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Bioinspired Iron *N*-Heterocyclic Carbene Complexes in C–H Bond Oxidation: Reactivity, Electronic Properties, and Catalytic Activity

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Dangerous and disturbing this puzzle is.

Yoda – Grand Jedi Master, Master of the Order

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Zusammenfassung

Bioinspirierte Eisen(II)komplexe mit multidentaten *N*-heterozyklischen Carbenliganden (NHC) als Ligandplattform werden als Katalysatoren in der Oxidation von unreaktiven Alkanen wie beispielsweise Cyclohexan eingesetzt. Vor dem Hintergrund der direkten Umwandlung von Methan zu Methanol wurde diesem Forschungsgebiet in den letzten Jahren zunehmende Bedeutung beigemessen. Dabei wurde das Nachempfinden von enzymatischen Reaktionen mittels synthetischer Katalysatoren angestrebt.

In dieser Arbeit werden elektronische Veränderungen von Eisen(II)-NHC-Komplexen untersucht, wobei sowohl Substitutionsreaktionen in den apikalen Positionen als auch Veränderungen an der vierzähnigen NHC-Ligandplattform durchgeführt werden. Dabei wird gezeigt, dass das Halbzellenpotential des Fe^{II}/Fe^{III} Redoxpaars über einen großen Bereich (> 1000 mV) beeinflusst werden kann. Dies wird auch mit theoretischen Berechnungen belegt. Darüber hinaus ist es möglich, mittels Dichtefunktionaltheorie (DFT) die Veränderung der Halbzellenpotentiale vorherzusagen.

Die Anwendung von ausgewählten Eisen(II)-NHC-Komplexen als nicht-häm Katalysatoren in der Oxidation von unreaktiven Alkanen wird untersucht. Ein Hauptaugenmerk liegt dabei auf Cyclohexan als Modelsubstrat. Modifikationen in den apikalen Koordinationsstellen der Eisenkomplexe werden verwendet um die Katalysatorstabilität zu erhöhen, ohne dabei die Selektivität negativ zu beeinflussen. Zudem werden eine große Bandbreite an Reaktionsparametern untersucht (beispielsweise Temperatur, Oxidationsmittel, Konzentration) um genaue Einblicke in den Ablauf der katalytischen Reaktion zu erhalten.

Da sich Eisenkatalysatoren in der Regel unter oxidierenden Bedingungen im Laufe der Zeit zersetzen, werden auch mögliche Zersetzungswege der Eisen(II)-NHC-Komplexe bei Ein-Elektronenoxidationen untersucht. Dabei wird ein organisches Abbauprodukt mit ungewöhnlichen strukturellen und elektronischen Eigenschaften isoliert. Dies kann für weitere Folgereaktionen ausgenutzt werden, beispielsweise dient das organische Abbauprodukt, ein 2,2‘-Biimidazolium Salz, als Vorstufe für weitere Übergangsmetall-NHC-Komplexe.

Abstract

Bioinspired iron(II) complexes with multidentate *N*-heterocyclic carbene (NHC) ligands as supporting ligands are applied as catalysts in the oxidation of unreactive alkanes, e.g., cyclohexane. Against the background of the direct conversion of methane to methanol this field of research became increasingly important in the last decades, attempting to resemble enzymatic reactivity with artificial systems.

Electronic manipulations of iron(II) NHC complexes by apical ligand substitution reactions as well as by variation of the tetradentate NHC ligand environment are investigated. In that context, the ability to tune the half-cell potential of the Fe^{II}/Fe^{III} redox couple over a broad potential range (>1000 mV) is demonstrated and correlated to theoretical calculations. Also, based on density functional theory (DFT) calculations the change in half-cell potential is identified to be predictable for a given supporting ligand system.

Application of selected modifications of iron(II) NHC complexes as non-heme iron catalysts in the oxidation of unreactive alkanes is demonstrated, with a main focus on cyclohexane as model substrate. Apical ligand modifications are used to increase catalyst stability without decreasing selectivity. Furthermore, a broad range of parameters, e.g. temperature, oxidant, and concentration, is varied to gain detailed insights into the catalytic reaction.

As iron catalysts tend to be unstable over time under oxidizing conditions, decomposition pathways of the iron(II) NHC complex upon one-electron oxidation are investigated. A defined organic decomposition product is identified, showing unusual structural and electronic properties which can be exploited for further reactivity. For instance, the organic decomposition product, a 2,2'-biimidazolium salt, can be used as precursor for other transition metal NHC complexes.

List of Abbreviations

A/K	alcohol-to-ketone
AMO	ammonia monooxygenase
aq.	aqueous
BDE	bond dissociation energy
bpym	2,2'-bipyrimidine
BTSA	bis(trimethylsilyl)amide
CV	cyclic voltammetry
CYP	cytochrome P450 oxidases
DFT	density functional theory
DMAP	4-dimethylaminopyridine
DMSO	dimethylsulfoxide
equiv.	equivalents
EPR	electron paramagnetic resonance
ESI	electrospray ionization
Fc	ferrocene
Fc^+	ferrocenium
GC	gas chromatography
His	histidine
HOMO	highest occupied molecular orbital
Glu	glutamic acid
KAUST	King Abdullah University of Science and Technology
Me^{i}nico	methyl isonicotinate
MMO	methane monooxygenase
MMOH	methane monohydroxylase
MO	molecular orbital
MS	mass spectrometry
MTA	methanol to aromatics
MTBA	methyl *tert*-butyl ether
MTG	methanol to gasoline
MTO	methanol to olefins
NCCN	bis(*o*-imidazol-2-ylidenepyridine)-methane

NHC	*N*-heterocyclic carbene
NMR	nuclear magnetic resonance
OCCO	bis(*o*-imidazol-2-ylidenefuran)-methane
OTf	triflate
PDB	The Protein Data Bank
pMMO	particulate methane monooxygenase
py	pyridine
Py_2N_2	*N*,*N*'-(biphenyl-2,2'-diyl)-*N*,*N*'-bis(2-pyridylmethyl)-*N*,*N*'-dimethyldiamine
Py_2S_2	1,6-bis(2'-pyridyl)-2,5-dithiahexane
SCCS	bis(*o*-imidazol-2-ylidenethiophene)-methane
sMMO	soluble methane monooxygenase
S,*S*-PDP	2-(((*S*)-2-[(*S*)-1-(pyridin-2-ylmethyl)pyrrolidin-2-yl]pyrrolidin-1-yl)methyl)pyridine
$Th^{\bullet+}$	thianthrene radical cation
TMC	1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane
TOF	turnover frequency
TPA	tris(2-pyridylmethyl)amine

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1 INTRODUCTION

1.1 Mineral Oil: Vital for the Chemical Industry

Easy and reliable access to carbon building blocks is vital for the chemical industry. Downstream processing of carbon-based bulk chemicals allows production of a broad range of industrial goods and consumer products, e.g., coatings, plastics, and pharmaceuticals. In 2012, 9.3 million tons mineral oil and 19.2 million tons (oil equivalents) natural gas were consumed by the chemical industry in the European Union, with natural gas being used mainly for energy production and not as carbon feedstock.[1,2] Therefore, mineral oil continues to play the major role as raw material. From a chemical point of view the greatest advantage of mineral oil is its composition, as crude oil already contains important basic chemicals such as aromatics, olefins, or acetylene beside alkanes in various chain lengths.[1] Refining processes for the separation of these compounds have been developed and enhanced over the past decades, allowing for a highly efficient crude oil utilization.

Consequently, great attention is paid to the development of both crude oil production and crude oil prices. As a fossil fuel, crude oil is doomed to be consumed at some point in the future as its natural formation requires several million years.[1,3] Starting with the oil crisis in 1973, the worldwide, public discussion on the finite nature of fossil fuel supply began.[4] Ever since, the amount of crude oil reserves that can be recovered economically has been adjusted every year and thus the predicted end date of the oil age has been shifted further and further into the future. Compared to 1990 the worldwide crude oil reserves increased by 76% from 136 to 240 billion tons in 2014 (Figure 1).[5]

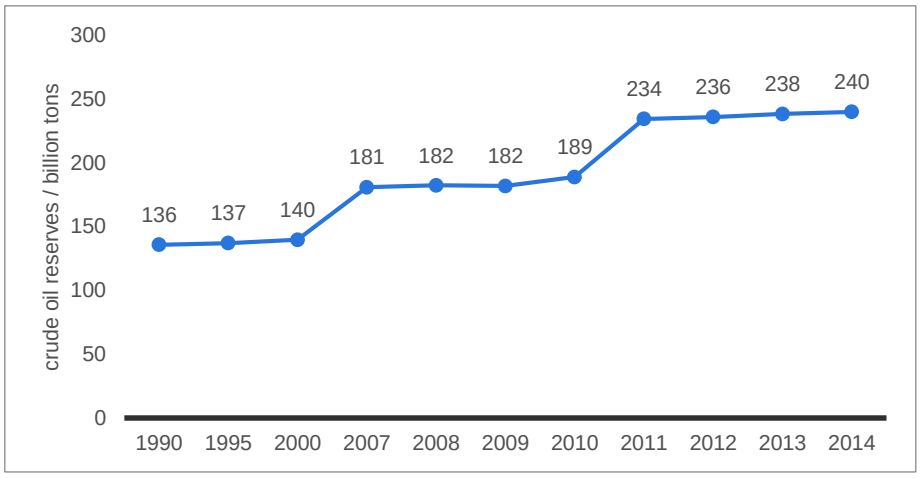


Figure 1. Development of worldwide crude oil reserves from 1990 to 2014 in billion tons.[5]

As a counterpart to the reserves, the crude oil consumption amounts to 4.2 billion tons in 2014 compared to 3.2 billion tons in 1990, corresponding to an increase of only 31%.[6] Based on these data

the complete consumption of crude oil reserves would have been estimated for the year 2032 in 1990 and for the year 2071 in 2014. This clearly illustrates that a precise prediction of the development of the crude oil market is rather challenging, mainly for two reasons: Technological advances and fluctuating prices.[1] Historically, both have supported an increase in the estimated total crude oil reserves that can be accessed economically. New technologies allow for a more cost efficient recovery from oil deposits and might even extend the number of accessible oil deposits. An increase in crude oil prices supports cost intense recovery from unconventional deposits, e.g., deepwater drilling, tar sand, and oil shale, which consequently leads to an increase of economically accessible crude oil reserves.[1] The oil price driven exploration of such unconventional oil deposits became increasingly important with the sharp increase in crude oil prices starting around the year 2000 (exemplary for UK Brent, Figure 2).[7]

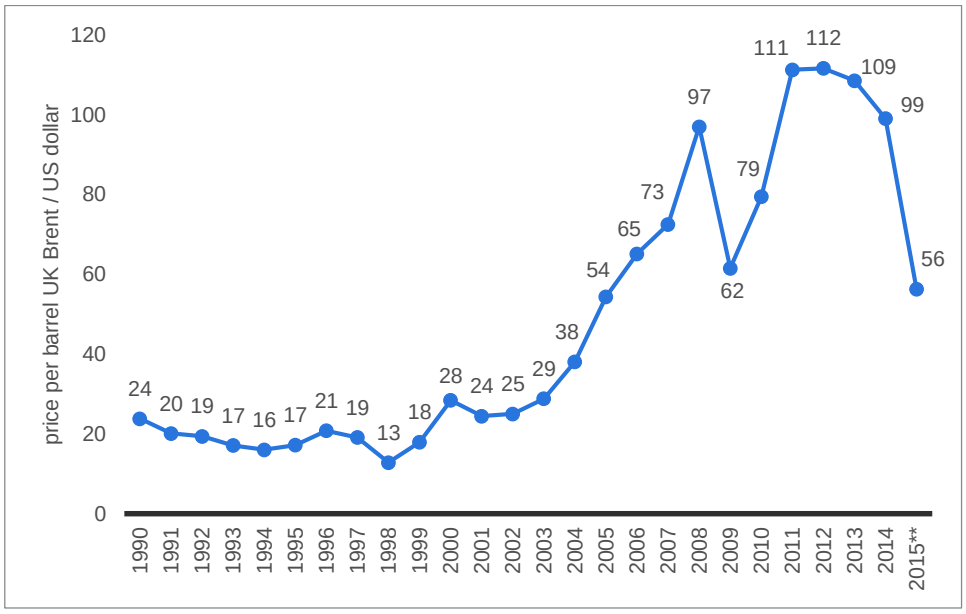


Figure 2. Development of the yearly average price per barrel crude oil (UK Brent) from 1990 to 2015 in US dollar. ** Averaged value based on data from January 2015 to August 2015.[7]

The development of crude oil prices correlates with the amount of worldwide reserves in Figure 1. Mining of oil sand mainly in Canada became economic in the early 2000s with crude oil prices constantly far above 20 $/barrel.[1,7] With further increasing prices also oil shale mining was targeted and thus a second sharp increase in crude oil reserves in 2011 occurred. However, in 2015 the profitability of oil shale mining was subject of numerous discussions, as it is controversial whether economic oil production from oil shale is possible or not after a sharp decline in crude oil prices in 2015.[8]

Against the background of these uncertainties of the future development of the crude oil markets and the potential end of the oil age within this century, both the chemical industry and the chemical scientific community is driven to develop technologies for the use of alternative carbon feedstocks for the downstream processing and production of value-added chemicals.[9]

1.2 Methane as Carbon Feedstock

1.2.1 Natural Gas and Methane Hydrates as Methane Sources

Natural gas is one of the most important primary energy sources beside mineral oil and coal. 3'380 billion m^3 natural gas have been consumed worldwide in 2012 with reported reserves of 185'000 billion m^3.[10,11] With methane being the main component of natural gas it is used mainly as fuel for heating and electricity generation. Similar to mineral oil, the exact composition of natural gas varies depending on the deposit. For instance, natural gas from Groningen (Netherlands) consists of 81.3% methane and 14.3% dinitrogen, natural gas from Lacq (France) of 69.3% methane, 15.2% hydrogen sulfide, and 9.6% carbon dioxide, and natural gas from the British deposit "Forties" (Northern Sea) of 44.5% methane and 53.6% other carbon hydrates (e.g., ethane and propane).[1] However, depending on the literature reference the reported values for the exact compositions may vary.[12]

Beside natural gas, methane hydrates are a highly interesting source of methane. Hydrates of methane are clathrate complexes with gaseous methane being trapped in a cage of frozen water.[12,13] Two different methane hydrates are known: $(CH_4)_9 \cdot (H_2O)_{46}$ and $(CH_4)_{24} \cdot (H_2O)_{136}$, although the exact compositions varies.[12] The nominal composition requires 5.75 moles of water for every 1 mole of methane.[14] Most of the known deposits of methane hydrate are located in deep sea beside permafrost, with isotopic patters indicating methane production by methanogenic archaea in absence of electron acceptors, e.g., dioxygen.[15] In addition to biogenic methane, also thermal decomposition of organic matter in deep sediments can result in methane hydrate formation, although this is less common.[14] Formation of methane hydrates can occur in depths greater than 300 m at water temperatures around 2 °C.[14] Since the discovery of these natural methane reservoirs the estimated amount of global methane bound in hydrates decreased constantly.[16] Still, today usually the global volume of hydrate-bound methane is cited with 10^{15} m^3.[16] The sheer size of the known global methane hydrate deposits render this an attractive alternative carbon feedstock. However, economic extraction is still in its infancy, requiring significant improvements in terms of commercial exploration.[16]

Although the majority of natural gas is used for energy production, several industrial processes exist for the conversion of methane to bulk chemicals, following the separation of methane from natural

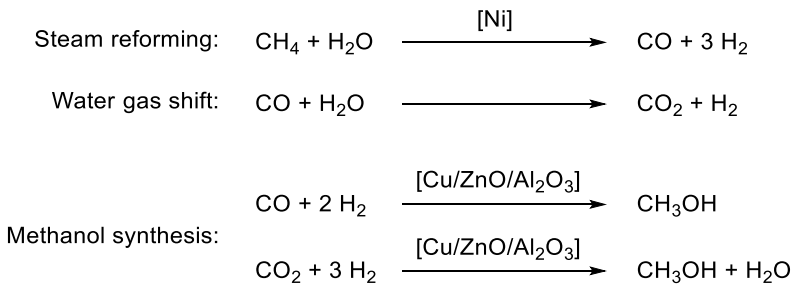
gas.[9] Important processes include the chlorination of methane to yield the respective chloromethanes, the conversion to hydrogen cyanide, and the production of synthesis gas (syngas) as crucial intermediate for several downstream processes.[1] Of special interest in this context is the downstream process route via methanol, which is formed from syngas in a worldwide scale of 65 million tons (2014).[9,12,17-19]

