electron oxidation of alkenes compound I is the most probable active species. It can directly transfer an oxygen atom to the alkene to form an epoxide. In turn it is reduced to iron(II) and coordinated by water to replace the epoxide. To close the cycle iron(II) can reduce dioxygen to form the iron(III) hydroperoxide (compound 0). Compound II is invoked in C-H oxidations and is formed from compound I by C-H abstraction. Consequently it then transfers the hydroxide to the resulting reactive carbon atom. However, it does not seem to have a major role in CYP catalyzed epoxidation reactions.



Scheme 9: Epoxidation mechanism of CYP oxidases using O_2 as oxidant invoking compounds 0 and I.^[81-82]

Inspired by these enzymes, the group of Groves synthesized the first bio-mimetic iron heme complexes that are active in various oxidation reactions including epoxidations.^[77] This work was developed further in the following years and high activities were achieved with heme ligands bearing fluorinated side-chains.^[83-86] The mechanism is believed to be similar to that of CYP catalysts. Compelling studies to prove this with detailed empirical and theoretical investigations were carried out in the group of Nam et al.^[84-86]

Inspired by sMMO, Que and coworkers published the first non-heme iron epoxidation catalyst in 1986 containing two iron centers.^[87] Subsequently the first non-heme iron epoxidation catalyst containing only one iron atom was reported in 1991 by Valentine et al.^[88] They succeeded in creating in a catalytic system that oxidizes alkenes in high yields and selectivity to epoxides using an iron(II) cyclam complex (cyclam=1,4,8,11-tetraazacyclotetradecane). In the following years mainly amino-pyridine

ligands, such as bpmnp [N,N'-bis(2-pyridylmethyl)-1,3-diaminopropane], have been used by Que et al. and other groups in order to investigate the structure-reactivity relationship of iron epoxidation catalysts.^[83, 89-102] Bipiperidine and bipyrrolidine were used in more recent years to explore their potential towards asymmetric epoxidation of prochiral alkenes (Figure 6).^[102-103]

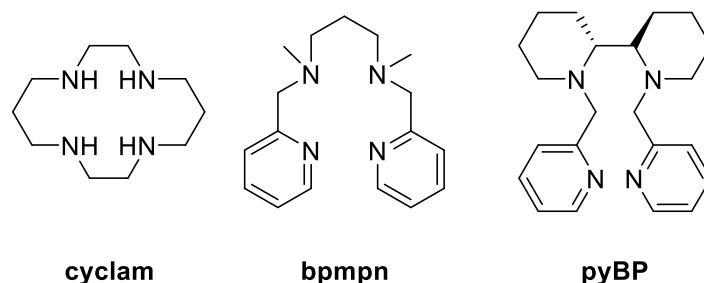
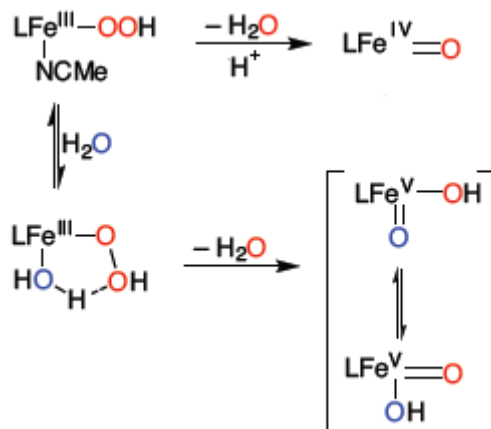


Figure 6: Ligand motifs commonly found in non-heme iron epoxidation catalysts.^[83, 103]

While expanding the ligand scope of these systems it became apparent that a more thorough picture of the mechanism of non-heme iron epoxidation catalysts was needed for an effective ligand design. In this context the groups of Valentine, Nam, and Que contributed valuable works in the discovery of the catalytic mechanism of iron(II)-catalyzed epoxidations with hydrogen peroxide.^[90-91, 94] The first step of the mechanism is a one-electron oxidation with subsequent ligand exchange forming an iron(III) hydroperoxide complex. Several routes to form high-valent iron complexes are possible yielding either iron(IV) oxo complexes or iron(V) oxo hydroxo complexes.^[83, 91, 99] A strong dependence on the ligand geometry is observed in these subsequent transformations, rendering the formation of the latter only possible for cis-labile coordination sites in the complex. For these water coordination can occur and a water assisted heterolytic bond cleavage is feasible.^[97] In case of a trans-labile ligand system this is not a possibility and in the absence of acids no iron(V) intermediate is formed (Scheme 10).^[97] These intermediates are key in understanding the selectivity of ligand precursors since the nature of the high-valent intermediates determines the products of the catalytic cycle. Iron (V) oxo hydroxo complexes are able to directly dihydroxylize alkenes while iron(IV) oxo complexes are only able to epoxidize olefins.^[97]



Scheme 10: Simplified reaction mechanisms for the water assisted and non-water assisted iron epoxidation reactions. The water assisted pathway is only accessible in a cis-labile ligand topology. Water assistance can be examined by the use of labelled water (blue).^[83]

However, the use of acidic additives can shift the reaction selectivity and activity of complex bearing cis-labile coordination sites significantly to favor epoxides.^[99] Doing so can however impair product and catalyst stability. This dependence of the selectivity on the ligand geometry was implied in the early works of Valentine^[88] and fully confirmed by in depth studies carried out in the group of Que.^[97] Que, Münck and Nam also were the first to structurally characterize an iron(IV) oxo complex by single crystal x-ray diffraction in 2003.^[92] While these bio-inspired works show great promise in order to understand the mechanism, highly active and selective catalysts are yet to be reported. Activities reported with amino-pyridine ligands are typically low, having TOFs of between 1,000 h⁻¹ and 10,000 h⁻¹, with the notable exception of the [(bpmen)Fe(MeCN)₂]²⁺ (bpmen=N,N'-dimethyl-N,N'-bis-(pyridin-2-ylmethyl)-1,2-diaminoethane) complex which shows TOFs of up to 25,000 h⁻¹.^[83] Typically, turnover numbers are an even greater problem with catalyst decomposition within a few minutes. Overall, these catalysis benchmarks show the great room for improvement possible in the catalytic performance of iron epoxidation catalysts.

