

Technische Universität München
Lehrstuhl für Anorganische Chemie

**A Bioinspired Tetra(NHC) Iron Complex:
Synthesis, Characterization and Catalytic Application of an
Organometallic Heme Analogue**

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Vollständiger Abdruck der von der Fakultät für Chemie der Technischen Universität München zur
Erlangung des akademischen Grades eines

Doktors der Naturwissenschaften (Dr. rer. nat.)

genehmigten Dissertation.

Vorsitzender: Univ.-Prof. Dr. K. Köhler

Prüfer der Dissertation:

1. Univ.-Prof. Dr. F. E. Kühn
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Die Dissertation wurde am 26.10.2016 bei der Technischen Universität München eingereicht und
durch die Fakultät für Chemie am 28.11.2016 angenommen.

Just as the constant increase of entropy

is the basic law of the universe,

so it is the basic law of life

to struggle against entropy.

Václav Havel

Die vorliegende Arbeit wurde am Anorganisch-Chemischen Institut der Technischen Universität München in der Zeit von Dezember 2012 bis Dezember 2016 angefertigt.

Mein besonderer Dank gilt meinem Doktorvater

Herrn Professor Dr. Fritz E. Kühn

für die Aufnahme in seinen Arbeitskreis, das mir entgegengebrachte Vertrauen und die forschersche Freiheit die mir zuteil geworden ist.

Weiterhin gilt mein besonderer Dank

Dr. Mirza Cokoja für die kompetente Betreuung und Anleitung meiner Arbeit, für die fachlichen Ratschläge und für die Korrektur von zahlreichen Publikationen, sowie

Dr. Alexander Pöthig für die hilfreichen Gespräche und die zahlreichen Kristallstrukturen, sowie für die exzellente Organisation der ACII-Praktika deren Betreuung mir besonders viel Freude bereitet hat.

Acknowledgement

Neben den oben genannten hat noch eine Vielzahl weiterer Personen zum Gelingen dieser Doktorarbeit beigetragen. Mein besonderer Dank gilt aus diesem Grund:

Dr. Valerio D'Elia und **Dr. Manuel Högerl** für die angenehme und produktive Zusammenarbeit im Rahmen des KAUST-Projektes, sowie den erlebnisreichen Aufenthalt in Saudi Arabien.

meinem langjährigen Laborpartner **Dr. Andreas Raba** für die vielen Hilfestellungen noch während meiner Master- und zu Beginn meiner Doktorarbeit, die mir den Einstieg in das Gebiet der Metall NHC-Chemie enorm erleichtert haben.

Daniel Weiß, dem besten Kollegen und Freund den man sich denken kann, für die gemeinsamen Spieleabende und für all die zahllosen Freundlichkeiten, die ich jemals von ihm erhalten habe. Ohne Dich hätte die Doktorarbeit maximal halb so viel Spaß gemacht! Danke Daniel!

meinen "Nach dem Umzug ist vor dem Umzug" Laborpartnern **Robert Reich**, **Özden Karaca** und **Tommy Hofmann**, für die freundschaftliche Atmosphäre und die stets angenehme und produktive Zusammenarbeit.

Dr. Marlene Kaposi, **Anja Windhorst** und **Dr. Patricia Wand** für die zahllosen kurzweiligen gemeinsamen Mittagessen, die kulinarisch auf höchstem Niveau durchgeführten Gourmet-Events und die freundliche Unterstützung, die sie mir stets entgegengebracht haben.

Stefan Haslinger für die Durchführung von theoretischen Berechnungen und das Messen zahlreicher Kristallstrukturen, sowie seinen unvergleichlich klaren und scharfen Blick beim Durchsehen diverser Manuskripte.

Jens Kück für die angenehme und reibungslose kollegiale Zusammenarbeit und den klugen Anregungen die ich von Ihm erhalten habe, sowie für die Erweiterung meines „Pilz-Repertoires“.

meinem langjährigen Laborpartner **Billy** für all die guten Gespräche im Labor und „on the road“.

der „Whisky Connection“ bestehend aus **Korbinian Riener, Christian Jandl** und **Philipp Altmann**, für die gemütlichen Umtrünke in angenehmer Gesellschaft.

den freundlichen Damen aus dem Sekretariat **Irmgard Grötsch, Roswitha Kaufmann, Renate Schuhbauer-Gerl** und **Ulla Hifinger** für die kompetente Unterstützung in jedweden organisatorischen Fragen.

unserem „Papa Bär“ **Jürgen Kudermann**, für die stets tatkräftige Unterstützung und kompetente Hilfe, die Erstellung der Methode zur Messung paramagnetischer Fe-Komplexe, sowie die zahlreichen immer sehr unterhaltsamen Gespräche.

Maria Weindl für die zahllosen Tieftemperaturmessungen und NMR-Kinetiken.

Ulrike Ammari, Petra Ankenbauer und **Bircan Dilki** für die Analyse zahlreicher Verbindungen

Abschließend möchte ich mich noch bei meiner ganzen Familie besonders aber bei meinen Eltern, meiner Schwester und meinem Großvater für all die Unterstützung, die sie mir mein ganzes Leben lang entgegengebracht haben, und die ebenso essentiell für das Gelingen dieser Doktorarbeit war, wie akademische Aspekte, von ganzem Herzen bedanken. Ein herzliches Danke Euch Allen!

English Abstract

This thesis focuses on the synthesis, reactivity and catalytic application of tetra *N*-heterocyclic carbene (NHC) iron complexes. Within this small but fast growing field of research it deals especially with complexes bearing cyclic tetra(NHC) ligands and their reactivity with small molecules such as carbon monoxide (CO), nitric oxide (NO), molecular oxygen (O₂) and hydrogen peroxide (H₂O₂). Furthermore a comprehensive review of all reported cyclic tetra(NHC) ligands and their metal complexes until September 2016 is given.

This thesis by publication is based on four first author full article publications. The first one published in *Inorganic Chemistry* in **2015** reports the synthesis and characterization of a new cyclic tetra(NHC) iron(II) complex, resembling the long known and biologically important heme system and explores its reactivity with various small molecules (NO, CO).

The second one was published in *Dalton Transactions* in **2016** and sheds light on the reactivity of the previously reported cyclic tetra(NHC) iron complex with molecular oxygen (O₂). The formation of a labile superoxo intermediate is proposed and supported by various independent methods. Two different decomposition products are isolated and characterized.

The third one was published in *ChemSusChem* in **2015** presenting the respective cyclic tetra(NHC) iron(III) complex and revealing its outstanding catalytic activity towards epoxidation of olefins utilizing H₂O₂ as oxidant. Hereby TOFs (Turn over frequency [h⁻¹]) of up to 183,000 are reported and various parameters are explored in depth.

The fourth one was published in *Organometallics* in **2015** and investigates the redox potential of the Iron(II/III) centers in relation to the number of coordinated NHC ligands and the overall ligand structure.

Four other publications with co-authorship covering a novel synthesis of *2-imidazolylpyridines* (*Tetrahedron Let.* **2013**), the reactivity of a cyclic bis(NHC)/Pyridine iron complex (*Organometallics* **2015**), the decomposition pathways of acyclic iron(III) NHCs (*Chem. Eur. J.* **2015**) and mechanistic insights to a Wittig type reaction catalysed by iron(II) NHCs (*J. Catal.* **2016**), are also briefly discussed.

Deutscher Abstract

Der Schwerpunkt dieser Doktorarbeit liegt in der Synthese, Reaktivität und katalytischen Anwendung von tetra *N*-hetero zyklischen Eisenkomplexen. Innerhalb dieses noch kleinen aber schnell wachsenden Wissenschaftsfeldes behandelt sie besonders zyklische tetra(NHC)-Eisenkomplexe und deren Reaktivität mit kleinen Molekülen wie Kohlenstoffmonoxid (CO), Stickstoffmonoxid (NO), molekularem Sauerstoff (O₂) und Wasserstoffperoxid (H₂O₂). Weiterhin gibt sie einen vollständigen Überblick über alle bis September 2016 bekannten cyclischen tetra(NHC)-Liganden und deren Metallkomplexe.

Diese kummulative Doktorarbeit basiert im Wesentlichen auf vier veröffentlichten Erstauthorenartikeln. Der erste - veröffentlicht **2015** in *Inorganic Chemistry* – befasst sich mit der Synthese und Charakterisierung eines neuen zyklischen tetra(NHC)-Eisen(II)komplexes mit hoher struktureller Ähnlichkeit zum bekannten und biologisch bedeutenden Häm-System und erkundet dabei dessen Reaktivität mit kleinen Molekülen (NO, CO).

Der zweite - veröffentlicht **2016** in *Dalton Transactions* – beleuchtet die Reaktivität des zuvor eingeführten Eisen(II)komplexes mit molekularem Sauerstoff (O₂). Dabei wird die Bildung eines labilen Superoxo-Intermediates postuliert und durch unabhängige Methoden bestätigt. Des weiteren erfolgt die Isolierung und Charakterisierung zweier Abbauprodukte der Reaktion des Eisen(II)komplexes mit Sauerstoff.

Der dritte - veröffentlicht **2015** in *ChemSusChem* – stellt den entsprechenden tetra(NHC) Eisen(III) Komplex vor und zeigt dessen herausragende katalytische Aktivität bei der Epoxidierung von Olefinen. Es werden TOFs (Turn over frequency [h⁻¹]) von bis zu 183.000 erreicht und es erfolgt eine tiefgehende Analyse verschiedener Reaktionsparameter.

Der vierte - veröffentlicht **2015** in *Organometallics* – untersucht die Abhängigkeit des Redox-Potenziales von Eisen(II/III) Zentren von der Anzahl koordinierter NHC-Liganden und der allgemeinen Ligandstruktur.

Vier weitere Co-Autor Publikationen, welche die neuartige Synthese von 2-Imidazolylpyridinen (*Tett. Lett.*, **2013**), die Reaktivität von zyklischen NHC/Pyridin Eisenkomplexen (*Organometallics*, **2015**), die Zerfallswege von azyklischen Eisen(III)-NHCs (*Chem. Eur. J.*, **2015**) und mechanistische Einblicke in von Eisen(II)-NHCs katalysierte Wittig Reaktionen (*J. Catal.*, **2016**) beinhalten, werden zudem kurz erläutert.

List of Abbreviations

CHD	1,4-Cyclohexadien
CM	Coinage Metal
Cp	Cyclopentdienyl
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
ESI	Electron Spray Ionization
Fc	Ferrocen
Fc ⁺	Ferrocenium
GC/FID	Gas Chromathography/ Flame Ionization Detector
HOMO	Highest Occupied Molecular Orbital
hs	High spin
-I-effect	Negative-Inductive-Effect
ls	Low spin
M	Metal
+M-effect	Positive Mesomeric Effect
MeCN	Acetonitrile
Na/Hg	Sodium-Amalgam
NHC	<i>N</i> -heterocyclic carbene
S	Spin
SQUID	Superconducting Quantum Interference Device
Th	Thianthrenyl
THF	Tetrahydrofuran
TM	Transition Metal
TOF	Turn over frequency
TON	Turn over number
Ts	Tosyl
VE	Valence Electron
X ⁻	Counter Ion

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1. Introduction

1.1. Preliminary Thoughts

Almost 50 years ago John Naisbitt, a specialist for future studies, said: “Biology will take the present rank of chemistry and physics in the 21st century”. On the one hand, he was right: In recent years science and industry as well as society changed to a more biological perspective. This may be observed in the efforts of e.g. Bayer strengthening its biological portfolio buying Monsanto or the strikingly obvious trend towards a more ecological and sustainable way of life in the most western industrialised countries. But on the other hand the more our understanding of chemistry and biology proceeds, the more we recognize that both scientific disciplines are not diametrically opposed, but very closely related to each other. We understand they are two sides of the same coin, the one – chemistry – starting on the microscopic side of things while the other – biology – starting from the macroscopic perspective. Nevertheless, the principal understanding of the fundamental laws of life and nature are their most important goal. Due to this new understanding chemistry and biology converged quickly within the last decades, created new disciplines such as molecular biology¹ and biomimetic chemistry² complementing the long existing biochemistry, the first scientific discipline mediating between chemistry and biology. From the chemical side of the coin the sophisticated elegance of biological systems - the efficiency and selectivity of enzymes or the cooperative effect of hemoglobine transporting oxygen through our veins – provide desirable goals. From the biological perspective, the simple applicability on a technical scale – the world changing impact of the Haber-Bosch-Process or the “artificial” synthesis of complex biomolecules like heme and erythromycin - made an appealing goal. The fact that eight of the last 20 nobel prizes in chemistry were awarded for biological topics³ can also be taken as a case in point for the ongoing blurring of borders between chemistry and biology. Mimicking of biological processes - especially catalytic processes – with less complex artificial molecules was a still fast growing field of research during the last couple of years. This dissertation will provide a deeper insight into this area of biologically inspired inorganic chemistry, especially into those parts using cyclic NHC iron compounds for the mimicking of heme-related biological structures.

1.2. N-heterocyclic Carbenes: Structure and Properties

During the last two decades, the thorough examination of N-heterocyclic carbenes as ligands for transition metals uncovered a very rich coordination chemistry with an increasing variety of applications:^{4,5,6,7,8} This includes homogeneous catalysis,^{9,10,11,12} medicinal chemistry,^{13,14,15} and photoluminescent materials.¹⁶ Polydentate NHC ligands - especially cyclic ones - were found to stabilize high-valence iron species, which are apparently key intermediates in catalytic oxidation and aziridation reactions.^{17,18,19,20,21,22,23} To understand the utmost importance which NHC ligands have gained in recent years, we have to take a closer look at the history and unique properties of this special kind of ligand.

As many important discoveries before, the first NHC-complexes were mere "lab curiosities". Even before the first NHC complexes were prepared in 1968 by Wanzlick and Öfele,^{24,25} simple carbene complexes of late transition metals had been reported.²⁶ For many decades the isolation of free carbenes was deemed impossible, due to their highly unstable and transitory nature, until Arduengo proved in 1991 that the isolation of free carbenes - NHCs in particular - is possible.²⁷ To completely understand those achievements a detailed look at the valence orbitals of a carbene is required. "Carbene" refers to divalent carbon atoms, which, in contrast to common tetravalent carbon atoms, have only six rather than eight valence electrons (Figure 1). Based on this vacancy in the valence orbitals two different electronic configurations are possible: First the usually energetically – according to Hund's rule - more favourable triplet state with two singly occupied sp^3 hybrid orbitals (**A**). Second the less favourable singlet state with both electrons paired in one sp^2 hybrid orbital and a perpendicular empty p orbital (**B**).

