Tuning Activity and Stability: Non-Heme Iron *N*-heterocyclic Carbene Complexes in the Catalytic Epoxidation of Olefins

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„Work is the best antidote to sorrow"

- Sir Arthur Conan Doyle

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KURZZUSAMMENFASSUNG

Im Rahmen dieser Arbeit wird die katalytische Anwendung von Eisen *N*-heterozyklischen Carben (NHC) Komplexen in Epoxidationsreaktionen mit Wasserstoffperoxid als Oxidans untersucht. Alle untersuchten Komplexe imitieren zu unterschiedlichen Ausmaßen die aktiven Zentren aus der Natur bekannter CYP Enzyme.

Zwei gemischte vierzähnige NHC/1,2,3-Triazol Fe^{II} Komplexe (Fe^{II}-$N_{trz}C_{im}C_{im}N_{trz}$) mit *cis* labilen Koordinationsstellen werden auf ihre Anwendbarkeit als Katalysatoren in der Epoxidation von *cis*-Cyclookten überprüft. Dabei wird insbesondere der Einfluss verschiedener Brønsted (AcOH, $HClO_4$) und Lewis Säuren ($Sc(OTf)_3$) als unterstützende Additive untersucht. In Anwesenheit von Essigsäure und unter optimierten Reaktionsbedingungen wurden hierbei die höchsten jemals veröffentlichten Wechselzahlen (76.000 h^{-1}) eines nicht Häm-basierten Fe^{II} Komplexes erreicht.

Tiefgreifende Studien zu den Effekten verschiedener Lewis Säuren auf die Fe^{II} und Fe^{III} Varianten eines zyklischen tetra-NHC Komplexes offenbarten zusätzlich signifikant erhöhte und nahezu identische katalytische Aktivität und Stabilität beider Komplexe mit Wechselzahlen von bis zu 410.000 h^{-1} und eine katalytische Produktivität von bis zu 1.200 bei 20°C. In Kombination mit diesen Resultaten zeigen UV/Vis spektroskopische Studien, dass sich die notwendige Oxidation des Fe^{II} Prä-Katalysators zum aktiven Fe^{III} Katalysator unter katalytischen Bedingungen und in Anwesenheit starker Lewis Säuren unverzögert vollzieht.

Abschließend werden strukturell eng verwandte Derivate des zyklischen Eisen tetra-NHC Komplexes untersucht, um die Auswirkungen von elektronen-schiebenden und elektronen-ziehenden Substituenten am NHC Rückgrat auf die katalytische Leistungsfähigkeit zu untersuchen. Das Methyl-substituierte Derivat zeigte dabei, angewendet in Epoxidationsreaktionen, eine deutlich niedrigere Stabilität im Vergleich zum unsubstituierten Derivat. Verantwortlich dafür ist die erhöhte Elektronendichte am Eisen-Zentrum resultierend aus dem +I Effekt induziert durch die Methyl-Gruppen. Im Gegensatz dazu hat der Austausch der Imidazolyliden-Einheiten mit Benzimidazolylidenen, zum Zweck des Entzugs von Elektronendichte am Eisen-Zentrum, einen deutlich positiven Effekt auf die Stabilität des Komplexes während der

katalytischen Reaktion, allerdings einhergehend mit einer allgemein niedrigeren Aktivität. Diese niedrigere Reaktivität ist allerdings vermutlich dafür verantwortlich, dass die Epoxidation schwieriger umzusetzender Olefine im Vergleich zu *cis*-Cyclookten deutlich erleichtert wird. Zusätzliche vergleichende Untersuchungen *via* Zyklovoltammetrie (CV), Kernspinresonanzspektroskopie (NMR) und Dichte-Funktional-Theorie (DFT) bestätigen den erheblichen Einfluss der Methyl-Gruppen und der Benzimidazolyliden-Einheiten auf die elektronischen Eigenschaften des Eisen-Zentrums.

ABSTRACT

Several novel iron *N*-heterocyclic carbene complexes are investigated with respect to their catalytic properties in epoxidation reactions using hydrogen peroxide as oxidant. The active sites of all complexes evaluated resemble those of CYP enzymes found in nature to a variable extent.

Two mixed tetradentate NHC/1,2,3-triazole Fe^{II} complexes (Fe^{II}-$N_{trz}C_{im}C_{im}N_{trz}$) exhibiting *cis* labile coordination sites were studied as catalysts in the epoxidation of *cis*-cyclooctene with particular emphasis on the influence of various Brønsted (AcOH, $HClO_4$) and Lewis acids ($Sc(OTf)_3$) as supporting additives. In presence of acetic acid and under optimized conditions, an unprecedented high activity for a non-heme Fe^{II} catalyst with turnover frequencies of up to 76,000 h^{-1} was observed.

Furthermore, in-depth studies of the effects of various Lewis acids on the performance of the Fe^{II} and Fe^{III} derivatives of a cyclic tetra-NHC iron complex revealed significantly improved activities (that also coincide) as well as stability of both complexes with TOFs of up to 410,000 h^{-1} and TONs of up to 1,200 at 20°C. These results, in combination with UV/Vis spectroscopic investigations, prove that the Fe^{II} pre-catalyst is instantly oxidized to the active Fe^{III} catalyst under catalytic conditions and in the presence of a strong Lewis acid.

Lastly, structurally closely related derivatives of the cyclic tetra-NHC complex were investigated with respect to the specific impact of electron donating and withdrawing substituents at the NHC backbone positions. The methyl-substituted derivative exhibits a considerably lower stability in epoxidation reactions compared to the unsubstituted derivative. This is attributed to the increased electron density at the iron center resulting from an +I effect induced by the methyl groups. In contrast, exchanging the imidazolylidene moieties with benzimidazolylidenes in order to withdraw electron density from the iron center results in an improved stability, however, a lower overall activity is observed. This lower overall activity, seems, however, to be favored if less reactive olefins compared to *cis*-cyclooctene are applied as substrates. Additionally, the particular electronic effects of the introduced methyl groups and benzimidazolylidene moieties on the iron center were studied *via* cyclic voltammetry (CV), NMR spectroscopy and density functional calculations (DFT).

LIST OF ABBREVIATIONS

Ar	aryl
AcOH	acetic acid
Bn	benzyl
BPMCN	*N,N*-bis(2-pyridylmethyl)-*N,N*-dimethyl-*trans*-1,2-diamino-cyclohexane
BPMEN	*N,N'*-bis(2-pyridylmethyl)-1,2-diaminoethane
btsa	bis(trimethylsilyl)amide
CV	cyclic voltammetry
cyclam	1,4,8,11-tetraazacyclotetradecane
CYP	cytochrome P450 oxidases
DFT	density functional theory
Dipp	diisopropylphenyl
ESI-MS	electro-spray ionization mass spectrometry
FCC	fluid catalytic cracking
HOMO	highest occupied molecular orbital
HPPO	hydrogen peroxide to propylene oxide
L	ligand
LA	Lewis acid
LUMO	lowest unoccupied molecular orbital
MTO	methyl-trioxorhenium(VII)
NHC	*N*-heterocyclic carbene
NMR	nuclear magnetic resonance
OTf$^-$	triflate
PDP	2-((*S*-2-[*S*-1-(pyridine-2-ylmethyl)pyrrolidin-2-yl]pyrrolidin-1-yl)-methyl)pyridine
PyTACN	bis(2-pyridylmethyl)-1,4,7-triaazacyclononane
QBPA	(2-quinolylmethyl)bis(2-pyridylmethyl)amine
ROMP	ring-opening metathesis polymerization
SC-XRD	single crystal x-ray diffraction
sMMO	soluble methane monooxygenases

| TAPH	1,4,8,12-tetraazacyclopentadecane
TAPM	1,4,8,12-tetramethyl-1,4,8,12-tetraazacyclopentadecane
TATM	1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclotridecane
TBHP	*tert*-butyl hydroperoxide
TMC	1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane
TOF	turnover frequency
TON	turnover number
TPA	tris(2-pyridylmethyl)amine

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1 INTRODUCTION

1.1 CARBON FEEDSTOCKS FOR THE CHEMICAL INDUSTRY

The tremendous growth of the chemical industry over the past 100 years was only possible because of the abundancy and reliable supply of carbon feedstocks.[1] Until a few decades ago, tar residues from coal-gas production represented the basis for organic chemistry providing a variety of aromatics.[2] In these processes, activation and manipulation of carbon bonds in order to successively obtain more complex organic molecules was a key procedure for increasing the value of chemical products.[3] However, using a coal-derived feedstock as hydrocarbon source entails severe disadvantages including the production of toxic wastes as byproducts, emission of nitrous and sulfuric gases, low overall yields and also the fact that coal-mining poses extreme danger to workers. Due to the rising demand for liquid mineral oil, driven by developments and growth in the automobile sector, certain fractions in the refinement process have become available to the chemical industry. Catalytic and thermal steam cracking with subsequent separation of the fractions constitute two key procedures in the production of chemically exploitable organic molecules (Scheme 1).[1]

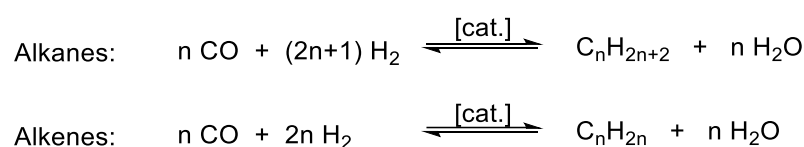**Thermal steam cracking:**
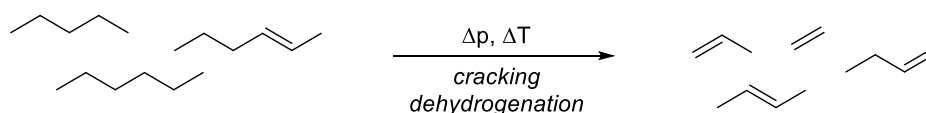
Fluid catalytic cracking:
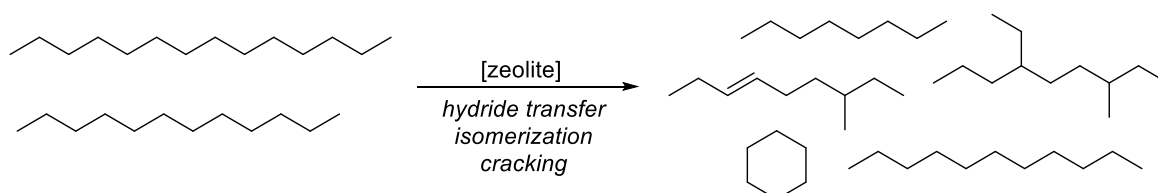
Scheme 1. Main chemical products in thermal steam cracking and fluid catalytic cracking (FCC) processes.[4-5]

Naphtha, which consists mainly of low boiling alkanes and alkenes is treated *via* steam or thermal cracking. High pressure and temperature cause C-C bond breaking and

dehydrogenation leading to various short-chain unsaturated hydrocarbons, depending on the conditions applied. Radical elimination reactions as a consequence of C-H bond homolysis taking place at extremely high pressure and temperature account for the retrieval of ethylene, propylene and various C_4-bodied olefins as the main products.[4] Longer chain hydrocarbons can be divided largely into lighter, mostly saturated hydrocarbons by fluid catalytic cracking (FCC) using in turn amorphous or crystalline zeolites as heterogeneous catalysts. The products are either used as gasoline fuel or subjected to thermal steam cracking, also depending on their current market value.[1, 4, 6]

Unfortunately, natural gas cannot be manipulated using the processes just described. Such a mixture consisting primarily of methane needs to be converted into syngas (n CO + m H$_2$) by partial oxidation prior to employing the Fischer-Tropsch process in order to obtain higher alkanes and olefins (Scheme 2). The products are either directly utilized or subjected to cracking processes.[7-8]

Fischer-Tropsch process:

$$\text{Alkanes:} \quad n\,CO \;+\; (2n+1)\,H_2 \;\underset{}{\overset{[cat.]}{\rightleftharpoons}}\; C_nH_{2n+2} \;+\; n\,H_2O$$

$$\text{Alkenes:} \quad n\,CO \;+\; 2n\,H_2 \;\underset{}{\overset{[cat.]}{\rightleftharpoons}}\; C_nH_{2n} \;+\; n\,H_2O$$

Scheme 2. Reaction equations of the Fischer-Tropsch syntheses of alkanes and alkenes.