2 OBJECTIVE

Following the investigations of non-heme iron(II) epoxidation catalysts, organometallic iron complexes based on N-heterocyclic carbenes (NHC) rather than amino-pyridine ligands seem to be a promising alternative. They combine a high synthetic modifiability with a strong σ -donating ability and have been applied in molybdenum oxidation catalysis. An iron(II) complex **1**, ligated by a tetradentate bis-NHC bis-pyridyl (NCCN) ligand was published by Herrmann and Kühn in 2012 (Figure 7).^[104] This complex is an ideal candidate to investigate catalytic behavior, find optimal conditions, and tune reactivity and activity in alkene epoxidation catalysis.

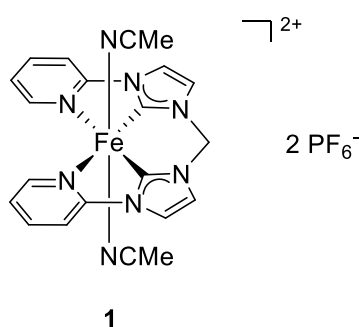


Figure 7: Complex **1** bearing a tetradentate bis-NHC-bis-carbene ligand in the following denoted as NCCN.^[104]

This complex combines the design principles previously laid out for N-donor ligated systems. Its trans-labile coordination sites are paramount for high selectivity, while the strongly donating character of the ligands should support the formation of high-valent iron oxo intermediates. Furthermore, the polydentate nature of the ligand should be beneficial for catalyst stability.

In order to further investigate the reactivity of **1** ligand exchange experiments are conducted. In the course of these investigations an influence of the axial ligands on the oxidation and reduction behavior can be studied electrochemically. The results can show whether an apical coordination analogously to the apical thiolate in CYPs are useful in the design of more active epoxidation catalysts. Concomitantly, a direct investigation of **1** in epoxidation catalysis is desirable in order to gauge activity and optimize conditions. Kinetic experiments can show the duration of activity as well as the initial TOFs at various temperatures. A variation of oxidants and alkenes can show the possible range of applications of **1** and the scope of further investigations.

The results of these investigations can then lead to the development of new and different iron NHC catalysts. Interesting prospects are offered by cyclic systems compared to open ligand systems. Furthermore, a development of tetra-NHC complexes can lead to more electron rich systems which in turn could lead to higher activity. Another interesting aspect is the use of iron(III) catalysts instead of

iron(II) catalysts. The use of iron(III) could be advantageous in terms of activity as it does not need a peroxidation step. Lastly, decomposition products of NCCN and other ligands should be investigated as they might be applied in ligand recovery.

3 Results – Publication Summaries

3.1 Molecular Epoxidation Reactions Catalyzed by Rhenium, Molybdenum, and Iron Complexes

JENS W. KÜCK,[#] ROBERT M. REICH,[#] AND FRITZ E. KÜHN

[#]J. W. KÜCK AND R. M. REICH CONTRIBUTED EQUALLY TO THIS WORK.

THE CHEMICAL RECORD **2016**, *16*, 349-464

This review article summarizes the approaches and results of 25 years of epoxidation research in the inorganic department at TUM. The first systems highlighted are based on rhenium as the catalytically active metal. Rhenium provides for reliable and stable catalysis using hydrogen peroxide as the oxidant. The catalytic cycle for rhenium-mediated epoxidation reactions is well understood in the case of methyltrioxo rhenium while allowing for optimization of catalytic conditions using fluorinated solvents and nitrogen donors. The high metal price and poor synthetic variability of the complexes warranted the use of other base metals that are equally or even more active as epoxidation catalysts. Piano-stool molybdenum complexes bearing N-heterocyclic carbene ligands show an equally promising performance, albeit under inert conditions and using TBHP as the oxidation agent. In contrast to MTO, these molybdenum complexes are highly modifiable and ligand design can be employed to boost activity and selectivity. Using arylated NHC ligands, turnover frequencies as high as 53,000 h⁻¹ for the epoxidation of *cis*-cyclooctene were obtained, significantly surpassing the highest TOFs obtained for MTO.

While molybdenum complexes are very suitable epoxidation catalysts, they too show significant drawbacks in terms of applicability. Molybdenum piano-stool complexes are highly sensitive against moisture and consequently need organic peroxides such as TBHP as oxidation agents. Furthermore the mechanism and the initiation phase are still very poorly understood. The substrate scope is quite limited and molybdenum compounds, especially the used carbonyls, are fairly toxic. In order to overcome some of these challenges the catalyst scope was broadened to include iron NHC complexes. Iron pyridine complexes have been used by other groups as epoxidation catalysts showing promising activity. As a first example, a tetradentate bis-NHC bis-pyridine ligated octahedral iron(II) complex was used as an epoxidation catalyst by our group, showing exclusively the epoxidation product under ambient conditions using hydrogen peroxide as oxidant. Changing the ligand motif to a cyclic tetradentate tetra-NHC ligand greatly increases activity by one order of magnitude. Moreover, subsequent oxidation to the respective iron(III) complex yields an extraordinary TOF of 183,600 h⁻¹. This is the highest value obtained for any homogeneous epoxidation catalyst so far. Unfortunately, stability and recyclability of the catalyst remains a challenge. Overall this article shows the great