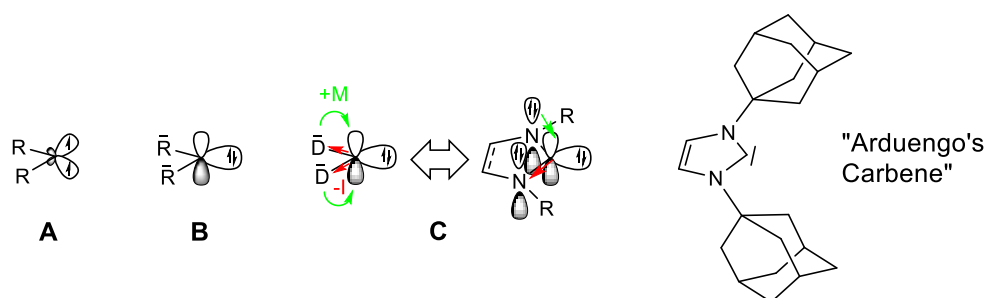


Fig. 1 Possible electronic structures of free carbenes (left **A/B**). Stabilization of free carbenes (middle **C**). Arduengos first isolated free carbene (right).

The obvious diradical character of **A** makes this type of particle highly reactive and prone to dimerization or the initiation of radical chain reactions. Despite its relatively higher energy, **B** should be less reactive due to its free electron pair (compare nitrogen). Consequently, if the preferred electronic configuration of a free carbene can be pushed from **A** to **B**, a more stable particle should arise. This can principally be achieved in two ways: First, by lowering the energy of the sp^2 orbital by adding electron withdrawing substituents to the carbon atom (**C**: -I-effect) and second, by stabilizing the empty p orbital by partially occupying it with electron density from adjacent atoms (**C**: +M-effect). These theoretical considerations lead to the conclusion that if R is an atom with high electronegativity and free electron pairs, the ground state of free carbenes can be changed from triplet **A** to singlet **B**,²⁸ which is realized in NHCs (**C**). Despite their higher stability, those singlet carbenes are still prone to dimerization. Besides binding the carbene to a transition metal, the easiest way to prevent this - finally enabling the isolation of free carbenes - is the introduction of bulky groups making dimerization highly unfavourable. We can see that all those considerations are realized in “Arduengo’s Carbene” (Figure 1).

None of this, however, explains why carbenes in general and NHCs in particular are such extraordinarily well-established and widely used class of ligands. It comes down to their special way of metal-carbon interaction and their high variability concerning the electron donating and accepting properties. Although it is widely accepted that NHCs are primarily σ -donor ligands, which is represented by drawing mere single bonds instead of double bonds between the metal center and the coordinating NHC carbon, in contrast to other famous carbene type ligands such as Fischer or Schrock carbenes,^{29,30} they are not limited to this type of interaction.³¹ To a minor but variable extent – strongly depending on the respective electronic situation both of the NHC and the coordinated metal fragment – NHCs can also function as π -donor- or π -acceptor-type ligands (Figure 2).

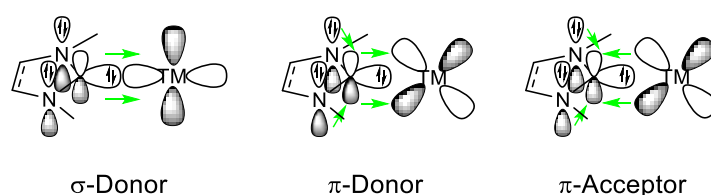
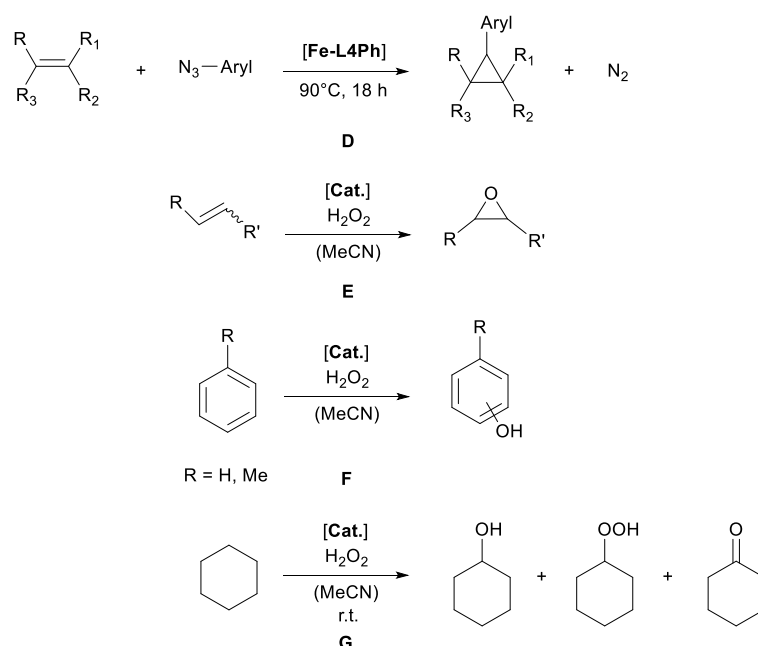


Fig. 2 Possible electronic interactions between a NHC and the coordinated transition metal (TM).

Due to these properties NHCs are significantly stronger ligands, both in terms of σ - and π -donor capability and kinetic stability, than phosphanes, to which they are often compared to. Thus rapid dissociation and association processes often observed for phosphanes are mostly prevented by the partial double bond character of the M-carbon bond.^{7,8} This makes coordinated NHCs less prone to oxidation than phosphanes, even if free NHCs are generally more sensitive towards oxygen than phosphanes, which are often air stable. However, the obstacle of the relative sensitivity of NHCs towards oxidation, especially in earlier transition metal complexes, was and is a significant hindrance in the broad application of those complexes as catalysts in oxidation reactions. Nevertheless, in the case of iron, Jenkins showed in 2011 and 2016 the advanced catalytic performance of two cyclic tetra(NHC) iron complexes as catalysts in the aziridination of a wide variety of substituted aliphatic alkenes using electron-donating aryl azides (**D**).^{22,32} In 2014 and 2015, Kühn could show that acyclic iron(II) NHCs are suitable catalysts for the epoxidation of olefins (**E**),^{33,34} the hydroxylation of aromatics³⁵ (**F**) and the even more challenging C-H activation in saturated hydrocarbons such as cyclohexane (**G**) (Scheme 1, Section 1.5 for details).³⁶



Scheme 1: Oxidation reactions catalysed by iron NHCs as reported by Jenkins and Kühn.

Considering those and other advances in the field of transition metal NHC chemistry, it is not surprising, that the number of publications and structures in this field of research is rapidly increasing.³⁷ This is reflected in an astonishing number and very high diversity of the

reported transition metal NHC complexes (Figure 3). Still, most of the approximately 5,900 crystallographically characterized compounds contain the “usual suspects”- Ru, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au – which altogether about are 5,000 or 85 % of all complexes. However, among the remaining 900 compounds, iron has by far taken the lead within the last years featuring close to 300 reported NHC compounds. Despite this, the overall count of cyclic iron tetra(NHC) species, is 17 (reported until September 2016), 7 of which are reported in this thesis alone.

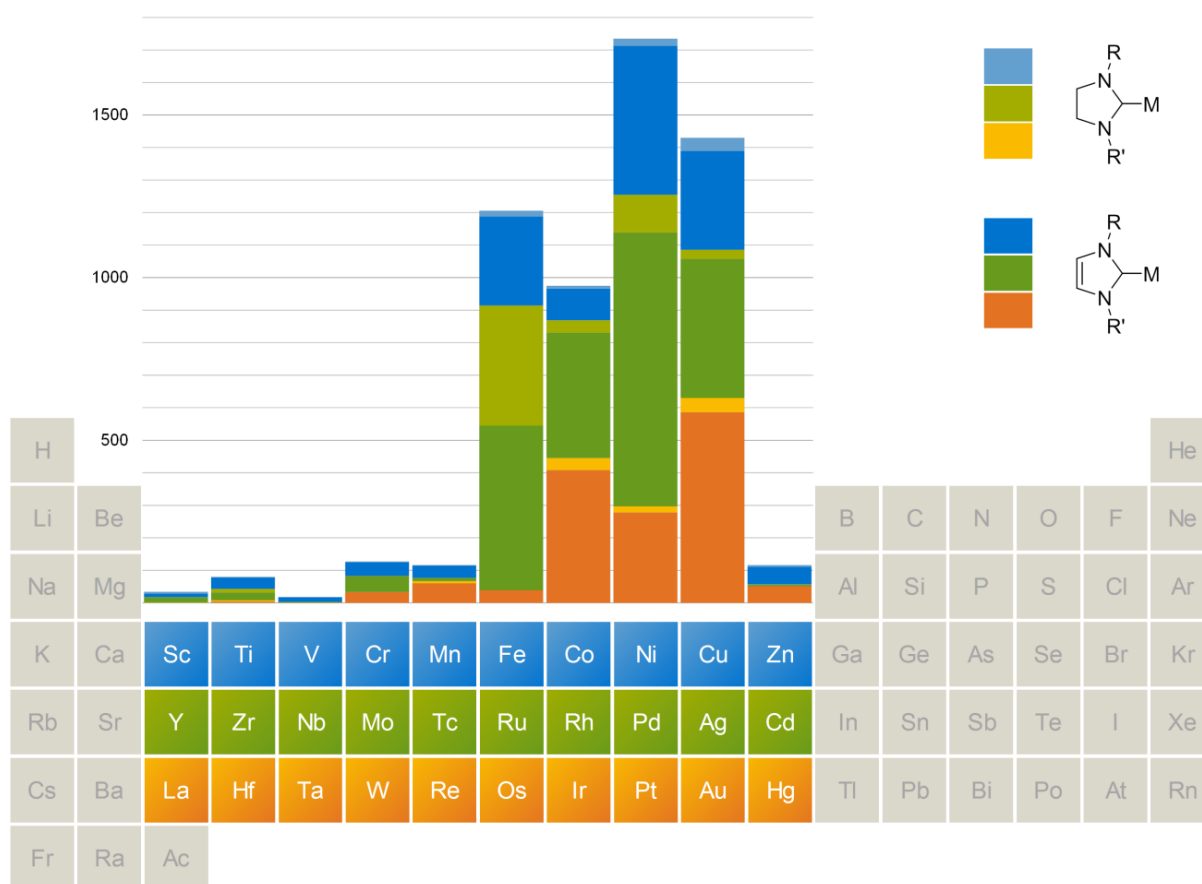


Fig. 3 Number of entries in the CCDC data base for metal complexes with N-heterocyclic carbene ligands based on imidazolylidenes (dark) and imidazolinylienes (bright) as drawn top right. The data set is sorted by transition metal and NHC type and was accessed at “<http://weccsd.ccdc.cam.ac.uk>” on August 31, 2015. (used with friendly permission of the author.)³⁷

All of those complexes were reported within the last 6 years, showing the intensified efforts made in this field of research. Why did especially cyclic iron NHC complexes become such a “hot topic” in recent years? To answer this question we will discuss the structural properties, the synthesis and the unique reactivity of those compounds in the following sections.

1.3. Tetra-NHC Ligands: Synthesis and their Metal Complexes

To provide a clear definition of a tetra(NHC) ligand and a complex of this type respectively, we explicitly exclude such tetra(NHC) complexes in which the NHC moieties are not covalently connected to each other. Examples for such complexes can be metals coordinated by four single NHC ligands, by two bis(NHC) ligands, or any combination thereof. In this well defined group of covalently connected tetra(NHC) ligands we will focus on the cyclic ligands and their complexes. Thus its synthesis was inspired through ideas from the early days of this work and its therefore very similar structure a non-cyclic tetra(NHC) ligand and its metal complexes are also described briefly later on. The reader may ask themselves why we focus on such an exclusive type of ligands, if thousands of metal NHC complexes and hundreds for iron alone are known? And this is exactly the point! While only a small number of iron NHC complexes displays sufficient stability for catalytic applications even less exceed comparable non-NHC complexes in the respective catalytic performance, such as epoxidation or hydrosilylation processes.^{38,39} The main reason for this is grounded in the lower kinetic and thermodynamic stability of the C-M bond of earlier transition metals compared to later ones such as Pd, Pt or Au.⁴⁰ Despite the generally high kinetic inertness of late TM-carbon bonds, early TM-carbon bonds tend to be thermodynamically and kinetically less stable.⁴¹ A simple explanation for this observation is smaller orbital overlap between the relatively hard early TMs and the soft NHC-carbon, resulting in a bonding situation with less covalent character compared to late-TM-NHC complexes. To overcome the emerging problems such as sensitivity towards water and/or oxygen, the chelate effect, which is widely found in coordination chemistry is also applied here. Originating from the ancient greek word "Χελας" meaning "crab claw", it describes the observation that two or more covalently connected ligating moieties which coordinate to the same metal atom, form more stable complexes than the same number of isolated ligating moieties. This increase in kinetic and thermodynamic stability is based on an entropy increase, because such chelate ligands losing less degrees of freedom compared to simple nonchelating ligands. This entropic gain and therefore the thermodynamic stability is further enhanced by using cyclic tetra(NHC) ligands, losing a smaller number of degrees of freedom on coordination due to their lower flexibility. The use of four NHC moieties per ligand was chosen as a compromise between stability and

free coordination sites for reactivity. In addition, many biologically active iron compounds bear a structurally related cyclic η^4 -ligand in their core structure, such as heme.

Before this work only a small number of cyclic tetra(NHC) systems and their metal complexes have been reported. One of the first of these kind of ligands (**L1**) was published in 2007 by Murphy⁴² together with its corresponding Ag(I), Cu(I) and Pd(II) complexes. In this case the four NHCs were linked by propylene bridges, resembling the structure of so called crown ether ligands. In 2009 and 2010, the Co(II)⁴³ and Ni(II)⁴⁴ complexes of **L1** were reported by the same group together with the first catalytic applications in the reduction of challenging organic substrates, throwing a first spotlight on the high catalytic potential of cyclic tetra(NHC) metal complexes (Section 1.5 for details). Two years before, in 2005, the first cyclic tetra(NHC) Pt complex (**Pt-L2**) was reported by Hahn.⁴⁵ In that work a template-controlled cyclization of β -functionalized phenyl isocyanides yielded four single Pt coordinated *N*-heterocyclic carbene ligands, which were subsequently linked *via* DMF/COCl₂ to the respective tetra(NHC) complex **Pt-L2**. In 2008, another tetra(NHC) ligand (**L3**) and its Ag(I) and Au(I) complexes were reported by Hahn.⁴⁶ Despite of its display of several different potential binding patterns **L3** was not mentioned ever since and no applications have been reported. The same is true for a very similar ligand **L3Py** which was also reported by Hahn in 2010 (Figure 4).^{47,48}

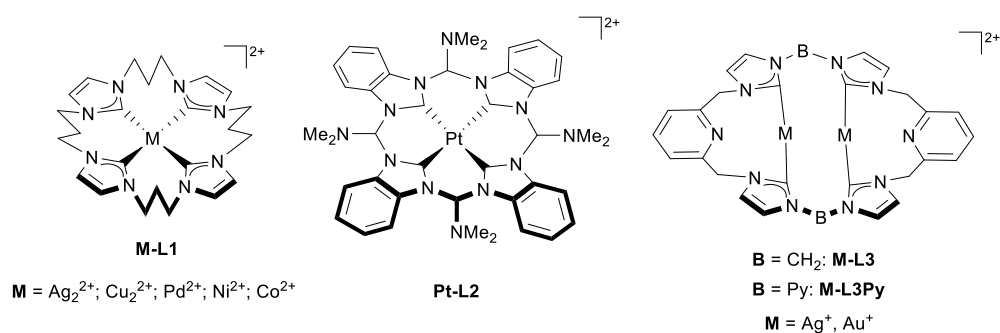


Fig. 4 Structures of the first reported cyclic tetra(NHC) ligands (**L1-3**) and their metal complexes.