The utilization of mineral oil and natural gas following the shift from coal also entailed change in the accessibility of different raw materials and the carbon building blocks for the chemical industry. Whereas coal derived chemistry was largely based on aromatics and alkynes, the rising use of mineral oil feedstocks paved the way for chemical utilization of alkenes as starting materials for a wide range of industrial applications.[1-2]

1.2 INDUSTRIAL EPOXIDATION CATALYSIS

For the chemical industry, catalytic epoxidation of olefins plays a major role in the synthesis of both fine and bulk chemicals.[9] Epoxides represent a key raw material in developing fragrances, detergents and pharmaceutical products (Figure 1).[1, 10-11] As an important intermediate in organic synthesis, epoxides are able to undergo ring-opening reactions with various nucleophilic reagents leading both to highly specific

organic molecules or products of industrial demand in megaton scales. In general, oxidants like hydrogen peroxide, various alkyl hydroperoxides, peracids or oxygen from air are applied to convert olefins to their respective epoxides in reactions catalyzed by transition metal complexes.[12-17]
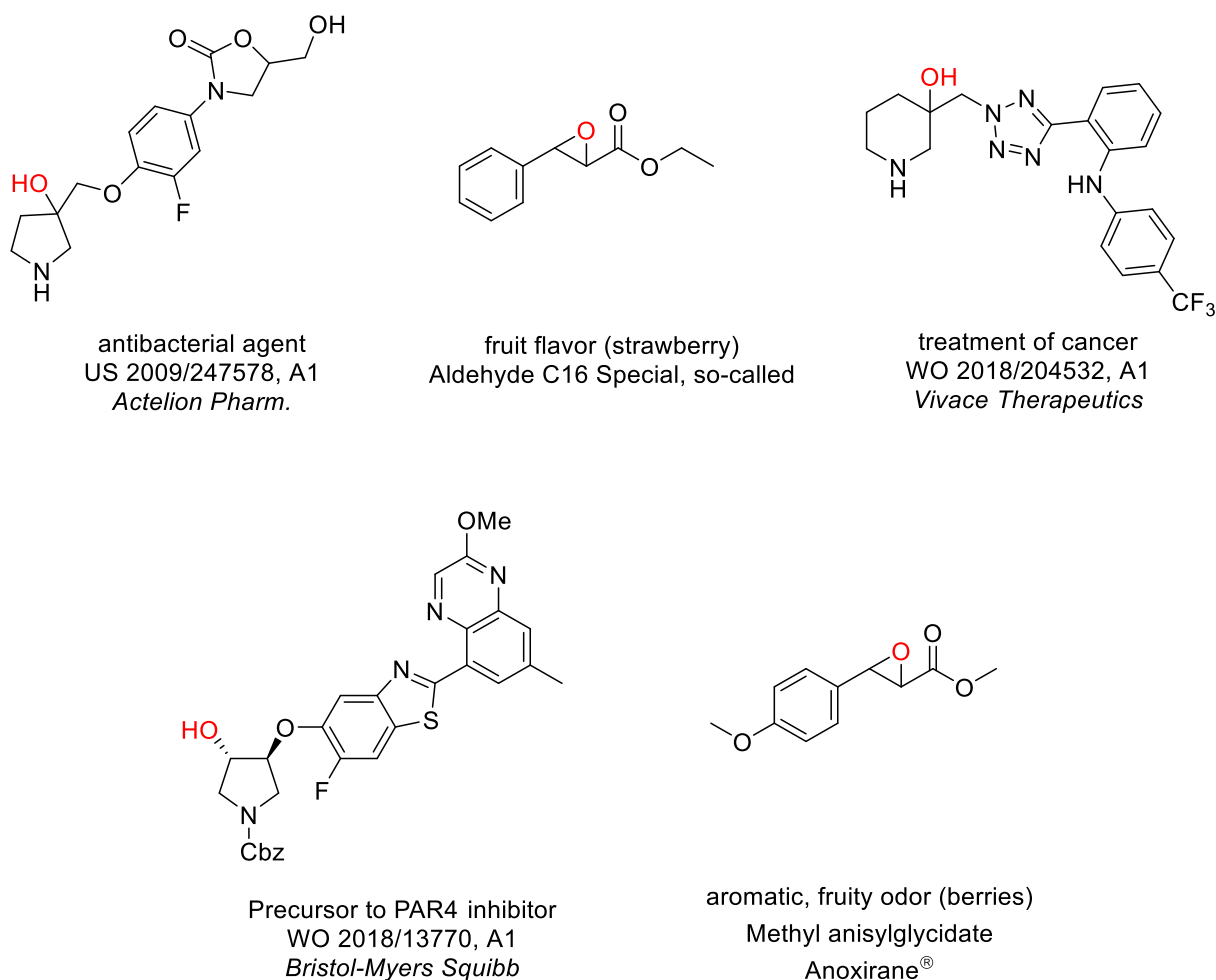

Figure 1. Structural examples of epoxides in fragrances/flavors and epoxide derived pharmaceutical products.[10, 18-20]

In terms of global demand, ethylene oxide and propylene oxide as products of olefin epoxidation account for the by far largest share of industrial production.[1, 21] Their subsequent processing into valuable products like polyglycols, polyurethanes, epoxy resins or organic carbonates, amongst others is of significant importance in polymer and material chemistry.[1] The ethylene epoxidation process was developed by Union Carbide (1937) and Shell (1958). Herein, ethylene oxide is synthesized by vapor-phase oxidation of ethylene with air or pure oxygen catalyzed by α-Al_2O_3 supported silver nanoparticles.[22-23] Unfortunately, this procedure is only applicable to olefins without allylic C-H bonds. Due to the competing oxidation of allylic C-H bonds, only low yields

and selectivity toward epoxide are achieved. For instance, applying propylene as a substrate in the process largely yields oxidation products like acroleine and acrylic acid due to the methyl group in allylic position.[21, 24] Therefore, for the epoxidation of higher olefins, the chlorhydrin process is still partly applied.

The chlorhydrin route follows a simple two-step process, depicted in Scheme 3, exemplified by the production of propylene oxide. Therein, propylene reacts with a solution of chlorine in water as the oxidizing agent to the respective propylenchlorohydrin isomers at 35-50°C and 2-3 bar.[1, 21]
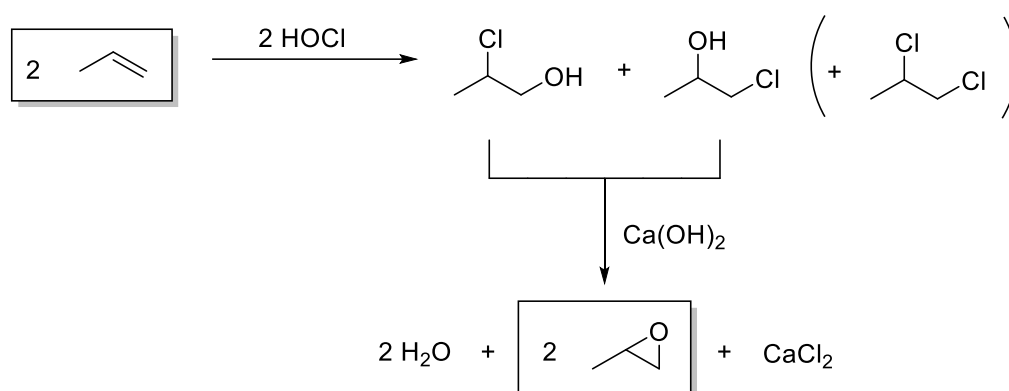
Scheme 3. Two-step reaction of the Chlorhydrin-process on the example of propylene oxide production.

The second step involves the *in-situ* dehydrochlorination of the isomers with calcium- or sodium hydroxide at 25°C yielding the desired epoxide. After separation of non-condensing byproducts and distillation, propylene oxide is obtained with an overall selectivity of ca. 90% in reference to the applied propylene. A critical disadvantage, however, is displayed by the large amounts of rather nugatory byproducts. 100-150 kg of 1,2-dichloropropane and 2.1/2.2 tons of $CaCl_2$/NaCl are produced per ton propylene oxide, respectively.[21] Therefore, alternative routes involving direct oxidation were developed independently by Halcon and Atlantic Richfield (ARCO) in 1967, applying organic hydroperoxides as oxidants and various high valent transition metal catalysts. Although molybdenum as catalyst metal (*e.g.* MoO_3, $Mo(CO)_6$) shows comparably high activity and selectivity if TBHP is applied as oxidant, in 1983 Enichem succeeded a breakthrough by introducing a titanium-substituted silicalite (TS-1) catalyst allowing for efficient liquid-phase oxidation and the application of H_2O_2 as an environmentally more benign and less expensive oxidant.[1, 21, 25-26] The absence of Lewis acidic sites with regard to the catalyst proved beneficial due to the decreased tendency to epoxide ring-opening and therefore reduced byproduct formation. By implementation of this route,

Dow, Solvay and BASF developed the HPPO (hydrogen peroxide to propylene oxide) industrial process. Therein, methanol is preferably applied as solvent and propylene is oxidized in a slurry consisting of the catalyst and hydrogen peroxide. Separation by distillation yields the purified propylene oxide product.[1, 21]

1.3 HOMOGENEOUS EPOXIDATION CATALYSIS

In comparison to heterogeneous epoxidation catalysts, homogeneous catalysts are considerably less prevalent in industry mainly due to the challenging separability and lower overall stability. However, homogeneous transition metal complexes exhibit, in general, superior activity and selectivity toward more intricate olefinic substrates and are far less substrate limited in comparison to well-established heterogeneous systems.[27-30]

1.3.1 ORGANORHENIUM COMPLEXES IN EPOXIDATION CATALYSIS

Beside molybdenum as epoxidation catalyst metal, rhenium plays a major role in the history of epoxidation catalysis.[31-35] Especially the by far most prominent organometallic rhenium complex methyltrioxorhenium(VII) (MTO), first synthesized by Beattie and Jones in 1978, shows immense versatility as catalyst with regard to oxidation reactions.[35-38] The groups of Herrmann and Espenson, in particular, put tremendous efforts into the study of the mechanisms involved in MTO catalyzed (ep)oxidation reactions.[39-46] The mechanistic proposal of Herrmann *et al.* displays two separate catalytic cycles consisting of the formation of a mono- and bis(η_2-peroxo) complex, respectively. A concerted mechanism is suggested for both cycles A and B following the attack of an olefinic double bond onto a peroxidic oxygen of the (mono-/bis-)peroxo rhenium complex (Scheme 4).[41]
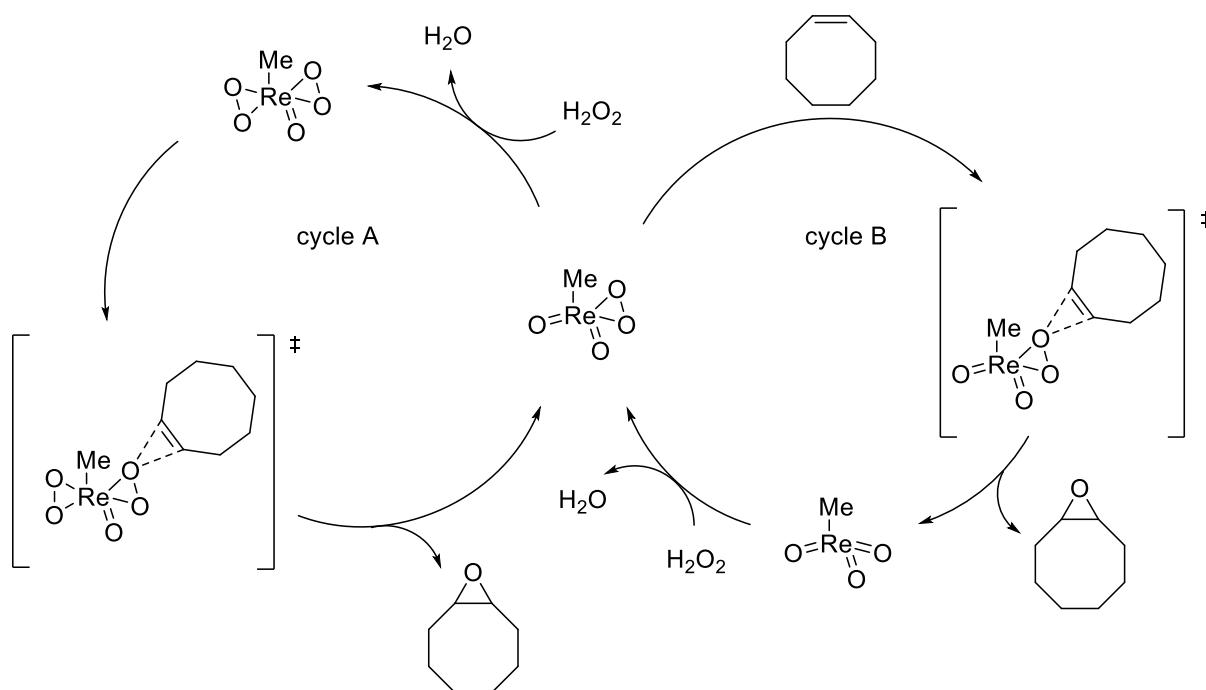
Scheme 4. Mechanism of the MTO-catalyzed epoxidation of *cis*-cyclooctene. Both mono- and bis(η_2-peroxo) species of cycles A and B are able to transfer oxygen, respectively.[41]

The applicability of organorhenium(VII) complexes as catalysts in epoxidation reactions was recently expanded to several aryl-substituted MTO derivatives. However, the critically low stability of all so far studied derivatives in comparison to the MTO benchmark is still a major challenge to overcome in order to develop promising alternatives and enhance catalytic performance.[33, 47-48]

## 1.3.2 IRON COMPLEXES IN EPOXIDATION CATALYSIS

Iron as a metal in homogeneous oxidation catalysts exhibits some major advantages in comparison to the (in academia) well-established rhenium and molybdenum based complexes. As a natural resource it is largely available, cheap and considered non-toxic, rendering iron complexes ideal alternatives in the development of novel and suitable oxidation catalysts.[16-17, 49-56] However, it is noteworthy that absolute environmental benignity is not given due to the possibility of leaching of metal ions or nanoparticles into products or waste or deficient biocompatibility of decomposed ligand systems.[57] In nature, the well-known and extensively studied methane monooxygenases (sMMO; Figure 2, right) and cytochrome P450 enzymes (CYP; Figure 2, left) both exhibit catalytically essential iron centers and play a key role in oxidative transformations in a multitude of organisms. CYP enzymes, for instance, are

potent catalysts in the oxidation of several substrates including alkenes, alkanes or aromatic compounds, formally using oxygen from air as the oxidizing agent.[58-63]
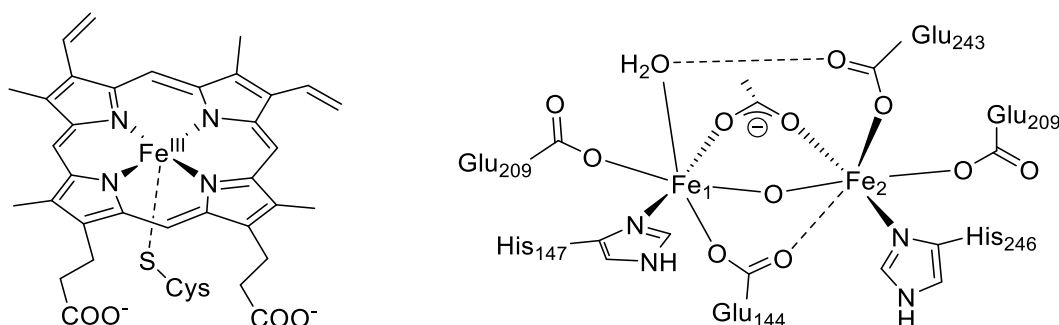
Figure 2. Chemical structures of the active sites of cytochrome P450 enzymes (left) and the methane monooxygenases sMMO subunit (right).[59, 64]