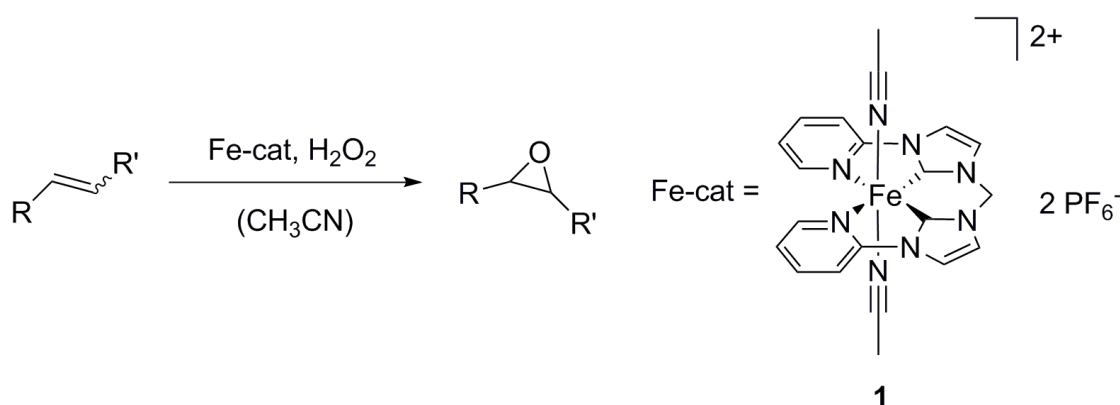
promise of base metals in epoxidation catalysis and the progress that has been made in the understanding and application of epoxidation catalysis in the last two decades. Further progress in iron mediated epoxidation is expected in the next year with the potential of developing a suitable alternative epoxidation catalyst for fine-chemical synthesis.

3.2 Epoxidation of Olefins Catalyzed by a Molecular Iron *N*-Heterocyclic Carbene Complex: Influence of Reaction Parameters on the Catalytic Activity

JENS. W. KÜCK, ANDREAS RABA, JULIUS I. E. MARKOVITS, MIRZA COKOJA, AND FRITZ E. KÜHN

CHEMCATCHEM 2014, 6, 1882-1886

Molecular epoxidation catalysis has been focused to a large extent on heme systems, while non-heme systems are now emerging as a viable alternative to the synthetically challenging heme complexes. These non-heme systems are largely based on N-donor ligands due to their ease of synthesis and biological analogs. The iron carbene complex **1** has been previously reported as a remarkably air and moisture stable organometallic iron complex. Based on its structural similarity to known non-heme iron complexes active in epoxidation catalysis complex **1** has been investigated in this type of reactions (Scheme 11).



Scheme 11: Complex **1** as an active epoxidation catalyst at ambient conditions using aqueous hydrogen peroxide.

In these investigations complex **1** proved to be a very active epoxidation catalyst using hydrogen peroxide as oxidant and *cis*-cyclooctene as the substrate. The reactions are remarkably fast with maximum conversions being reached in less than 60 seconds. Typical catalyst concentrations are in the order of 1 mol% catalyst relative to substrate under excess oxidant conditions (150 mol%). Under these conditions no byproducts were detected and the overall yield determined as 66 % epoxide. After the reaction time no further activity of the catalyst was observed. Under excess substrate conditions the catalyst stays active and a second addition of oxidant leads to further substrate conversion. Using extreme excess of oxidant leads to fast catalyst decomposition, thus lowering yields. Other substrates have been investigated with lower yields but comparable selectivities, with the only exception of aromatic olefins such as styrene. Interestingly the yields in the epoxidation of *cis*-cyclooctene were significantly higher at decreased temperatures. Monitoring the time-dependent yields at various temperatures showed that the reaction rate as indicated by the turnover frequencies

was lowered. However, this decrease in activity was compensated by a longer catalyst lifetime thus giving higher yields (Figure 8).

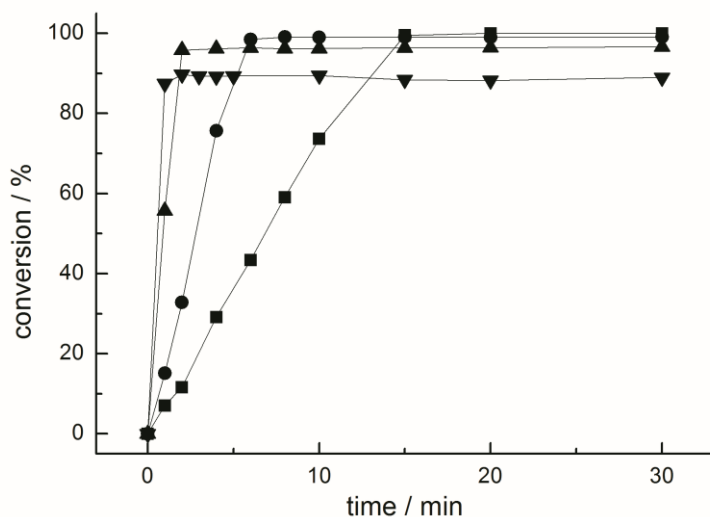


Figure 8: Effect of lowering the temperature in the catalytic oxidation of cis-cyclooctene using **1** (■: 10°C, ●: 0°C, ▲: 10°C, ▼: 25°C).

Under optimized conditions the catalyst reached turnover frequencies of up to 2614 h^{-1} which is comparable to most non-heme complexes previously known. Complex **1** constitutes a new type of epoxidation catalyst since no previously reported catalyst incorporated a Fe-C bond, thus making this the first organometallic iron epoxidation catalyst using the strict definition of organometallic compounds.