1.2.2 Methanol as a Bulk Chemical

Synthetic access to methanol on an industrial scale via syngas is well established.[18] Syngas can be provided from either natural gas or light naphtha (low boiling fraction of crude oil) by steam reforming or from coal by partial oxidation (also applicable to high boiling fractions of crude oil).[1] In the context of this work only natural gas with a high methane content is considered as raw material in the following. In the steam reforming process, the process gas reacts with an excess of water (ratios of H_2O/C are 2.8 to 3.5) at temperatures between 500 °C and 1000 °C to yield a mixture of H_2, CO, CO_2, H_2O, and CH_4.[1,20] A common side reaction is the water gas shift, transforming CO with H_2O to CO_2 and H_2.[21] Prior to the process the natural gas is desulfurized via hydrotreating to protect the nickel catalysts during the steam reforming process. The reaction conditions can be tuned to exactly adjust the product ratio, e.g., higher reaction temperatures are used to thermodynamically reduce residual amounts of methane in the syngas.[1] Beside the synthesis of methanol, syngas is used for ammonia synthesis, hydroformylation, and the Fischer-Tropsch process, for instance.[1,22,23]

For methanol synthesis the syngas is required to contain H_2 and CO in a ratio of 2:1.[1,24] Thus, especially for methanol production often syngas from light naphtha is used as in this the H_2/CO ratio is already close to the required value. In case the syngas contains larger H_2 amounts, CO_2 is added to the syngas as CO_2 also can be converted with H_2 to methanol under reaction conditions. Catalyzed by Cu/ZnO/Al_2O_3 at temperatures between 230 °C and 270 °C, methanol is formed in exothermic reactions (Scheme 1).[1,9] The interest in methanol is mainly caused by the broad range of accessible downstream products. A range of organic intermediates derives from methanol, with the most important being formaldehyde for applications in synthetic resins.[25] Furthermore, methanol is converted to formic acid and acidic acid as well as methyl *tert*-butyl ether (MTBA), an important additive for automotive fuels.[1,25] Most importantly, however, are the MTG (methanol to gasoline), MTO (methanol to olefins), and MTA (methanol to aromatics) processes with respect to the target of potentially substitute mineral oil as carbon feedstock.[9,26-28]

Scheme 1. Chemical reactions of steam reforming (from natural gas) and of methanol synthesis. Depending on the composition of the syngas used for methanol synthesis both reactions shown here might occur in parallel. Potential byproducts and side reactions (apart from water gas shift) that can be found under specific reaction conditions are not shown.[1,21]

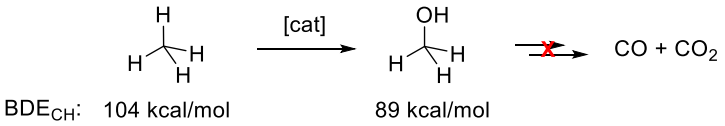


All three product classes are major reasons for the growing demand on mineral oil, as they can be provided easily upon refinement of crude oil. Perspectively, an alternative carbon source that allows economic access to these product classes – especially gasoline with potential use as automotive fuel – would be a milestone for reducing the dependence on mineral oil. Hence, methanol is an ideal candidate with tremendous potential in case it can be provided at prices capable of competing with those of mineral oil.[18,19,24] However, with the current energy-intense, two-step process for methanol synthesis it is not possible to establish a methanol-based instead of the well-established oil-based economy. A more efficient production of methanol is required, preferably from methane with respect to the enormous methane hydrate deposits (chapter 1.2.1). An efficient conversion of methane to methanol would also be beneficial for transportation of this main energy carrier, as cost-intensive liquefaction is no longer required.[17]

1.2.3 Methane to Methanol: Chances and Challenges

A direct and selective oxidation of methane to methanol is considered as one of the “dream reactions” in chemistry (Scheme 2).[17] Such a reaction would reduce the number of steps required for methanol synthesis and thus reduce costs significantly.[12,21] Also, as the currently established steam reforming of methane requires high temperature which is achieved by methane-fueled burners, a direct conversion without steam reforming would save enormous amounts of methane from burning. Although a lot of effort was put into research on pyrolysis of methane in order to yield methanol, so far it could not be demonstrated that a process capable of competing with the syngas-based route is feasible.[12,21,29-31] The main obstacle is the (un)reactivity of methane itself. Although thermodynamically the conversion of methane to methanol is favorable (-28 kcal/mol),[32] the C–H bond dissociation energy (BDE) of methane is with 104.9 kcal/mol very high, making it the least reactive hydrocarbon molecule.[9,17,33,34]

Scheme 2. Schematic drawing of the direct conversion of methane to methanol. A suitable catalyst is required to avoid over-oxidation of methane in addition to various potential side reactions. The values of the C–H bond dissociation energies (BDE) underline the challenges that need to be faced in order to control this reaction, as methanol is more reactive than methane.[9,17]



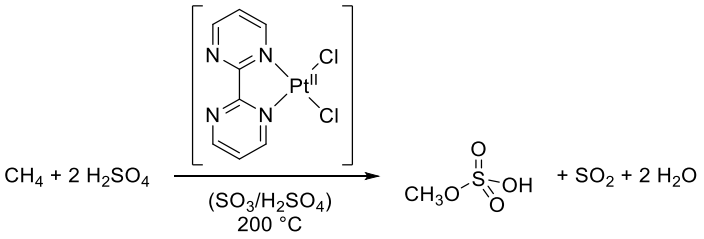
Unfortunately, the oxidation of methane to CO_2 by O_2 (combustion) is significantly stronger favored (-196 kcal/mol) compared to the formation of methanol.[32] Cleavage of the C–H bond requires drastic conditions, lowering any selectivity towards a specific product. Also, due to the perfect tetrahedral symmetry of methane and its poor basicity ($pK_a \approx 48$)[35] the reactivity towards nucleophiles, electrophiles, or bases is almost negligible.[9,17] These data become even more problematic when looking at the desired oxygenated product, methanol, which is more basic and has a lower C–H BDE (89 kcal/mol).[9,17] Thus, over-oxidation is a major challenge that needs to be faced beside a range of additional side reactions based on the formation of highly reactive methyl radicals.

1.2.4 Homogeneous Catalysis in Methane Oxidation

Low temperature approaches for methane conversion are one possibility to reduce unwanted side reactions and thus for increasing selectivity.[9] Looking at the high C–H BDE of methane (chapter 1.2.3) it is immediately evident that such low temperature reactions require extremely active catalyst systems. Homogeneous catalysis offers great potential for catalytic transformations under mild conditions, as catalytically active sites can be tuned comparably easily and thus suppression of side reactions is achievable.[36]

Pioneering work on homogeneously catalyted C–H bond oxidation was done by Shilov, introducing platinum salts as catalysts for methane activation.[36-39] While platinum(II) was used as catalyst, the stoichiometric use of $[Pt^{IV}Cl_6]^{2-}$ as oxidation was required, illustrating the major drawback of this approach. Knowledge about these systems was constantly refined and extended to other metals especially by Periana, who also provided the most prominent example of homogeneous methane activation (Scheme 3).[40-43]

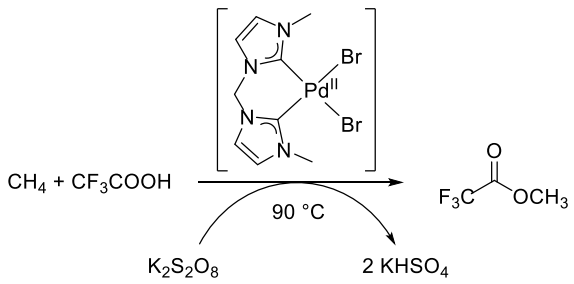
Scheme 3. Conversion of methane to methyl bisulfate in yields greater than 70%. The reaction is catalyzed by (bpym)$PtCl_2$ (bpym = 2,2'-bipyrimidine), with sulfuric acid (oleum SO_3/H_2SO_4) being both oxidant and solvent.[17,42]



Oleum as reaction medium serves several purposes in this context. First, sulfur in the oxidation state +VI acts as strong oxidant which allows the Pt^0/Pt^{II} redox couple to serve as catalyst, compared to the Pt^{II}/Pt^{IV} redox couple in Shilov's system. Second, the product formed from methane is extremely stable under these reaction conditions. Methyl bisulfate as reaction product is oxidized with a rate of 1/100 compared to methane, thus being protected efficiently from over-oxidation.[43] Limiting for potential applications on a larger scale is mainly the required low concentration of less than 1 molar with respect to the product.

Ligand platforms used for transition metal complexes in methane activation were extended by Herrmann, who introduced *N*-heterocyclic carbene (NHC) ligands as supporting ligands for palladium complexes.[44] Using these complexes as catalysts, methane is converted to trifluoroacetic acid methyl ester at temperatures of 80-100 °C, with the best results being obtained for the complex shown in Scheme 4 at 90 °C.

Scheme 4. Conversion of methane to trifluoroacetic acid methyl ester, catalyzed by a palladium(II) NHC complex. Potassium peroxodisulfate is used as oxidant.[44]



Beside those selected examples a range of additional homogeneous approaches exist to tackle the problem of catalytic methane functionalization. For instance, Asensio, Etienne, and Pérez introduced C–C bond formation between methane and ethyl diazoacetate catalyzed by silver compounds.[45] Also, Groves and Gunnoe recently presented an unusual approach to oxidize methane to the

trifluoroacetate methyl ester, using iodate salts and catalytic amounts of chloride as reagents.[33] Conversion of methane to methyl esters catalyzed by main group compounds (Tl^{III}, Pb^{IV}) was introduced by Periana, continuing his extensive research in this field.[46]

For the full potential of tunable active sites in homogeneous catalysis to be unlocked, immobilization is required as it would allow easier product separation and thus longer cycles for every catalyst batch. Basset reported pioneering work on the functionalization of methane catalyzed by silica- and alumina-supported tantalum and tungsten hydride species.[47-49] Although these reports did not focus on oxidation of methane to methanol, the potential of well-defined, immobilized single-site catalysis for methane upgrading was demonstrated and these results might help in the future to increase the efficiency of homogeneous systems for methanol formation. A heterogeneous analog to Periana's system was reported by Schüth, embedding platinum active sites in a polymer-based framework (Figure 3).[50,51] As a result of the heterogenization, a better reusability of the catalyst was achieved under similar conditions compared to Periana.

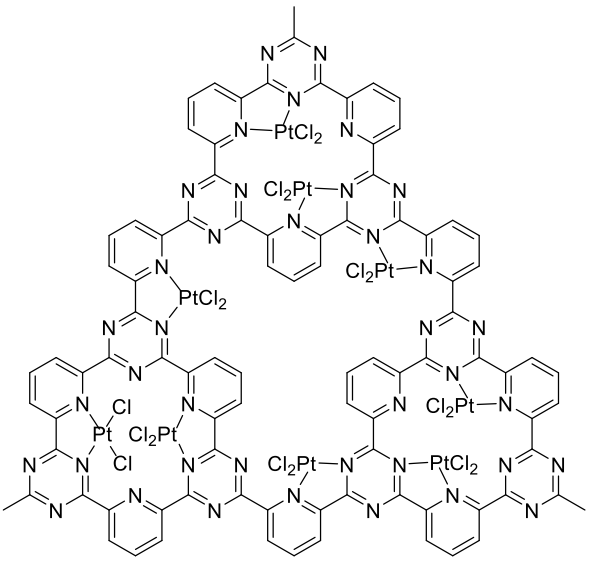


Figure 3. Heterogeneous system introduced by Schüth as analogue to Periana's catalyst for catalytic methane oxidation.[51]

1.3 Alkane Hydroxylation in Nature

The idea to homogeneously oxidize methane is based on natural archetypes. Alkane oxidation plays an important role in various biological systems and thus nature developed a whole class of metalloenzymes capable of C–H hydroxylation with dioxygen as the terminal oxidant.[52] Within this so-called monooxygenases, a subclass of the oxidoreductases, the methane monooxygenase (MMO) deserves particular interest in the context of methane to methanol conversion.[53] Also, the cytochrome P450 oxidases (CYP) deserve attention as they are among the most important monooxygenases, being able to catalyze a broad range of oxidative hydrocarbon conversions.[54-56]

1.3.1 Methane Monooxygenases (MMO)

As the name states itself, MMOs are capable of catalytically convert methane to methanol, using dioxygen as terminal oxidant.[9,53] Most interestingly, the reaction takes place under mild conditions in aqueous media at temperatures below 100 °C, rendering MMOs exciting archetypes for homogeneous methane oxidation catalysts. Also, an extremely high selectivity toward methanol is given without formation of common byproducts, e.g., formaldehyde, formic acid, and CO_x.[9] Methanotropic bacteria use MMOs for metabolizing methane as carbon and energy source, with one of the best studied example being *Methylococcus capsulatus* (Bath, England).[57,58] Two different forms of MMO have been studied in great detail: the particulate form (pMMO) and the soluble form (sMMO).[53,59,60] Details on the structure of sMMO have been known for more than two decades, reported by Frederick, Lippard, and Nordlund in 1993:[61] In addition to a reductase and a coupling protein, sMMO contains a hydroxylase subunit (MMOH) with a carboxylate-bridged diiron(III) center, responsible for the hydroxylation of methane (Figure 4).[61-63]

Formation of significant amounts of sMMO in several strains of methanotrophs requires copper-limiting conditions in its environment.[64] If sufficient amounts of copper are accessible, membrane-bound pMMO with copper active sites is formed for methane metabolism.[64,65] Detailed understanding of pMMO is still in its infancy, although today it is agreed that pMMO of the Bath enzyme consists of three metal centers: a mononuclear copper active site, a binuclear copper active site, and a zinc center.[65-68] The dicopper center, which is made responsible for methane hydroxylation, is shown in Figure 5, as determined by X-ray diffraction (PDB code: 1YEW).[67 65]

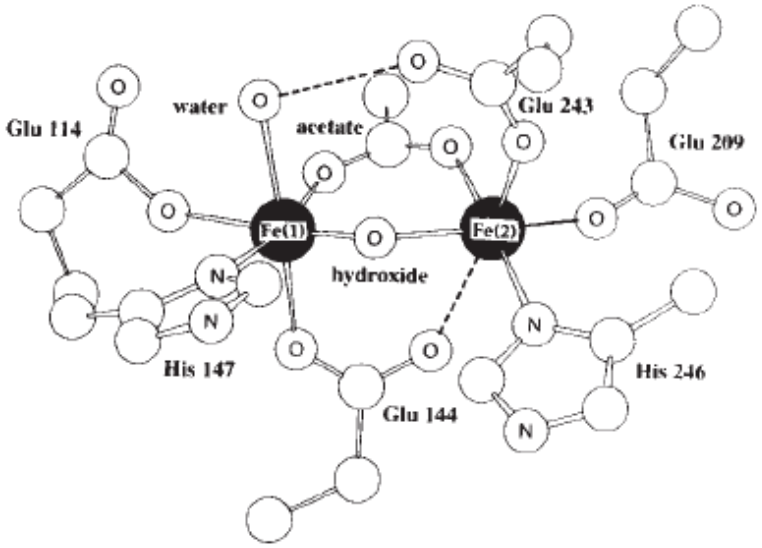


Figure 4. Active site of the hydroxylase subunit in sMMO. Two iron(III) atoms are bridged by two carboxylate groups and one hydroxide.[61] Reprinted by permission from Macmillan Publishers Ltd: *Nature* 1993, *366*, 537-543, copyright 1993.