The enzyme's active site contains an Fe^{III} porphyrin cofactor. A cysteine residue is coordinated axially to the iron center (Figure 2, left), anchoring the heme-iron complex to a protein. Additionally, the electron donating properties of the *trans* located cysteine-*S* play a pivotal role in the coordination and reduction of molecular oxygen.[65] The largely accepted mechanism of the oxidation reaction cycle, developed by Groves *et al.* in the late 1970s, involves the formation of an Fe^{III}-OOH (compound 0) species either by coordination of O_2 with an one-electron reduction or coordination of H_2O_2 ("peroxide shunt" pathway) with subsequent heterolytic cleavage of the O-O bond (Scheme 5).[66-68] The formed Fe^{V}=O is considered the active species capable of oxygen transfer to an available substrate. The porphyrin ligand's ability to stabilize this high-valent iron intermediate is key to its formation and reactivity. Due to the fact that this stabilization occurs through delocalization of the positive charge onto the porphyrin scaffold, electronically this intermediate is more accurately described as an Fe^{IV}=O porphyrin radical $[(por·)Fe^{IV}=O]^+$ (compound 1).[59, 69-73]
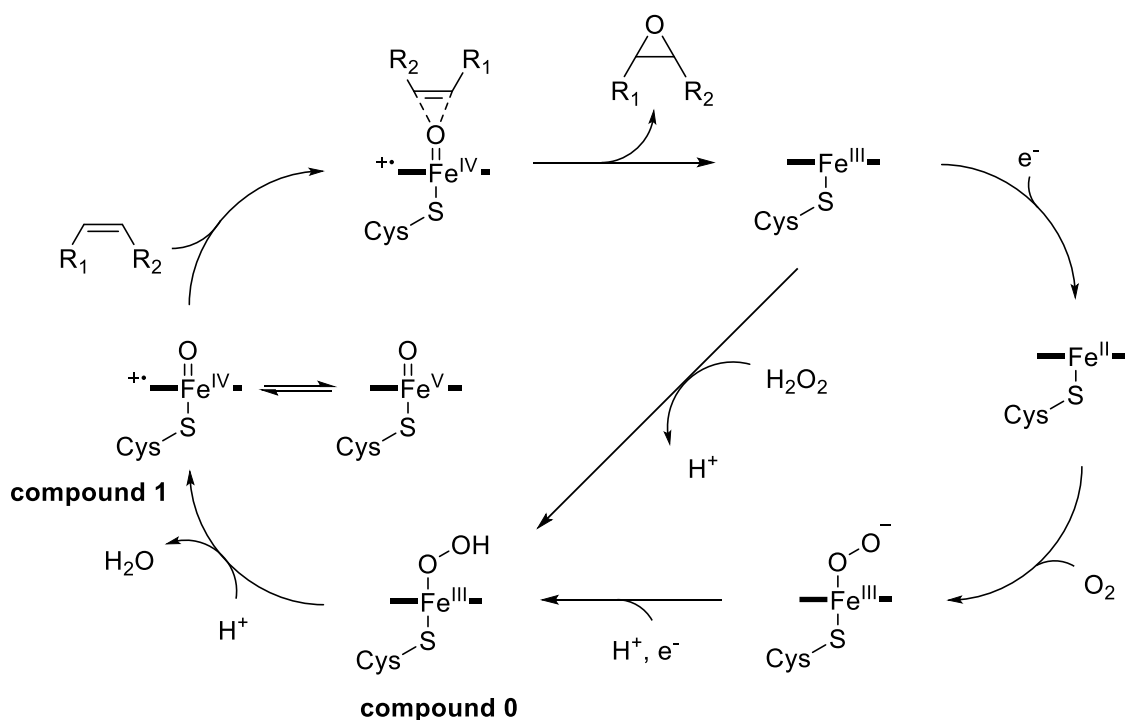
Scheme 5. Epoxidation mechanism of cytochrome P450 enzymes using O_2 as oxidant including the formation and reaction of compounds 0 and 1.[59, 70-71]

Inspired by the high selectivity and general reactivity of biological iron containing enzymes toward oxidation reactions, tremendous efforts have been directed into the development of biomimetic iron catalysts over the past 50 years. Synthesis and study of novel biomimetic catalysts serve not only the purpose of designing commercially applicable systems, but also drive the increasing understanding of the biological systems they originate in. Due to the active intermediates of synthetic complexes possibly being more stable than their biological counterparts, characterization may sometimes be considerably facilitated.[69, 74]

Biomimetic iron complexes, mimicking the structure of the active sites of naturally occurring enzymes, are generally divided into two major types: heme and non-heme compounds. While the first class includes only complexes in which the iron center is ligated by porphyrin or closely related ligand systems, non-heme iron complexes may exhibit a variety of ligands, *i.a.* bearing *N*-, *O*- or *C*-donating moieties.[17]

1.3.2.1 BIOMIMETIC HEME-IRON CATALYSTS

The first biomimetic iron-heme complexes were synthesized by Groves *et al.* in the 1970s. Their ferric porphyrin derivatives catalyzed the epoxidation of cyclohexene and

stilbene and the hydroxylation of cyclohexane and adamantine amongst others, using iodosylbenzene as oxidant.[68] Advancements in terms of stability were achieved by modification of the porphyrin scaffold. Investigation of the decomposition pathways revealed oxidation of the ligand structure to be crucial in the degradation of the catalyst.[75-76]
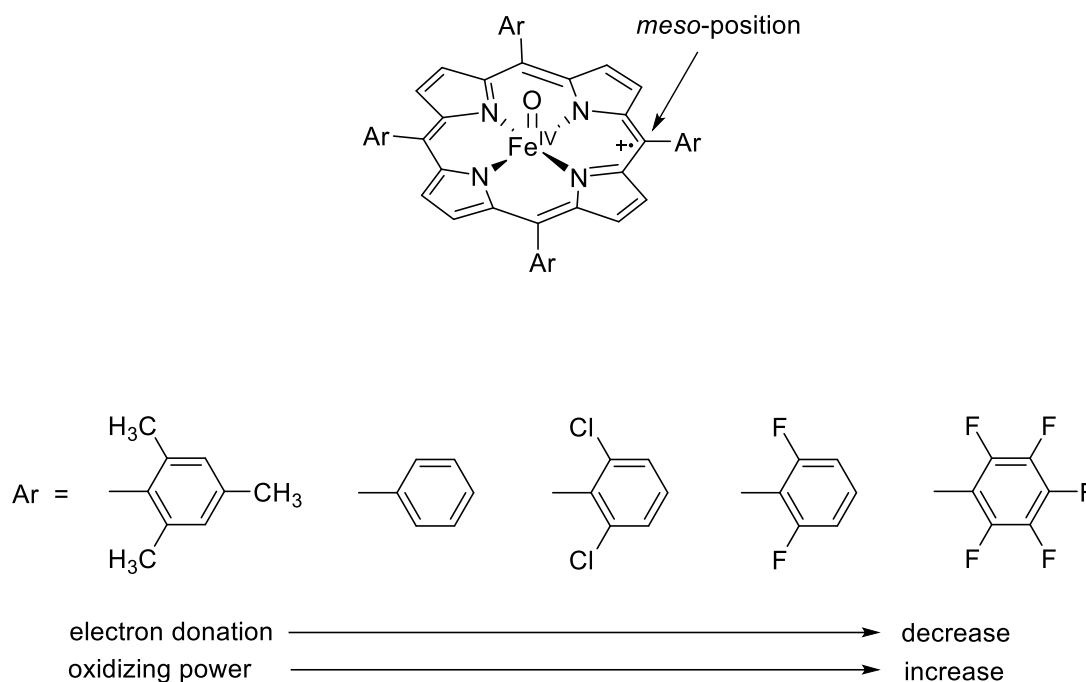

Figure 3. Possibiliy of porphyrin modification and its stereo-electronic influence on the catalytic reaction progression.[74]

Therefore, bulky substituents were introduced at the *meso*-positions in order to enhance catalytic performance by increasing stability and electrophilicity at the iron center. Arylic substituents at the *meso*-positions, for instance, inhibit the formation of catalytically rather inactive μ_2-oxo bridged dimers. Additionally, electron withdrawing substituents such as fluoride or chloride increase the catalyst's oxidizing abilities by decreasing electron density at the iron center, as illustrated in Figure 3.[54, 74, 77-78]

1.3.2.2 BIOMIMETIC NON-HEME-IRON CATALYSTS

In contrast to iron-heme complexes, which comprise only of iron compounds bearing porphyrin or closely related ligands, the field of non-heme iron complexes is considerably broader. Although the structures of non-heme ligands include a variety of donors, *e.g. N*-, *O*- or *C*-, tetradentate exclusively *N*-donor ligated iron complexes are by far the most extensively studied catalysts with regard to their reaction mechanism

and catalytic applicability.[54, 74] The first non-heme iron epoxidation catalyst was reported in 1986 by Que and coworkers. As it was inspired by the sMMO subunit, the catalyst consisted of two iron centers bridged by a phenolate moiety and two acetates.[79] Five years later, the first non-heme iron epoxidation catalyst with only one iron center was reported by Nam *et al.* (Figure 4).[80]
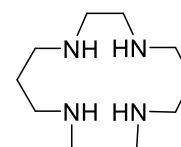
trans-Fe^{II}(cyclam)   *cis*-Fe^{II}(BPMEN)(OTf)$_2$ *cis*-Fe^{II}(PyTACN)(OTf)$_2$
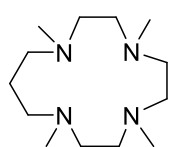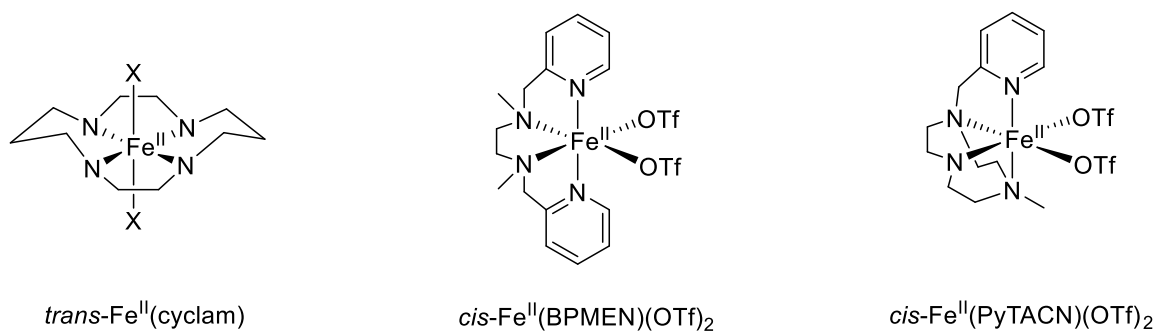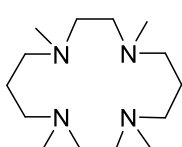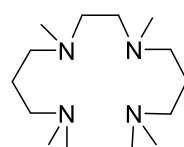
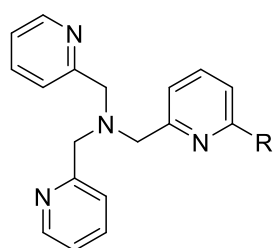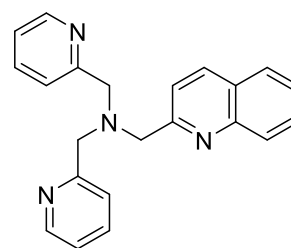TATM   TMC   TAPM   TAPH

R-TPA (R = H, Me)   QBPA
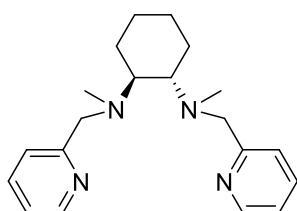
BPMCN   PDP
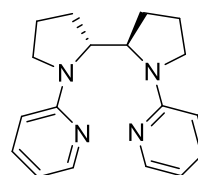
Figure 4. Examples of non-heme iron oxidation catalysts bearing *cis* and *trans* labile coordination sites (top) and chemical structures of various ligand motifs for non-heme metal complexes (bottom).[74, 80-82]

This Fe^{II} cyclam complex (cyclam = 1,4,8,11-tetraazacyclotetradecane) proved to be an efficient catalyst in the epoxidation of various olefins (*e.g.* cyclohexene, 1-octene,

trans/cis-stilbene) with turnover numbers of up to 20 using hydrogen peroxide (30% aqueous solution) as oxidant.[80] In the following decades, a variety of non-heme iron complexes bearing mostly tetradentate amino-pyridine ligands (Figure 4) were introduced in order to investigate their structure-reactivity relationship.[54, 83-94] Especially the groups of Nam, Que and Valentine took the leading role in exploring the mechanisms involved in Fe[II] catalyzed epoxidation reactions and the particular role of hydrogen peroxide.[57, 74, 80, 85, 88, 94] The more detailed picture of the influence of the electronic and overall ligand structure proved to be key in the targeted development of new catalysts for specific oxidation reaction types and substrate scope. Based on the ground-breaking work of Nam, Que and Valentine and their groups, in 2007 Chen and White were able to report the selective oxidation of intricate and functionalized organic substrates with hydrogen peroxide and even the stereoselective oxidation of natural products using a chiral *N,N'*-Bis(2-pyridylmethyl)-2,2'-bipyrrolidine Fe[II] complex.[95]

However, despite of the unambiguous progress in understanding and improving non-heme iron catalysts, they still fall short in terms of efficiency and stability under oxidative conditions if compared to their naturally occurring archetypes.[54] Especially the fact that oxygen is not utilizable as oxidant demonstrates how much room for improvement there still is.