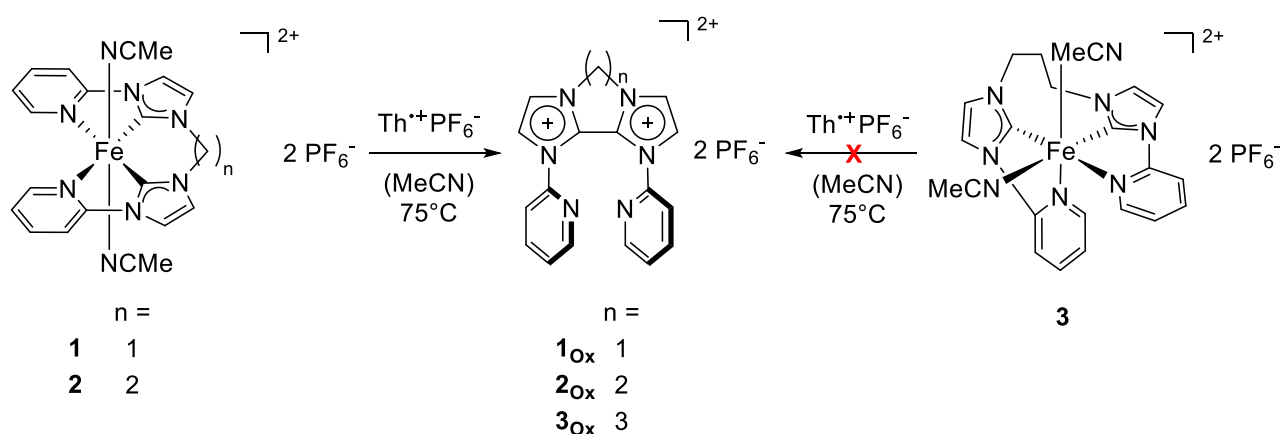
3.3 Formation of Highly-Strained *N*-Heterocycles via Decomposition of Iron *N*-Heterocyclic Carbene Complexes: The Value of Labile Fe – C Bonds

STEFAN HASLINGER,[#] JENS. W. KÜCK,[#] MARKUS R. ANNESER, MIRZA COKOJA, ALEXANDER PÖTHIG, AND FRITZ E. KÜHN

[#]J. W. KÜCK AND S. HASLINGER CONTRIBUTED EQUALLY TO THIS WORK.

CHEMISTRY – A EUROPEAN JOURNAL 2015, 21, 17860-17869

Oxidation states of non-heme iron oxidation catalysts are of great interest for mechanistic insights and catalyst fine tuning. For this reason a one-electron oxidation of complex **1** was investigated. Unexpectedly, the resulting iron(III) NCCN complex is not stable but decomposes, yielding an unusual annulated heteropolycyclic product **1_{ox}**. For the analogous complexes **2-3** the product formation was highly dependent on coordination geometry (Scheme 12).

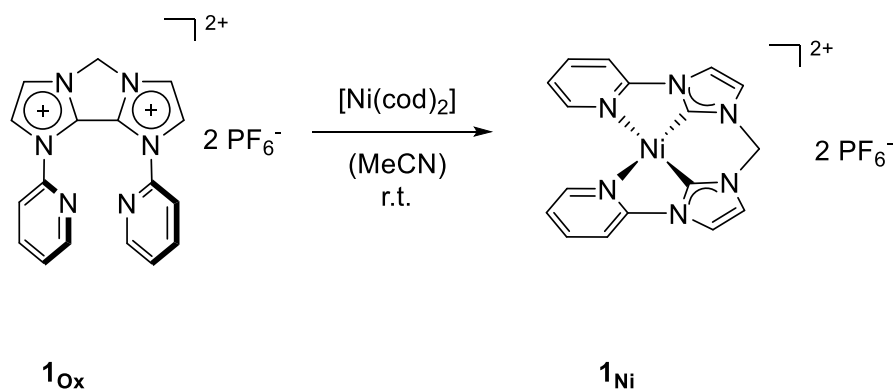


Scheme 12: Syntheses of annulated 2,2'-biimidazoles **1_{ox}** and **2_{ox}** by one-electron oxidation of **1** and **2**, respectively. Oxidation of **3** did not yield **3_{ox}**. Th²⁺: Thianthrene cation radical.

The obtained compounds were investigated electrochemically and compared to their reduced tetraazafulvalene counterparts. In this investigation the observed reversibility of the two one-electron reduction steps was highly dependent on the nature of the bridge between the imidazole moieties. Subtle changes such as the introduction of methyl substituents or an elongation by a methylene group gave large improvements in the reversibility of the redox steps. The methylene tethered tetraazafulvalene could not be observed or inferred, but a dimeric macrocyclic tetraazafulvalene seems most likely as indicated by NMR spectroscopy.

The reactivity of the observed bisimidazolium salts is of a highly interesting nature as they allow for oxidative addition in order to form NHC-complexes as well as deprotonation of the bridging

methylene tether (Scheme 13). These applications might introduce new tools in the synthesis of bis-NHC complexes or recycling of ligands.



Scheme 13: Reaction of dicationic annulated 2,2'-biimidazole $\mathbf{1}_{\text{ox}}$ with $[\text{Ni}(\text{cod})_2]$ to yield the square-planar Ni complexes $\mathbf{1}_{\text{Ni}}$.