Noteworthy, beside pMMO and sMMO the related ammonia monooxygenase (AMO) is the only known additional enzyme capable of methane hydroxylation.[65,69] AMO mainly oxidizes NH_3 to NO_2^- as energy source for *Nitrosomonas europaea*, but is also capable of oxidizing a broad range of additional substrates including light alkanes.[69]

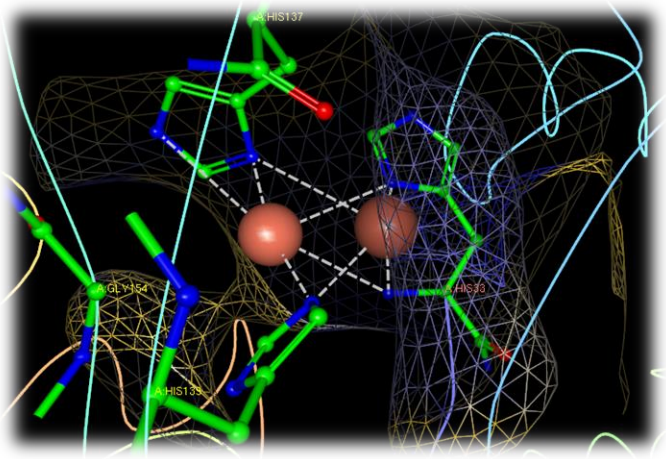


Figure 5. Dicopper active site of pMMO as determined by X-ray diffraction (PDB code: 1YEW).[65,70] The two copper atoms (pale red) are surrounded by three histidine residues (His33, His137, His139) and one glutamic acid residue (Glu35).[66]

1.3.2 Cytochrome P450 Oxidases (CYP)

Although not capable of oxidizing methane itself, the monooxygenases of the CYP family attracted great interest of researchers.[54] On the one hand, these enzymes catalyze a broad range of challenging C–H oxidations with dioxygen as terminal oxidant. In the human body they play a key role in drug metabolism, for instance.[55] On the other hand, CYPs exhibit a well-defined coordination environment – a single heme *b* cofactor – at the catalytically active site, rendering CYPs a powerful archetype for biomimetic chemists.[55] The heme *b* cofactor consist of an iron(III) center coordinated by a tetradentate porphyrin ligand. Characteristic for CYPs, the iron(III) center is additionally coordinated by an apical thiolate from a cysteine residue which acts as an anchor to the protein structure (Figure 6).[54,71] Due to the heme cofactor all CYPs belong to the family of hemoproteins.[71] Heme-based enzymes and in that context also CYPs have been subjected to extensive mechanistic studies with major breakthroughs made by Groves in the 1970s.[72-74] He was able to reveal a metal-centered, non-radical oxidation mechanism via high-valent iron-oxo intermediates. The catalytic cycle of CYPs consists of three high-valent iron-oxo key intermediates: Compound 0, Compound I, and Compound II.[54,55] Outstanding work of Green in the last decade, who provided a high-yield route to Compound I for mechanistic studies, finally led to a fully understood mechanism of the CYP-mediated hydroxylation of alkanes.[55,75,76]

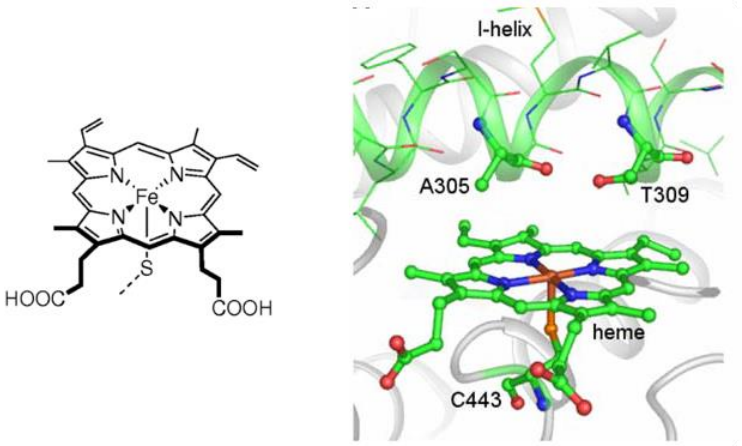
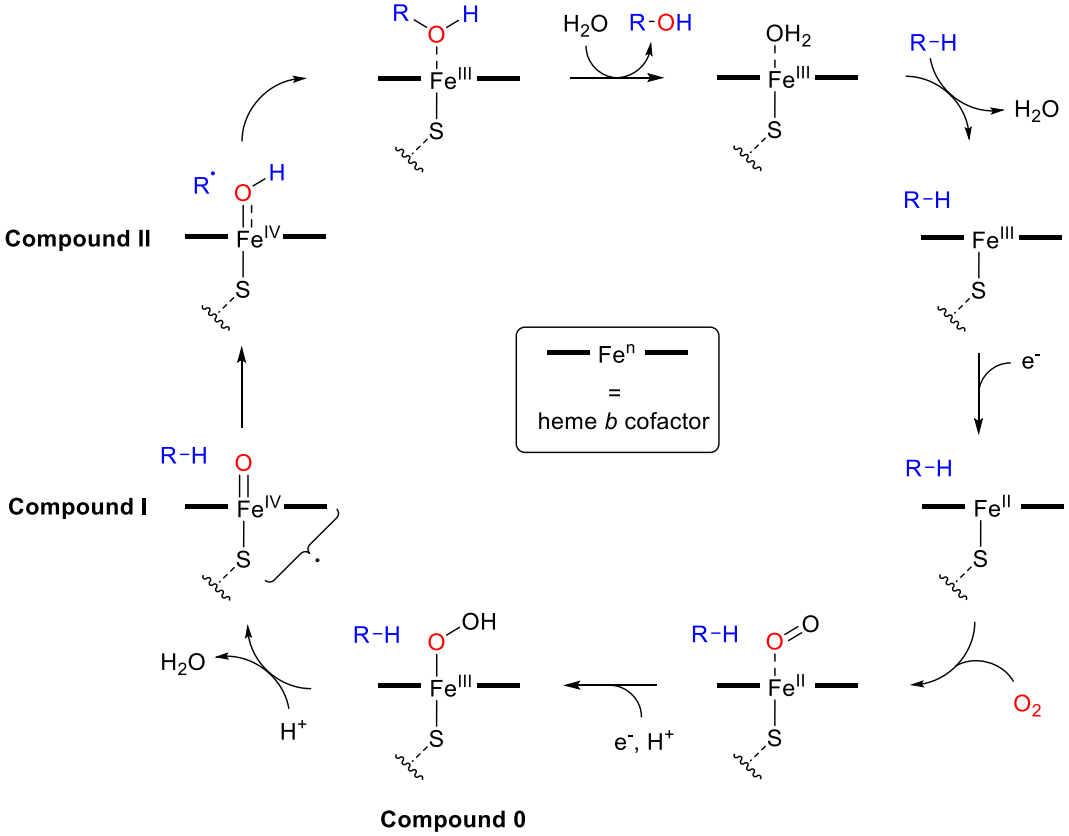


Figure 6. Left: Structure of the heme *b* cofactor with an iron(III) center and an apical thiolate characteristic for CYPs. Right: Structure of the catalytically active site of CYP2D6, playing a major role in human drug metabolism (PDB code: 2F9Q).[77] The iron center is coordinated by a tetradentate porphyrin ligand and in apical position by a cysteine residue (C443) as anchor to the protein structure. Reprinted by permission from Springer Publishing Company: *JBIC* 2007, *12*, 645-654, copyright 2007 This is an open access article distributed under the terms of the Creative Commons Attribution.

Compound 0 is formed from the heme *b* resting state by a one-electron reduction, the end-on coordination of dioxygen, and finally the proton-coupled one-electron reduction of the coordinating

dioxygen, yielding an Fe^{III}–OOH intermediate. Subsequently, proton-assisted O–O bond splitting of the hydroperoxide results in formation of the iron(IV) oxo intermediate, Compound I. In Compound I also the redox-active porphyrin ligand is oxidized, as the O–O bond splitting is heterolytic and therefore a two-electron oxidation of the heme cofactor is required. Thus, Compound I can be described as iron(IV) and an oxidized porphyrin ligand containing a delocalized radical in its π-electron system, or as iron(V) without a porphyrin-based radical in the π-electron system of the ligand. However, with recent studies based on modern experimental techniques at hand, the oxidation state of +IV for the iron oxo unit with a spin state of S = 1 was confirmed by EPR spectroscopy.[76] A doublet overall ground state was found for Compound I as a consequence of the antiferromagnetic coupling of the iron(IV) oxo species (S = 1) with the porphyrin-based radical (S = ½).[76] Being highly reactive and short-lived, Compound I is able to abstract a hydrogen from unreactive alkanes, resulting in formation of Compound II, an Fe^{IV}–OH intermediate. Hydroxylation of the carbon-based radical of the substrate that is formed upon H abstraction finally leads to the hydroxylated alkane as the product. A schematic description of the catalytic cycle is given in Scheme 5.[54,55]

Scheme 5. Mechanism of alkane hydroxylation with dioxygen mediated by CYPs. Three high-valent iron-oxo compounds are formed as key intermediates: Compound 0, Compound I, and Compound II.[54,55]



For the C–H bond activation to occur – namely the H atom abstraction by Compound I – both the reduction potential of Compound I and the basicity of Compound II are required to be within a certain range.[78] In that context special attention has to be paid to the apical thiolate ligand at the heme *b* cofactor, as its comparably strong electron donating properties make the Fe^{IV}–O unit more basic and therefore allows for H atom abstraction to form Compound II. The experimentally obtained pK_a value for Compound II is with ≈12 significantly higher for an apical thiolate compared to an apical histidine (pK_a ≈ 3.5).[55]

Based on the detailed understanding of the oxidation mechanism of CYPs, attempts to synthetically mimic the catalytic activity came into focus by creating artificial systems.[79,80] The ability to use bioinspired or biomimetic catalysts can help to develop tailor-made systems for the oxidation of specific substrates with the desired selectivity. In the given context, especially the oxidation of light alkanes (including methane) catalyzed by artificial systems that mimic biological reactivity is of interest.

1.4 Homogeneous Iron-Based C–H Bond Oxidation Catalysis[1]

1.4.1 Model Compounds and Substrates

Iron was chosen by nature as metal in the active sites of enzymes capable of oxidizing methane and other alkanes (compare chapter 1.3), mainly due to its abundant availability in the earth's crust and its broad range of accessible oxidation states (up to +VI).[81] Its use by nature in combination with a relative low toxicity renders iron also a highly interesting candidate for applications in catalysis.[81] Implementing iron active sites in homogeneous catalysis is a reasonable choice based on the given natural archetypes and the advantages provided by the precise synthetic approaches toward defined active sites in homogeneous catalysts.[36,82] Thus, a variety of artificial heme and non-heme iron complexes have been developed and applied in C–H bond oxidation.[79,83] Heme complexes often intend to directly mimic the oxidation chemistry found in CYPs, while non-heme complexes are either dinuclear iron structures

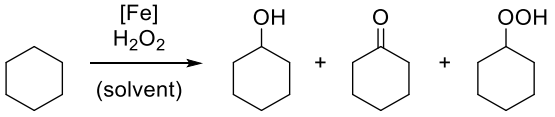
[1] This topic has been reviewed extensively as a part of this PhD thesis in *Chemical Communications* (A. C. Lindhorst, S. Haslinger, F. E. Kühn, "Molecular Iron Complexes as Catalysts for Selective C–H Bond Oxygenation Reactions", *Chem. Commun.* 2015, DOI: 10.1039/C5CC07146A) and the respective article is summarized in chapter 3.2. Therefore, here only a brief introduction on this topic is given, highlighting the most important factors affecting research in homogeneous iron-based C–H bond oxidation catalysis.

mimicking sMMO or mononuclear iron complexes inspired by CYPs with structural or electronic resemblance to their biological archetype.

Although various substrates are investigated in the context of homogeneous, iron-catalyzed C–H bond oxidation, the most common model substrate is cyclohexane being oxidized with hydrogen peroxide.[84,85] For cyclohexane, the C–H BDE is with 99.3 kcal/mol relatively close to methane (104.9 kcal/mol).[34,86] Also, as a result of its high symmetry only CH_2 groups are present in cyclohexane, eliminating potential problems with selectivity. Finally, as cyclohexane and its major oxidation products are all liquid, it is not only easy to handle but also perfectly suited for homogeneous catalysis in solution. As an interesting side fact, the oxidation of cyclohexane plays an important role in industry: In the DuPont process a mixture of cyclohexanol and cyclohexanone is obtained upon oxidation of cyclohexane with dioxygen at cobalt or manganese catalysts.[87,88] This process is critical for providing the raw materials for the production of the polyamides Nylon 6 and Nylon 6.6'.

On a bench top scale in research laboratories the oxidation of cyclohexane usually yields three different products: the afore-mentioned cyclohexanol and cyclohexanone, and in addition cyclohexyl hydroperoxide (Scheme 6). Apart from hydrogen peroxide also other peroxides are applied as oxidants; however, as hydrogen peroxide is the most economic option beside dioxygen, it is usually the oxidant of choice for these model reactions.[89]

Scheme 6. Iron-catalyzed oxidation of cyclohexane in homogeneous solution: Three major products can be obtained, depending on the reaction conditions and the catalyst: cyclohexanol, cyclohexanone, and cyclohexyl hydroperoxide.

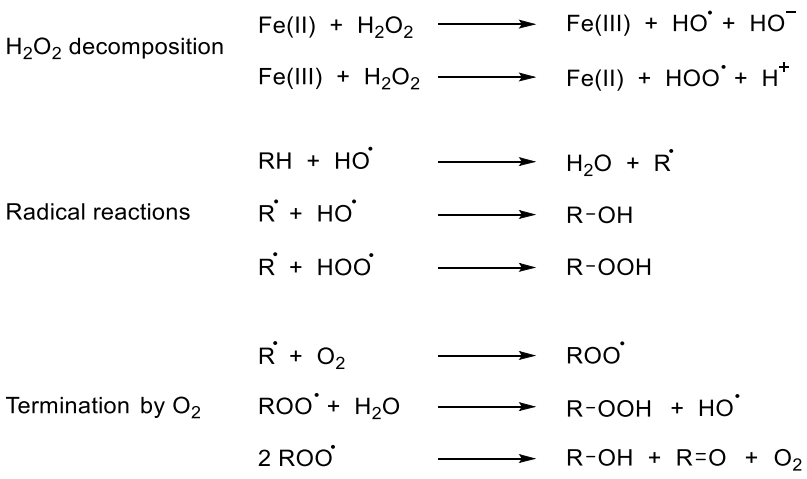


1.4.2 Mechanistic Considerations

The selectivity and therefore the product distribution is considered as mainly dependent on the type of mechanism the respective catalyst undergoes in its catalytic cycle.[84] In general, two competing mechanistic pathways are discussed in the literature: an unselective Fenton-type pathway via long-lived radicals and a metal-centered oxidation mechanism via high-valent iron oxo intermediates (compare CYP, chapter 1.3.2).[79,84,90]

Studied by Fenton already at the end of the 19th century, hydrogen peroxide reacts with simple iron(II) salts to form highly reactive hydroxyl radicals.[91,92] This basic principle of reactivity holds true still today, rendering selective iron-catalyzed oxidation reactions with hydrogen peroxide as oxidant an enormous challenge. Hydroxyl radicals are highly reactive and thus they immediately undergo several possible radical-based subsequent reactions (Scheme 7) in presence of organic substrates (e.g., cyclohexane).[90,93]

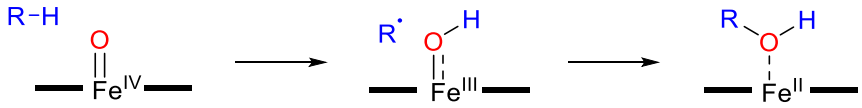
Scheme 7. Possible reactions following the Fenton-typ reaction pathway. Hydrogen peroxide decomposes at Fe(II) or Fe(III), leading to highly reactive radicals that subsequently react with organic substrates. In the presence of dioxygen, a termination step of the radical reactions can occur (auto-oxidative pathway), leading to equal amounts of alcohol and ketone as oxidation products.[90,93]



Alkyl radicals formed upon H atom abstraction by hydroxyl radicals are long-lived. This is relevant especially in the presence of dioxygen, as alkyl radicals react with dioxygen in an auto-oxidative pathway and alkyl peroxide radicals are formed as a consequence (Scheme 7). Subsequently, either alkyl hydroperoxides are formed as final reaction product or two of the alkyl peroxides recombine to yield equal amounts of the respective alcohol and ketone (Russel-type termination).[90,93] This is a very typical results of Fenton-type reactions, as dioxygen is formed as a side-product from the hydrogen peroxide decomposition according to the Haber-Weiss reaction, and thus dioxygen is always present in the reaction medium.[91,92] Analytically, the observed formation of equal amounts of alcohol and ketone is thus a hint towards a Fenton-type mechanism. Typically this is expressed in form of the alcohol-to-ketone (A/K) ratio, which in such a case is close to 1. Furthermore, accumulation of alkyl hydroperoxide as major oxidation product is indicative of the auto-oxidative pathway. However, exact quantification of alkyl hydroperoxide often faces analytical challenges due to its thermal instability.[37]

In contrast to the radical-based Fenton-type reaction pathway stands the metal-centered oxidation, in analogy to the mechanism of CYPs (see chapter 1.3.2). This has been proven for the first time by Groves, introducing a biomimetic heme iron catalyst for the oxidation of unreactive alkanes.[73] In case of the metal-centered mechanism the H atom abstraction is not a result of hydroxyl radicals but of a highly reactive high-valent iron oxo intermediate.[79,80,84,94]

Scheme 8. Simplified schematic drawing of the metal-centered oxidation mechanism of biomimetic iron-based oxidation catalysts: H atom abstraction from alkanes is achieved by a high-valent iron oxo intermediate (compare Compound I of CYPs) with the alkyl radical formed in this process staying in close proximity. Thus, it reacts immediately with the hydroxyl ligand to yield the hydroxylated alkane (compare Compound II of CYPs).[79,80,84,94]



Systems proceeding solely via the metal-centered pathway would in consequence selectively form the alcohol as oxidation product, resulting in a very high A/K ratio.[79,84] The required high-valent iron oxo intermediate can be formed from an iron(II) precursor and hydrogen peroxide;[79,95] however, so far decomposition of hydrogen peroxide resulting in radical formation always occurs in parallel. Thus, optimizing the electronic structure of the iron(II) precursor and balancing the reaction conditions for the catalytic conversion means usually balancing on a knife's edge: suppression of Fenton-type decomposition of hydrogen peroxide is required, while formation of high-valent iron oxo intermediates and their subsequent reactivity towards alkanes needs to be maintained.[96] Consequently, tremendous effort has been put into understanding the nature of the intermediates as well as into optimizing electronic and structural properties of iron complexes for catalytic applications.[95,97]

1.4.3 Important Milestones

Looking at artificial iron-based catalysts for the homogeneous, selective oxidation of alkanes, Groves achieved a first major milestone by identifying the metal-based mechanism (compare chapter 1.4.2).[74] At that point, porphyrin-based ligands were used in order to create artificial heme systems and these complexes were successfully used as catalysts for the oxidation of cyclohexane to cyclohexanol among other substrates.[73] Experimental evidence for an iron(IV) oxo intermediate as catalytically active species for artificial heme iron catalysts was given also by Groves a few years later in 1981.[98]

As for heme systems the possibilities for electronic and steric modifications are limited, non-heme systems with similar geometric features came into focus in the early 1990s.[84,90,96,97] For non-heme iron oxidation catalysts, also high-valent iron(IV) oxo intermediates are understood as catalytically active species. In that context a major breakthrough was achieved by Münck, Nam, and Que in 2003, as they provided a high yield route towards such an intermediate and they even were able to identify it unambiguously via single-crystal X-ray diffraction.[99] With the molecular structure at hand, a direct Fe=O bond with a length of 1.65 Å was identified, proving the existence of iron(IV) oxo units without the support of porphyrin-based ligands (Figure 7).