1.3.2.3 MECHANISTIC CONSIDERATIONS WITH REGARD TO IRON-BASED OXIDATION CATALYSIS

As previously mentioned, the groups of Que, Nam and Valentine played a key role in unravelling the mechanistic modes of action in Fe[II]-catalyzed oxidation using hydrogen peroxide as oxidant. However, the origins in this field of chemistry reach back as far as the late 1800s, when Henry Fenton described the oxidation of tartaric acid in presence of iron.[96] The nowadays well-known Fenton's reagent is a solution containing hydrogen peroxide and a simple iron salt, typically $FeSO_4$, capable of oxidizing a wide range of organic molecules.[97] For example, it has been used to oxidize contaminants and waste waters or to destroy and quench toxic compounds such as trichloroethylene or tetrachloroethylene.[98] In 1934, Haber and Weiss reached a milestone by identifying the hydroxyl radical to be the actual oxidant in Fenton-type reagents, formed upon reaction of hydrogen peroxide with iron cations (Scheme 6).[99]

$$Fe^{II} + H_2O_2 \longrightarrow Fe^{III} + {}^{\cdot}OH + {}^{-}OH$$

$$Fe^{III} + H_2O_2 \longrightarrow Fe^{II} + {}^{\cdot}OOH + H^+$$
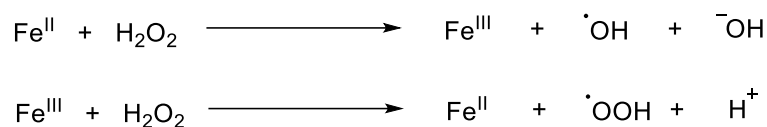
Scheme 6. Reactions of Fe^{II} and Fe^{III} ions with hydrogen peroxide and the formation of a hydroxyl radical as a potent oxidant.[99]

In reactions with organic substrates the hydroxyl radical is able to initiate radical chain reactions resulting in the formation of alkyl radicals, which can recombine or react with dioxygen due to their longevity compared to the original hydroxyl radicals. These Fenton-type radical reactions result in a drastic loss in selectivity and are therefore attempted to be suppressed with regard to the development of biomimetic iron catalysts for oxidation reactions.[54, 100] In both heme-iron and non-heme-iron catalysts, the catalytic cycle involves the formation of a ferric peroxide species upon reaction with hydrogen peroxide (Scheme 7).[74, 101]
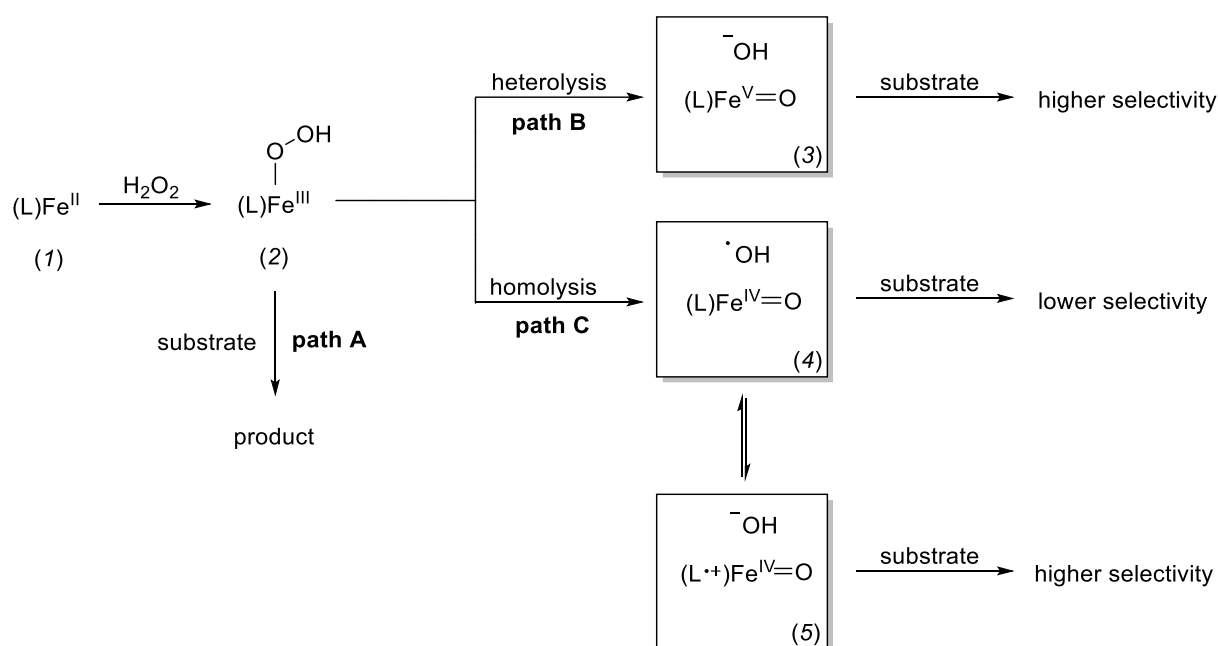
Scheme 7. Different pathways of iron oxo active species formation in the reaction of biomimetic iron compounds with hydrogen peroxide.[74, 101]

This intermediate (*2*) is either able to react directly with a substrate (path A) or undergoes heterolytic (path B) or homolytic (path C) O-O bond cleavage. The resulting high-valent (L)Fe=O (*3* or *4*) species in both cases consequentially differ with regard to their electronic structure. In contrast to path B, the formation of (L)Fe^{IV}=O (*4*; path C) features the generation of a hydroxyl radical prone to act as an initiator for radical chain reactions, subsequently leading to lower selectivity with regard to the targeted

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oxidation product. Heterolytic O-O bond cleavage (path C) prevents hydroxyl radical generation due to the formation of a (L)Fe^V=O species (*3*) accompanied by a hydroxyl anion not capable of performing radical chain reaction initiation, rendering path C more selective. Heavily depending on the electronic structure of the iron center surrounding ligand system, the ideal strategy in iron oxidation catalyst development includes pushing the respective mechanism toward path C and (L)Fe^V=O (*3*) formation eliminating the possibility of generating radicals. However, the capability of some ligands to distribute electron density across the ligand system allows the formation of a (L·+)Fe^{IV}=O species (*5*) without generating a hydroxyl radical, being one reason for the high selectivity of CYP enzyme catalyzed oxidation reactions.[54, 74, 85]

Additional to the mechanisms described in Scheme 7, a water- and acid-assisted pathway in the formation of the active iron oxo species was proposed by Que *et al.*, however only applicable in reactions with iron catalysts bearing *cis* labile coordination sites (Scheme 8).[54, 85, 91-92] After formation of the Fe^{III} hydroperoxo compound, coordination of a water molecule or acetic acid leads to a 5- or 6-membered ring structured intermediate, respectively.
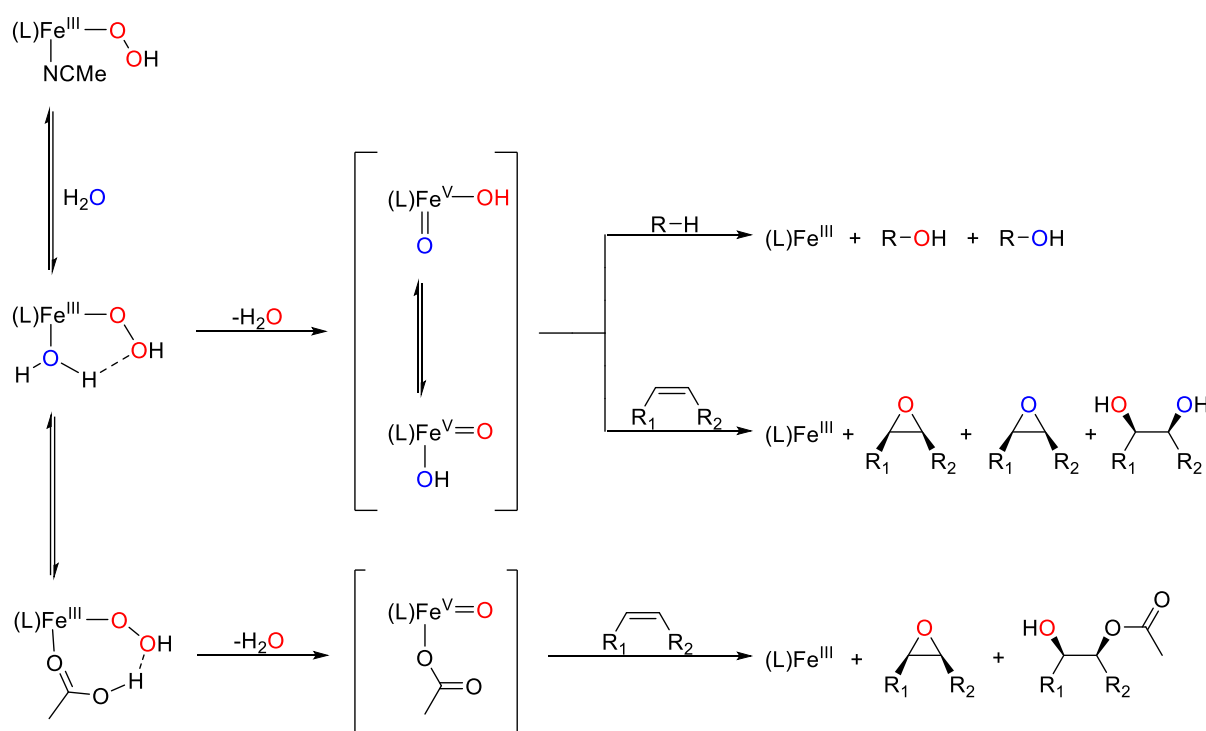
Scheme 8. Water- and acid-assisted pathways of Fe^V oxo hydroxo/acetate formation and their reactivity toward alkanes and olefins (blue oxygen: ^{18}O-labeled H_2O; red oxygen: unlabeled).[54]

In case of the solely water-assisted pathway, heterolytic fission of H_2O forms a $(L)Fe^V$ oxo hydroxo active species capable of epoxidation and alkyl hydroxylation. By using ^{18}O labeled water, it was demonstrated that the $(L)Fe^V$ oxo hydroxo species occurs in a mesomeric equilibrium due to the incorporation of both oxygen isotopes in the respective oxidation products (Scheme 8, blue and red).[85, 102] Particularly instructive was the formation of a *cis*-diol from an alkene containing one labeled and one unlabeled oxygen, demonstrating the crucial role a proximal proton donor (metal-bound water) plays in promoting heterolytic O-O bond cleavage. The acid-assisted pathway, in contrast, does not offer a mesomeric equilibrium of the formed $(L)Fe^V$ oxo acetate species, however the proximal proton provided by the acetic acid is suggested to promote the heterolytic H_2O elimination more effectively compared to water.[54, 85, 91, 94, 102-103]

Brønsted acid promoted O-O bond cleavage of the previously formed Fe^{III} hydroperoxo compound, however, is not limited to coordinating Brønsted acids (*e.g.* acetic acid).[104] Non-coordinating Brønsted acids like $HClO_4$ have been shown to accelerate the $Fe^{IV/V}=O$ active species formation as well, solely providing H^+ ions in solution. These readily protonate the Fe^{III} hydroperoxo compound ($\rightarrow Fe^{III}\text{-}O\text{-}OH_2^+$) resulting in the elimination of H_2O.[104-105] In recent years, additional to Brønsted acids, various Lewis acids with scandium triflate ($Sc(OTf)_3$) being the most widely applied emerged as alternatives to enhance catalytic performance of iron (and manganese) catalysts in the hydroxylation of cyclohexane and benzene and the epoxidation of olefins.[104-110]

Reflecting the role of Ca^{2+} in combination with a high-valent oxomanganese cluster species involved in the photosystem II, Sc^{3+} (or other Lewis acidic metal ions LA^{n+}) is supposed to interact with non-heme iron (or manganese) complexes during the catalytic reaction similar to Brønsted acids.[104, 106, 111-112] However, the innocence of Sc^{3+} with regard to its particular function is still highly debated.[113] Beside the possibility of LA^{n+} merely generating protons in the presence of water or directly cleaving a hydroxyl group from the Fe^{III}-hydroperoxo compound, crystal structure analyses and molecular modelling studies found evidence for Sc^{3+} binding to the oxygen or nitrogen of several oxo-iron,[106, 114] -cobalt[115-116] and nitrene-copper[117] complexes, which could have significant impact on the electronic environment of the metal center and therefore confer considerable differences with regard to catalytic behavior. Furthermore, the metal center oxidation state of these species is still not entirely clear

raising doubts about the prevailing catalytic mechanism, if Lewis acids like Sc^{3+} are involved. Mössbauer spectroscopy could unequivocally solve these issues, however, such species happen to be highly elusive.[113, 115, 118]