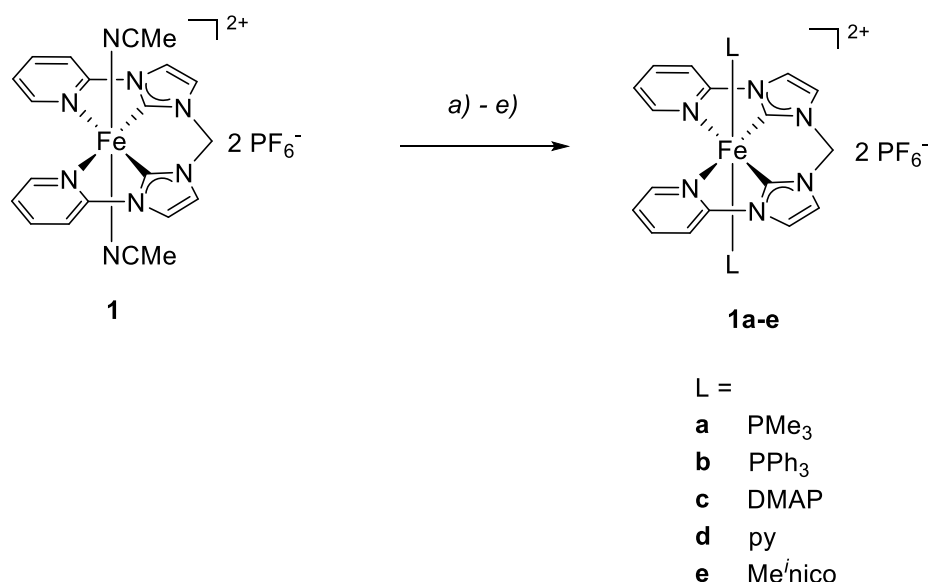
complex only produced a fraction of the final yield in the first 10 s. In order to elucidate the initial reaction behavior of complexes **4** and **4a** the reaction temperature was decreased significantly. The observed reaction behavior was similar to the previously investigated complex **1** with higher yields, longer catalyst life-times and lowered activity at decreased temperatures. At -30°C the catalyst loadings can be reduced by several orders of magnitude with noticeable conversions even at relative catalyst concentrations of 0.005 mol%. The highest observed turnover number under these conditions is 4,300. Kinetic investigations revealed that the sum of all reaction orders is 2 and complex **4** passes an initiation phase before showing a linear reaction behavior. These findings show that the initial oxidation is indeed a recognizable factor in molecular epoxidation catalysis using non-heme iron complexes and the catalytic yields strongly favor iron(III) complexes.

3.5 Making Oxidation Potentials Predictable: Coordination of Additives Applied to the Electronic Fine Tuning of an Iron(II) Complex

STEFAN HASLINGER, JENS W. KÜCK, EVA M. HAHN, MIRZA COKOJA, ALEXANDER PÖTHIG, JEAN-MARIE-BASSET, AND FRITZ E. KÜHN

INORGANIC CHEMISTRY 2014, 53, 11573-11583

In this article the influence of axially coordinating ligands on the electronic structure and oxidation behavior of complex **1** were investigated. To this end several pyridine-derived N-donor ligands and phosphine derived P-donor ligands were coordinated to complex **1** (Scheme 15).



Scheme 15: Reactions of complex **1** with phosphines and pyridines forming **1a-e**, respectively. *a)* excess PMe_3 , MeCN, r.t. *b)* excess PPh_3 , acetone, -78°C to r.t. *c)* excess 4-dimethylaminopyridine (DMAP), MeCN, r.t. *d)* excess pyridine (py), acetone, -78°C to r.t. *e)* excess methyl isonicotinate (Me'nico), acetone, -78°C to r.t.

Several of the resulting complexes were crystallized and their structure confirmed by single crystal x-ray diffraction. Their geometrical parameters were consecutively reproduced and the molecular orbital levels determined by DFT calculations using the same functional and basis set. Complexes **1a-e** were also investigated with regard to their electrochemical properties. It was found that the oxidation potential of the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ redox couple is shifted significantly upon coordination of axial ligands. While the lowest oxidation potential is exhibited by the bis-dimethylamino pyridine substituted complex **1c** (79 mV vs Fc/Fc^+) the highest oxidation potential for the bis-triphenyl phosphine substituted complex **1b** is shifted to 440 mV vs Fc/Fc^+ . This shows the extraordinary influence of axially coordinating ligands on the electronic structure of complexes like **1**. Using Koopman's theorem, a correlation between the

calculated energy levels of the highest occupied molecular orbital and the determined half-cell potential for the Fe^{II}/Fe^{III} redox couple of complexes **1a-e** was shown to be linear (Figure 9).

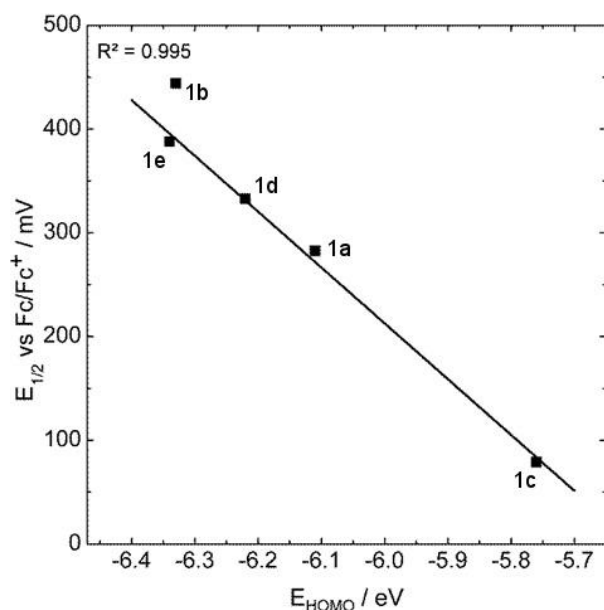


Figure 9: Linear relationship between experimental half-cell potential $E_{1/2}$ versus Fc/Fc⁺ as determined by cyclic voltammetry and DFT-calculated energies of HOMOs (E_{HOMO}) on a B3LYP/B2 level of theory for complexes **1a-e**. Values of **1b** were not included in the linear fit as **1b** did not exhibit full reversibility for at least 10 cycles in the CV experiment. Linear equation: $E_{1/2} = -538 \times E_{\text{HOMO}} - 3016$.