The next step towards a smaller and more rigid tetra(NHC) ligand (**L4**) was made by Jenkins in 2010.⁴⁹ Starting from easily accessible methylene(bisimidazole), the 18 membered cyclic tetra(NHC) ligands **L4H** and **L4Ph** were synthesized, along with the respective Pt(II) complexes. In 2013, he have been the smallest cyclic tetra(NHC) ligands until a 16 membered tetra(NHC) ligand (**L5**) and another 18 membered ligand (**L6**) were described, by Jenkins.⁵⁰

However, they were not able to synthesize any metal complexes of **L5** while the respective Ni(II) and Pd(II) complexes of **L6** could be prepared in low yields (Figure 5).

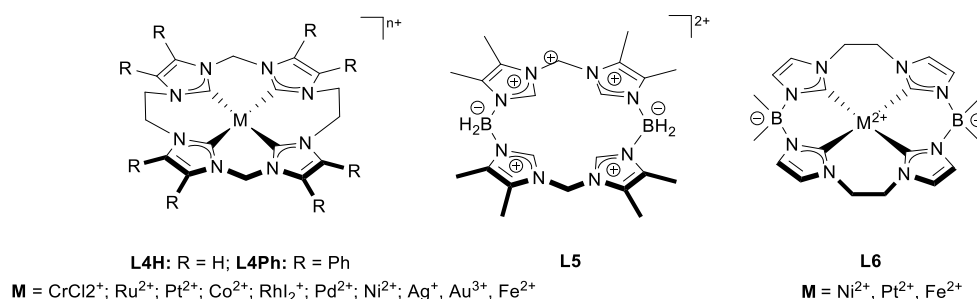


Fig. 5 Structures of several cyclic tetra(NHC) ligands (**L4-6**) and their metal complexes, as reported by Jenkins *et al.*

A different synthetic approach, namely utilizing the Ag-complexes of **L4** as transmetalation reagent, allowed synthesis of a broad array of **L4**-based metal complexes in 2012 and set the stage for catalytic applications.⁵¹ The research on **Fe-L4Ph** as an active and recyclable catalyst in the aziridination of olefins is still ongoing.^{52,53} Besides Murphy, Meyer has been exploring **Fe-L4H** its potential for the stabilization of high iron oxidation states²¹ and its reactivity with small molecules such as S₈ or NO since 2013 (Section 1.5 for details).^{54,55,56} Based on this work, the Ag(I)- and Au(I)-complexes of **L0** have been published recently.⁵⁷ Both exhibit a unique molecular box type structure and the Ag(I) compound was utilized for transmetalation to the corresponding Ni(II), Pd(II) and Pt(II) complexes. Less surprising, all of these show the anticipated square planar geometry (Figure 6).

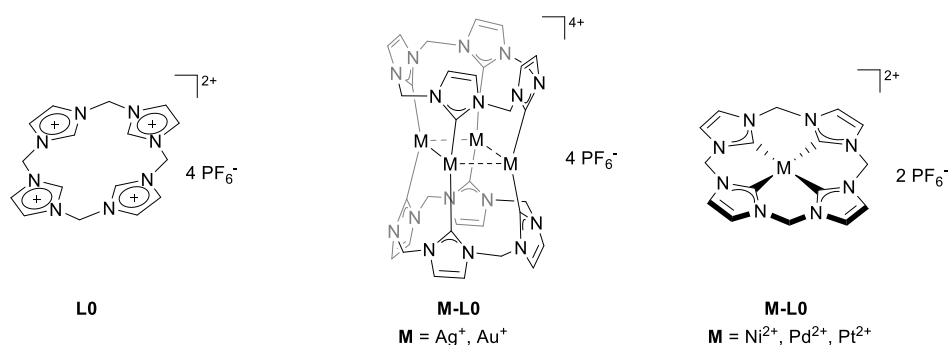


Fig. 6 Structure of ligand **L0** (left) and its metal complexes with Ag(I) and Au(I) (middle) and group 10 metals (right), as reported by Kühn *et al.*⁵⁷

Although a number of acyclic tetra(NHC) ligands exists in literature, most of them have a very different coordination behaviour than their cyclic counterparts due to the reasons mentioned above.^{58,59,60,61} However, two of them, which are inspired by **L0**, **L1** and **L4**, depict

a comparable structure and reactivity. The synthesis as well as the preparation of the corresponding Ag(I) complexes of these acyclic tetra(NHC) ligands (**L7/L8**) was first reported by Kühn and coworkers in 2014 (Figure 7).⁶²

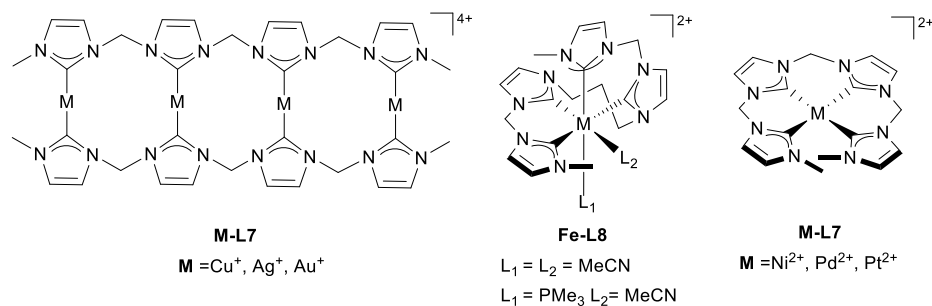


Fig. 7 Structures of two acyclic tetra(NHC) Ligands (**L7/L8**) and their metal complexes, as reported by Kühn et al.

Subsequently, a number of metal complexes containing **L7** and **L8** was reported in 2015, revealing an interesting connection between the structure of the complex (square planar vs. sawhorse type) and the different linker used in the backbone of the ligands (CH₂ vs. (CH₂)₃).⁶³ A remarkable structural flexibility especially of **Fe-L7** opened possible catalytic applications for reactions in need of two *cis*-oriented free coordination sites, which can hardly be provided by any of the cyclic tetra(NHC) complexes. In 2016, it was shown that for the **Ru-L7/L8** complexes a similar behaviour could be observed and proven for both complexes, that they are highly active transfer hydrogenation catalysts,⁶⁴ which need *cis*-oriented free coordination sites to operate effectively.⁶⁵ The structural resemblance among the coinage metal complexes of **CM-L7** and the afore mentioned **CM-L0** are remarkable, thus showing a certain amount of flexibility even in the relatively rigid structure of **L0**, allowing the CMs to keep their strongly preferred linear coordination.

1.4. Structure and Synthesis of Cyclic Tetra(NHC) Iron Complexes

“The field of iron NHC chemistry has emerged as a diverse area of organometallic chemistry, and the iron compounds display a broad range of geometric and electronic variations. With regard to oxidation states, examples range from low-valent iron(0) and iron(I) over the most common iron(II) and iron(III) to high-valent iron(IV) and even iron(V). In terms of geometry, most reports describe tetrahedral or octahedral coordination at the iron center, however, some iron NHC compounds appear as trigonal bipyramidal or square planar complexes.”¹⁷ In case of cyclic tetra(NHC) iron complexes, despite the little variation in the equatorial positions (per definition 4 NHCs), significant differences in terms of geometry and electronic structure (oxidation state) are reported. Most of the cyclic tetra(NHC) iron complexes display octahedral coordination, bearing two axial ligands, but the nitrosyl compounds show mostly a square pyramidal geometry. In one case even a purely square planar structure without any axial ligands is reported (Figure 8).³²

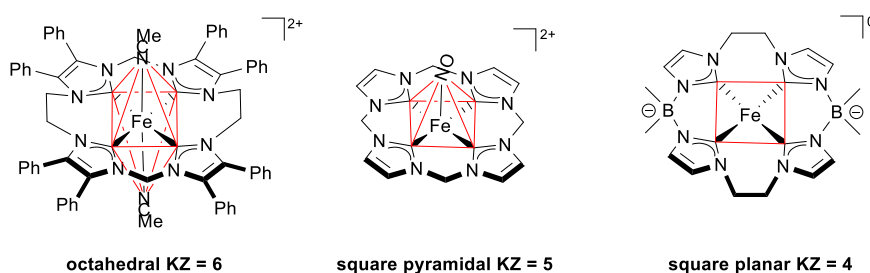


Fig. 8 Coordination geometry of iron in various cyclic tetra(NHC) complexes.

Regarding the electronic situation and oxidation state the level of variation is even larger. While in most compounds the oxidation state of +II is preferred by the iron center – due to the high ligand field splitting induced by the four strong NHC-donors - in many cases the respective +III state can easily be reached (Figure 9), often by simple addition of molecular oxygen.²¹ If the strong donating character of the tetra(NHC) ligands are combined with other strong donors like oxide (O^{2-})²¹ or amide (NR_2^-)²² iron(IV) species can also be stabilized for

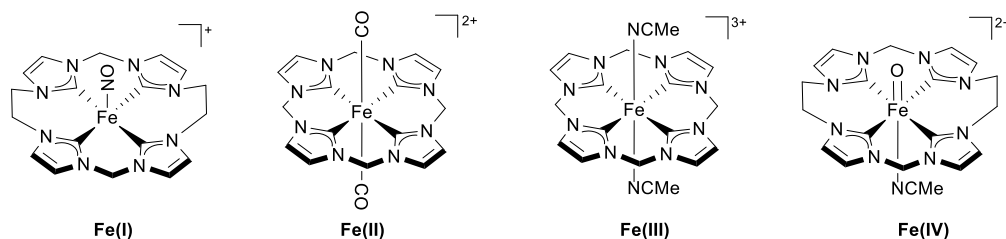
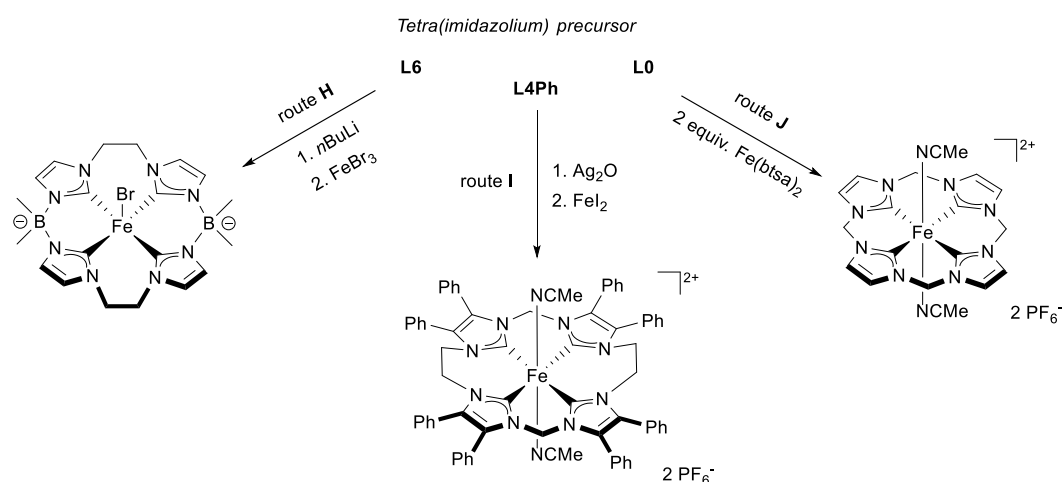


Fig. 9 Different oxidation states of iron in various cyclic tetra(NHC) complexes.

characterization or even be isolated. On the other hand if axial ligands with strong electron accepting properties such as isonitriles (CNR) or nitrosyls (NO) are applied, a rarely observed oxidation state of iron +I can be found.⁵⁶

Although there are several synthetic routes known from literature for the preparation of iron NHC complexes in general¹⁷ only three of them were successfully applied in the formation of cyclic tetra(NHC) iron compounds (Scheme 2). Even more, only two of them have been proven to provide the desired complexes in good yields. The first method (H),



Scheme 2: Three different routes (H-J) applied for the synthesis of cyclic tetra(NHC) iron complexes.

known for twenty years and first applied by Fehlhhammer,⁶⁶ includes the *in situ* generation of free NHC from the respective imidazolium salt, followed by addition of a suitable metal precursor. However, the reported yields for this synthetic route are only moderate (<25%),³² but can be applied for every kind of metal. The second synthetic route (I) - the transmetallation of a Ag(I) carbenes prepared from Ag₂O and the respective imidazolium salt - became the most common approach for the synthesis of any kind of NHC metal complex, since it was first reported by Lin in 1998.^{67,68} Even though the preparation of cyclic tetra(NHC) Ag(I) complexes can sometimes be challenging, due to Ag(I) mostly featuring linear coordination, resulting in complex polynuclear structures.^{51,57,59} However, the transmetallation to the respective iron compounds as well as to most other metals proceeds relatively smooth and in high yields (40-93%).⁵¹ This can be attributed to the high thermodynamic driving force provided by the formation of insoluble Ag(I) halides and their simple separation from the reaction product by filtration. Especially for smaller sized (16- and 18-membered) cyclic tetra(NHC) ligands the use of iron bis(trimethylsilyl)amide

([Fe{N(SiMe₃)₂}]₂) is preferred.^{21,69} Its first usage as a metal precursor was reported in 2004 by Danopoulos and co-workers.⁷⁰ Iron bis(trimethylsilyl)amide was introduced as an iron(II) precursor bearing two equiv. of internal base for deprotonation of the imidazolium salts, thus making it perfectly suitable for the synthesis of halide-free iron(II) complexes with two NHC ligands. A main drawback of [Fe{N(SiMe₃)₂}]₂ is its high sensitivity to air and moisture, making both preparation and transformation of this compound extremely demanding. However, the reactions usually proceed cleanly and with high yields, as the resulting amine can be removed *in vacuo*. Therefore, this synthetic route has become the preferred path to access Fe(II) NHC complexes in recent years.¹⁷ Using two equivalents has proven to provide moderate to very high yield (30-90%) for cyclic tetra(NHC) iron complexes. The resulting byproduct [Fe(MeCN)₆]²⁺ 2X can be easily separated by filtration over silica. However, this protocol is limited to acetonitrile (MeCN) as the solvent of choice. Not only their relatively straightforward accessibility made cyclic tetra(NHC) iron complexes and NHC iron complexes in general popular target molecules, but also their diverse reactivity, and their possible catalytic applications. Both will be discussed in further detail in the following section.