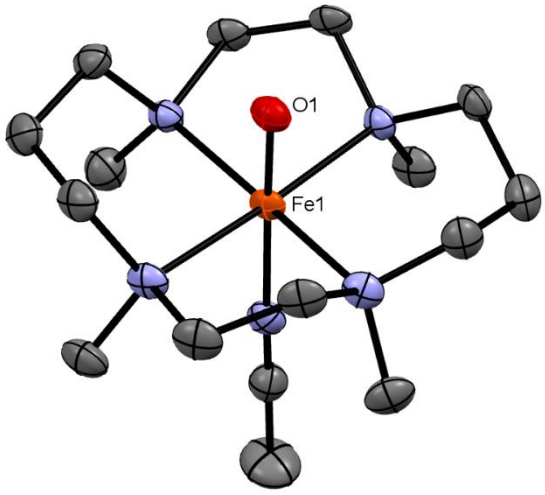
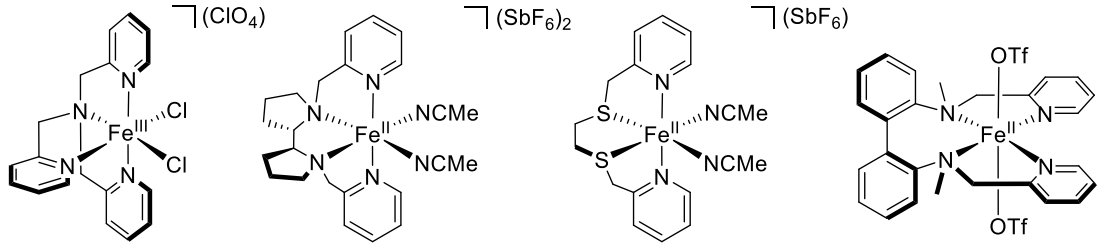


Figure 7. Molecular structure of $[Fe^{IV}O(TMC)(MeCN)]^{2+}$ obtained through single-crystal X-ray diffraction by Münck, Nam, and Que (structural data obtained from the Cambridge Crystallographic Data Centre, CCDC 192768).[99] TMC: 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane.

The use of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC) as supporting ligand was crucial for the isolation and crystallization of this intermediate. In the given case, the oxo ligand is surrounded by six H atoms of the alkylene bridges of the TMC ligand, hindering external reactants to access the oxo ligand easily.[99] Ever since, various research groups have been expanding the knowledge on a range of iron-oxygen intermediates which has been review comprehensively by Ray and Nam just recently.[95]

Beside mechanistic investigations Que also reported ground breaking work focusing on the catalytic oxidation of cyclohexane, starting in the early 1990s. For instance, Que introduced iron(III) complexes with tris(2-pyridylmethyl)amine (TPA) as supporting ligands ($[Fe^{III}(TPA)Cl_2](ClO_4)$, see Figure 8), exhibiting *cis* labile coordination sites.[100] With this approach, the idea of using non-heme iron

complexes that still resemble the geometric features of CYPs was abandoned and the basis for a broad range of TPA-derived ligand platforms was developed during the following years.[84,90,96]



$[Fe^{III}(TPA)Cl_2](ClO_4)$ $[Fe^{II}(Py_2S_2)(MeCN)_2](SbF_6)_2$

$[Fe^{II}(S,S\text{-PDP})(MeCN)_2](SbF_6)_2$ $[Fe^{II}(Py_2N_2)(OTf)_2]$

Figure 8. Selected examples of non-heme iron oxidation catalysts.[100-103] TPA: tris(2-pyridylmethyl)amine; *S*,*S*-PDP: 2-(((*S*)-2-[(*S*)-1-(pyridin-2-ylmethyl)pyrrolidin-2-yl]pyrrolidin-1-yl)methyl)pyridine; Py_2S_2: 1,6-bis(2'-pyridyl)-2,5-dithiahexane; Py_2N_2: *N*,*N*'-(biphenyl-2,2'-diyl)-*N*,*N*'-bis(2-pyridylmethyl)-*N*,*N*'-dimethyldiamine.

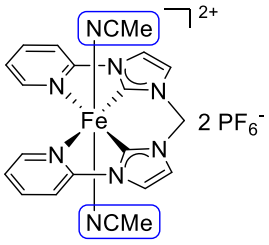
Great attention was paid to the work of White in 2007, who used molecular iron catalysts for the selective oxidation of highly functionalized molecules and therefore this type of reaction became interesting also for synthetic chemists.[102] In their work, White used the chiral, tetradentate supporting ligand *S*,*S*-PDP on iron(II), exhibiting *cis* labile coordination sites (Figure 8). Detailed investigations on chemoselectivity and siteselectivity in the oxidation of secondary C–H bonds to the respective ketones were conducted on a range of substrates.[104]

Examples of cyclohexane oxidation catalyzed by non-heme iron complexes are numerous.[84] As a selected example, Pombeiro used a modified version of a complex originally reported by Britovsek as non-heme iron catalyst.[101,105] With 1,6-bis(2'-pyridyl)-2,5-dithiahexane (Py_2S_2) as supporting ligand on a *cis*-α iron(II) complex (Figure 8), Pombeiro oxidized cyclohexane with 122 turnovers and an A/K ratio of 5, attesting this system a comparably good compromise of stability and selectivity.

Interestingly, reports on non-heme *trans* iron complexes as catalysts for cyclohexane oxidation are rare. This is surprising, as the CYP family as natural archetype is more comparable to a *trans* complex than a *cis* complex. Britovsek described the *trans* non-heme iron(II) complex $[Fe^{II}(Py_2N_2)(OTf)_2]$ as catalyst for the oxidation of cyclohexane (Figure 8).[103] However, compared to known *cis* complexes both stability (turnovers <5) and selectivity (A/K 1.9) are drastically lower. These data show that there is still significant room for improvement for non-heme *trans* iron complexes, as tuning of the ligand environment might help to better mimic the reactivity of CYPs.

2 OBJECTIVE

Inspired by the reactivity of CYPs in C–H bond oxidation and the given shortage of investigations on non-heme *trans* iron complexes as catalysts for this reaction, the iron(II) *N*-heterocyclic carbene (NHC) complex **1** provides a good starting point for such studies. **1** has been reported by Herrmann and Kühn in 2012 (Figure 9).[106]



1

Figure 9. Iron(II) NHC complex **1** bearing a tetradentate, methylene-bridged NCCN ligand and exhibiting *trans* labile coordination sites (blue frames).[106]

This non-heme iron(II) complex has geometric features comparable to CYPs, although the equatorial ligand is not a macrocycle. With *trans* labile sites at hand, **1** offers great potential for manifold modifications. Understanding the reactivity, the electronic properties, and the catalytic activity in C–H bond oxidation of **1** was the main target of this thesis.

In an initial step, substitution of the labile acetonitrile ligands in the apical positions of **1** was targeted (Figure 9, blue frames). Depending on the coordinating substituent in these positions, the electronic structure and the correlated electrochemical redox behavior needs to be studied both experimentally and theoretically. In that context an irreversible monosubstitution in only one of the two apical positions is a very interesting reaction, as this would result in a single active site *trans* to the apical ligand similar to CYPs. Also, such modifications will help to understand the general reactivity of **1** towards different potential reactants.

With that knowledge at hand, in a second step the impact of various electronic modifications and different apical substitution on the catalytic activity in C–H bond oxidation needs to be investigated. In the context of homogeneous oxidation of light alkanes, cyclohexane is the model substrate of choice (compare chapter 1.4.1 and Scheme 6). Furthermore, as it is well-known that iron-based coordination compounds often lack stability under oxidizing conditions, identification of possible decomposition pathways of the oxidation catalyst **1** and its modifications is of great interest and is also considered an additional aim of this work.

Beside modifications in the apical coordination sites of **1** also a synthetic modification of the tetradentate NCCN ligand itself is of interest. For instance, the number of NHC moieties can be varied, resulting in a different ratio of NHC-to-pyridine donors. As NHCs are considered as much stronger σ-donors, this can influence the electronic structure and thus the electrochemical redox behavior quite significantly. Another approach in that context is the change of the tetradentate ligand from an acyclic to a macrocyclic system, creating a geometric analog to the heme cofactor.

All investigations described here are part of a collaboration with the King Abdullah University of Science and Technology (KAUST), Saudi Arabia, within the *Catalytic oxidation of light hydrocarbons* project. Prof. Jean-Marie Basset acts as the principal investigator at KAUST.

3 RESULTS –

PUBLICATION SUMMARIES

3.1 Chemistry of Iron *N*-Heterocyclic Carbene Complexes: Syntheses, Structures, Reactivities, and Catalytic Applications

KORBINIAN RIENER,[#] **STEFAN HASLINGER**,[#] ANDREAS RABA,[#] MANUEL P. HÖGERL, MIRZA COKOJA, WOLFGANG A. HERRMANN, AND FRITZ E. KÜHN

[#] K. RIENER, S. HASLINGER, AND A. RABA CONTRIBUTED EQUALLY TO THIS WORK.

CHEMICAL REVIEWS **2014**, *114*, 5215-5272

In this comprehensive review article the vast development of the field of iron NHC complexes is surveyed. During the past decade, the focus on synthesizing bioinspired transition metal complexes and the urge to provide environmentally friendly catalysts resulted in an increasing number of iron-based complexes, including those relying on NHC ligands. Beside a plethora of novel structural motifs, the catalytic applicability of iron NHC complexes was extended to a variety of reactions, including C–C cross coupling, hydrosilylation, and polymerization reactions.

Mono- and bidentate NHC ligands were the first to be used for the formation of iron NHC complexes, which often derived from iron pentacarbonyl as precursor. Until today the majority of known iron NHC complexes still consists of mono- and bidentate NHC ligands. However, with the increasing interest in mimicking biological systems the focus shifted towards the application of polydentate ligands, a trend that is observed for both NHC and non-NHC containing ligand platforms. Consequently, the number of reported iron NHC complexes bearing polydentate (tri-, tetra-, and pentadentate) ligands with at least one NHC moiety increased drastically within the last few years. Supported by this development, iron compounds in unusual oxidation states such as +IV and +V could be accessed and characterized. Playing a crucial role as intermediates in biological processes, high-valent iron oxo and iron nitrite complexes are highly relevant for understanding enzymatic reactions in detail.

The application of iron NHC complexes as molecular catalysts still faces significant challenges, especially concerning mechanistic studies. Compared to late transition metals of the 4d and 5d rows iron easily undergoes one electron elementary steps. While on the one hand this allows access to a multitude of electronically different complexes, it increases on the other hand the probability of radical side reactions and thus the occurrence of less-defined reaction pathways. Nevertheless, the large number of catalytic reactions mediated by iron complexes underlines the potential of this metal in catalysis. Especially for C–C bond formation a number of examples is known where simple iron salts (e.g., $FeCl_3$) act as catalysts in the presence of NHC ligands. Well-defined, molecular iron NHC

complexes have been used to catalyze reduction reactions such as hydrosilylation or transfer hydrogenation reaction.

With respect to the goal of this thesis and the overall project that the thesis is part of, the lack of examples for iron NHC-catalyzed oxidation reaction is worth mentioning. Only added as *Note in Proof* to the review article, the application of an iron NHC complex as catalyst for olefin epoxidation by our group was the first example of C–O bond formation.

3.2 Molecular Iron Complexes as Catalysts for Selective C–H Bond Oxygenation Reactions

ANJA C. LINDHORST, **STEFAN HASLINGER**, AND FRITZ E. KÜHN

CHEMICAL COMMUNICATIONS **2015**, ADVANCE ARTICLE, DOI: 10.1039/C5CC07146A

In this Feature Article a comprehensive review on molecular iron catalysts and their application in selective C–H bond oxygenation reactions is given. Two main types of reactions are presented in detail: hydroxylation of alkanes and hydroxylation of aromatics.

Many catalytic systems described in the literature are inspired by biological archetypes, e.g., sMMO, CYPs, and the Rieske dioxygenases. Great potential is shown by non-heme iron catalysts with tetradentate ligands consisting solely of *N*-donor functionalities, for instance the TPA ligand. With TPA as supporting ligand on iron, the first example of a non-heme iron-catalyzed oxidation of alkanes via a metal-centered mechanism with hydrogen peroxide as the oxidant was given. Competition between a metal-centered reaction pathway and a radical-based pathway remains one of the main challenges in this field of research. Formation of radicals drastically reduces selectivity. Also, stability of iron-based coordination compounds under oxidizing conditions is still an issues that needs to be addressed, as catalyst degradation often results in very low turnover numbers (< 100, for many systems even < 20). Intending to increase both selectivity and stability, great efforts were spent on mechanistic studies, trying to understand the behavior of key intermediates such as high-valent iron oxo complexes. Compared to biological systems, the artificial mimics have the advantage of increased intermediate stability in many cases, allowing for a more detailed investigation on these compounds.

Despite enormous achievements during the last decades, artificial systems still are less active and less selective compared to enzymes. Thus, additional research is required to improve the overall catalyst performance. As iron is considered an environmentally friendly metal due to its abundance and its low toxicity, it is worth to further invest in molecular iron oxidation catalysts.

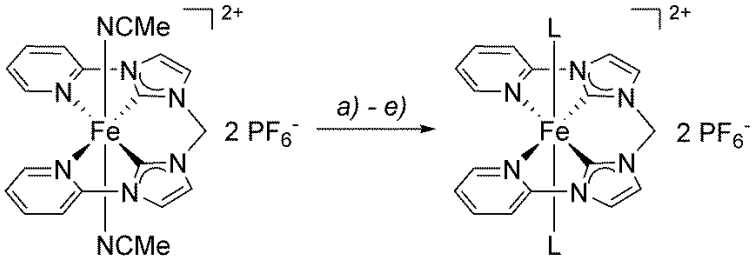
3.3 Making Oxidation Potentials Predictable: Coordination of Additives Applied to the Electronic Fine Tuning of an Iron(II) Complex

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 different phosphine- and pyridine-based ligands were used as axially coordinating additives for the bioinspired iron(II) NHC complex **1** (Scheme 9).