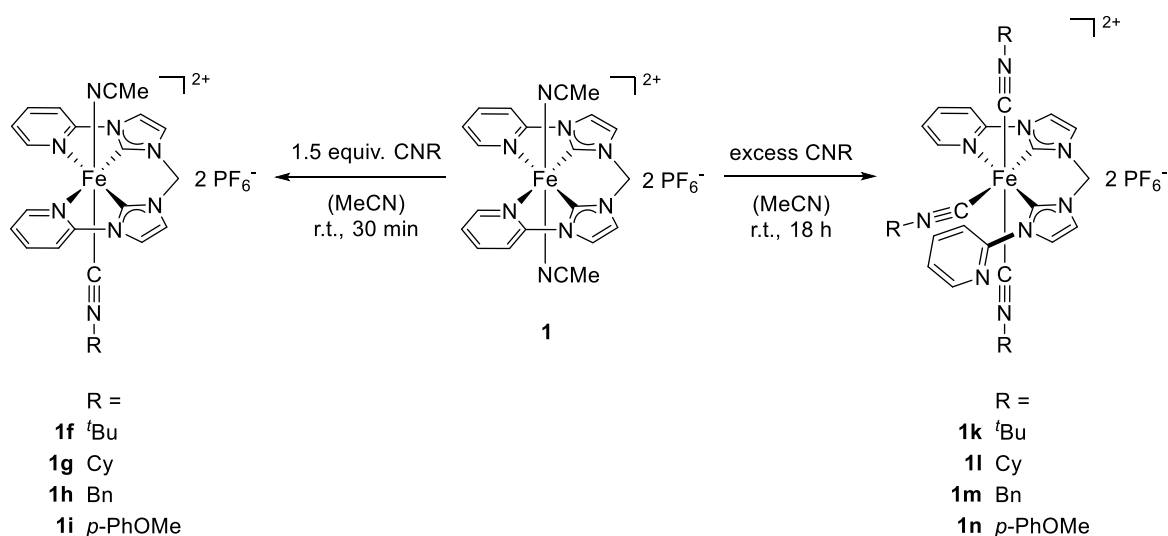
To further prove the potential of the applied DFT model the oxidation potentials for the mono-substituted complexes analogous to **1a-e** were calculated using again Koopman's theorem. The experimental half-cell potential for the Fe^{II}/Fe^{III} redox couple of the mono-trimethylphosphine substituted analogue of complex **1a** was found to deviate within the experimental margin of error from the values predicted by the computational model (325 mV vs. 330 mV). These mono-substituted complexes are of scientific interest due to their similarity to the apically coordinated cytochromes found in nature. Predicting their oxidation behavior, suitable synthetic targets for applications in oxidation chemistry can be determined *in silico* rather than through tedious synthetic and electrochemical procedures.

3.6 Isocyanide Substitution Reactions at the Trans Labile Sites of an Iron(II) *N*-Heterocyclic Carbene Complex

STEFAN HASLINGER, ANJA C. LINDHORST, JENS W. KÜCK, MIRZA COKOJA, ALEXANDER PÖTHIG, AND FRITZ E. KÜHN

RSC ADVANCES 2015, 5, 85486-85493

Starting from the previously investigated iron(II) NHC complex bearing an equatorially coordinating bis(pyridyl-NHC) ligand, several ligand exchanged isocyanide-substituted complexes were synthesized. The complexes exhibit an unusual substitution pattern as they can either bear one or three isocyanide ligands depending on reaction stoichiometry, while the bis-substituted complexes were not accessible. This stands to contrast donating ligands such as phosphines and amines that have been presented earlier. The tris(isocyanide) complexes show that under suitable reaction conditions one of the two pyridyl coordination sites of the chelating ligand is labile and can be exchanged with strongly coordinating ligands such as isocyanides (Scheme 16).



Scheme 16: Syntheses of mono(isocyanide)-substituted complexes **1f-i** and tri(isocyanide)-substituted complexes **1k-1n** from **1**.

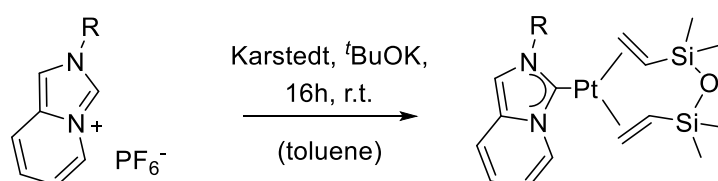
This unexpected coordination behavior was first observed in the solid state structure determined via single crystal XRD analysis and matches NMR spectroscopy data in solution. In the course of these NMR investigations a transient bis(isocyanide) complex could be identified. Interestingly, for these compounds the coordination of the second isocyanide moiety takes place in the equatorial plane rather than the second axial position. The change in electronic structure was investigated by cyclic voltammetry, confirming that the required oxidation potential for the iron(II)/iron(III) redox couple is significantly increased from 423 mV to up to 1092 mV after substitution.