1.3.2.4 *N*-HETEROCYCLIC CARBENE COMPLEXES IN OXIDATION CATALYSIS

In recent years, *N*-heterocyclic carbenes (NHCs) emerged as ligand alternatives to the widely studied and applied purely *N*-donating ligands introduced by Que, Nam and others.[17, 119-120] In oxidation catalysis non-heme iron NHC complexes show great potential so far.[17, 53, 121-122] Structurally, these complexes mostly comprise of tetradentate ligand scaffolds bearing four NHCs or a mixture of two NHCs and two *N*-donating moieties. Two weakly coordinating ancillary ligands such as acetonitrile or triflate complete the octahedral structure of the majority of reported compounds.[17]

The first *N*-heterocyclic carbene metal complexes were synthesized independently by Wanzlick and Öfele in 1968 (Figure 5).[123-124] However, due to their highly unstable and elusive nature, NHCs were merely regarded as "lab curiosities" for many years before Arduengo *et al.* isolated the first "free" and thermally stable NHC in 1991 (Figure 5).[125] Over the last three decades, NHCs started to gain increasing interest in homogeneous catalysis due to their rich coordination chemistry for a variety of transition metals and their unique structural and electronic properties.[17, 119, 126]

Wanzlick 1968   Öfele 1968   Arduengo 1991
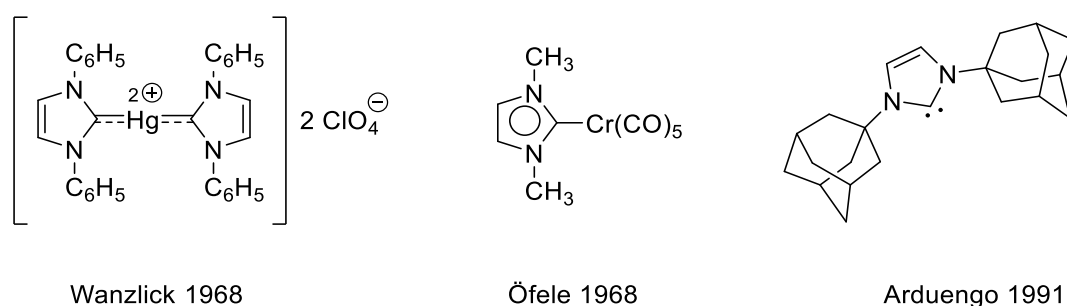
Figure 5. Chemical structures of the first metal NHC complexes reported by Wanzlick and Öfele and the structure of the first "free" NHC synthesized by Arduengo.[123-125]

In general, a *N*-heterocyclic carbene consists of a ring structure containing a carbene and at least one nitrogen atom, forming a heterocycle, in most cases based on an imidazole scaffold.[120] A carbene refers to a divalent carbon atom possessing six valence electrons. This vacancy of carbene atoms, in comparison to tetra-valent carbon atoms which possess eight valence electrons, allows two different electronic configurations. The energetically more favorable triplet ground-state with two singly

occupied sp^3 hybrid orbitals is common with most carbene species. *N*-heterocyclic carbenes, however, exhibit a singlet ground-state electronic configuration, which is attributed to the stabilizing effect of the adjacent nitrogen atom.[127-128] Therein, both electrons are paired in one sp^2 hybrid orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) exhibits properties of an empty π-orbital. The adjacent nitrogen is responsible for the stabilization of the HOMO by withdrawing σ-electron density, while also donating π-electron density into the empty LUMO, also referred to as "push-pull" effect (Figure 6).[119-120, 126]
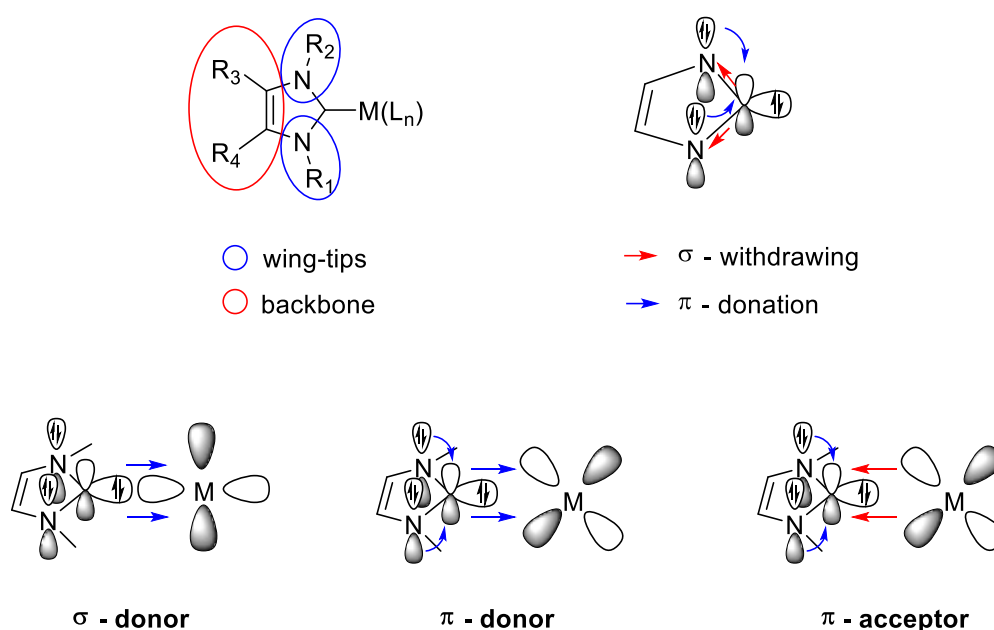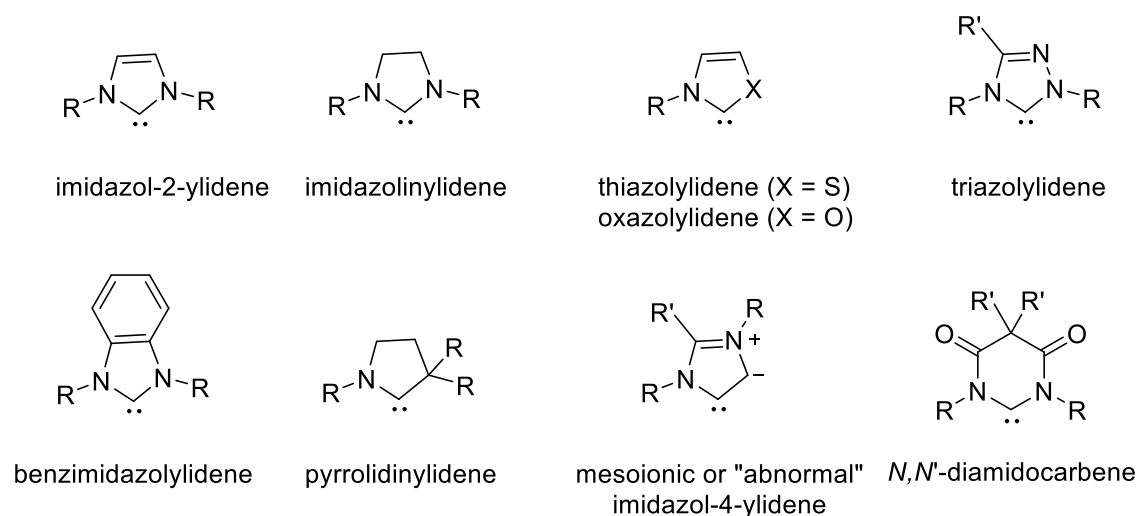

Figure 6. Modification opportunities at the NHC scaffold and the unique bonding properties of NHCs when coordinated to a metal center.[129-130]

Therefore, NHCs offer strong σ-donor abilities and react as nucleophiles making them capable of stabilizing metal ions in high oxidation states (*e.g.* iron oxo). The partial double bond character of the metal-NHC bond also renders NHCs less susceptible toward dissociation and subsequent oxidation compared to phosphines, for instance. The additional ability to act as a π-donor or π-acceptor (Figure 6) separates NHCs from other known carbene-type ligands such as Fischer or Schrock carbenes, which are rather limited to σ-donation.[131-132] Whether a NHC ligand acts as a π-donor or π-acceptor depends heavily on the electronic characteristics of both the NHC and the ligated metal and the presence of other metal coordinated ligands and is therefore to some degree controllable. Combined with the synthetically feasible modifiability with regard to wing-tip and backbone substituents in order to tailor electronic and steric

properties (Figure 6), NHCs give access to a wide range of purposively tuned metal complexes for a variety of applications.[119, 126, 129, 133]

In addition to the most widely applied common imidazolylidene type of NHCs, several derivatives have gained increasing interest in recent years as ligand alternatives in various homogeneous catalysts (Figure 7).[120, 126, 134-135] The mesoionic or "abnormal" NHCs, in particular, are generally stronger electron donors in comparison to the classic imidazol-2-ylidene NHCs and therefore may contribute to even better stabilization of metals in high oxidation states.[136-137]


imidazol-2-ylidene   imidazolinylidene   thiazolylidene (X = S)   triazolylidene
                                           oxazolylidene (X = O)

benzimidazolylidene   pyrrolidinylidene   mesoionic or "abnormal"   N,N'-diamidocarbene
                                            imidazol-4-ylidene

Figure 7. Examples of N-heterocyclic carbene motifs with varying electron donor properties.[120]

The most widely reported applications of N-heterocyclic carbene metal complexes in homogeneous catalysis are cross-coupling reactions (e.g. Pd-NHCs),[138-140] olefin metathesis (e.g. Grubbs 3rd generation)[141-142] and asymmetric catalysis[143] by introducing chiral elements into the NHC scaffold. However, employing metal NHC complexes in oxidation catalysis has been gaining increasing interest over the last years.[120, 144-145] Therein, mostly palladium-, ruthenium- and iridium-based NHC complexes showed promising performance in reactions such as alcohol oxidation, Wacker-type oxidation and methane oxidation using Pd-NHCs, alkane oxidation and Oppenauer oxidation using Ir-NHCs and oxidative alkene cleavage using Ru-NHCs as catalysts.[146]

Despite the first Fe-NHC complex already being reported in 1969, iron N-heterocyclic carbene complexes only started to receive attention since the 1990s, when their first catalytic applications were uncovered.[147] Over the last two decades, the number of

publications on Fe-NHC complexes and especially their catalytic application has been increasing steadily.[17, 130] Nowadays, several routes to access Fe-NHC complexes are known. The most widely applied methods include transmetallation from an easily accessible Ag- or Mg-NHC complex by addition of an iron precursor (Scheme 9, a), using NHC dimers and an iron precursor (b), deprotonation of an imidazolium salt with a base to create a "free" carbene followed by *in-situ* addition of an iron halide (c) or directly reacting an imidazolium salt with an iron precursor containing an internal base (*e.g.* Fe(btsa)$_2$, btsa = bis(trimethylsilyl)amide; d).[130, 148]
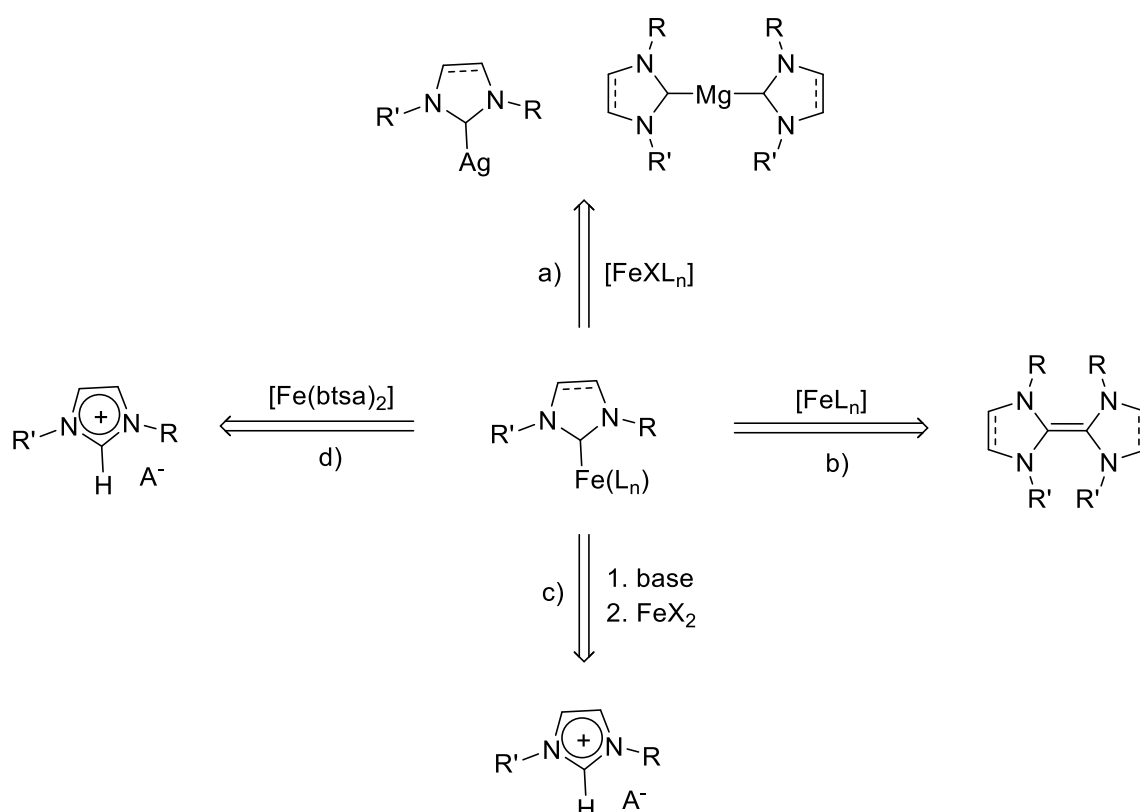
Scheme 9. Examples of the most widely applied synthetic routes to Fe-NHC complexes.[130]

In contrast to the early Fe-NHC complexes, bearing mostly mono- and bidentate carbenes, the past decade showed an increasing number of chelating polydentate ligands and macrocycles.[149-152] Especially cyclic and acyclic tetradentate ligand motifs have been receiving increasing attention, partly due to their structural similarities with respect to the purely *N*-donating non-heme iron complexes established by Que, Nam and others.[54, 74, 130] Also, the presence of two accessible coordination sites in an octahedral configuration allows the adoption of prevalent reaction mechanisms.