Scheme 9. Reactions of complex **1** with trimethylphosphine, triphenylphosphine, 4-dimethylaminopyridine (DMAP), pyridine (py), and methyl isonicotinate (Me^{i}nico) to form complexes **2**-**6**, respectively. *a)* excess PMe_3, MeCN, r.t. *b)* excess PPh_3, acetone, –78°C to r.t. *c)* excess DMAP, MeCN, r.t. *d)* excess pyridine, acetone, –78°C to r.t. *e)* excess Me^{i}nico, acetone, –78°C to r.t.



1

2 PMe_3
3 PPh_3
4 DMAP
5 py
6 Me^{i}nico

The trans-labile sites of **1** undergo axial ligand exchange easily. Depending on the donor strength of the additives for the ligand exchange reactions either acetonitrile (**2** and **4**) or acetone (**3**, **5**, and **6**) is required as solvent. Based on the resulting complexes **2-6** the predictability of oxidation potentials for the redox couple Fe^{II}/Fe^{III} was demonstrated. A linear correlation was found between the half-cell potentials obtained by cyclic voltammetry experiments and the DFT-calculated molecular orbital (MO) energies. Upon axial ligand exchange, the half-cell potentials of **1-6** cover a range of 79 mV to 440 mV (versus the ferrocene/ferrocenium (Fc/Fc^+) redox couple), showing the strong impact of the axial ligands on the electronic structure of the iron(II) atom. For the correlation with DFT-derived MO energies an approach known from Koopman's theorem was chosen: The energy required for ionization

– or, in this context, for oxidation – depends on the energy of the highest occupied MO. Hence, for **1-6** the HOMO energies were determined by DFT with a range of −5.76 eV to −6.34 eV, showing a distinct linear correlation to the experimentally obtained half-cell potentials.

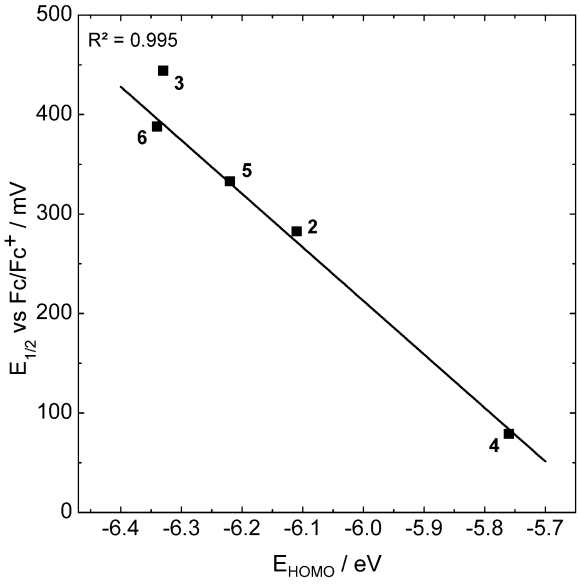


Figure 10. Linear relationship between experimental half-cell potential $E_{1/2}$ versus Fc/Fc^+ as determined by cyclic voltammetry and DFT-calculated energies of HOMOs (E_{HOMO}) on a B3LYP/B2 level of theory for complexes **2-6**. Values of **3** were not included in the linear fit as **3** did not exhibit full reversibility for at least 10 cycles in the CV experiment. Linear equation: $E_{1/2} = –538 \times E_{HOMO} – 3016$.

Furthermore, the applicability of this concept was proven by the mono(PMe_3)-substituted derivative of **1** with a predicted half-cell potential of 330 mV and an experimentally obtained value of 325 mV. The possibility to gain insights into the electronic properties on both a theoretical and experimental basis will help to created tailor-made catalyst systems and will allow an effective tuning o of bioinspired systems in terms of reactivity.

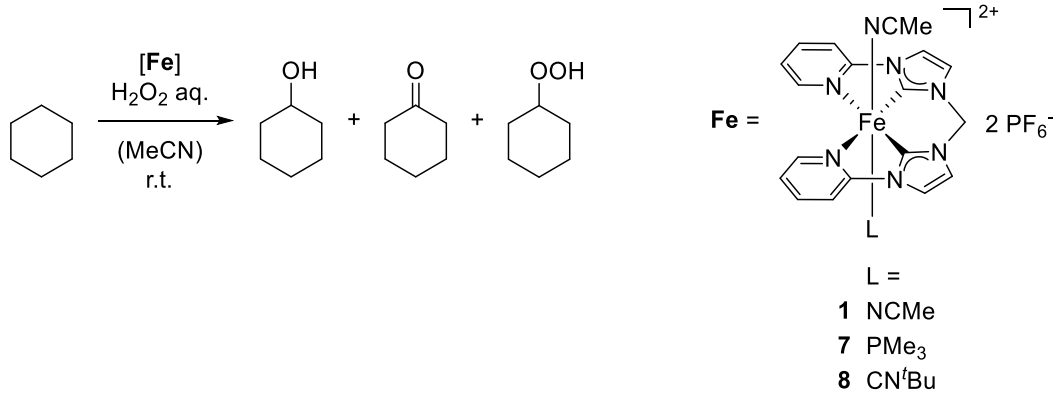
3.4 Iron-catalyzed Oxidation of Unreactive C–H Bonds: Utilizing Bio-Inspired Axial Ligand Modification to Increase Catalyst Stability

STEFAN HASLINGER, ANDREAS RABA, MIRZA COKOJA, ALEXANDER PÖTHIG, AND FRITZ E. KÜHN

JOURNAL OF CATALYSIS **2015**, *331*, 147-153

Bioinspired, iron-mediated oxidation of hydrocarbons is one of the focus areas of today's research in the field of catalysis. In this article we applied three different iron(II) complexes **1**, **7**, and **8** as catalysts for the oxidation of unreactive C–H bonds. With cyclohexane being a well-established model substrate, special focus laid on its oxidation to yield cyclohexanol, cyclohexanone, and cyclohexyl hydroperoxide (Scheme 10).

Scheme 10. Catalytic oxidation of cyclohexane to form cyclohexanol and cyclohexanone as well as cyclohexyl hydroperoxide. Complexes **1**, **7**, and **8** are used as catalysts [**Fe**] and aqueous hydrogen peroxide (50%) as the oxidant in an acetonitrile solution at room temperature.



It was shown that the introduction of an irreversibly bound axial ligand, e.g., trimethylphosphine or *tert*-butyl isocyanide, increased the stability of the catalyst under catalytic reaction conditions. For instance, with **8** as catalyst an increase in turnovers of up to 34% was observed compared to **1**. Achieving reasonable stability of molecular iron oxidation catalysts is one of the key challenges that still have to be addressed. Compared to recent other examples from the literature, the catalysts presented in this article show high stability with turnovers up to 43, depending on the reaction conditions. Significantly higher turnovers are typically only obtained under reaction conditions that are

optimized for the formation of the ketone as primary oxidation product. For catalysts **1**, **7**, and **8** almost no ketone formation was observed as shown by the very high alcohol + cyclohexyl hydroperoxide to ketone ration ((A+H/K) of up to 26. Overall, complex **8** showed the best combined results for both turnovers and high (A+H)/K ratio (43 turnovers, (A+H)/K = 19). To ensure a precise quantification of cyclohexyl hydroperoxide by gas chromatography, the samples were treated with triphenylphosphine prior to injection, resulting in the reduction of cyclohexyl hydroperoxide to cyclohexanol. Based on data obtained from double injections with selected samples before and after reduction with triphenylphosphine it was shown that cyclohexyl hydroperoxide is the major oxidation product of the catalytic reaction, indicating the significance of radical-chain autooxidative pathways.

Time-dependent monitoring of the turnovers for all three catalysts revealed a significant slower reaction for **8** (TOF = 4 h^{-1}) and **7** (TOF = 8 h^{-1}) compared to **1** (TOF = 47 h^{-1}). As expected, an increase in temperature resulted in a faster reaction (Figure 11).

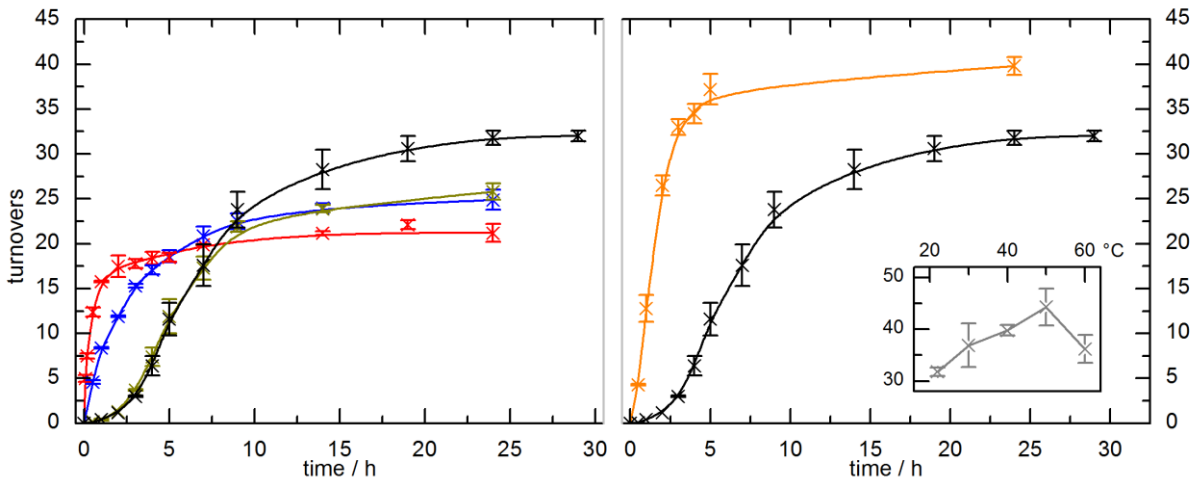


Figure 11. Kinetic plots for the oxidation of cyclohexane (569 µmol) with complexes **1**, **7**, and **8** at a relative catalyst concentration of 0.5 mol% (2.486 µmol). The turnovers are presented as combined turnovers for cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone (determined by GC). *Left*: Time-dependent turnovers at r.t. with 2 equiv. H_2O_2 for **1** (red), **7** (blue), and **8** (dark yellow) as well as for **8** with 3 equiv. H_2O_2 at r.t. (black). *Right*: Time-dependent turnovers for **8** with 3 equiv. H_2O_2 at r.t. (black) and 40 °C (orange). *Inset*: Number of turnovers after 24 hours for **8** with 3 equiv. H_2O_2 at various temperatures.

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

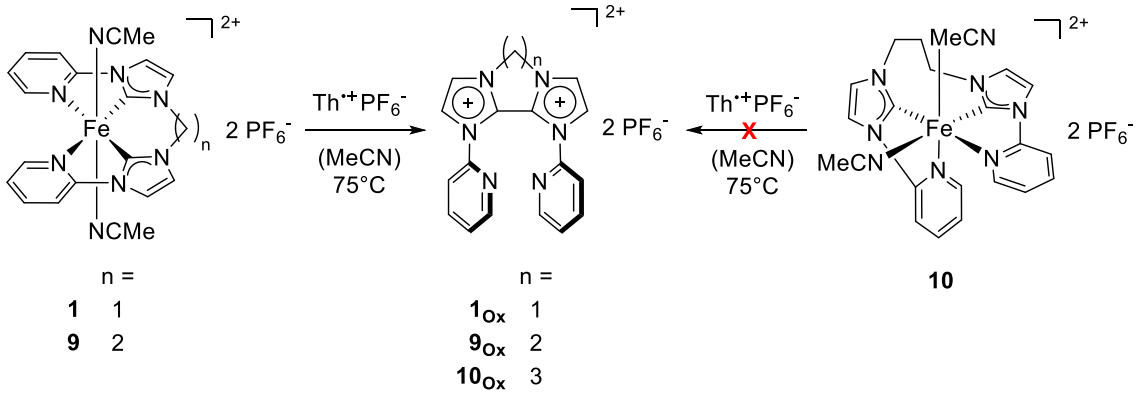
STEFAN HASLINGER,[#] JENS W. KÜCK,[#] MARKUS R. ANNESER, MIRZA COKOJA, ALEXANDER PÖTHIG, AND FRITZ E. KÜHN

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

CHEMISTRY – A EUROPEAN JOURNAL **2015**, EARLY VIEW, DOI: 10.1002/CHEM.201503282

In iron-catalyzed oxidation reactions the elimination of one-electron redox-steps potentially leads to a higher selectivity, as the formation of free radicals is less likely. It is well-known that the reaction of Fe(II) complexes with hydrogen peroxide results in an initial one-electron oxidation of iron(II) to iron(III) in many cases. A selective oxidation of iron(II) catalysts to their respective iron(III) derivatives prior to the application as catalysts can help to eliminate this initial oxidation that results in formation of highly reactive, free radicals. Thus, iron(II) oxidation catalyst **1** was reacted with the outer-sphere, one-electron oxidant thianthrene radical cation hexafluorophosphate ($Th^{\bullet+}PF_6^-$), expecting the formation of the respective iron (III) derivative. However, the annulated 2,2'-biimidazolium salt $\mathbf{1_{Ox}}$ was yielded as a defined decomposition product of the tetradentate ligand (Scheme 11) and the structure was identified without doubt by single crystal X-ray diffraction.

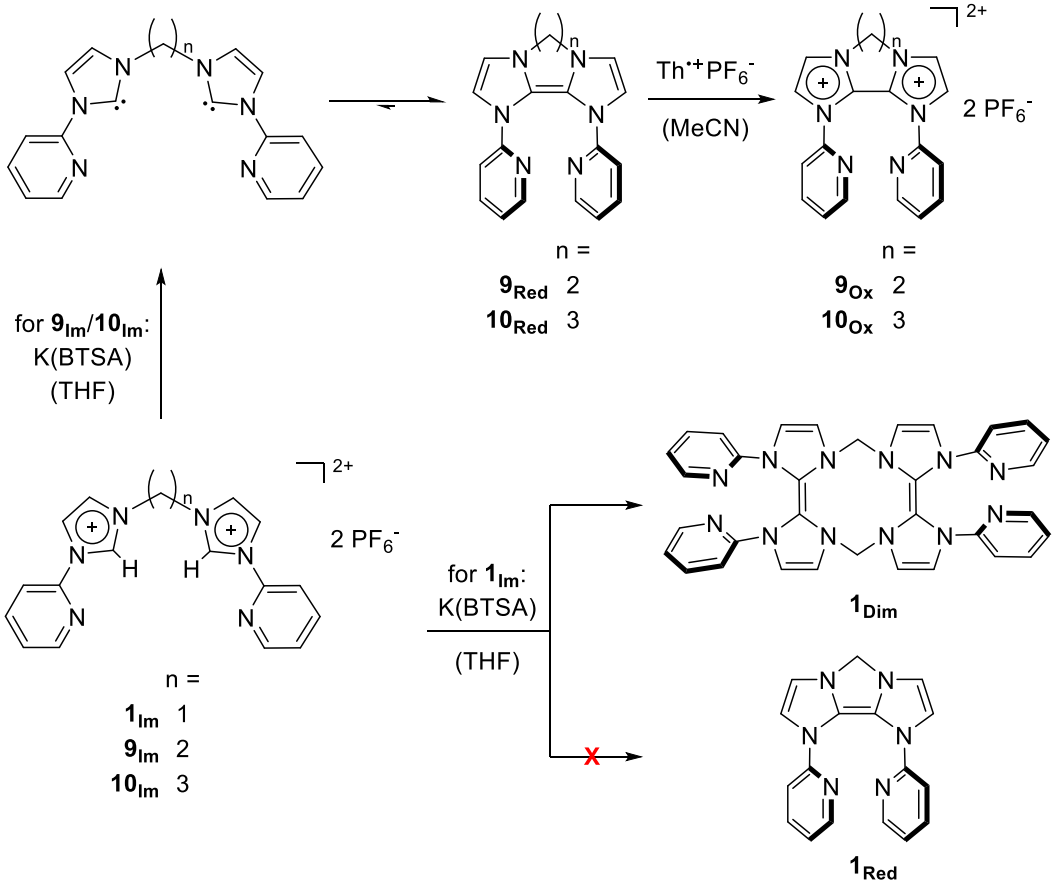
Scheme 11. Reaction of iron(II) complexes **1**, **9**, and **10** with the outer-sphere, one-electron oxidant thianthrene radical cation hexafluorophosphate ($Th^{\bullet+}PF_6^-$). In case of **1** and **9** the annulated 2,2'-biimidazolium salts $\mathbf{1_{Ox}}$ and $\mathbf{9_{Ox}}$ are obtained, while for **10** no reaction was observed.