3.7 Decoding Catalytic Activity of Platinum Carbene Hydrosilylation Catalysts

TERESA K. MEISTER, JENS W. KÜCK, KORBINIAN RIENER, ALEXANDER PÖTHIG, WOLFGANG A. HERRMANN, AND FRITZ E. KÜHN

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Platinum catalyzed hydrosilylation reactions are among the most used applications of homogeneous catalysis. The most commonly used compound in these reactions is Karstedt's catalyst which comprises two platinum(0) centers and three bi-dentate olefin ligands. Partially substituting these olefins with symmetrical NHC ligands leads to Markó's catalyst which has significantly higher activity and an overall very favorable performance. In this article asymmetric imidazo[1,5-a]pyridine-3-ylidenes are used rather than symmetrical NHC ligands due to the former's strong σ -donating qualities as well as their similar steric hindrance (Scheme 17). However, they invoke a stereoelectronic environment that is unique and substantially different from the previously described Markó systems. The synthesis uses the standard approach of ligand exchange using a free NHC ligand obtained via deprotonation of the corresponding imidazolium salt with a strong organic oxide base.



Scheme 17: Syntheses of Marko type catalysts bearing substituted imidazo[1,5-a]pyridine-3-ylidene ligands.

The obtained complexes are investigated by cyclic voltammetry and the results compared to calculated orbital energies of the highest occupied molecular orbitals. The correlation is linear and fits Koopmans theorem showing an isostructural oxidation behavior. These complexes show outstanding activities in hydrosilylation reactions with TOFs up to 22,600 h^{-1} and a very short induction period. Interestingly, a good linear relationship between the Hammett coefficient and the first order reaction constant was observed for complexes bearing para substituents. These results show that efficient ligand design can be used to optimize Markó's catalysts and that current methods of predicting steric and electronic ligand properties are useful in revealing promising new hydrosilylation catalysts.

4 CONCLUSION AND OUTLOOK

In conclusion, this work is the first investigation of iron NHC complexes in homogeneous epoxidation catalysis. Complex **1** was the first organometallic iron complex (defined as containing at least one metal carbon bond) active in epoxidation catalysis. It was found that the overall epoxide yield is not only highly dependant on the activity of **1** but rather a function of balanced activity and stability. At low loadings and decreased temperatures the epoxide yield could be increased to a considerable extent. Moreover, it was concluded that hydrogen peroxide is the best oxidant for these systems that epoxidize various alkenes in high selectivity.

Through substituting the axial ligands of **1**, a variety of new disubstituted complexes were synthesized and characterized (**1a-1n**). First pyridines and phosphines were used and later isocyanides were added as suitable substitution partners. The electrochemical properties were investigated and enabled the development of a model that allows for predictions of achievable oxidation potentials. In the course of these investigations this model was tested for monosubstituted analogs of complex **1** and the predictions matched empirical results.

A cyclic tetra-NHC analog of **1** was synthesized and oxidized to the iron(III) complex in good yields. Both complexes were applied in epoxidation catalysis and found to be very active. In fact both complexes were more active than the benchmark rhenium system MTO. Complex **4a** is the most active homogeneous epoxidation catalyst to date with a TOF of 183,600 h⁻¹. More importantly the difference in behavior between the two complexes in different oxidation states becomes obvious at reduced temperatures. At -30°C complex **4a** is instantly active while complex **4** shows an induction period. This implies that **4** needs to transform to **4a** before the reaction can take place. This confirms the hypothesis of a peroxidation step before the active catalyst is formed. The remaining trends are all in good accordance with previous studies in the literature and studies conducted with **1**.

In contrast to **4**, complex **1** cannot be oxidized with a strong outer sphere one-electron oxidant. Instead of an oxidized complex only a decomposition product of the ligand can be isolated in good yields. The product is a bisimidazolium salt that is formed by the reductive elimination of the ligand forming a C-C bond between the former carbenes. This motif of a heterocyclic cationic polycycle of three five membered rings has not been reported before. More importantly, it displays an interesting reductive behavior which is highly dependent on the tether length. Molecules with a longer tether and thus a larger ring size of the central ring show a higher reversibility in their reduction behavior, while complexes with a methylene tether show an irreversible reduction. Similarly, methylene-tethered bisimidazolium salts can be deprotonated at the methylene bridge yielding an unusual imidazolium salt.

Future investigations based on this dissertation can lead in a variety of directions. First and foremost, the range of iron complexes active in epoxidation catalysis can be extended considerably. The investigated systems show great promise, but only comprise two ligands. The amount of variations of different tetradentate ligands is vast considering the progress that has been made within the Kühn group and the published works thereof. Also, axial ligand substitutions are tools that are so far not explored in epoxidation catalysis. Secondly, substitution experiments should also be conducted with complexes in which the ligand does not coordinate equatorially. This could prevent side reactions that lead to dihydroxylation and thus improve existing systems to a large extent. For all of these catalysts a single electron oxidation could lead to higher activities or to interesting decomposition products that in turn should be studied for their redox properties.

Concerning the methylene bridged NCCN ligand and its bisimidazolium decomposition product, the already vast reaction network should be extended. After deprotonation it could lead to an interesting new type of NHC ligand with very low steric demand, yet high donor ability. Furthermore, first insertion experiments show that the bisimidazolium salt can be used in a rare type of NHC complex formation through oxidative addition via a C-C single bond. This could be interesting for the exploration of new NHC complexes and their properties. This route should be thoroughly examined with late electron-rich transition metals. Overall, iron complexes and their reaction products remain worthwhile synthetic targets. Catalytic studies will produce sought-after alternatives to known systems and their ability to substitute late and toxic transition metals is potentially transformative for the future of homogeneous catalysis. This work could barely scratch the surface of epoxidation applications of iron catalysts and the future will hold great things in store for researchers of organometallic iron compounds.