The first macrocyclic tetracarbene iron complex and its successful application in the aziridination of olefins was reported by Cramer and Jenkins in 2011.[153] Their catalytic results and the isolation and characterization of the first $Fe^{IV}=O$ compound ligated by a tetra-NHC scaffold by Meyer and coworkers in 2013 proved tetra-NHCs to be a promising ligand class in account with being able to stabilize iron intermediates in high oxidation states and therefore potentially expedient in oxidation catalysis.[153-154] In the following years, Kühn and coworkers reported the synthesis of several new *N*-heterocyclic carbene Fe^{II} complexes (Figure 8; **1**, **2** and **3**) comprising of acyclic tetradentate ligand motifs bearing two imidazolylidene *C*-donors and two pyridine *N*-donor moieties, among them the first Fe^{II}-NHC complex (**1**) applied in olefin epoxidation catalysis.[122, 155-156] Complexes **1** and **2** exhibit a planar coordination sphere with *trans* labile coordination sites due to the rather rigid structure of the tetradentate ligand induced by the short NHC bridges (**1**, methylene; **2**, ethylene). The C_3-membered propylene bridges of complex **3**, in contrast, allow for a more flexible arrangement resulting in a sawhorse-type configuration including *cis* labile coordination sites (Figure 8).
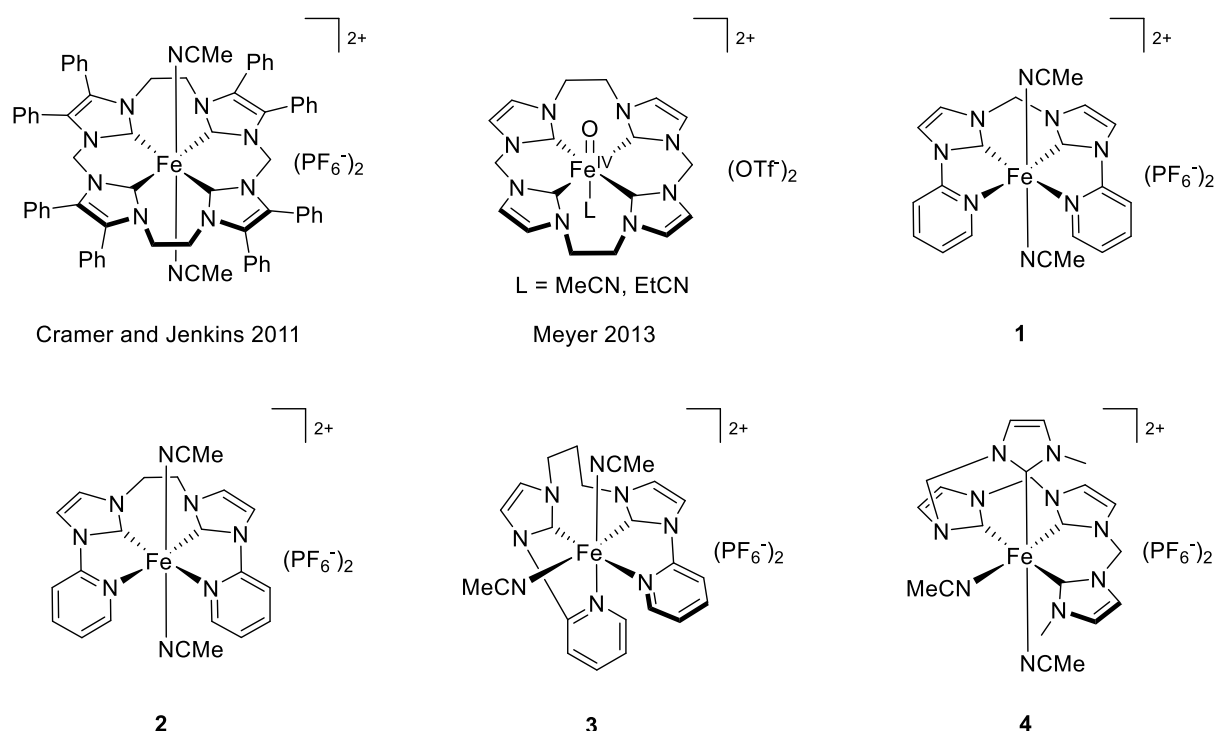
Figure 8. Chemical structures of cyclic and acyclic tetradentate Fe-NHC complexes reported by Jenkins, Meyer and Kühn.[122, 153-156]

The evaluation of complex **1** as an epoxidation catalyst was performed using *cis*-cyclooctene as a model substrate and hydrogen peroxide as oxidant. The nearly

selective (>99%) reaction reached its maximum conversion of 92% after five minutes at ambient conditions using 2.0 mol% of the catalyst. Kinetic investigation resulted in turnover frequencies (TOF) of up to 2,600 h^{-1}, which at the time were among the highest reported values under acid-free conditions, however, is considerably lower than the by Que *et al.* reported TOF of 25,200 h^{-1} for the [Fe(BPMEN)(MeCN)$_2$]$^{2+}$ catalyst (*cf.* Figure 4) in presence of acetic acid.[17, 52, 86, 91, 122, 157-158] Additionally, it was found that lowered reaction temperatures resulted in higher maximum conversions due to the fact that degradation of the catalyst is significantly more impacted by temperature than the epoxidation reaction. Prompted by the promising results in the catalytic application of catalyst **1**, the focus of Kühn's group shifted toward the development of purely *C*-donating tetradentate ligand scaffolds (CCCC) for the application in Fe^{II} catalysts.[156, 159] The acyclic iron tetra-NHC complex **4** (Figure 8) exhibits a sawhorse-type structure with *cis* labile coordination sites. The twistable methylene bridges between all NHC moieties allow for a tilting of the ligand scaffold, subsequently resulting in the observed coordination arrangement. Fe^{II} complex **5** (Scheme 10), in contrast, is restricted to a planar ligand coordination due to the cyclic structure in consequence of the rather rigid methylene bridges of the tetra-NHC ligand.[121, 159]
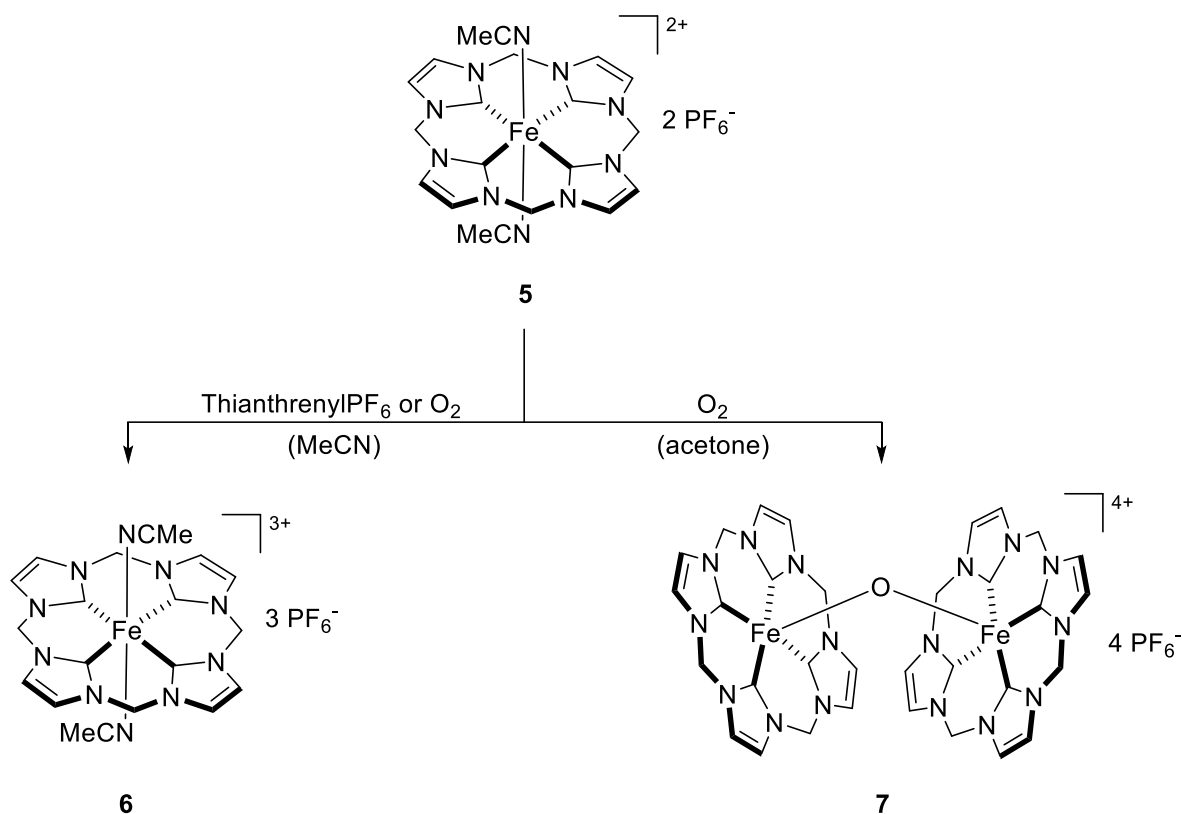
Scheme 10. Reactivity of a cyclic Fe^{II} tetra-NHC complex to form the respective Fe^{III} compound or an oxo-bridged Fe^{III}-O-Fe^{III} dimer.[121, 159]

Complex **5** was intended to closely resemble the structure of the active sites of heme-based enzymes (CYP). Under the same reaction conditions used for catalyst **1** (Figure 8), 82% conversion (selectivity >99%) is reached after five minutes under ambient conditions using 0.25 mol% of the Fe^{II} catalyst **5**. If the respective Fe^{III} catalyst **6** is employed, conversion increases to 96% at 0.25 mol% catalyst concentration due to a skipping of the initial step of one-electron $Fe^{II} \rightarrow Fe^{III}$ oxidation (induction phase) by hydrogen peroxide, also resulting in a rise in initial activity with TOFs up to 183,000 h^{-1} determined for catalyst **6**. Catalyst **5**, in comparison, exhibits a significantly lower TOF of 50,000 h^{-1}, which however, is still considerably higher than for any reported iron catalyst in the epoxidation of *cis*-cyclooctene.[17, 121]

Despite the significantly improved activity of catalysts **5** and **6** in comparison to all other reported non-heme iron epoxidation catalysts, their limited stability under oxidative conditions still presents a major challenge on the path to sustainable application. Well-studied decomposition pathways of non-heme iron oxidation catalysts include oxidation or dissociation of the ligand structure or formation of an inactive oxo-bridged Fe^{III}-O-Fe^{III} dimer, which for instance, is also formed of complex **5** in acetone under aerobic conditions (**7**, Scheme 10).[160-168] In addition, some mechanistic implications are still elusive and the substrate scope of most non-heme iron catalysts remains rather limited, deferring real-life application for industrially relevant processes into the future.

2 OBJECTIVE

The unprecedented high activity of the cyclic iron tetra-NHC complex **1** (Figure 9) in epoxidation catalysis reported by Kühn and coworkers in 2015 represents a promising starting point for further investigation and the development and catalytic evaluation of structurally related derivatives.[121]
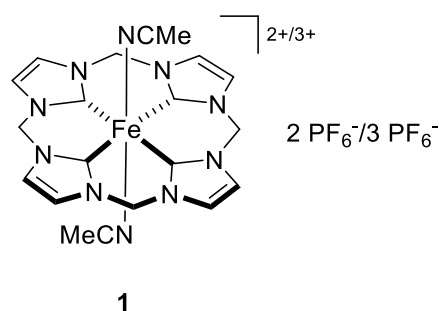
Figure 9. Chemical structure of the cyclic tetra-NHC Fe$^{II/III}$ complex **1**.

Only a few of the tetradentate iron NHC complexes synthesized so far have been investigated with regard to their catalytic applicability in oxidation reactions. Therefore, in addition to designing novel derivatives, systematic evaluation and comparison of existing complexes with structurally related compounds is imperative in order to increase our understanding of the particular electronic effects of different tetradentate NHC ligand motifs on the catalytic performance of the respective iron complexes. In particular, modification of the ligand structure of complex **1** by introducing electron withdrawing and electron donating substituents could provide valuable information with regard to their impact on the electronic properties of the iron center and subsequently on the stability and activity of the catalyst.

Furthermore, the beneficial effects of acidic additives known in the literature should be studied when applied in oxidation reactions catalyzed by iron NHC catalysts. Lastly, catalyst degradation pathways should be investigated by identifying possible decomposition products formed under catalytic conditions.