As $\mathbf{1_{Ox}}$ is a very unusual example of a highly-strained fused *N*-heterocycle, the study was extended to iron(II) complexes bearing tetradentate NCCN ligands with longer alkylene tetheres (**9**: ethylene, **10**:

propylene). Interestingly, formation of the respective 2,2'-biimidazolium salts only was observed in case of trans complexes **1** and **9**. With respect to the extensive investigations of Wanzlick a different approach for the syntheses of these fused *N*-heterocycles was investigated, too, exploiting the tendency of NHCs to dimerize under certain conditions. Consequently, for ethylene- and propylene-tethered derivatives an iron-free access to the respective 2,2-biimidazolium salts $\mathbf{9_{Ox}}$ and $\mathbf{10_{Ox}}$ was found, while $\mathbf{1_{Ox}}$ can be obtained only via the iron(II) complex which acts as template for the C–C bond formation (Scheme 12).

Scheme 12. Dimerization of NHC ligands based on the Wanzlick equilibrium and subsequent oxidation to the respective 2,2'-biimidazolium salts in case of $\mathbf{9_{Ox}}$ and $\mathbf{10_{Ox}}$.



A similar reactivity was found after introduction of methyl substituents to the methylene bridge. As 2,2'-biimidazolium salts correspond to the oxidized form of tetraazafulvalenes (which are known to be strong reducing agents), electrochemical investigations were made in order to link the oxidized to the reduced form of these structures. It could be demonstrated that the reversibility of the electrochemical redox process strongly depends on the alkylene tether. While for ethylene-tethered $\mathbf{9_{Ox}}$ two fully reversible one-electron redox steps are evident from the cyclic voltammogram, methylene-tethered

1_{ox} undergoes only a single reduction wave which is irreversible. Remarkably, with two methyl substituents being present in the methylene tether the reversibility increases significantly, showing improved stability of the reduced form even after the second reduction wave (Figure 12).

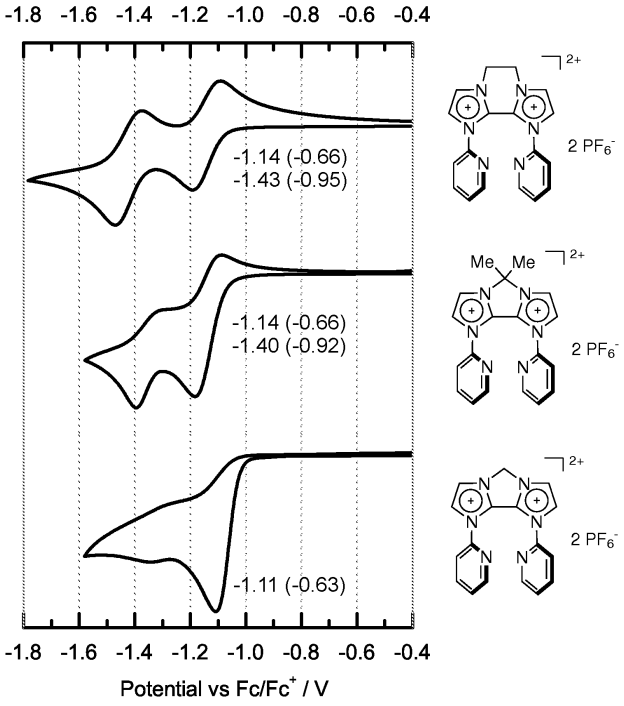


Figure 12. Electrochemical investigations of dimerized products with different alkylene tethers. While two fully reversible one-electron redox steps are found for the ethylene-tethered dimer (top), only one irreversible reduction occurs in case of the methylene-tethered derivative (bottom). Introduction of methyl substituents in the methylene tether increases the electrochemical reversibility (middle).

Furthermore, possible applications of this class of molecules were revealed. Oxidative addition of low-valent nickel(0) to the C–C bond gives access to the respective nickel(II) complex, a previously unknown synthesis of transition metal NHC complexes. Also, the CH_2 tether of **1_{ox}** is highly acidic and can be deprotonated to yield an uncommon, monocationic imidazolium salt with potential application in organometallic chemistry as ligand precursor.

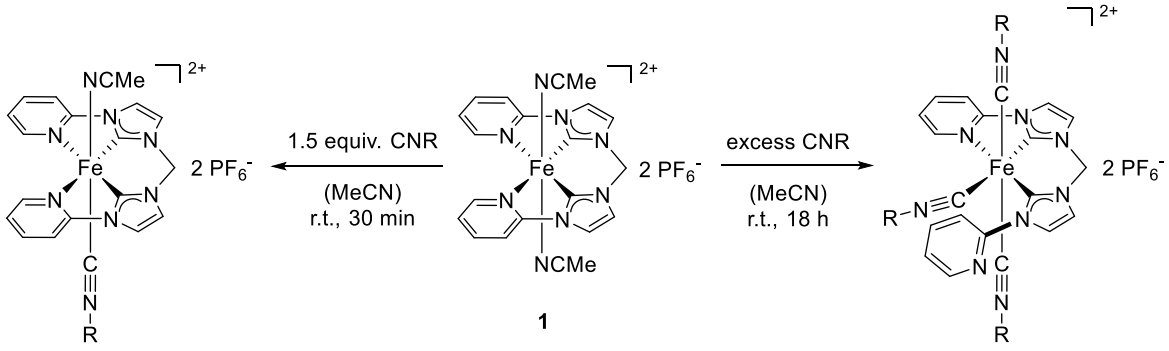
3.6 Isocyanide Substitution Reactions at the Trans Labile Sites of an Iron(II) *N*-Heterocyclic Carbene Complex

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

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

Based on the application of mono(CN^{t}Bu)-substituted iron(II) complex **8** as oxidation catalyst (see chapter 3.2) the range of isocyanide-substituted derivatives was extended. Also, the behavior of starting complex **1** under presence of larger amounts of isocyanide was investigated. Depending on the exact amount of isocyanide (CN^{t}Bu, CNCy, CNBn, CN(*p*-PhOMe)) either monosubstituted iron(II) complexes **8** and **11-13** or trisubstituted complexes **14-17** are obtained, while it is not possible to isolate *trans* disubstituted derivatives (Scheme 13).

Scheme 13. Reaction of **1** with different isocyanides to yield either monosubstituted complexes **8** and **11-13** or trisubstituted complexes **14-17**.



Upon formation of trisubstituted **14-17** the coordination mode of the tetradentate NCCN ligand changes to a trisdentate, meridional geometry. This was proven both in solution by NMR spectroscopy and in solid state by single crystal X-ray diffraction (for **14**, **15**, and **17**). The progress of the formation of **14** was monitored in detail by ^{1}H NMR spectroscopy in order to reveal possible intermediates.

Starting from **1**, **8** is formed within seconds, followed by accumulation of an intermediate up to 73% within 45 minutes (red line, Figure 13).

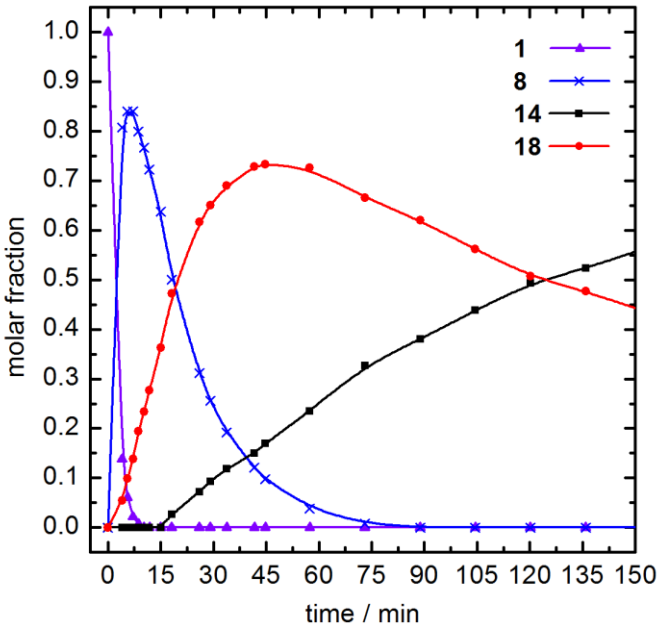


Figure 13. Time-dependent, relative amount of differently substituted iron(II) complexes upon reaction of **1** with 5 equiv. CN^{t}Bu. Data collected via ^{1}H NMR spectroscopy.

Integration of the NMR data at the point of maximum accumulation of the intermediate allowed identification of this species as the disubstituted iron(II) derivative **18**. In **18** the two isocyanide ligands coordinate *cis* and one of the pyridyl moieties of the NCCN ligand has already been removed from the coordination sphere.

All compounds were subjected to electrochemical investigations by cyclic voltammetry in order to understand the impact of the different substitution patterns on the electronic structure of the iron(II) atom. Compared to starting complex **1** (423 mV vs. Fc/Fc+) the half-cell potential of the Fe^{II}/Fe^{III} redox step is increased for all compounds **8** and **11-17**. The effect is more severe in case of trisubstituted **14-17** (up to 1092 mV) compared to monosubstituted **8** and **11-13** (up to 573 mV) as a consequence of the larger number of π–acceptor ligands coordinating to iron(II).

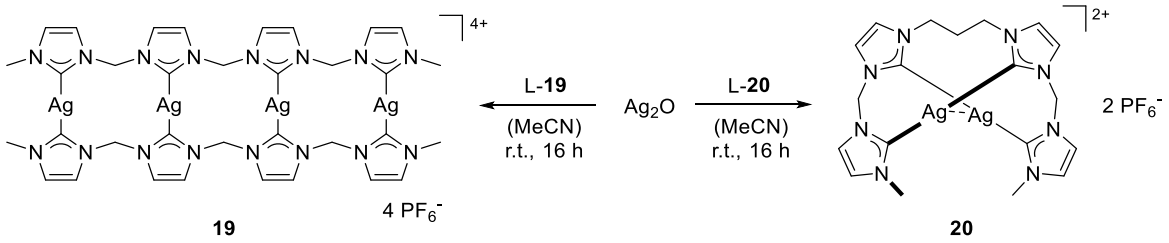
3.7 Application of Open Chain Tetraimidazolium Salts as Precursors for the Synthesis of Silver Tetra(NHC) Complexes

DANIEL T. WEISS, **STEFAN HASLINGER**, CHRISTIAN JANDL, ALEXANDER PÖTHIG, MIRZA COKOJA, AND FRITZ E. KÜHN

INORGANIC CHEMISTRY **2015**, *54*, 415-417

Tetra(NHC) ligands usually are reported as macrocyclic systems with a central cavity for a coordinated metal atom. In this work, acyclic open chain tetra(NHC) ligands were reported together with the respective silver complexes (Scheme 14). The use of acyclic ligands compared to macrocyclic ligands allows for different coordination geometries due to higher flexibility in the ligand backbone.

Scheme 14. Syntheses of silver tetra(NHC) complexes **19** and **20** with different geometries in dependence of the length of the alkylene bridge.



The syntheses of the two different tetra(NHC) ligands was achieved via an initial methylation of a methylene-bridged diimidazole as a crucial step. The resulting silver complexes **19** and **20** were obtained based on standard procedures for silver NHC complexes. It was shown by single crystal X-ray diffraction that the coordination geometry of **19** and **20** directly depends on the length of the alkylene tethere (**19**: methylene, **20**: propylene). While **19** exhibits a double helix structure with four silver cations being coordinated by two tetra(NHC) ligands, only one tetra(NHC) ligand is wrapped around two silver cations in case of **20**. With respect to the well-known use of silver complexes as transmetalation agents, **19** and **20** can help to access a range of transition metal complexes supported by acyclic, open chain tetra(NHC) ligands (see chapter 3.8).

3.8 Structural diversity of late transition metal complexes with flexible tetra-NHC ligands

DANIEL T. WEISS, PHILIPP J. ALTMANN, **STEFAN HASLINGER**, CHRISTIAN JANDL, ALEXANDER PÖTHIG, MIRZA COKOJA, AND FRITZ E. KÜHN

DALTON TRANSACTIONS **2015**, ADVANCE ARTICLE, DOI: 10.1039/C5DT02386F

Starting from two silver tetra(NHC) complexes **19** and **20** with different coordination geometry (see chapter 3.7), a range of d-block metal complexes was accessed via transmetalation to copper(I), gold(I), nickel(II), palladium(II), platinum(II), and iron(II). Depending on both length of the alkylene bridges of the tetra(NHC) ligands and the type of metal, different coordination geometries of the isolated complexes were obtained. In case of the coinage metals the geometry is similar to the silver complexes used as starting material: For methylene-bridged tetra(NHC) ligands a dimeric, tetranuclear double helix structure is obtained, for propylene-bridged tetra(NHC) ligands a monomeric, dinuclear structure is found with the ligand being wrapped around two metal atoms. Transmetalation to the group 10 metals nickel(II), palladium(II), and platinum(II) results in the expected formation of distorted square-planar complexes, with the degree of distortion depending on the length of the alkylene bridge of the tetra(NHC) ligand. Investigated in more detail, transmetalation to iron(II) yields complexes with octahedral coordination geometry. In case of the methylene-bridged tetra(NHC) ligand, the coordination mode fluctuates between *trans* and *cis*-β for the respective iron(II) complex at room temperature. Substitution of the acetonitrile ligands by irreversibly bound PMe_3 freezes the *trans* coordination mode as shown by single crystal X-ray diffraction. The more flexible propylene-bridged tetra(NHC) ligand facilitates *cis*-β coordination, which is the only observed geometry for the respective iron(II) complex. Compared to macrocyclic tetra(NHC) ligands this is the first known example for an iron(II) tetra(NHC) complex with *cis*-labile binding sites.

3.9 Synthesis and Characterization of an Iron Complex Bearing a Cyclic Tetra-*N*-heterocyclic Carbene Ligand: An Artifical Heme Analogue?

MARKUS R. ANNESER, **STEFAN HASLINGER**, ALEXANDER PÖTHIG, MIRZA COKOJA, JEAN-MARIE BASSET, AND FRITZ E. KÜHN

INORGANIC CHEMISTRY **2015**, *54*, 3797-3804

In this article the work on tetra(NHC) ligands (compare chapters 3.7 and 3.8) was extended to macrocyclic systems. An octahedral iron(II) complex with *trans* geometry bearing a macrocyclic tetra(NHC) ligand (molecular structure see Figure 14) was synthesized and investigated in terms of reactivity and electronic properties.

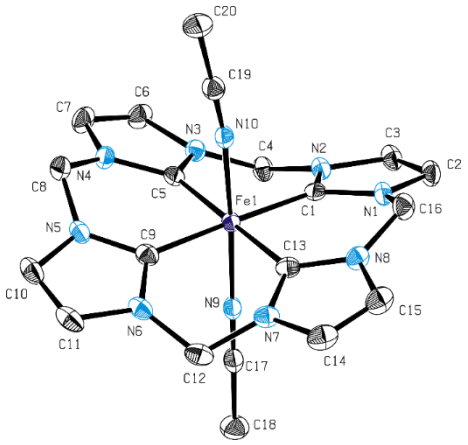
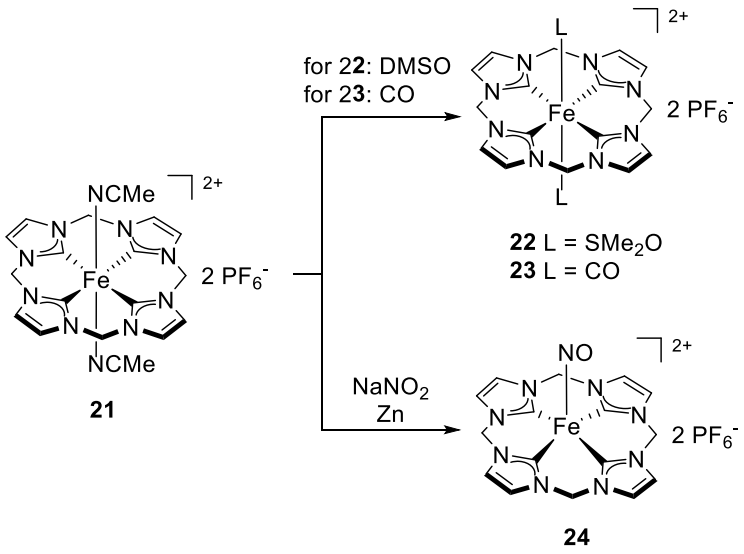


Figure 14. ORTEP-style representation of the cationic fragment of compound **21**. Hydrogen atoms and two PF_6^- anions are omitted for clarity and thermal ellipsoids are shown at a 50% probability level. Selected bond lengths (Å) and angles (°): Fe1−C1: 1.912(3), Fe1−C5: 1.904(3); Fe1−N9: 1.930(1), Fe1−N10: 1.933(1), N9−C17: 1.140(1), N10−C19: 1.133(1), C1−Fe1−C5: 90.31(2), N9−Fe1−N10: 177.08(3), Fe1−N9−C17: 173.25(3), Fe1−N10−C19: 177.50(4).