1.5. Reactivity and Catalytic Applications of Cyclic Tetra(NHC) Transition Metal Complexes

While most cyclic tetra(NHC) transition metal complexes have only been investigated from a structural point of view, the reactivity of five of them, namely **Co/Ni-L1**, **Fe-L4H**, **Fe-L4-Ph** and **Fe-L6** are discussed in greater detail (Figure 10). This was done by the three groups of Murphy, Jenkins and Meyer, each of them performing pioneering work on this rather new topic of organometallic chemistry. Although no iron complex of **L1** is known up to date, as the cyclic tetra(NHC) ligand with the first report of the reactivity of its Co(II)- and Ni(II)-complexes, both closely related to iron, it may not miss on this list. In the following, all five of them, their reactivity and catalytic activity are described in more detail.

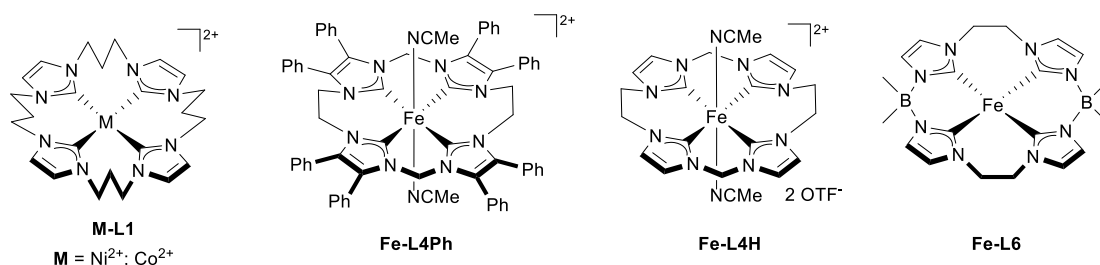
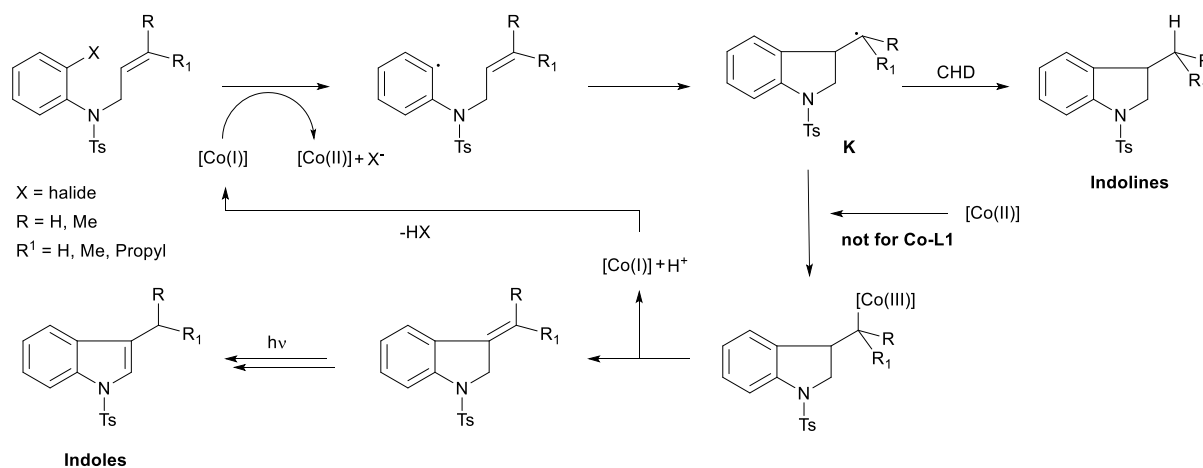


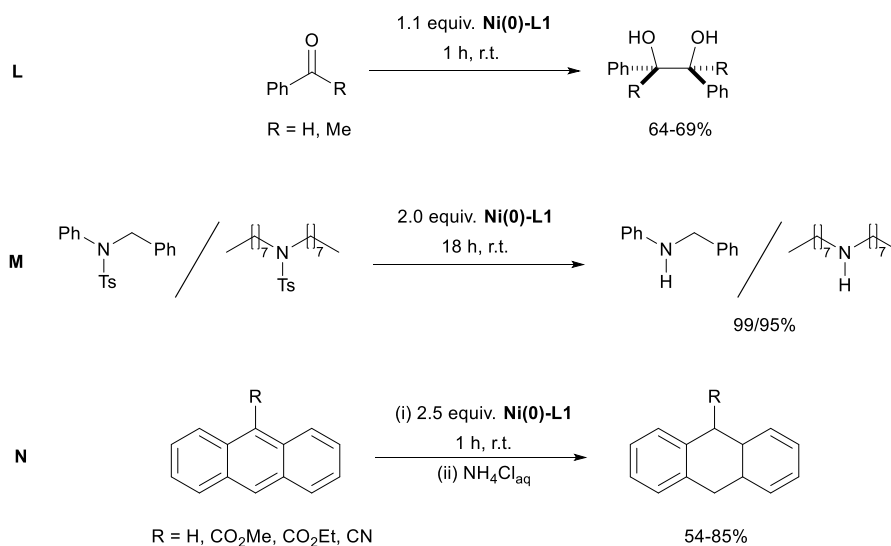
Fig. 10 Cyclic tetra(NHC) iron complexes for which reactivity has been investigated (**M-L1**, **Fe-L4H**, **Fe-L4Ph** and **Fe-L6**).

The electronic properties of **Co(II)-L1** were investigated by cyclic voltammetry. This revealed that its reduced **Co(I)-L1** state is reversibly formed at a potential of -1.15 V in DMF. Its Co(III) state, however, is only and irreversible achievable at + 2.00 V. These are very unusual results, since Co(II) normally tends to easily undergo oxidation to Co(III), especially if coordinated by strong ligands (Is d⁶ strongly favoured over hs d⁷!). A possible reason for this abnormal behaviour is the crown like shape of **L1** and the tetrahedral geometry of the Co(II) complex. For an easy oxidation an octahedral geometry must be accessible, as the strongly electron donating character of the NHC ligands should favour oxidation of Co(II). Cobalt(III) complexes highly favour octahedral geometry, and the ligand conformation is such that no facile rearrangement to such a geometry is possible.⁴³ The reduction potential of -1.15 V made the respective **Co(I)-L1** – generated *in situ* from Na/Hg in DMF – a suitable candidate for the consecutive reduction, cyclisation and isomerisation of aryl iodides (Scheme 3).⁷¹



Scheme 3: Proposed catalytic cycle of the cyclisation of aryl iodides using **Co(I/II)-L1** as a reagent/catalyst.

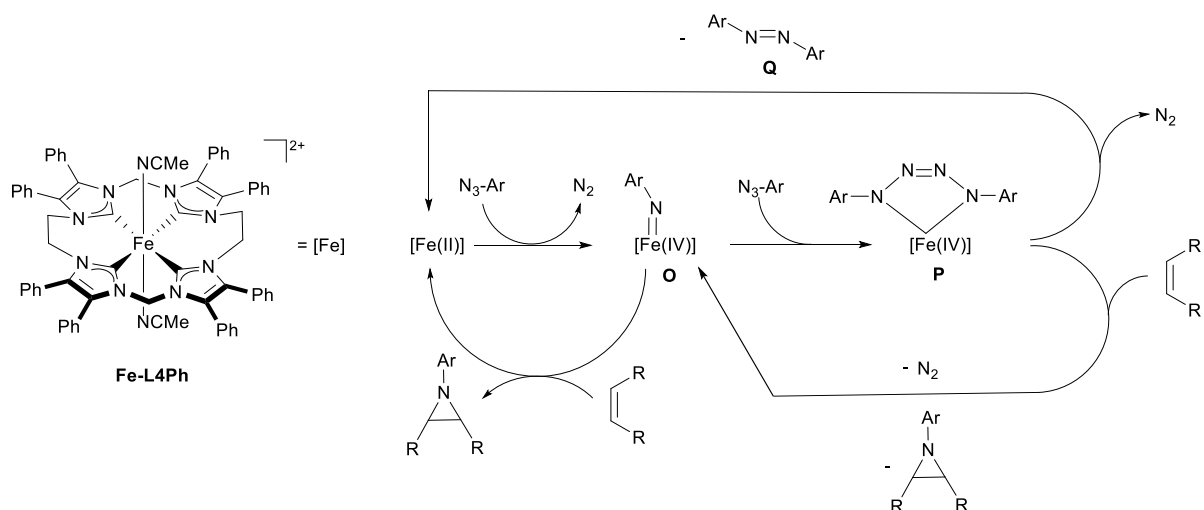
However, the initially desired isolation of **indoles** was not possible or, if at all, only in low yields, resulting from the difficulty to oxidize **Co(II)-L1**, which was unable to trap radical **K**. The formation of **indolines**, on the other hand was performed very well, especially if the H-radical donor 1,4-cyclohexadiene (CHD) was added. Even more challenging substrates such as aryl bromides and chlorides could be transformed in moderate to high yields. If the formation of the Co(I)-species was not induced by Na/Hg, but electrochemically, the reaction could be performed catalytically in **Co-L1** for the case of aryl iodides. Overall, this first reported (catalytic) application of a cyclic tetra(NHC) transition metal complex paved the way for more advanced and selective catalytic processes in the following years. Next in line was **Ni(II)-L1** and its application as a reducing reagent for challenging organic substrates.⁴⁴ In contrast to its Co(II) counterpart, this complex showed a square planar coordination of the metal cation. Treated with Na/Hg, a presumable Ni(0)-species is formed being able to reduce I₂ in an equimolar fashion. DFT calculations, however, reveal a ligand centered nature of the HOMO in the reduced species, thus **Ni(0)-L1** may best be viewed as a ligand dianion. This shows the non-innocence of the macrocyclic tetra(NHC) ligand in this case, which is rarely known for NHC ligands.^{72,73,74} Due to the strong reduction potential of **Ni(0)-L1** at -2.4 V (no **Ni(III)-L1** was detected up to +2.5 V), it was applied as a reagent for reductions of challenging compounds such as the reductive coupling of aromatic aldehydes, reductive cleavage of N-aryl bonds and the reduction of aromatic rings (Birch Reduction) (Scheme 4). While the reductive coupling of aldehydes **L** is not extremely challenging, it has to be mentioned that the (*d,l*)-isomer of the corresponding pinacol products was formed exclusively.



Scheme 4: A selection of organic substrates reduced by **Ni(0)-L1**.

The high selectivity stands in contrast with other Ni-based reductions of ketones and aldehydes, where mixtures of pinacol and alcohol products are seen.^{75,76} The reductive cleavage of the N-aryl bonds **M** was performed in excellent yields (95-99%) and high selectivity. The reduction of aromatic rings **N**, usually involving alkali metals in liquid ammonia,⁷⁷ was also performed in good yields (54-85%) and mild conditions (1h, r.t.). Again, this shows the high importance of ligand design and the immense impact of noninnocent ligands on the reactivity of their coordinated metal. Both **Co-L1** and **Ni-L1** are examples for the destabilisation of lower oxidation states (Co(I), Ni(0)) evoked by the strong donation of electron density to the metal center, but for sterical reasons no higher oxidation states could be achieved in those cases. In the following reports about the cyclic tetra(NHC) iron complexes (**Fe-L4H**, **Fe-L4Ph** and **Fe-L6**) we will see that in their case, the full potential of this ligand type lies in the stabilisation of the higher oxidation states of iron (III/IV).

The first tetra(NHC) iron complex (**Fe-L4Ph**) used as a catalyst was reported by Jenkins in 2011.²² During his first investigations he proposed an iron(IV) imide **O** and proved its existence during the catalytic cycle by mass spectroscopy (Scheme 5). In a subsequent work published in 2014,²³ he had a closer look at the mechanistic details of the reaction and revealed that an iron(IV) tetraazene complex **P** was formed as an intermediate in the catalytic aziridination reaction. Even more surprisingly, the tetraazene was also capable of yielding 4,4-dimethylazobenzene **Q** when heated, which is the first reported metal assisted formation of this type of compound.

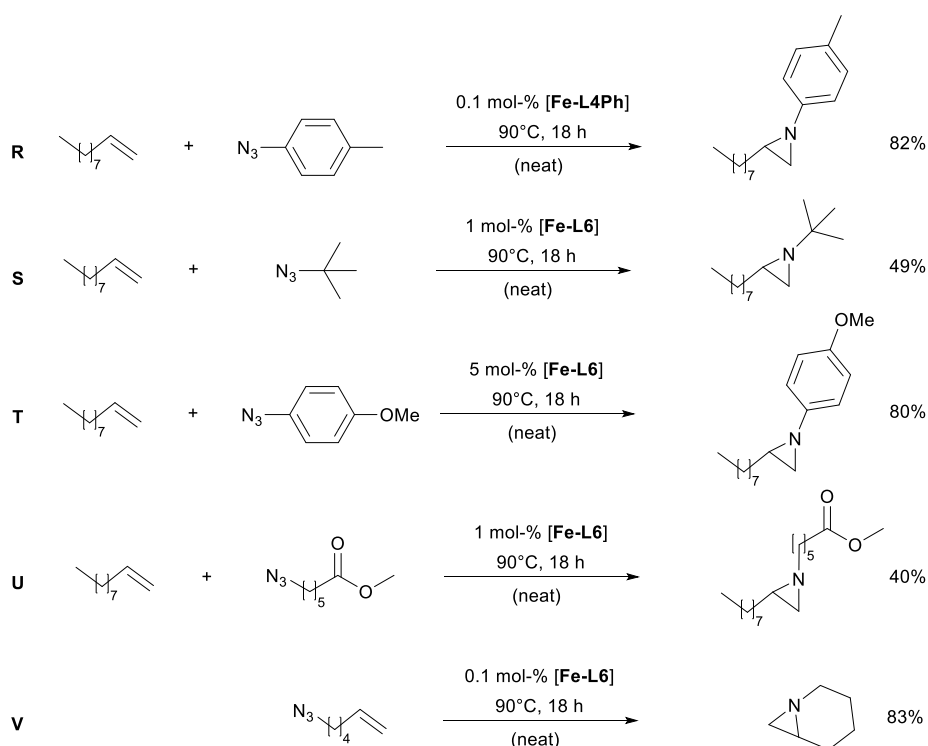


Scheme 5: Proposed catalytic cycle of the catalytic aziridination of olefins using **Fe-L4Ph** as a catalyst (**O**). Alternative reaction pathway over (**P**) and catalytic formation of 4,4-dimethylazobenzene (**Q**) - if no olefin substrate is available - are also depicted.