3 RESULTS – PUBLICATION SUMMARIES

3.1 Mixed tetradentate NHC/1,2,3-triazole iron complexes bearing *cis* labile coordination sites as highly active catalysts in Lewis and Brønsted acid mediated olefin epoxidation

Jonas F. Schlagintweit,[#] **Florian Dyckhoff**,[#] Linda Nguyen, Christian H.G. Jakob, Robert M. Reich and Fritz E. Kühn

Homogeneous epoxidation catalysis using iron compounds has largely been focusing on complexes bearing purely *N*-donating pyridine derived ligand motifs.[17, 74] In this article, the first mixed tetradentate NHC/1,2,3-triazole iron complexes studied in olefin epoxidation catalysis are reported. 1,2,3-triazle moieties are exploited as *N*-donors (N_{trz}) and form, in combination with the imidazol-2-ylidene *C*-donors (C_{im}) a $N_{trz}C_{im}C_{im}N_{trz}$ coordination arrangement. The reported derivatives, differing only with regard to the organic substituents at the triazole's N-3 positions (diisopropylphenyl **3** and benzyl **4**) exhibit a sawhorse-type configuration and therefore *cis* labile coordination sites.
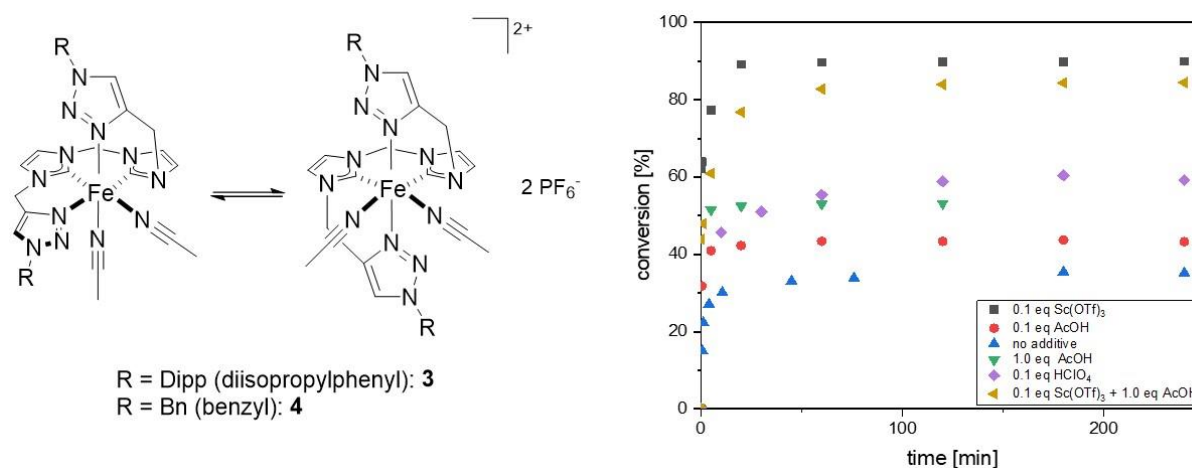
Figure 10. Chemical structures of complexes **3** and **4** (left) and catalytic impact of various acidic additives on the performance of complex **4** (right).

Kinetic studies demonstrate the unambiguous difference of both catalysts **3** and **4** with regard to their performance in the epoxidation of *cis*-cyclooctene, using hydrogen

peroxide as oxidant. The benzyl substituted derivative **4** exceeds the performance of **3** in terms of activity, stability and selectivity, proving the considerable influence of the substituents' electronic properties on the catalytically active iron center. Addition of various Brønsted (AcOH, $HClO_4$) and Lewis ($Sc(OTf)_3$) acids to the reaction showed that the beneficial effects of acidic support also apply to Fe-NHC complexes in epoxidation reactions. Furthermore, catalyst **4** enables the epoxidation of more challenging substrates, such as allyl alcohol and allyl chloride with remarkable selectivities of 84% and >99%, respectively. Under optimized conditions with support of AcOH, catalyst **4** exhibits unprecedented activity (TOF up to 76,000 h^{-1}) and notable stability with a TON of 200 at 20°C. Preliminary decomposition studies under oxidative conditions *via* ESI-MS revealed oxidation of the CH_2-bridges and NHC protonation to be potential deactivation pathways, providing leads for future catalyst design in order to improve stability.

3.2 Pushing the limits of activity and stability: the effects of Lewis acids on non-heme iron-NHC epoxidation catalysts

Florian Dyckhoff,[#] Jonas F. Schlagintweit,[#] Robert M. Reich and Fritz E. Kühn

In this communication, the influence of Lewis acidic additives on the performance of a cyclic tetra-NHC complex in epoxidation reactions using hydrogen peroxide as oxidant was studied. Therein, various lanthanoid (Ce^{4+}, Ce^{3+}, Sm^{3+}, Nd^{3+}, Dy^{3+}) as well as first (Sc^{3+}, Fe^{3+}) and second (Y^{3+}) row metal salts were applied as Lewis acidic additives to promote the active species formation of the iron catalyst. The employed iron complex reportedly exhibits the by far highest activity in the epoxidation of *cis*-cyclooctene of any literature known non-heme iron complex, even without the presence of a supporting acidic additive. Turnover frequencies (TOF) of 50,000 h^{-1} for the Fe^{II} complex **1** and up to 183,000 h^{-1} were reported when Fe^{III} complex **2** is employed as catalyst (Figure 11).[121]
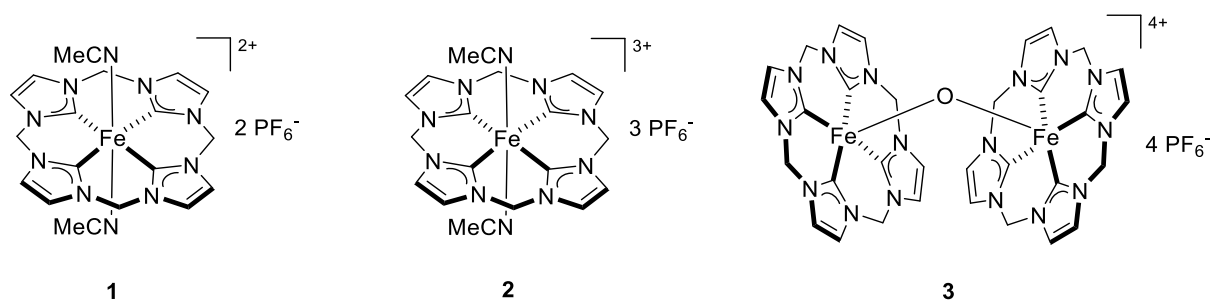
Figure 11. Chemical structures of the cyclic tetra-NHC Fe^{II} (**1**) and Fe^{III} (**2**) complexes and of the oxo-bridged Fe^{III}-O-Fe^{III} dimer (**3**).

This notable difference in initial reaction rates is attributed to the short induction period of the essential one-electron oxidation of Fe^{II} pre-catalyst **1** to the active Fe^{III} catalyst **2**. In presence of a strong Lewis acid (Ce^{4+}, Fe^{3+}, Sc^{3+}), however, this oxidation step occurs instantaneously upon the initiation of the reaction, resulting in coinciding initial reaction rates of both (pre-)catalysts **1** and **2**. The additional facilitation of acid-assisted O-O bond cleavage of the (L)Fe^{III}-OOH intermediate leads to significantly increased TOFs of up to 410,000 h^{-1}, which is more than 15-fold higher than for any other reported

non-heme iron catalyst in the epoxidation of *cis*-cyclooctene. Furthermore, employing the oxo-bridged Fe^{III}-O-Fe^{III} dimer, which is formed from **1** or **2** under oxidative conditions and considered an inactive deactivation product, yields nearly identical initial reaction rates and final conversions as complexes **1** and **2**. Therefore, one crucial deactivation pathway of dimer **3** formation during the catalytic reaction can easily be prevented by addition of a strong Lewis acid. Additionally, both transformations of Lewis acid assisted oxidation of pre-catalyst **1** and the reactivation of the rather inactive dimer **3** to the active catalyst **2** were evidenced by UV/Vis spectroscopic studies, respectively.

3.3 Synthesis, characterization and application of organo-rhenium(VII) trioxides in metathesis reactions and epoxidation catalysis

Florian Dyckhoff,[#] Su Li,[#] Robert M. Reich, Benjamin J. Hofmann, Eberhardt Herdtweck and Fritz E. Kühn

[#] F. Dyckhoff and S. Li equally contributed to this work.

In oxidation catalysis, methyl trioxorhenium(VII) (MTO) is well-established in academia as an efficient catalyst for a variety of reactions including olefin oxidation, olefin metathesis, aldehyde olefination and arene oxidation.[35, 37-38] Arylic derivatives of MTO, however, have not received much attention so far.[47] In this article, the synthesis and characterization of several novel aryl-trioxorhenium(VII) complexes and an amido-trioxorhenium(VII) complex are reported. Due to the Lewis acidity of the Re^{VII} center being one of the key reasons for the catalytic performance of MTO, all reported aryl-trioxorhenium(VII) compounds bear electron withdrawing substituents to a variable extent. Complexes **1b-3b** were characterized by means of NMR and IR spectroscopic techniques in order to investigate the particular effects of the varying degree of substitution at the aryl moieties on rhenium-ligand bond lengths and overall electronic structure.
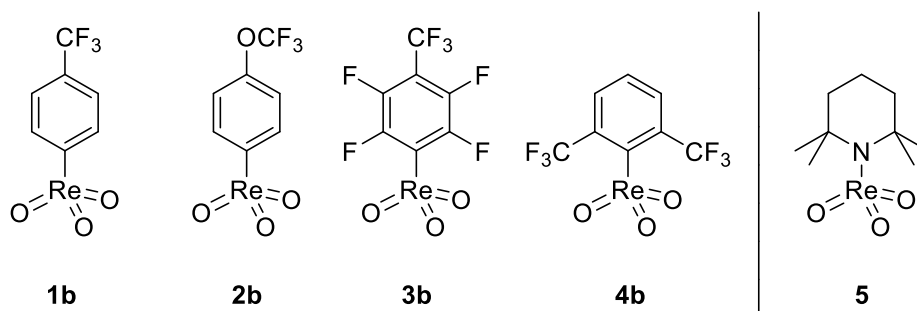
Figure 12. Chemical structures of aryl-trioxorhenium(VII) complexes **1b-4b** and amido-trioxorhenium(VII) complex **5**.

The results confirm the rising Lewis acidity at the Re^{VII} center in the order of an increasing number of electron withdrawing substituents at the arylic ring.

Complexes **1b**, **2b** and **3b** were successfully applied in the epoxidation of *cis*-cyclooctene using TBHP (*tert*-butyl hydroperoxide) as oxidant resulting in turnover

frequencies of up to 1,420 h^{-1} at 55°C. However, a distinct correlation between an increase of Lewis acidity at the Re^{VII} center and improved catalytic performance could not be shown. Additionally, **1b** and **5** proved to be suitable catalysts in the ROMP (ring-opening metathesis polymerization) of norbornene and **1b** showed promising performance in the self-metathesis of 1-hexene using Et$_2$AlCl as a supporting additive, demonstrating that the remarkable catalytic versatility of organorhenium(VII) complexes is not limited to MTO.

3.4 Exploring different coordination modes of the first tetradentate NHC/1,2,3-triazole hybrid ligand for group 10 complexes

Jonas F. Schlagintweit, Linda Nguyen, **Florian Dyckhoff**, Felix Kaiser, Robert M. Reich and Fritz E. Kühn

In this article, the first mixed tetradentate NHC/1,2,3-triazole hybrid ligand and its respective Pd^{II}, Pt^{II} and Ni^{II} complexes are reported. The ligand consists of two *C*-donating imidazol-2-ylidene (C_{im}) and two *N*-donating 1,2,3-triazole (N_{trz}) moieties allowing for a $N_{trz}C_{im}C_{im}N_{trz}$ coordination sphere. As d^{10} metals, Pd^{II}, Pt^{II} and Ni^{II} favor a square planar coordination geometry, rendering two different coordination modes feasible: Coordination of one ligand to the metal center with the above mentioned $N_{trz}C_{im}C_{im}N_{trz}$ donation system or involvement of a second identical ligand resulting in an exclusively NHC donation system ($C_{im}C_{im}C_{im}C_{im}$), as illustrated in Figure 13.
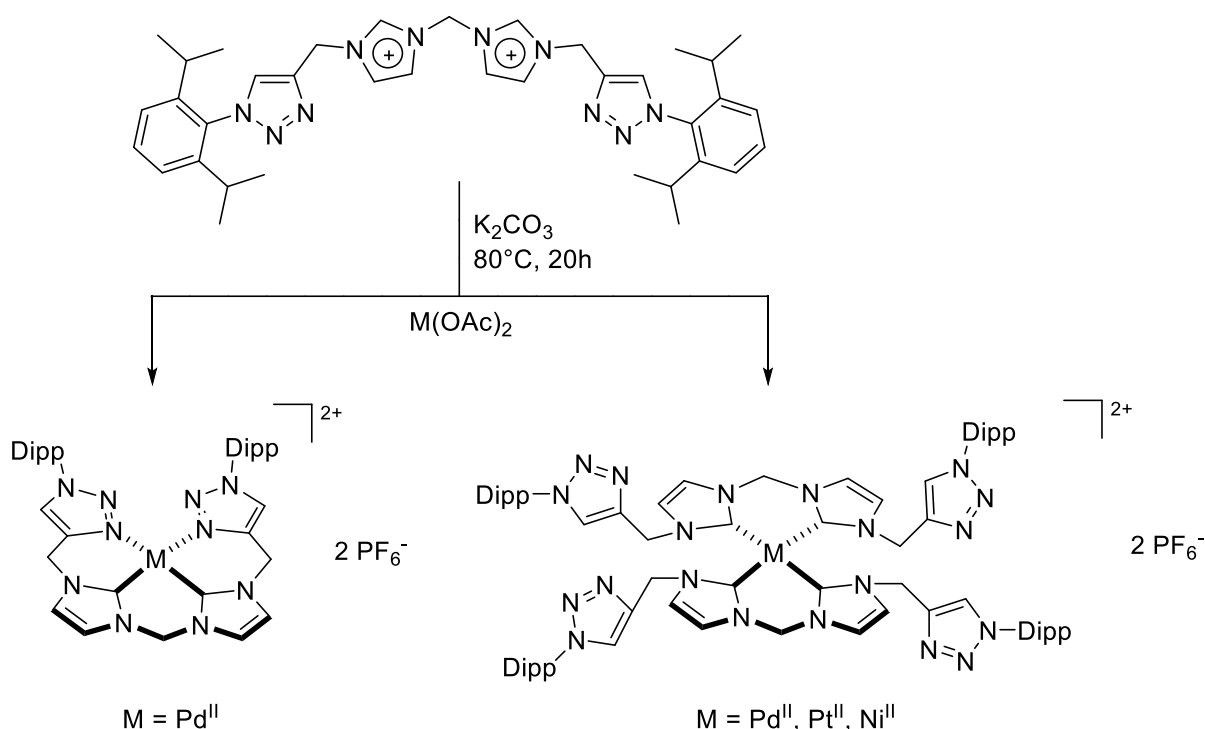
Figure 13. Synthesis and chemical structures of the mono-ligated Pd^{II} complex (left) and the bis-ligated Pd^{II}, Pt^{II} and Ni^{II} complexes (right).