Based on cyclic voltammetry, the half-cell potential for the fully reversible Fe^{II}/Fe^{III} redox couple of **21** is 0.15 V versus Fc/Fc^+. This relatively low value is a direct consequence of the strong σ-donor potential of the tetra(NHC) ligand, resulting in a high electron density at the iron(II) atom. Ligand exchange reactions with DMSO, CO, and $NaNO_2$ were conducted in order to replace the *trans* acetonitrile ligands and to investigate the impact on the electronic structure (Scheme 15).

Scheme 15. Reaction of iron(II) tetra(NHC) complex **21** with DMSO, CO, and $NaNO_2$ to form substituted derivatives **22**, **23**, and **24**, respectively.



In case of DMSO and CO the *trans*-disubstituted iron(II) complexes **22** and **23** were yielded and the required oxidation potentials of the Fe^{II}/Fe^{III} redox couple were shifted to 0.74 V and 1.25 V, respectively. The effect is remarkable especially for CO-substituted **23** as a result of the strong π-acceptor properties of CO as ligand. This is also reflected by the IR stretching vibration band of the coordinated CO at 2010 cm^{-1}. NO-substituted iron(II) complex **24** exhibits a distorted square-pyramidal coordination geometry with the iron(II) atom being located slightly above the plane spanned by the four coordinating carbon atoms. Single crystal X-ray diffraction of **24** showed a significant increase in the N–O bond length from 1.14 Å to 1.159(3) Å upon coordination. Electrochemically, no oxidation of **24** was obtained in the accessible range of potential. Instead, an irreversible NO-centered reduction was revealed at a potential of –1.06 V, resulting in removal of the NO ligand from the coordination sphere.

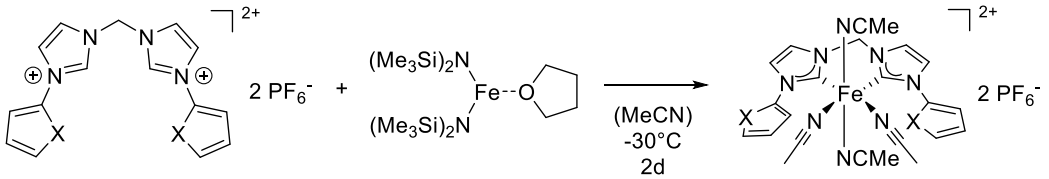
3.10 Synthesis, Characterization, and Reactivity of Furan- and Thiophene-Functionalized Bis(N-heterocyclic carbene) Complexes of Iron(II)

JULIA RIEB, ANDREAS RABA, **STEFAN HASLINGER**, MANUEL KASPAR, ALEXANDER PÖTHIG, MIRZA COKOJA, JEAN-MARIE BASSET, AND FRITZ E. KÜHN

INORGANIC CHEMISTRY **2014**, *53*, 9598-9606

Modification of the previously described tetradentate NCCN ligand (see chapters 3.3 to 3.6) by substitution of the pyridyl moieties with furan and thiophene groups leads to ligands of the type OCCO (**25a**) and SCCS (**25b**). These ligands were applied in the syntheses of iron(II) complexes using $[Fe(N(SiMe_3)_2)_2]\cdot THF$ as iron precursor, expecting to yield *trans* geometry as observed for the analog Fe(NCCN) complexes. However, in contrast to the tetradentate, equatorial coordination of the NCCN ligand the OCCO and SCCS motif coordinates only via the two NHC units to the iron(II) atom, as revealed by single crystal X-ray diffraction. Consequently, four acetonitrile molecules complete the octahedral geometry of complexes **26a** and **26b** (Scheme 16).

Scheme 16. Formation of iron(II) NHC complexes **26a** and **26b** from imidazolium salts **25a** and **25b**, respectively.



Exemplary it was demonstrated for **26a** that the acetonitrile ligands are prone to ligand exchange reactions and can be replaced by PMe_3, for instance. NMR scale reactions were conducted to investigate the differently substituted iron(II) complexes that derive from **26a** upon reaction with a varied relative amount of PMe_3 (1, 2, 3, 4, and 10 equivalents). Although four labile acetonitrile sites are given in **26a**, ^{31}P NMR revealed only two different substitution products upon stepwise addition of PMe_3: A mono(PMe_3)-substituted derivative of **26a** and a tetra(PMe_3)-substituted complex, with either one or all four acetonitrile ligands being replaced by PMe_3. Formation of di- or tri(PMe_3) substitution patterns were not observed (Figure 15).

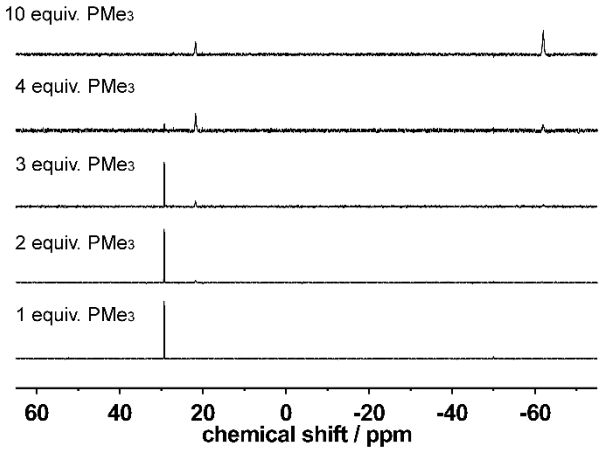


Figure 15. Reaction of **26a** with PMe_3 at room temperature: ^{31}P NMR reveals three different signals at 29.28 ppm (monosubstituted complex), 21.72 ppm (tetrasubstituted complex), and –61.98 ppm (free PMe_3), depending on the relative amount of PMe_3.

DFT calculations were used in order to reveal the nature of the mono(PMe_3)-substituted complex. As thermodynamically most favored product a coordination of PMe_3 *cis* to the NHC ligand was found, with PMe_3 directing away from the methylene bridge between the two NHC moieties. These findings are supported by evaluation of ^1H NMR data, showing characteristic signal patterns of the CH_2 bridge that indicate asymmetry in the equatorial plane upon addition of 1 equiv. PMe_3.

3.11 NHC versus Pyridine: How "Teeth" Change the Redox Behavior of Iron(II) Complexes

DANIEL T. WEISS,[#] MARKUS R. ANNESER,[#] **STEFAN HASLINGER**, ALEXANDER PÖTHIG, MIRZA COKOJA, JEAN-MARIE BASSET, AND FRITZ E. KÜHN

[#] D. T. WEISS AND M. R. ANNESER CONTRIBUTED EQUALLY TO THIS WORK.

ORGANOMETALLICS **2015**, *34*, 5155-5166

The motif of the supporting, tetradentate NCCN ligand on iron(II) was varied in terms of the exact number of NHC moieties within the acyclic tetradentate ligand. Four different cases were studied: one NHC/three pyridyl (NCNN), two NHC/two pyridyl (NCCN), three NHC/one pyridyl (NCCC), and four NHC/no pyridyl moieties (CCCC). For the first time the structural motif containing an NCNN or NCCC ligand was described in this work (Figure 16).

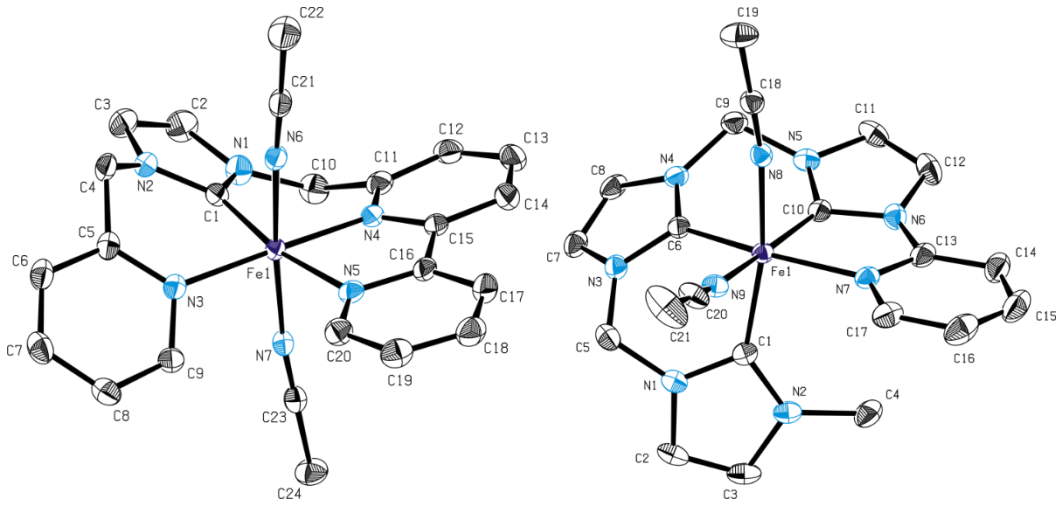


Figure 16. Molecular structures of dicationic iron(II) complexes bearing tetradentate ligands with either one NHC moiety (left) or three NHC moieties (right). The geometry in the given examples changes from *trans* (left) to *cis*-β (right) as a result of the terminal methyl group, which is pushed away from the pyridyl unit.

Of special interest in this context was the impact of the different ligands on the electronic structure of the iron(II) complexes and the electrochemical redox behavior. As revealed by cyclic voltammetry, the impact on the half-cell potential of the Fe^{II}/Fe^{III} redox step is quite severe. In case of mono-NHC ligands potentials of 0.68 and 0.58 V versus the Fc/Fc^{+} redox couple were found, while the half-cell potentials decreased to 0.35-0.42 V (di-NHC ligands), 0.25 V (tri-NHC ligand), and even 0.02-0.08 V (tetra-NHC

ligands). A more detailed look into the respective half-cell potentials revealed a direct correlation between the number of NHC donors and the potential. The linear correlation of this behavior is shown in Figure 17.

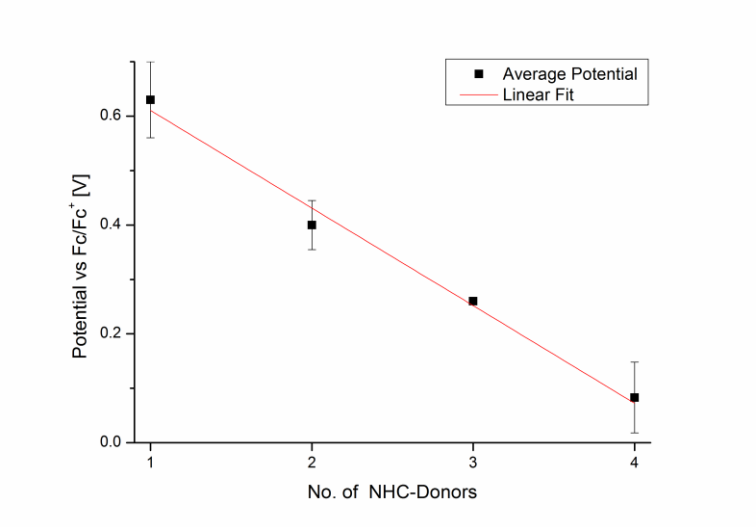


Figure 17. Correlation between the average half-cell potential $E_{1/2}$ to the number of carbene donors in the tetradentate ligand.

3.12 Iron Complexes of a Macrocyclic *N*-Heterocyclic Carbene/Pyridine Hybrid Ligand

IRIS KLAWITTER, MARKUS R. ANNESER, SEBASTIAN DECHERT, STEFFEN MEYER, SERHIY DEMESHKO, **STEFAN HASLINGER**, ALEXANDER PÖTHIG, FRITZ E. KÜHN, AND FRANC MEYER

ORGANOMETALLICS **2015**, *34*, 2819-2825

Linking the acyclic NHC pyridine hybrid ligands to the macrocyclic tetra(NHC) ligand, a macrocyclic NCNC ligand is presented in this work as supporting ligand on iron(II). Two *trans* labile coordination sites allow for various ligand exchange reactions, in this work the substitution with carbon monoxide as neutral ligand and azide as anionic ligand is investigated.

Most interestingly in this context, however, is the outer-sphere one electron oxidation of the iron(II) complex bearing the macrocylic NCNC ligand. Using thianthrene hexafluorophosphate $Th^{\bullet+}PF_6$ as oxidant the respective iron(III) complex is yielded as stable compound. This one electron oxidation step can also be achieved by electrochemical approaches, as demonstrated by UV/vis spectro-electrochemistry. Upon oxidation, formation of a broad asymmetric band at 660 nm is observed, which is characteristic for the iron(III) compound. Single crystal X-ray diffraction showed that the overall geometry is almost unaffected upon the oxidation from iron(II) to iron(III) (Figure 18).

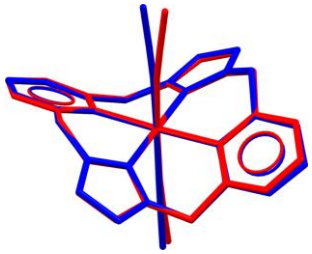


Figure 18. Overlay of the molecular structure of the cationic fragments of the iron(NCNC) complexes in oxidation states +II (blue) and +III (red).

The formation of a stable iron(III) derivative upon oxidation with $Th^{\bullet+}PF_6$ stands in clear contrast to the decomposition observed in case of the acyclic NCCN ligand supporting iron(II), as described in chapter 3.5. Apparently, macrocyclic ligand scaffolds are a useful approach to avoid cleavage of the Fe–C bond via reductive elimination.

4 CONCLUSION AND OUTLOOK

In this work the iron(II) NCCN complex **1** has been investigated in detail with a major focus on reactivity, electronic structure, and catalytic activity in alkane oxidation. The *trans* labile sites of **1** allowed for a broad range of modifications without altering the structure of the supporting, tetradentate NCCN ligand. An overview of all modifications of **1** that have been made by substitution reactions in the apical positions is given in Figure 19 (see also chapters 3.3, 3.4, and 3.6).

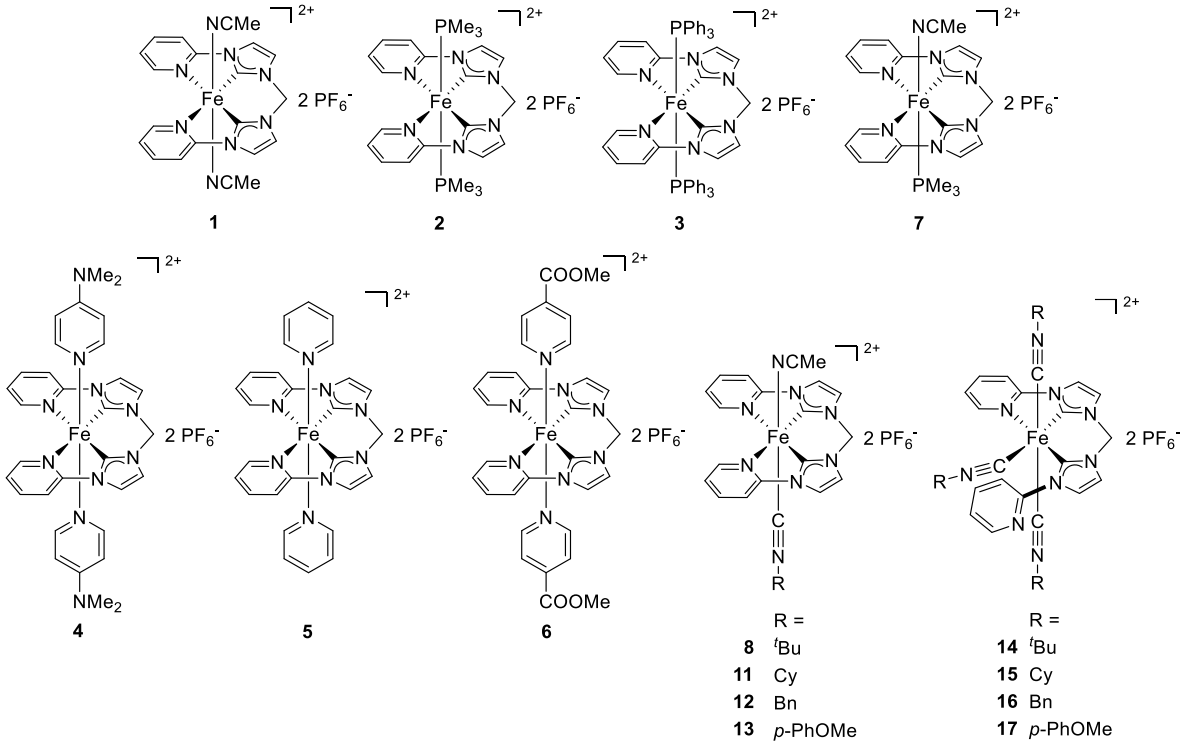


Figure 19. Overview of all modifications made to iron(II) complex **1** upon ligand exchange reactions in the apical positions without altering the structure of the supporting NCCN ligand (see chapters 3.3, 3.4, and 3.6).