To sum up the reactivity of **Fe-L4Ph** with a broad range of donor- and acceptor-substituted aryl azides, one can say that even supposedly straightforward reactions - more often than not - reveal alternative reaction pathways, if one is willing to take them into consideration.

In 2016, Jenkins reported a second-generation iron aziridination catalyst **Fe-L6**, featuring a dianionic cyclic tetra(NHC) ligand, with even higher activity.³² This complex has a unique structure, exhibiting an iron(II) center with an unusual square planar coordination geometry lacking any additional axial ligands. The result of a square planar - formally counting 14 VE - iron(II) tetracarbene, whose highly unsaturated structure is even retained in coordinating solvents such as acetonitrile supports two assumptions: Firstly the dianionic cyclic tetra(NHC) ligand **L6** significantly exceeds its neutral counterparts in terms of donor capacity. Secondly the two vacant coordination sites make a high catalytic activity very likely, which was shown later on. Not only from a structural point of view is **Fe-L6** extraordinary, its electronic properties are also unique. In contrast to any other known tetra(NHC) iron(II) complex it displays a paramagnetic electronic ground state with two unpaired electrons ($S = 1$). In addition, while other iron(II) tetra(NHC) are relatively weak reducing agents, **Fe-L6** exhibits an iron(II/III) potential of -0.95 V. This is more than 1.1 V lower than for **Fe-L4Ph**, making it a strong reducing agent. The - thus far completely unknown - reasons for its unique electronic behaviour might be the key for a deeper understanding of this standalone tetra(NHC) iron complex. After discussing the structural and electronic features of **Fe-L4Ph** and **Fe-L6**, we will take a look at their catalytic performances. While **Fe-L4Ph** is able to

catalyze the transformation of moderately electron rich aromatic azides (**R**) to aziridines (0.1 mol-% loading, 90°C, 18 h) in moderate to excellent yields (20-97 %), **Fe-L6** can also convert aliphatic azides (**S**) (1 mol-% loading, 90°C, 18 h) and very electron rich aromatic (**T**) azides in good to excellent yields (47-95 %) (Scheme 6). Even more surprisingly, functionalized aliphatic azides (**U**) can also be converted by **Fe-L6**, still in moderate to good yields (33-50 %). In addition, the intramolecular aziridination to 5- and 6-membered heterocycles can be catalysed (**V**), which makes **Fe-L6** unmatched considering both activity and variability with respect to the range of possible substrates.

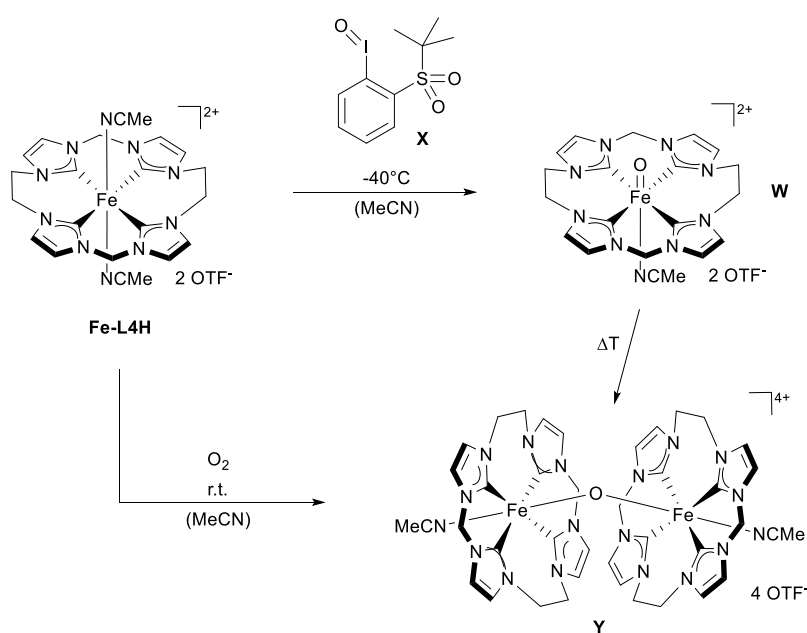


Scheme 6. Selection of challenging catalytic aziridination reactions of olefins performed by using **Fe-L4Ph** or **Fe-L6** as a catalyst.

Overall the work reported by Jenkins is a huge step in the field of catalytic aziridination of olefins, because for the first time, **Fe-L4Ph** and to an even higher degree, **Fe-L6** enabled simple access to the catalytic formation of electron rich aromatic and aliphatic azides. Previous reaction protocols included costly and difficult multistep reactions, if they could be achieved at all.^{78,79,80}

In 2013, Meyer reported the synthesis and characterization of another cyclic tetra(NHC) iron(II) complex (**Fe-L4H**) utilizing a ligand system previously reported by Jenkins in 2010.^{21,49} Although no catalytic application of **Fe-L4H** has been reported up to date, a very thorough

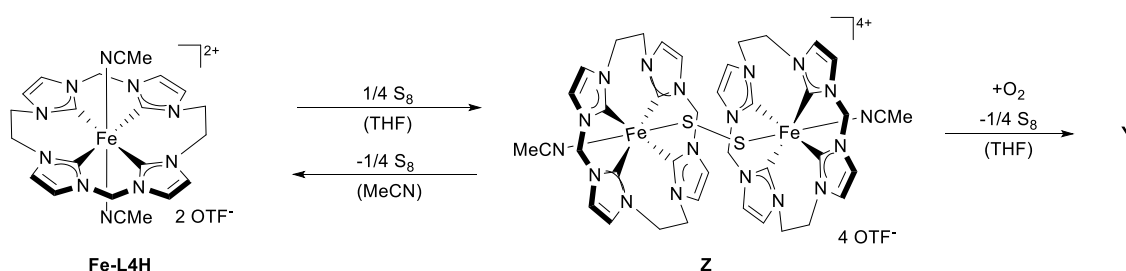
investigations of its reactivity towards oxidants, especially molecular oxygen (O_2), nitric oxide (NO) and even sulfur (S_8), is reported.^{54,55,56} In his first publication on this topic in 2013, the crystallographic characterization of an iron(IV) oxo species (**W**) was reported. Being the first iron(IV) oxo species - bearing a cyclic terta(NHC) ligand - ever isolated, a number of interesting properties are described (Scheme 7). Its synthesis was only successful with a special iodosylbenzene derivative (**X**) at $-40\text{ }^\circ\text{C}$ and could not be achieved by either H_2O_2 or simple iodosylbenzene. The green iron(IV) oxo species is relatively stable in acetonitrile solution, exhibiting a half-life of about five hours at room temperature and almost indefinite stability at $-40\text{ }^\circ\text{C}$. It is noteworthy that this high kinetic stability might be favoured by secondary interactions – namely hydrogen bonds – from the backbone of the cyclic tetra(NHC) ligand. Besides SQUID measurements the complex was also characterized by advanced Mössbauer spectroscopy, revealing an almost linear correlation between the oxidation state of the iron center and the respective isomer shift (-0.19 mm s^{-1}), when compared to the initial iron(II) compound **Fe-L4H** and its iron(III) dimer (**Y**) formed with oxygen. The iron(III) oxide dimer - formed from oxygen and **Fe-L4H** in acetonitrile at room



Scheme 7. Formation of iron(IV) oxo species (**W**) by iodosylbenzene (**X**) from **Fe-L4H** and formation of dimer (**Y**) by both oxygen or by heating of **W**.

temperature - is another interesting and rare $1s\ d^5$ iron compound. Unfortunately no further reactivity of **Y** is reported, it potentially being a capable oxidant. In another publication from 2015, Meyer reported the formation of a disulfide linked iron(III) dimer (**Z**), rather similar to

Y, which could be prepared by stirring a suspension of complex **Fe-L4H** with freshly sublimated sulfur in THF. The formed complex **Z** is an analogue for [2Fe-2S]-clusters naturally occurring in a number of metalloproteins.⁸¹ Interestingly **Z** is not stable in more polar solvent such as acetonitrile or acetone, because in those solvents the equilibrium of the reaction is shifted towards **Fe-L4H** and sulfur. **Z** is also sensitive to oxygen, which smoothly transforms it into complex **Y** and colloidal sulfur (Scheme 8). Despite the labile character of the Fe-S bond Mössbauer spectra and DFT calculations confirm the oxidation state of the iron centers to be +III and consequently the one of sulfur is -I.

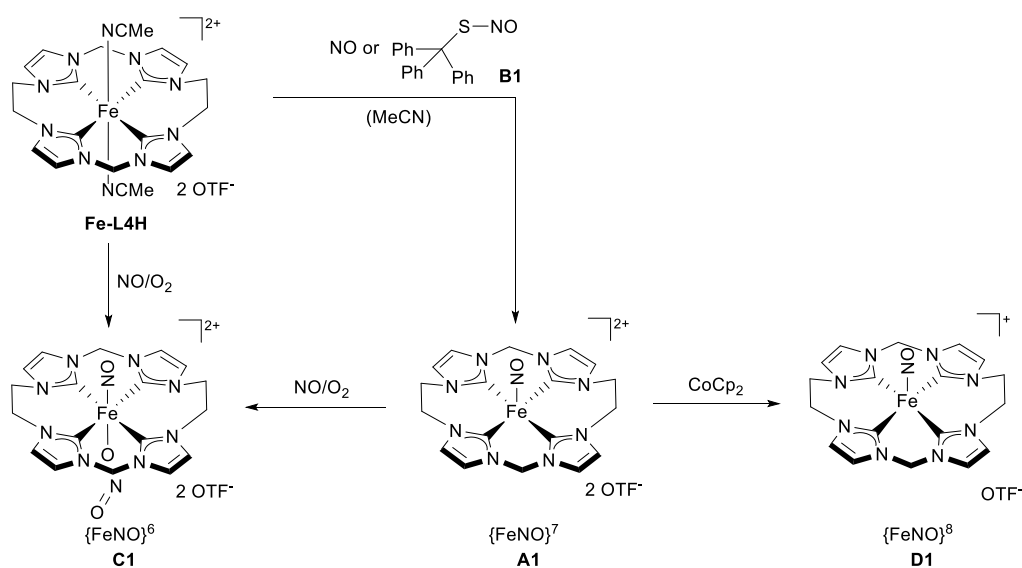


Scheme 8. Formation of iron(III) disulfide species (**Z**) from sulfur and **Fe-L4H**. Formation of dimer **Y** and sulfur upon contact of **Z** and oxygen.

To conclude, this is an interesting example for the progress made in biomimetic chemistry, being aware of the essential role of iron in countless biological processes and not least in our very own existence.

The reactivity of **Fe-L4H** and another biologically active small molecule, NO,⁸² was investigated by Meyer in 2015 and 2016.^{54,56} He was able to isolate and fully characterize the full series of {FeNO}^x (x = 6, 7, 8) complexes and derive a consistent picture of the electronic structure of these unique organometallic variants of the bioinorganic {FeNO}^x functional unit. For the preparation of the blue {FeNO}⁷ complex (**A1**), **Fe-L4H** was treated with either gaseous NO or 1 equiv. of trityl S-nitrosothiol (**B1**) in acetonitrile at room temperature. According to the unusually high $\nu_{\text{N-O}}$ absorption at 1742 cm⁻¹, the almost linear Fe-N-O angle of 176.9° and DFT calculations, the complex might be viewed best as a Fe^I(NO⁺) compound. Consequently, the reduced green {FeNO}⁸ (**C1**) complex could be prepared by treating **A1** with the strong reductant CoCp₂. This stable, diamagnetic complex is probably best described as a Fe⁰(NO⁺), because DFT calculations reveal a metal centered reduction. The yellow, oxidized {FeNO}⁶ complex **D1** can be prepared by exposing either **Fe-L4H** or the {FeNO}⁷ complex **A1** to an atmosphere of excess NO and molecular oxygen. This leads to a

rare example of an octahedrally coordinated non-heme $\{\text{FeNO}\}^6$ complex, bearing an *in situ* generated O-bound nitrito ligand in the second axial position (**D1**). In agreement with the previous compounds the $\{\text{FeNO}\}^6$ complex is best described as an $\text{Fe}^{\text{II}}(\text{NO}^+)$ complex. This also matches the spectroscopic observations that both the reduced $\{\text{FeNO}\}^8$ species **D1** and the oxidized $\{\text{FeNO}\}^6$ species **C1** show very different $\nu_{\text{N-O}}$ absorptions at 1590 cm^{-1} and 1877 cm^{-1} . This is in perfect accordance with the assigned oxidation state of the respective iron centers (Scheme 9).



Scheme 9. Formation of $\{\text{FeNO}\}^7$ complex **A1** from **Fe-L4H** via *NO* or trityl *S*-nitrosothiol **B1** and further preparation of the oxidized/reduced derivatives **C1/D1** by using either *NO/O₂* or *CoCp₂*.

Since much of the work presented in chapter 3 was performed simultaneously to the work reported by Meyer, inspirations were taken from one another. Also a cooperation with the Meyer group is reported herein (see 3.6). However, despite the high structural similarity of the cyclic terta(NHC) iron complexes **Fe-L1H** and **1**, many differences regarding the reactivity of those closely related systems were revealed in the publications central to this dissertation.

2. Objective

Taking into consideration that iron is the most abundant and cheap transition metal in earth's crust and is widely used by nature supporting countless biological processes, it is a reasonable choice to further explore its nature for future applications. Taking further into account that its heavier homologues (Ru/Os) and especially its neighbours to the right in the periodic table (Co, Rh, Ir; Ni, Pd, Pt), are known foremost for their catalytic activity, it seems even more true.

In particular, NHC complexes of iron show a high potential for enabling new catalytic pathways and applications, combining the unique traits of both iron and NHCs. Taking nature as a model, especially cyclic tetra(NHC) iron complexes, structurally and electronically closely related to naturally occurring "heme", might be a promising way to go (Scheme 11).

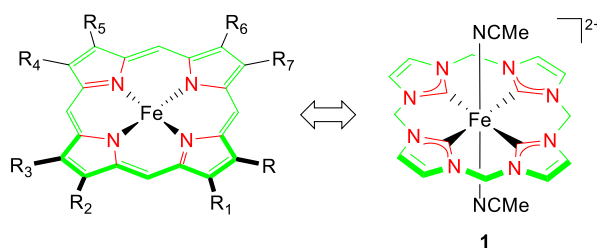


Fig. 11 Strong structural resemblance between **heme** and **1** – the central complex of this thesis – the structure of the latter emerging from the former by “simply” changing the “CNC”-motive of pyrrole against the “NCN”-motive of NHCs.