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Molecular Epoxidation Reactions Catalyzed by Rhenium, Molybdenum, and Iron Complexes

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Epoxidation of Olefins Catalyzed by a Molecular Iron *N*-Heterocyclic Carbene Complex: Influence of Reaction Parameters on the Catalytic Activity

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Formation of Highly-Strained *N*-Heterocycles via Decomposition of Iron *N*-Heterocyclic Carbene Complexes: The Value of Labile Fe – C Bonds

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Fighting Fenton Chemistry: A Highly Active Iron(III)-Tetracarbene Complex in Epoxidation Catalysis

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Making Oxidation Potentials Predictable: Coordination of Additives Applied to the Electronic Fine Tuning of an Iron(II) Complex



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S. Haslinger, A. C. Lindhorst, J. W. Kück, M. Cokoja, A. Pöthig and F. E. Kühn, *RSC Adv.*, 2015, 5, 85486
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Decoding Catalytic Activity of Platinum Carbene Hydrosilylation Catalysts

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JENS. W. KÜCK,[#] ROBERT. M. REICH,[#] AND FRITZ E. KÜHN

[#]J. W. KÜCK AND R. M. REICH CONTRIBUTED EQUALLY TO THIS WORK.

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Influence of Reaction Parameters on the Catalytic Activity

JENS. W. KÜCK, ANDREAS RABA, JULIUS I. E. MARKOVITS, MIRZA COKOJA, AND FRITZ E. KÜHN

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Formation of Highly-Strained *N*-Heterocycles via Decomposition of Iron *N*-Heterocyclic Carbene Complexes: The Value of Labile Fe – C Bonds

STEFAN HASLINGER,^{a,#} JENS. W. KÜCK,^{a,#} MARKUS R. ANNESER,^a MIRZA COKOJA,^b ALEXANDER PÖTHIG,^c AND FRITZ E. KÜHN^a

[#]J. W. KÜCK AND S. HASLINGER CONTRIBUTED EQUALLY TO THIS WORK.

CHEMISTRY – A EUROPEAN JOURNAL **2015**, *21*, 17860-17869

^a Chair of Inorganic Chemistry/Molecular Catalysis, Technische Universität München (TUM), Ernst-Otto-Fischer-Straße 1, D-85747 Garching b. München. E-mail: fritz.kuehn@ch.tum.de

^b Chair of Inorganic and Organometallic Chemistry, Technische Universität München (TUM), Ernst-Otto-Fischer-Straße 1, D-85747 Garching b. München

^c Catalysis Research Center, Technische Universität München (TUM), Ernst-Otto-Fischer-Straße 1, D-85747 Garching b. München

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Fighting Fenton Chemistry: A Highly Active Iron(III)-Tetracarbene Complex in Epoxidation Catalysis

JENS. W. KÜCK,^{a,#} MARKUS R. ANNESER,^{a,#} BENJAMIN HOFMANN,^a MIRZA COKOJA,^b ALEXANDER PÖTHIG,^c AND FRITZ E. KÜHN^a

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CHEMSUSCHEM **2015**, *8*, 4056-4063

^a Molecular Catalysis/Inorganic Chemistry, Department of Chemistry, Catalysis Research Center, Technische Universität München (TUM), Lichtenbergstr. 4, D-85747 Garching bei München, Germany

^b Catalysis Research Center, Technische Universität München (TUM), Ernst-Otto-Fischer-Straße 1, D-85747 Garching bei München, Germany

^c Faculty of Chemistry, TUM, Lichtenbergstr. 4, D-85747 Garching bei München, Germany

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Making Oxidation Potentials Predictable: Coordination of Additives Applied to the Electronic Fine Tuning of an Iron(II) Complex

STEFAN HASLINGER,[†] JENS W. KÜCK,[†] EVA M. HAHN,[†] MIRZA COKOJA,[†] ALEXANDER PÖTHIG,[†] JEAN-MARIE-BASSET,[‡]
AND FRITZ E. KÜHN[†]

INORGANIC CHEMISTRY **2014**, *53*, 11573-11583

[†] Inorganic Chemistry/Molecular Catalysis, Catalysis Research Center, Technische Universität München (TUM), Ernst-Otto-Fischer-Straße 1, 85747 Garching bei München, Germany

[‡] Catalysis Center, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia

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STEFAN HASLINGER,^a ANJA C. LINDHORST,^a **JENS W. KÜCK,**^a MIRZA COKOJA,^b ALEXANDER PÖTHIG,^c AND FRITZ E. KÜHN^a

RSC ADVANCES **2015**, *5*, 85486-85493

^a Chair of Inorganic Chemistry/Molecular Catalysis, Technische Universität München (TUM), Department of Chemistry/Catalysis Research Center, Lichtenbergstr. 4, D-85747 Garching bei München, Germany

^b Chair of Inorganic and Organometallic Chemistry, Technische Universität München (TUM), Ernst-Otto-Fischer-Straße 1, D-85747 Garching bei München, Germany

^c Catalysis Research Center, Technische Universität München (TUM), Ernst-Otto-Fischer-Straße 1, D-85747 Garching bei München, Germany

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TERESA K. MEISTER,^{a,b} **JENS W. KÜCK,**^a KORBINIAN RIENER,^{b,c} ALEXANDER PÖTHIG,^d WOLFGANG A. HERRMANN,^c AND FRITZ E. KÜHN^{a,c,d}

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^a Molecular Catalysis, Technische Universität München, Lichtenbergstrasse 4, 85747 Garching b. München, Germany

^b Institut für Siliciumchemie, Technische Universität München, Lichtenbergstrasse 4, 85747 Garching b. München, Germany

^c Chair of Inorganic Chemistry, Department of Chemistry, Technische Universität München, Lichtenbergstrasse 4, 85747 Garching b. München, Germany

^d Catalysis Research Center, Technische Universität München, Lichtenbergstrasse 4, 85747 Garching b. München, Germany

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8 COMPLETE LIST OF PUBLICATIONS

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Conference Contributions

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