By choosing the appropriate reaction conditions, *i.e.* adding one equivalent or two equivalents of the ligand, both types of coordination are obtainable in the case of

palladium. In contrast, employing Pt^{II} or Ni^{II} precursors exclusively yields complexes with two coordinated ligands and a $C_{im}C_{im}C_{im}C_{im}$ donation structure, regardless of the amount of ligand and reaction conditions (temperature, reaction time, amount of base) applied. However, the exact reasons for this diverse behavior of platinum and nickel in comparison to palladium is not entirely clear since Pd^{II} and Pt^{II} share, in general, very similar chemical properties including ionic radii.

3.5 Synthesis and Characterization of New N-Heterocyclic Silylazides

Florian Dyckhoff,# Felix Kaiser,# Sebastian Hölzl and Fritz E. Kühn

This article presents a new synthetic strategy toward *N*-heterocyclic silylene metal complexes. Silylazides have not been receiving much attention so far as potential precursors for applicable silylene generation. Additional to the ability of azides (N_3^-) to act as a leaving group, azido compounds are known to be capable of eliminating gaseous nitrogen if exposed to heat or radiation. Therefore, *N*-heterocyclic silylazides could give access to a variety of silylene complexes, if added to a suitable metal precursor under the right conditions.
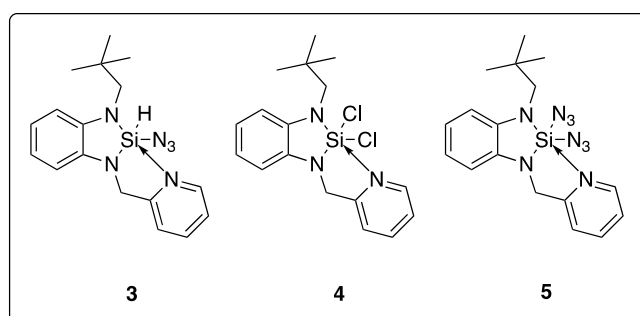
Figure 14. Chemical structures of *N*-heterocyclic mono- (**3**) and diazide (**5**) and their –dichloro (**4**) derivative. The strong dative interaction of the *N*-donor of the pyridine moiety induces a penta-coordination configuration with regard to the silicon center.

Herein, the synthesis and characterization of two novel *N*-heterocyclic silylazides are reported. The strong dative interaction of an attached pyridine-*N* donor induces a penta-coordination at the silicon center. The two compounds bearing either one or two azide groups, respectively, are characterized with regard to the electronic effects of the azide(s) on the Si center and compared to their *N*-heterocyclic chlorosilane analogues, using single-crystal x-ray diffraction (SC-XRD) and several NMR spectroscopic techniques. Additional preliminary decomposition studies reveal that both silylazide compounds are considerably less stable at elevated temperatures than their chloro derivative.

4 CONCLUSIONS AND OUTLOOK

In this thesis, the catalytic properties of several Fe-NHC complexes in epoxidation reactions have been studied. Epoxidation catalysis represents a key process for the chemical industry. The transformation of olefins as a rather cheap raw material into their respective epoxides gives rise to a significant added value due to the broad applications of epoxides in a variety of further chemical reactions.

Two closely related mixed tetradentate NHC/1,2,3-triazole Fe^{II} complexes exhibiting *cis* labile coordination sites showed great potential as epoxidation catalysts (*cf.* Figure 10). Both the selectivity and the activity of the more active catalyst was significantly increased as a result of the employment of acetic acid as a supporting additive, resulting in turnover frequencies of up to 76,000 h^{-1}, a selectivity of 97% toward epoxide and turnover numbers of up to 200 at 20°C using *cis*-cyclooctene as a model substrate under optimized reaction conditions. Additionally, the catalyst enables the epoxidation of more challenging substrates such as allyl alcohol and ally chloride with remarkable selectivities of 84% and >99%, respectively. Preliminary decomposition studies *via* ESI-MS revealed methylene bridge oxidation of the ligand scaffold and NHC protonation to be crucial deactivation pathways of the catalyst under catalytic oxidative conditions.

Furthermore, in-depth catalytic studies of the Fe^{II} and Fe^{III} derivatives (*cf.* Figure 11) of the reportedly most active non-heme iron epoxidation catalyst were conducted by investigating the particular effects of various Lewis acidic additives on their catalytic performance. These complexes, bearing a cyclic tetra-NHC ligand, respectively, exhibit TOFs of up to 50,000 h^{-1} for the Fe^{II} complex and up to 183,000 h^{-1} in case of the Fe^{III} complex even in the absence of any supporting acid. If strong Lewis acids (*e.g.* $Sc(OTf)_3$, $Ce(OTf)_4$, $Fe(ClO_4)_3 \cdot H_2O$) are applied, the considerable difference between the Fe^{II} and Fe^{III} complexes with regard to their initial activity, which stems from the short induction period of one-electron oxidation of the Fe^{II} pre-catalyst to the active Fe^{III} catalyst, disappears. This results in significantly increased and coinciding TOFs for both Fe^{II} and Fe^{III} catalysts of up to 410,000 h^{-1} in the epoxidation of *cis*-cyclooctene, representing by far the highest activity of a non-heme iron oxidation catalyst to date. Additionally, Lewis acids are able to contribute to the reactivation of a μ_2-oxo-bridged Fe^{III}-O-Fe^{III} dimer, which is considered an inactive deactivation product formed under

oxidative conditions during the catalytic reaction. Therefore, employing the Fe^{III}-O-Fe^{III} dimer as catalyst in the presence of $Sc(OTf)_3$ or $Fe(ClO_4)_3 \cdot H_2O$ results in nearly identical initial reaction rates and maximum conversion as to applying the Fe^{II} or Fe^{III} complexes as catalysts. The instantaneous oxidation of the Fe^{II} pre-catalyst and reactivation of the Fe^{III}-O-Fe^{III} dimer to the active Fe^{III} catalyst upon initiation of the reaction was additionally confirmed by UV/Vis spectroscopic studies.

In order to further increase our understanding of the particular role the varying electron density at the iron centers of different non-heme iron complexes plays with regard to the performance as epoxidation catalysts, two derivatives of the above-mentioned cyclic tetra-NHC iron complex with electron density donating and withdrawing substituents were investigated. The results unequivocally show that an increased electron density at the iron center, induced by methyl groups at the imidazolylidene backbone positions, has a disadvantageous effect on the stability of the respective catalyst under oxidative conditions. In contrast, exchanging the imidazolylidene moieties with benzimidazolylidenes and therefore inducing a lower electron density at the iron center proved to be beneficial with regard to the catalyst's stability. In addition, the inevitably accompanying lower overall activity of the catalyst seems to be advantageous if more challenging olefins compared to *cis*-cyclooctene are applied as substrates.

Ultimately, the results demonstrate the numerous options how influence on the properties of Fe-NHC catalysts can be exerted. Impacting the catalytic cycle by addition of supporting additives and especially targeted modification of ligand systems present key tools for tailoring more robust and selective complexes for future real-life application in industrially relevant processes.

5 REPRINT PERMISSIONS

5.1 RSC JOURNALS

"Pushing the limits of activity and stability: the effects of Lewis acids on non-heme iron-NHC epoxidation catalysts"

Catalysis Science & Technology **2020**, *10*, 3532-3536. DOI: 10.1039/D0CY00631A

"Synthesis, characterization and application of organorhenium(VII) trioxides in metathesis reactions and epoxidation catalysis"

Dalton Transactions **2018**, *47*, 9755-9764. DOI: 10.1039/C8DT02326C

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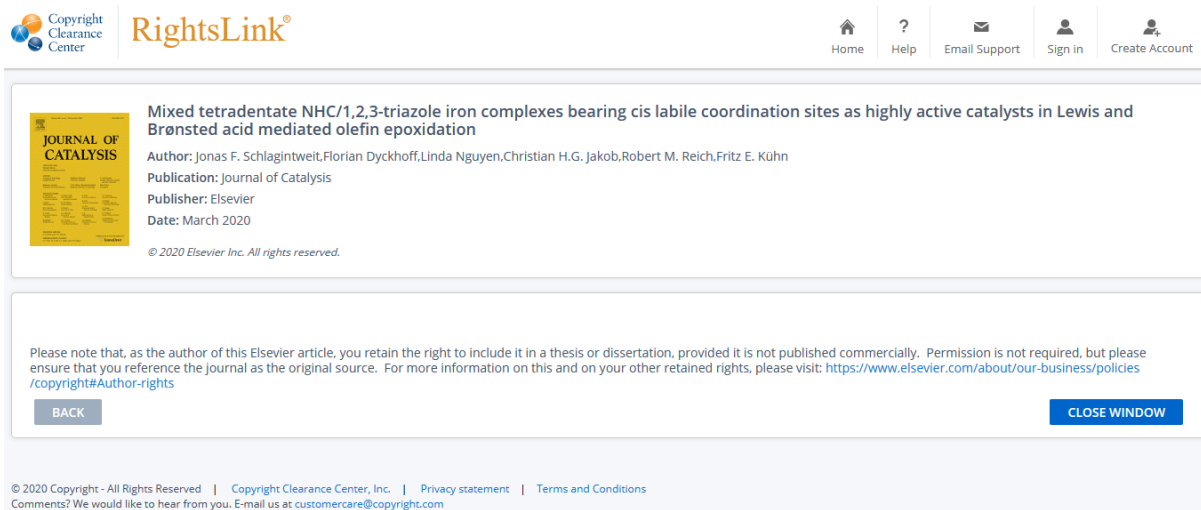
5.2 ELSEVIER JOURNALS

"Mixed tetradentate NHC/1,2,3-triazole iron complexes bearing *cis* labile coordination sites as highly active catalysts in Lewis and Brønsted acid mediated olefin epoxidation"

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6 BIBLIOGRAPHIC DATA OF COMPLETE PUBLICATIONS

6.1 Mixed tetradentate NHC/1,2,3-triazole iron complexes bearing *cis* labile coordination sites as highly active catalysts in Lewis and Brønsted acid mediated olefin epoxidation

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6.2 Pushing the limits of activity and stability: the effects of Lewis acids on non-heme iron-NHC epoxidation catalysts

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6.3 Synthesis, characterization and application of organorhenium(VII) trioxides in metathesis reactions and epoxidation catalysis

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6.4 EXPLORING DIFFERENT COORDINATION MODES OF THE FIRST TETRADENTATE NHC/1,2,3-TRIAZOLE HYBRID LIGAND FOR GROUP 10 COMPLEXES

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8 COMPLETE LIST OF PUBLICATIONS

8.1 JOURNAL ARTICLES

Mixed tetradentate NHC/1,2,3-triazole iron complexes bearing *cis* labile coordination sites as highly active catalysts in Lewis and Brønsted acid mediated olefin epoxidation

J. F. Schlagintweit, **F. Dyckhoff**, L. Nguyen, C. H. G. Jakob, R. M. Reich, F. E. Kühn

Journal of Catalysis **2020**, *383*, 144-152.

Pushing the limits of activity and stability: the effects of Lewis acids on non-heme iron-NHC epoxidation catalysts

F. Dyckhoff, J. F. Schlagintweit, R. M. Reich, F. E. Kühn

Catalysis Science & Technology **2020**, *10*, 3532-3536.

Synthesis, characterization and application of organorhenium(VII) trioxides in metathesis reactions and epoxidation catalysis

F. Dyckhoff, S. Li, R. M. Reich, B. J. Hofmann, E. Herdtweck, F. E. Kühn

Dalton Transactions **2018**, *47*, 9755-9764.

Exploring different coordination modes of the first tetradentate NHC/1,2,3-triazole hybrid ligand for group 10 complexes

J. F. Schlagintweit, L. Nguyen, **F. Dyckhoff**, F. Kaiser, R. M. Reich, F. E. Kühn

Dalton Transactions **2019**, *48*, 14820-14828.

Synthesis and Characterization of New N-Heterocyclic Silylazides

F. Dyckhoff, F. Kaiser, S. Hölzl, F. E. Kühn

Zeitschrift für anorganische und allgemeine Chemie **2019**, *645*, 207-211.

8.2 CONFERENCE CONTRIBUTIONS

Cis-labile Iron NHC Complexes in Oxidation Catalysis

F. Dyckhoff, J. F. Schlagintweit, F. E. Kühn

Conference Poster, Fourth International Conference on Catalysis and Chemical Engineering, Los Angeles, CA, United States, **February 2020**.