The investigations reported in this thesis were performed to broaden the scope and the understanding of biomimetic iron compounds and pave the way for future research and applications.

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

3. Paper Discussions

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

In this first publication the synthesis of bioinspired cyclic tetra(NHC) Iron(II) complex **1** is presented. Also included is an alternative halide-free synthesis of its ligand precursor **L0**, a macrocyclic 16 membered tetraimidazolium salt. Furthermore the reactivity of **1** with a variety of small molecules such as dimethylsulfoxide (DMSO), nitric monoxide (NO) and carbon monoxide (CO) is explored in depth.

The crystal structure depicted below shows the structure of complex **1** (Figure 12). The cyclic tetra(NHC) ligand coordinates the iron(II) center in an almost ideally square planar fashion and the octahedral coordination geometry is completed by two axial acetonitrile ligands.

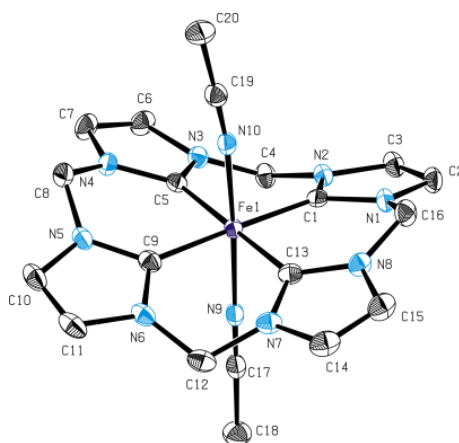


Fig. 12 ORTEP-style drawing of the cationic fragment of compound **1**. Hydrogen atoms and two PF_6^- anions are omitted for clarity and thermal ellipsoids are shown at a 50% probability level. Selected bond lengths (Å) and angles (°): Fe1–C1: 1.912(3), Fe1–C5: 1.904(3); Fe1–N9: 1.930(1), Fe1–N10: 1.933(1), 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).

$^1\text{H-NMR}$ experiments reveal a fast inversion of the saddle shaped ligand so that **1** appears to have a symmetry of D_{4h} . In addition they show the labile nature of the axial acetonitrile ligands, which readily exchange even at low temperatures. This finding is utilized for the straightforward synthesis of the corresponding DMSO, CO and NO complexes **5**, **6** and **7**. The aforementioned flexible nature of the ligand is confirmed by the crystal structures of these complexes, all exhibiting different conformations: Almost planar for **5**, saddle shaped for **6**

and ruffled for **7** (Figure 13). This clearly shows the strong influence of the axial ligands in this complexes on both the conformation of the ligand and the coordination geometry of the iron center.

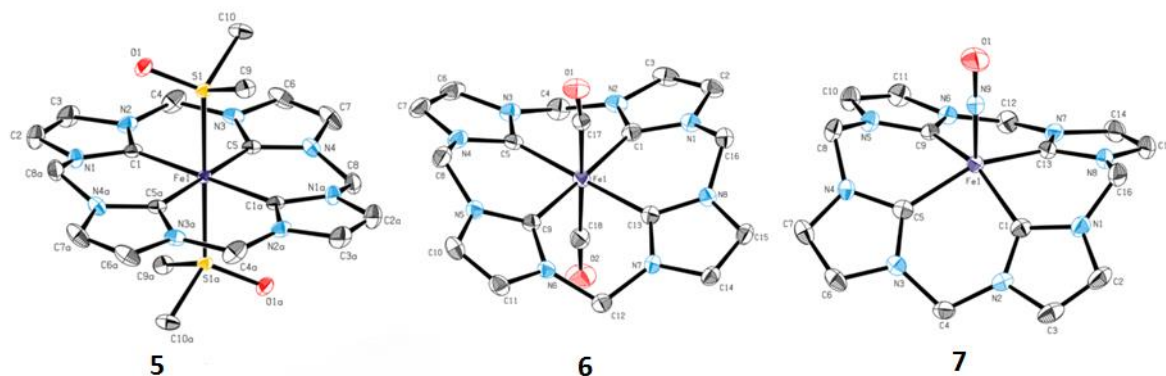


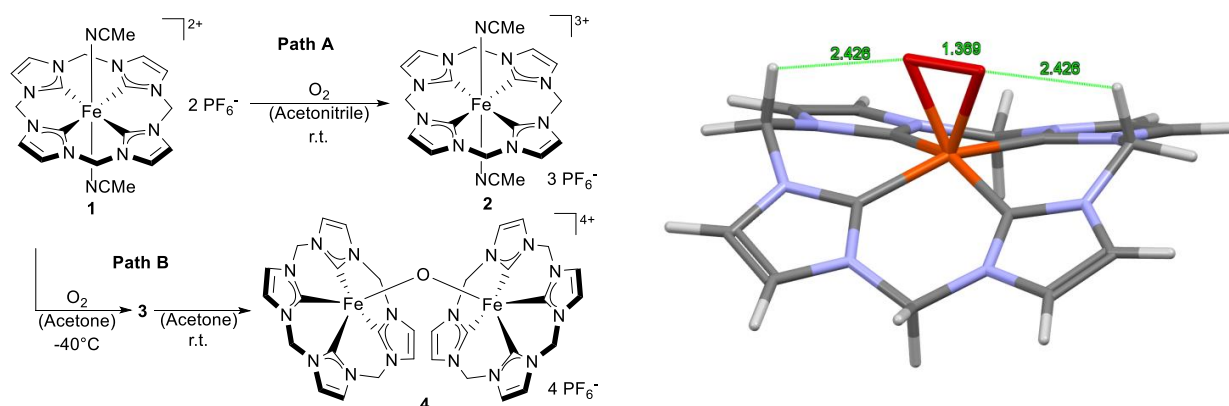
Fig. 13 ORTEP-style drawing of the cationic fragment of compounds **5-7**. Hydrogen atoms and PF_6^- anions are omitted for clarity and thermal ellipsoids are shown at a 50% probability level. Selected bond lengths (Å) and angles (°): **5**: Fe1–C1 1.936(3), Fe1–C5 1.938(3), Fe1–S1 2.205(1), S1–O1 1.479(1), C1–Fe1–C5 90.41(2), **6**: Fe1–C1 1.915(3), Fe1–C5 1.913(3), Fe1–C17 1.826(1), C17–O1 1.127(1), Fe1–C18 1.815(1), C18–O2 1.128(1), C1–Fe1–C5 89.27(10), C1–Fe1–C13 90.21(10), Fe1–C18–O2 177.39(3), Fe1–C17–O1 173.14(3); C18–Fe1–C17 177.11(2) **7**: Fe1–C1 1.950(3), Fe1–C5 1.952(3), Fe1–N9 1.673(2), N9–O1 1.159(3), C1–Fe1–C5 86.77(10), Fe1–N9–O1 172.13(10).

Electrochemical investigations of all the resulting iron(II) complexes revealed a strong influence of the coordinating ligands on the electronic properties of the complexes. Despite all - except **7** - showing a reversible iron(II/III) redox couple, their potential is strongly dependent on the respective ligand. While the redox potential of **1** is at 0.15 V those of **5** and **6** are significantly altered to 0.74 V and 1.25 V, respectively. However, the $\{FeNO\}^7$ complex **7** can not be easily oxidized, most probably due to the strength of the Fe-NO bond, but it can be reduced to the respective $\{FeNO\}^8$ compound at -1.06 V. This work paved the way for a deeper understanding of the synthesis and reactivity of **1** in particular and for cyclic tetra(NHC) iron complexes in general. This knowledge was the basis for more elaborate applications such as the utilization of **1** in epoxidation catalysis or the bonding of molecular oxygen, both described in the following sections.

3.2. Binding of Molecular Oxygen by an Artificial Heme Analogue: Investigation on the Formation of an Fe-Tetracarbene Superoxo Complex

This second publication - building up on the investigations reported in section 3.1 - focuses on the reactivity of **1** with molecular oxygen. Divergent oxidation behavior of **1** is observed depending on the choice of solvent (acetonitrile or acetone). In the first case, exposure to molecular oxygen leads to an oxygen free iron(III) complex **2**, whereas in the latter case an oxide-bridged iron(III) dimer **4** is formed. In acetone, an iron(III)-superoxo can be trapped, isolated and characterized as an intermediate at low temperatures. It is shown that the oxidation of the iron(II) complex in both solvents is a reversible process, thus **1** can be easily regenerated from both **2** and **4** by a number of organic and inorganic reducing agents.

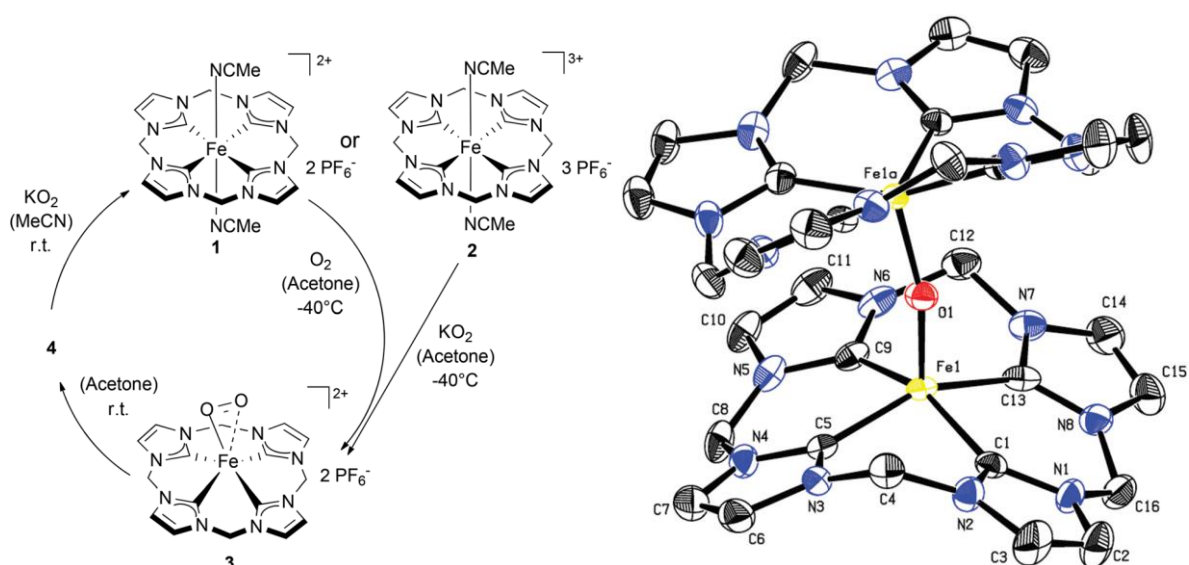
As depicted in scheme 10, in acetonitrile an one electron oxidation of **1** is observed resulting in the corresponding iron(III) complex **2**, which was first reported by independent oxygen free experiments described in section 3.3. Despite being relatively similar in regard to structure and polarity, in acetone an oxide linked Fe(III)OFe(III) dimer (**4**) can be isolated in good yields, precipitating as a dark blue powder from the reaction mixture (Scheme 10).



Scheme 10: Reactivity of **1** with molecular oxygen in acetonitrile/acetone. (left) DFT-derived structure of the cationic fragment $[Fe(O_2)CCCC]^{2+}$ of **3**. Selected calculated bond lengths (\AA) and angles ($^\circ$): Fe1-C1: 1.966, Fe1-C5: 1.956, Fe1-O1: 1.883, O1-O1*: 1.369, O1-H8: 2.426, C1-Fe1-C5: 87.62, C5-Fe1-C9: 89.73, O1-Fe-O1*: 42.63, C8-H8-O1: 105.79. (right)

However, at low temperatures a defined intermediate in the transformation of **1** into **4** can be trapped and isolated. This extremely sensitive reddish orange compound **3** was characterized by various analytical methods such as 1H -NMR, UV/Vis, EPR spin trapping and different reactivity studies including kinetics of its formation and decay. All of those

experiments along with DFT calculations confirm **3** being an paramagnetically coupled iron(III) side on superoxo compound. Unfortunately, due to its high sensitivity no X-ray structure could be obtained, but the calculated structure matches perfectly with those reported for similar compounds (Scheme 10). Being diamagnetic, the formation and decay of **3** could be monitored by ^1H NMR showing a smooth reaction of **1** to **3** at -40°C . and, upon warming, a subsequent reaction of **3** to **4** (Scheme 11). The same reaction was observed when starting with **2** and KO_2 , unambiguously proving the superoxidic nature of intermediate **3**.

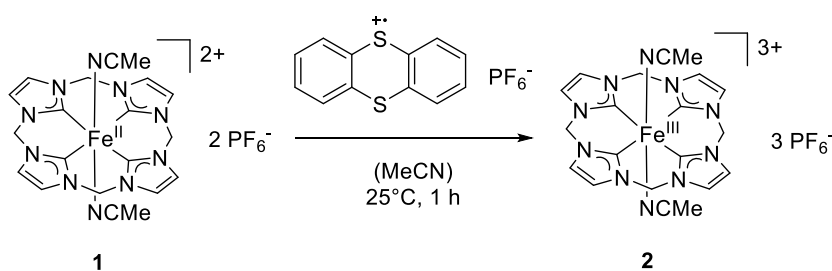


Scheme 11: Formation of **3** and subsequent conversion to **4** from both **1** and O_2 and **2** and KO_2 . (left) ORTEP-style drawing of the cationic fragment of $\text{O}[\text{Fe}(\text{III})\text{CCCC}]_2^{4+}$ of **4**. Hydrogen atoms and PF_6^- anions are omitted for clarity and thermal ellipsoids are shown at a 50% probability level. Selected bond lengths (Å) and angles (°): Fe1-C1 : 1.948(4), Fe1-C5 : 1.941(1), Fe1-C9 : 1.943(4), Fe1-C13 : 1.966(4), Fe1-O1 : 1.7322(7), C1-Fe1-C5 : 87.28(16) C5-Fe1-C9 : 87.84(17), C9-Fe1-C13 : 87.20(17), C1-Fe1-N13 : 86.92(16), C1-Fe1-O1 : 101.55(16), C5-Fe1-O1 : 100.80(12), C9-Fe1-O1 : 102.30(16), C13-Fe1-O1 : 105.47(12), Fe1-O1-Fe1a : 162.7(2). (right)

The stable product of both reactions, **4** could be easily isolated in high purity and good yields due to its insolubility in acetone. Its dual core iron(III) structure linked by an oxide was revealed by X-ray crystallography (Scheme 11). Reactivity studies revealed **4** being a capable oxidizing agent, smoothly transforming PPh_3 into OPPh_3 under regeneration of starting compound **1**. The utilization of this high oxophilicity in catalysis is subject of the third publication.