Three different classes of neutral ligands proved to be suitable for apical modifications: pyridine-based, phosphine-based, and isocyanide-based molecules. In addition, a monocarbonyl derivative of **1** exists which was reported by Herrmann and Kühn prior to the start of the work described in this thesis.[106] Based on the disubstituted complexes **2-6** the impact of the apical ligands on the electronic structure of the iron(II) complexes and thus on the half-cell potential of the Fe^{II}/Fe^{III} redox couple was investigated. It was found that depending on the chosen apical ligands the half-cell potentials cover a range of 79 mV to 440 mV versus the Fc/Fc^{+} redox couple (chapter 3.3). Furthermore, predictability of half-cell potentials for this class of compounds by DFT calculations was demonstrated and extended to monosubstituted complexes, e.g., complex **7**.

These monosubstituted complexes are of special interest as they exhibit geometric similarities to CYPs as natural archetypes. Both monosubstituted complexes **7** and **8** have only one accessible coordination site, which is *trans* to one irreversibly bound apical ligand. Geometrically this is similar to CYPs (1.3.2), where the accessible coordination site for all reactions is positioned *trans* to an apical thiolate ligand (Figure 20). Thus, complexes **7** and **8** were investigated in more detail as catalysts for alkane oxidation together with the unsubstituted starting complex **1** (chapter 3.4).

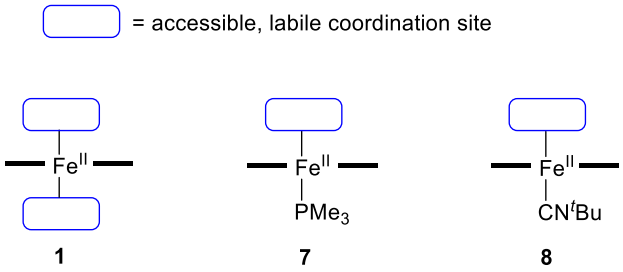


Figure 20. Schematic visualization of accessible, labile coordination sites in the apical positions of unsubstituted complex **1** and monosubstituted complexes **7** and **8**.

It was shown that blocking one of the two accessible coordination sites of **1** results in a slower catalytic oxidation of cyclohexane, but at the same time more turnovers (up to 34%) can be achieved, indicating an increased catalyst stability. The impact on selectivity is negligible. In all cases cyclohexyl hydroperoxide is formed as major oxidation product from cyclohexane with ratios of up to 80%. This clearly hints towards a radical auto-oxidative pathway (compare chapter 1.4.2) with metal-centered oxidation playing only a minor role. Nevertheless, as cyclohexyl hydroperoxide is fairly stable under the reaction conditions and accumulates during the reaction, it is easily reduced to the desired cyclohexanol during the quenching process by addition of phosphines. As a consequence, high A/K ratios of up to 26 were achieved.

With the catalyst stability being a critical issue, the elimination of the initial one-electron oxidation step from the iron(II) precursor **1** to the respective iron(III) derivative was targeted. Using an iron(III) catalyst precursor might help to reduce unproductive hydrogen peroxide decomposition during the reaction. The outer-sphere one-electron oxidation of **1**, however, resulted in defined decomposition of the complex and the highly-strained, fused *N*-heterocyclic compound $\mathbf{1_{ox}}$ as reductive elimination product was isolated (Figure 21 and chapter 3.5). A change of the supporting ligand to a macrocyclic system suppressed this decomposition, as the respective iron(III) derivatives are no longer prone to Fe–C bond cleavage (chapter 0).

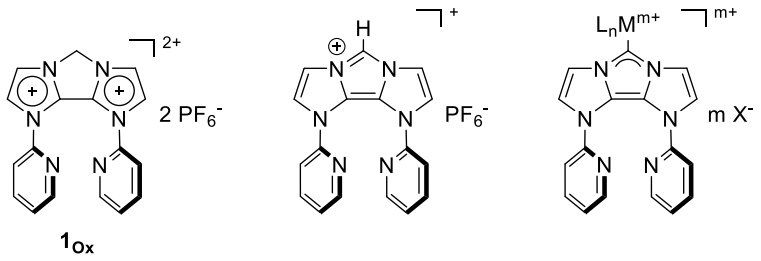


Figure 21. Fused *N*-heterocycle $\mathbf{1_{ox}}$ as decomposition product of the oxidation of iron(II) complex **1**. Due to its highly acidic methylene bridge it can form uncommon imidazolium salts upon deprotonation (middle), which have potential to lead to a novel class of electron rich NHC ligands with very low steric demand (right).

Properties of $\mathbf{1_{ox}}$ and some derivatives were investigated in detail to understand this type of molecule and to reveal any potential for possible applications. Perspectively, $\mathbf{1_{ox}}$ bears potential as precursor for electron rich NHC ligands with very low steric demand (Figure 21). Initial experiments in that context showed that formation of silver NHC complexes derived from $\mathbf{1_{ox}}$ might be achievable. The subsequent chemistry holds potential for future investigations, especially as the $\mathbf{1_{ox}}$-derived NHC ligand is most likely redox active, based on the findings presented in chapter 3.5.

Apart from all the derivatives of **1** (see Figure 19) that have been presented in this work several additional modifications to the ligand environment of the iron(II) complex have been made. By altering the tetradentate, supporting ligand a broad range of iron(II) complexes with different geometric and electronic features were accessed (chapters 3.7-3.12). With all these structures at hand, a strong basis is given to further investigate catalytic applications and decomposition routes under oxidizing conditions. Furthermore and probably most interestingly, mechanistic investigations on the catalytic oxidation of cyclohexane and on the reaction of the iron(II) complexes with hydrogen peroxide or even dioxygen can be pursued. Initial experiments on the reactivity of **1** towards hydrogen peroxide show a defined reaction at low temperatures, that eventually allows isolation of temperature sensitive intermediates (Figure 22).

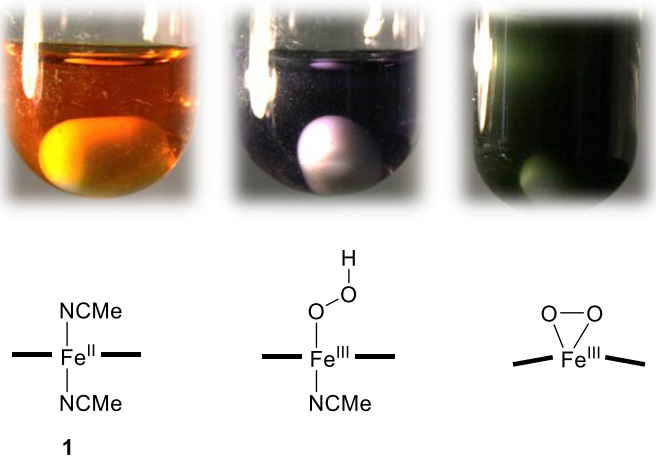


Figure 22. Reaction of a solution of iron(II) complex **1** (left) with hydrogen peroxide at low temperature leads to formation of a purple, temperature sensitive intermediate (middle). This intermediate reacts with bases to form a green product, which is even more temperature sensitive (right).

The true nature of these intermediates has not been revealed so far. Based on reports in the literature it is possible that an iron(III) hydroperoxide complex is formed from **1** upon reaction with hydrogen peroxide, which in a subsequent reaction can be deprotonated.[95,107] Being little understood so far, this reaction offers great potential for additional research on iron oxo intermediates. Characterization of an iron(III) hydroperoxide or an iron(III) peroxo complex with detailed understanding of their reactivity certainly would enrich the scientific community, as among all iron oxo intermediates known today only few examples of these two compound classes are reported.[95]

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A. C. Lindhorst, S. Haslinger and F. E. Kühn, *Chem. Commun.*, 2015, Advance Article, DOI: 10.1039/C5CC07146A

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

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Iron-catalyzed Oxidation of Unreactive C–H Bonds: Utilizing Bio-Inspired Axial Ligand Modification to Increase Catalyst Stability

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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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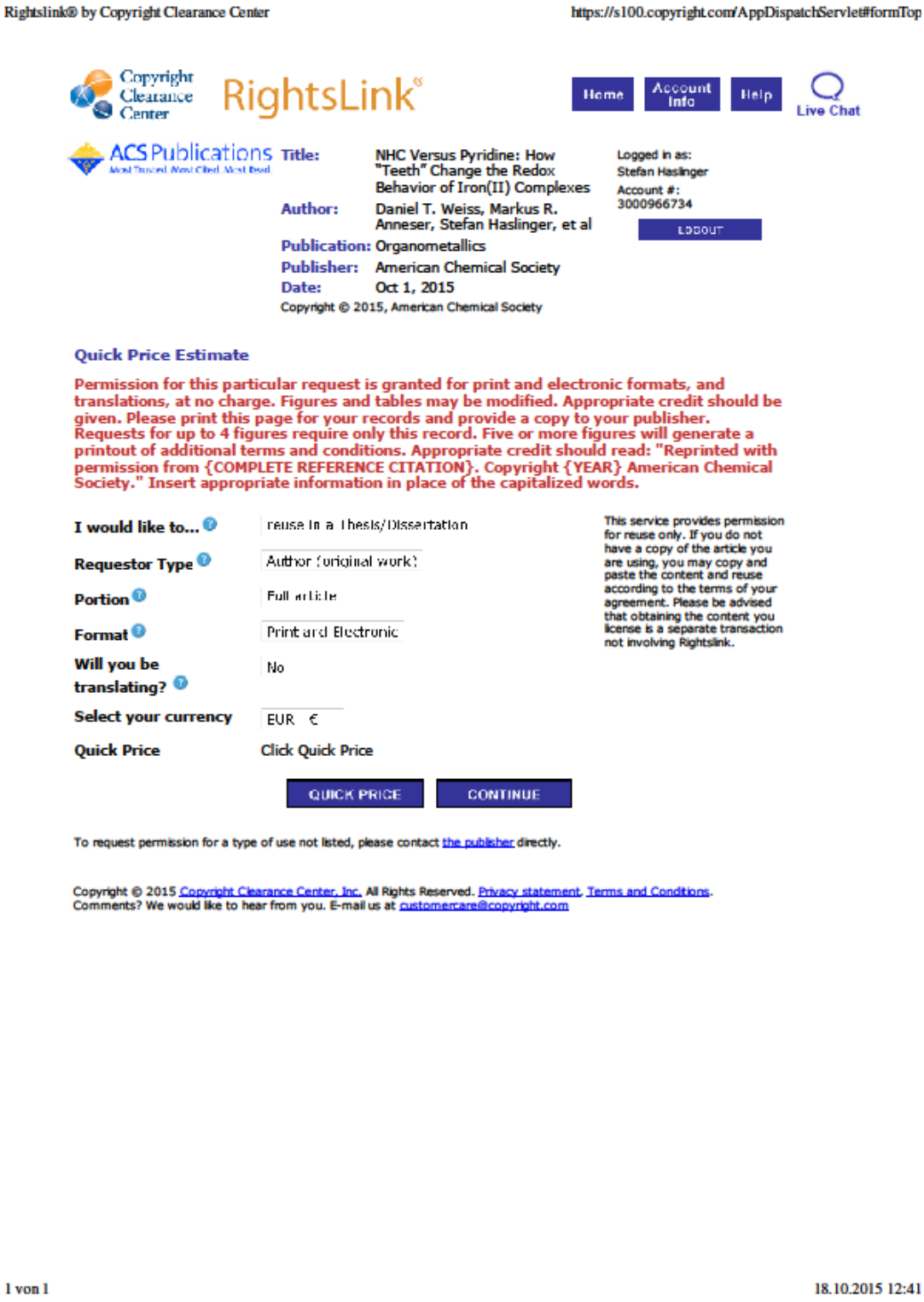

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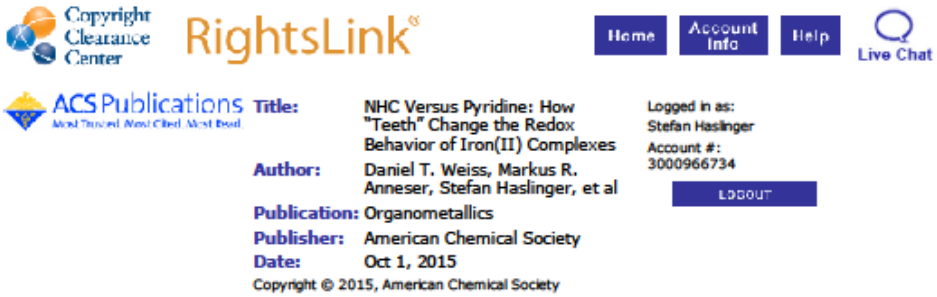

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6 BIBLIOGRAPHIC DATA OF COMPLETE PUBLICATIONS

Chemistry of Iron N-Heterocyclic Carbene Complexes: Syntheses, Structures, Reactivities, and Catalytic Applications

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Molecular Iron Complexes as Catalysts for Selective C–H Bond Oxygenation Reactions

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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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Iron-catalyzed Oxidation of Unreactive C–H Bonds: Utilizing Bio-Inspired Axial Ligand Modification to Increase Catalyst Stability

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

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Application of Open Chain Tetraimidazolium Salts as Precursors for the Synthesis of Silver Tetra(NHC) Complexes

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Structural diversity of late transition metal complexes with flexible tetra-NHC ligands

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Synthesis and Characterization of an Iron Complex Bearing a Cyclic Tetra-N-heterocyclic Carbene Ligand: An Artifical Heme Analogue?

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Synthesis, Characterization, and Reactivity of Furan- and Thiophene-Functionalized Bis(N-heterocyclic carbene) Complexes of Iron(II)

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NHC versus Pyridine: How "Teeth" Change the Redox Behavior of Iron(II) Complexes

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Iron Complexes of a Macrocyclic N-Heterocyclic Carbene/Pyridine Hybrid Ligand

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8 COMPLETE LIST OF PUBLICATIONS

Publications

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

S. Haslinger,* J. W. Kück,* M. R. Anneser, M. Cokoja, A. Pöthig, F. E. Kühn
Chemistry – A European Journal **2015**, Early View, DOI: 10.1002/chem.201503282

[15] *Molecular Iron Complexes as Catalysts for Selective C−H Bond Oxygenation Reactions*

A. C. Lindhorst, **S. Haslinger**, F. E. Kühn
Chemical Communications **2015**, Advance Article, DOI: 10.1039/C5CC07146A

[14] *NHC Versus Pyridine: How "Teeth" Change the Redox Behavior of Iron(II) Complexes*

D. T. Weiss,* M. R. Anneser,* **S. Haslinger**, A. Pöthig, M. Cokoja, J.-M. Basset, F. E. Kühn
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[13] *Isocyanide substitution reactions at the trans labile sites of an iron(II) N-heterocyclic carbene complex*

S. Haslinger, A. C. Lindhorst, J. W. Kück, M. Cokoja, A. Pöthig, F. E. Kühn
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[12] *Iron-catalyzed Oxidation of Unreactive C–H Bonds: Utilizing Bioinspired Axial Ligand Modification to Increase Catalyst Stability*

S. Haslinger, A. Raba, M. Cokoja, A. Pöthig, F. E. Kühn
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[11] *Structural Diversity of Late Transition Metal Complexes with Flexible Tetra-NHC ligands*

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M. R. Anneser, **S. Haslinger**, A. Pöthig, M. Cokoja, J.-M. Basset, F. E. Kühn
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[08] *Application of Open Chain Tetraimidazolium Salts as Precursors for the Synthesis of Silver Tetra(NHC) Complexes*

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

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[06] *Synthesis, Characterization, and Reactivity of Furan- and Thiophene-Functionalized Bis(N-heterocyclic carbene) Complexes of Iron(II)*

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[02] *Synthesis and Characterization of Dimolybdenum(II) Complexes Connected by Carboxylate Linkers*

X.-M. Cai,* D. Höhne,* M. Köberl, M. Cokoja, A. Pöthig, E. Herdtweck, **S. Haslinger**, W. A. Herrmann, F. E. Kühn
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