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

This third publication around **1** focuses - besides the preparation and characterization of a rare example of a stable iron(III) NHC complex (Scheme 12) - on the extraordinary catalytic activity of complex **2** in terms of epoxidation of unfunctionalized olefins: Activities up to 183,000 turnovers per hour at room temperature and turnover numbers of up to 4300 at -30°C were reported for the most active iron(III) system. In addition, significant negative influence of Fenton chemistry in the case of the iron(II) complex and the impact of various reaction parameters (water content, loading, temperature and various oxidants) were investigated. Complex **2** was prepared from **1** by using [Th][PF₆] as a one electron oxidant. **2** was characterized by means of single-crystal XRD, UV/Vis spectroscopy, cyclic voltammetry, ESI-MS, and elemental analysis, which confirmed its purity and bulk composition.



Scheme 12: Synthesis of iron(III) complex **2** by reacting thianthrenyl hexafluorophosphate as one electron oxidant with iron(II) complex **1**.

Both complexes **1** and **2** are examined with respect to selectivity and epoxide yield formed from *cis*-cyclooctene. In addition, they are compared to a previously reported bis(NHC) iron(II) complex. As shown in table 1 the activity of tetra(NHC) complexes exceeds that of the bis(NHC) complexes by far. They do not only deliver quantitative yield and perfect selectivities in about ten seconds, but can also be used at very low catalyst loadings of below 0.5 mol%. Especially at low concentrations (<0.5%) **2** shows a higher activity than **1**. This may be attributed to Fenton type deactivation processes becoming more relevant at lower concentrations. Thus, the formation of **2** from **1** as a first step in the catalytic cycle is indicated (Table 1). The evaluation of different reaction parameter revealed that low temperatures (-30°C) and high concentrated H₂O₂ (50%) as oxidant are favourable for the stability of **1** and **2**.

Table 1. Performance of iron carbene complexes in epoxidation of *cis*-cyclooctene.

rel. cat. conc. [mol %]	Epoxide yield (selectivity) [%]		
	[FeNCCN ^{Me}](PF ₆) ₂ ^a	[Fe ^{II} cCCCC](PF ₆) ₂ (1)	[Fe ^{III} cCCCC](PF ₆) ₃ (2)
2.0	92 (>99)	100 (>99)	100 (>99)
1.0	66 (>99)	100 (>99)	100 (>99)
0.5	–	99 (>99)	100 (>99)
0.25	–	82 (>99)	96 (>99)
0.1	4 (>99)	37 (>99)	55 (>99)

Reaction conditions: *Cis*-cyclooctene (269 μ mol, 100 mol %), H₂O₂ (aq. 50%, 403 μ mol, 150 mol %), solvent MeCN, *t* = 5 min, *T* = 25°C. Yields and selectivities were determined by GC/FID analysis. Reactions without catalyst did not yield any epoxide.

Although the rate of the reaction is lowered, quantitative yield and selectivity can be achieved in still 10 min with a catalyst loading of 0.05 mol% (Figure 14). Further an almost linear relation between yield and catalyst loading could be observed under these reaction conditions. Kinetic measurements indicate an overall order of 2 for both **1** and **2**. Nevertheless, **1** shows a significant initiation phase, while **2**, being already oxidized to iron(III), does not.

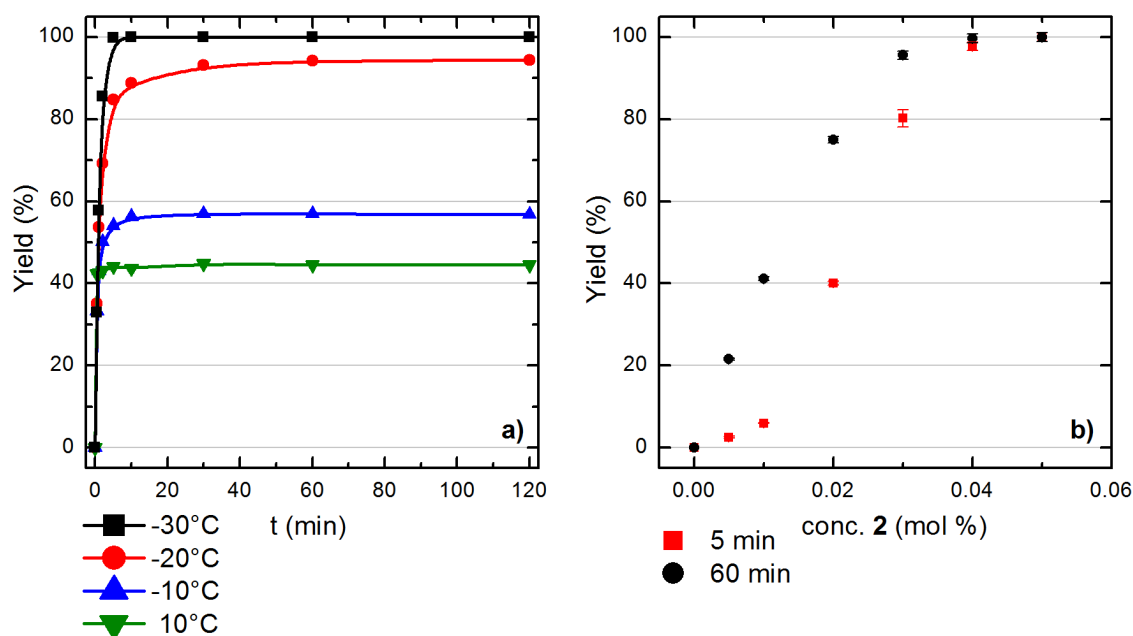


Fig. 14 Kinetic experiments at low temperatures for the epoxidation of *cis*-cyclooctene using 0.05 mol% of **2** as catalyst in a solvent mixture of MeCN/methylene chloride (1:1). (left) Dependency of yield after 5 and 60 min on the catalyst concentration of **2**. (right)

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

This fourth publication is divided into two parts with different focuses. The first one is centered around a systematic approach towards the synthesis of non cyclic tetradentate ligands, as well as the synthesis and characterization of their respective iron(II) complexes. The second part focuses on the electrochemical investigation of the various iron(II/III) redox potentials of those and comparable iron complexes, including complexes **1/2** (Figure 15).

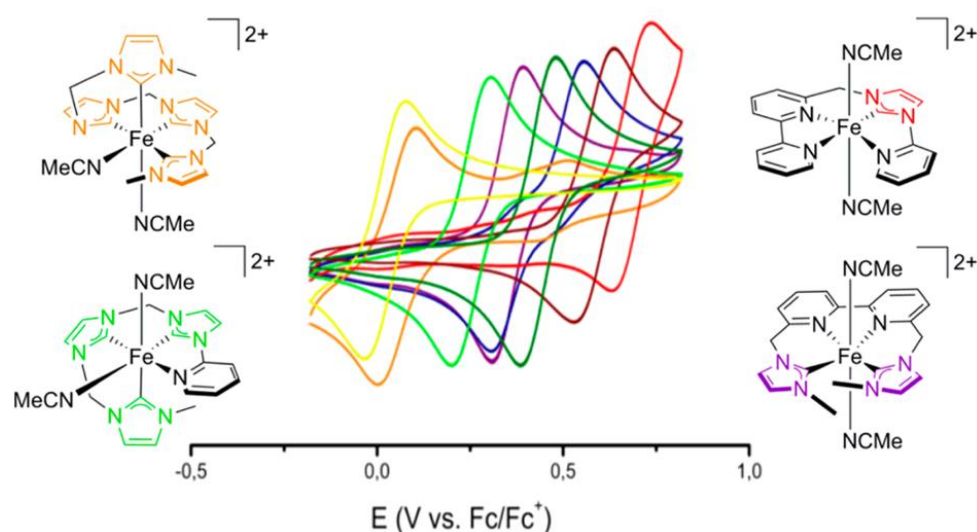


Fig. 15 Selection of various tetradentate NHC iron(II) complexes bearing 1 - 4 NHC moieties reported in 3.4 (left and right) and their different redox potentials depending on the number of coordinated NHCs using Fc as a reference (middle).

The synthetic section gives access to a number of previously unreported imidazolium salts and iron(II) carbenes and sheds light on conditions met for tetradentate pyridine NHC ligands to coordinate either in a square planar or a saw horse like fashion. All new complexes are fully characterized by ¹H/¹³C-NMR, single-crystal XRD, cyclic voltammetry, ESI-MS, and elemental analysis.

The electrochemical evaluation of these ten compounds reveals a linear relationship between the number of coordinated NHCs and the redox potential of the corresponding complexes (Figure 16). This insight might be useful for future catalytic applications, thus allowing fine-tuning of the electrochemical properties. Further it clarifies the strong impact of NHCs on the electronic situation at the iron(II) center, which is much larger than those of the pyridine.

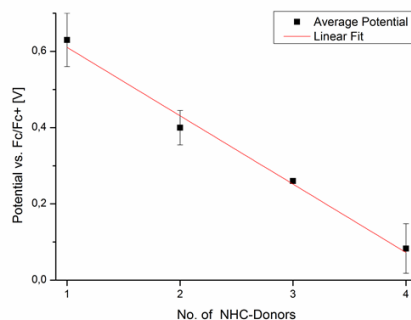


Fig. 16 Average $E_{1/2}$ plotted against the number of carbene donors. A linear relation for the compared systems **C1** to **C10** is shown. Error bars indicate standard deviation.

One of the complexes, **C4**, shows an especially interesting redox behaviour: Upon oxidation/reduction not only its overall charge, but also its structure changes (Figure 17). If oxidized at a potential of 0.56 V, the former κ^3 -coordinated bis(NHC) iron(II) complex is subjected to a conformational change. The non-coordinating pyridine unit switches places with one acetonitrile: Whether it is an axial or an equatorial one is uncertain, but due to steric reasons, an exchange on the axial position seems more likely. However, this change is completely reversible and the κ^4 -form switches back to its former κ^3 -form upon reduction at 0.31 V. This strongly suggests that the conformational change is driven by the enhanced Lewis acidity of the iron(III) center, since pyridine is a better donor than acetonitrile.

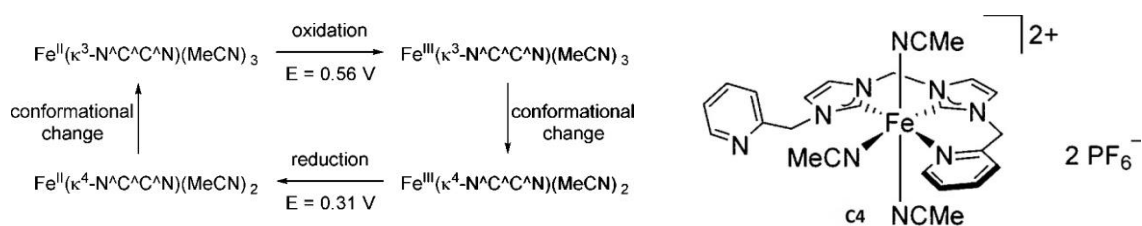


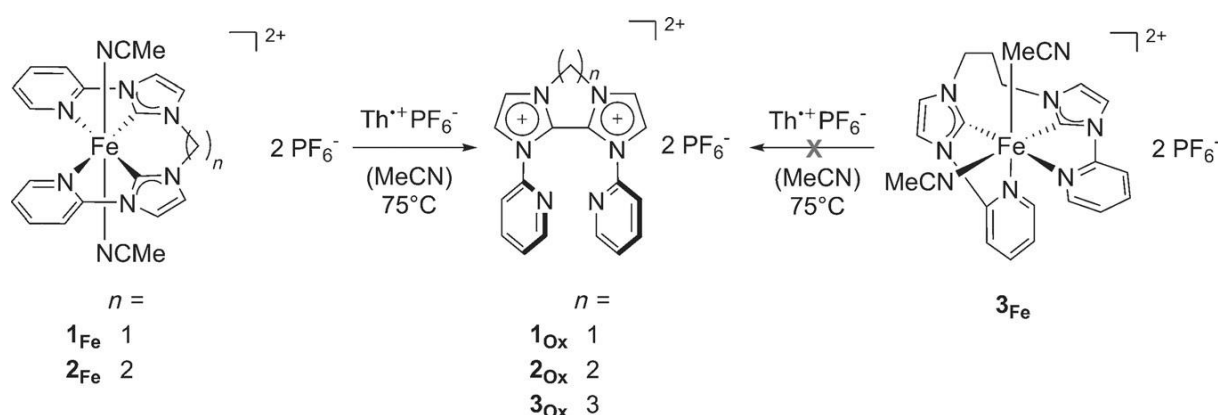
Fig. 17 Structural transformations during cyclic voltammetry of **C4** at a low scan rate of 100 mV/s.

Overall this work provided deeper insight into and understanding of both steric and electronic influences on the structure of iron(II) NHC complexes.

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

The utilization of the relative instability of open-chain iron(III) NHCs for the formation of highly strained annulated 2,2'-bisimidazoles by reductive elimination is the central point of this work. It is demonstrated that by this method highly strained systems such as **1_{Ox}** could be synthesized, which are not accessible via established synthetic methods. Furthermore, some of the resulting highly strained 2,2'-bisimidazoles were applied in the synthesis of Ni(II) complexes by oxidative addition to Ni(0) precursors.

The annulated 2,2'-bisimidazoles are obtained via the intermediately formed iron(III) species. Unlike its cyclic counterparts (e.g. **2**), acyclic iron(III) complex of **1_{Fe}** is not stable and reacts to soluble iron(II) salts by reductive elimination. Using this approach formerly inaccessible highly strained systems like **1_{Ox}** can be synthesized (Scheme 13).

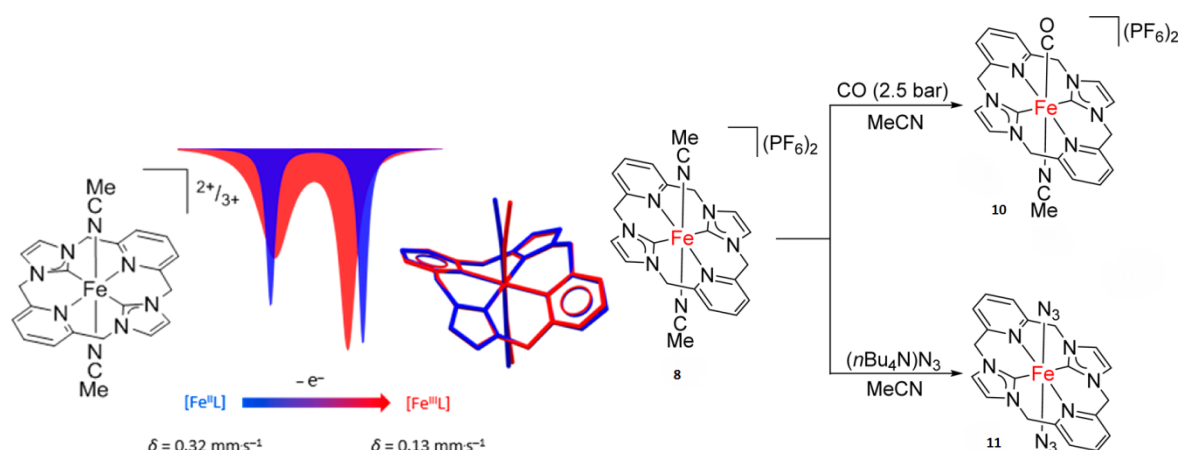


Scheme 13: Syntheses of annulated 2,2'-bisimidazolium salts **1_{Ox}** and **2_{Ox}** by one-electron oxidation of **1_{Fe}** and **2_{Fe}**, respectively. Oxidation of **3_{Fe}** did not yield **3_{Ox}**. $\text{Th}^{\cdot+}$: thianthrene cation radical.

The interesting redox properties of the resulting annulated compounds are investigated using cyclic voltammetry, showing a significant influence of the stability of reduced species of ring size as well as substitution pattern. Further this work delivers the first example of NHC ligand formation by oxidative C-C bond activation, showing the fascinating reactivity of 2,2'-bisimidazolium salts. Thereby these findings significantly increase the understanding of the Fe-C bond stability and show that dissociation of NHC ligands can selectively lead to useful and defined decomposition products.

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

This work is the result of a cooperation with the group of Franc Meyer from the University of Göttingen. The synthesis and advanced characterization (Mössbauer spectroscopy, SQUID) of a new cyclic FeNCNC complex **8** and its oxidation to the respective stable iron(III) complex **9** are described. In addition, the bisazido- and monocarbonyl-derivatives of the Fe(II) complex are presented (**10/11**) (Scheme 14).



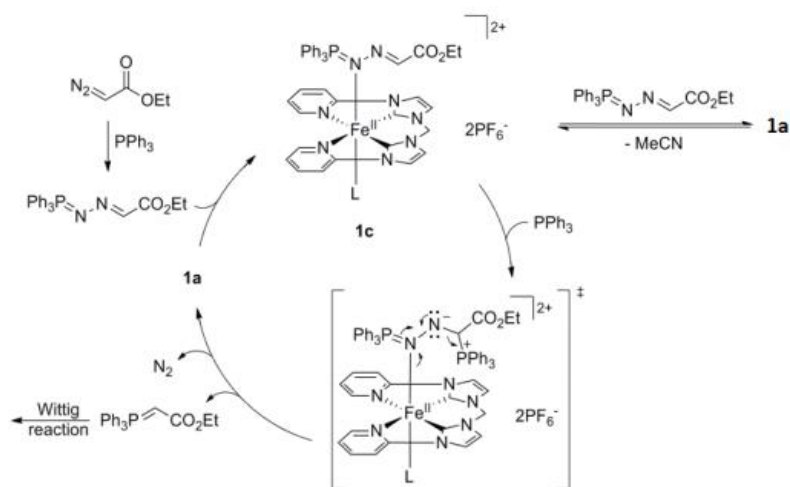
Scheme 14: Mössbauer spectra of the depicted iron(II) complex **8** and its oxidized counterpart **9**. (left) Synthesis of $[\text{FeL}(\text{MeCN})(\text{CO})](\text{PF}_6)_2$ (**10**) and $[\text{FeL}(\text{N}_3)_2](\text{PF}_6)_2$ (**11**). (right)

SQUID and Mössbauer experiments coherently showed that **9** has a $S = 1/2$ ground state, which corresponds to a $1s d^5$ configuration of the iron(III) atom. However, crystallographic analyses of **8** and **9** revealed no significant difference of both structures, which may be attributed to the rigid structure of the applied ligand. The macrocyclic ligand in **8** is puckered and shows a significant barrier for ring inversion ($\Delta H^\ddagger = 15.1 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = -4.7 \text{ cal mol}^{-1} \text{ K}^{-1}$). The detailed structural and electronic characterization allowed useful comparison with the related tetra(NHC) iron(II) complex **Fe-L4H** (see introduction). In its essence this investigation confirmed the supreme donor capacity of NHC vs. pyridine ligands and the improved stability of cyclic vs. acyclic iron NHCs.

3.7. Iron(II) N-Heterocyclic Carbene Complexes in Catalytic One-Pot Wittig Reactions: Mechanistic Insights

An NHC iron(II) complex is used as catalyst for aldehyde olefination with ethyl diazoacetate (EDA) in the presence of triphenylphosphine. The reaction leads to high olefin yields with very good *E*-selectivities. The key step of the reaction is the catalytic *in situ* generation of a phosphorus ylide. Based on the experimental observations, a new mechanism for the transformation of phosphazine is proposed.

While the Wittig reaction is long and well known in organic chemistry, there were some attempts to perform the reaction catalytically and not stoichiometrically in recent years. Iron complexes were reported to form iron(IV) carbenes as key intermediates in the catalytic cycle. This work, however, revealed that at least in case of iron(II) biscarbene **1a** no carbene, but an iron-phosphazine complex is involved under catalytic conditions, resulting in the catalytic generation of the phosphorus ylide (Scheme 15). The previously reported cyclic tetra(NHC) iron(II) complex **1** does actually form a carbene intermediate with diazoacetate,



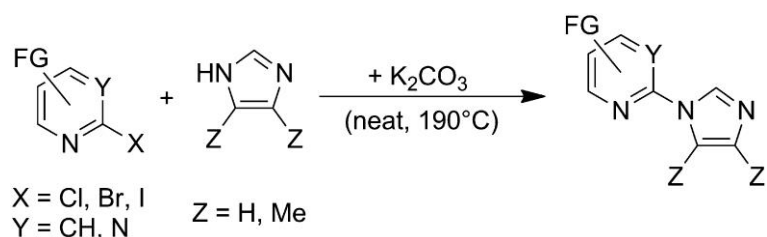
Scheme 15: Proposed catalytic cycle of the reaction.

but is not an active catalyst for this type of reaction. Thus, the overall reaction can be divided into two independent steps: First, the catalytic formation of phosphorus ylide followed by second, a Wittig-type conversion of the aldehyde to the respective olefin. The overall olefination reaction proceeds with yields of up to 90% and very good *E*-selectivity ($\geq 94\%$) at 70 °C.

3.8. Facile and Scalable Preparation of 2-Imidazolylpyridines

A novel method for the synthesis of 2-imidazolylpyridines is presented. The reaction of 2-halopyridines, potassium carbonate, and imidazole at high temperatures under inert gas atmosphere leads exclusively to the formation of 2-imidazolylpyridines in high yields. The synthesis is scalable, comparatively inexpensive and the products can easily be isolated.

2-imidazolylpyridines are important feedstocks in a broad range of applications such as *N*-heterocyclic carbene ligands (NHCs) and ionic liquids and serve as organic building blocks for pharmaceuticals. The most common method for their preparation is copper catalyzed coupling, which is relatively expensive and requires high effort. The presented novel, simple and cheap method is metal free and can also applied for multigram scale synthesis (Scheme 16). It can be applied to a broad range of substrates and even pyridines with weak donor substituents.



Scheme 16: Novel synthesis of 2-imidazolylpyridines.

Fast and simple aqueous work-up gives good to excellent yields and high purities. Overall, a significant progress in the efficient synthesis of 2-imidazolylpyridines is reported in this work.

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Author: Markus R. Anneser, Stefan Haslinger, Alexander Pöthig, et al

Publication: Inorganic Chemistry

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M. R. Anneser, S. Haslinger, A. Pöthig, M. Cokoja, V. D'Elia, M. P. Högerl, J. Basset and F. E. Kühn, *Dalton Trans.*, **2016**, 45, 6449

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

Markus R. Anneser,^a Stefan Haslinger,^a Alexander Pöthig,^a Mirza Cokoja,^a Jean-Marie Basset,^b Fritz E. Kühn^{*,a}

^aChair of Inorganic Chemistry/Molecular Catalysis, Catalysis Research Center, Ernst-Otto-Fischer-Straße 1 and Faculty of Chemistry, Lichtenbergstraße 4, Technische Universität München (TUM), D-85747 Garching bei München, Germany

^bKAUST Catalysis Center, King Abdullah University of Science and Technology (KAUST), Thuwal, Kingdom of Saudi Arabia

Originally published in: *Inorg. Chem.* **2015**, *54*, 3797–3804.

DOI:10.1021/ic503043h

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5.2. Binding of Molecular Oxygen by an Artificial Heme Analogue: Investigation on the Formation of an Fe-Tetracarbene Superoxo Complex

Markus R. Anneser,^a Stefan Haslinger,^a Alexander Pöthig,^a Mirza Cokoja,^a Valerio D'Elia,^{b,§} Manuel P. Högerl,^b Jean-Marie Basset,^b Fritz E. Kühn,^{a,*}

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5.3. NHC Versus Pyridine: How "teeth" Change the Redox Behavior of Iron(II) Complexes

Daniel T. Weiss,^{a,‡} Markus R. Anneser,^{a,‡} Stefan Haslinger,^a Alexander Pöthig,^a Mirza Cokoja,^a Jean-Marie Basset,^b Fritz E. Kühn*^a

^aChair of Inorganic Chemistry/Molecular Catalysis, Catalysis Research Center, Ernst-Otto-Fischer-Straße 1 and Faculty of Chemistry, Lichtenbergstraße 4, Technische Universität München (TUM), D-85747 Garching bei München, Germany

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[‡]Authors contribute equally to this work.

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

Jens W Kück,^{a,‡} Markus R Anneser,^{a,‡} Benjamin Hofmann,^a Alexander Pöthig,^a Mirza Cokoja,^a Fritz E Kühn*^a

^aChair of Inorganic Chemistry/Molecular Catalysis, Catalysis Research Center, Ernst-Otto-Fischer-Straße 1 and Faculty of Chemistry, Lichtenbergstraße 4, Technische Universität München (TUM), D-85747 Garching bei München, Germany

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

Stefan Haslinger,^a Jens W Kück,^a Markus R Anneser,^a Mirza Cokoja,^a Alexander Pöthig,^a Fritz E Kühn^{*,a}

^aChair of Inorganic Chemistry/Molecular Catalysis, Catalysis Research Center, Ernst-Otto-Fischer-Straße 1 and Faculty of Chemistry, Lichtenbergstraße 4, Technische Universität München (TUM), D-85747 Garching bei München, Germany

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5.6. Iron Complexes of a Macrocyclic *N*-Heterocyclic Carbene/PyridineHybrid Ligand

Iris Klawitter,^a Markus R Anneser,^b Sebastian Dechert,^a Steffen Meyer,[†] Serhiy Demeshko,^a Stefan Haslinger,^b Alexander Pöthig,^b Fritz E Kühn,^{*b} Franc Meyer^{*a}

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5.7. Iron(II) *N*-Heterocyclic Carbene Complexes in Catalytic One-Pot Wittig Reactions: Mechanistic Insights

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Originally published in: *J. Catal.* **2016**, *344*, 213-220.

DOI: 10.1016/j.jcat.2016.09.029

Hyperlink: <http://www.sciencedirect.com/science/article/pii/S0021951716302019>

5.8. Facile and Scalable Preparation of 2-Imidazolylpyridines.

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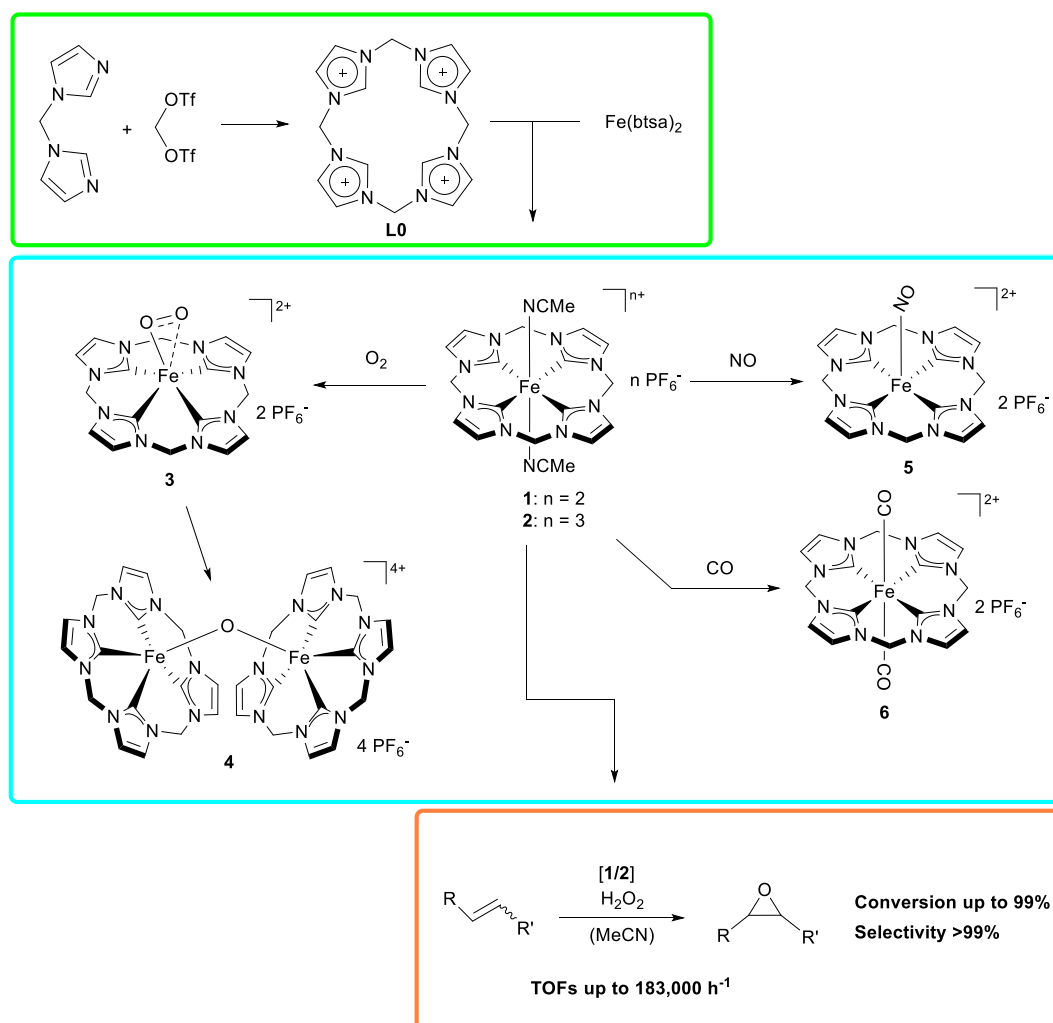
Originally published in: *Tetrahedron Lett.* **2013**, *54*, 3383–3387.

DOI: 10.1016/j.tetlet.2013.04.060

Hyperlink: <http://www.sciencedirect.com/science/article/pii/S0040403913006552>

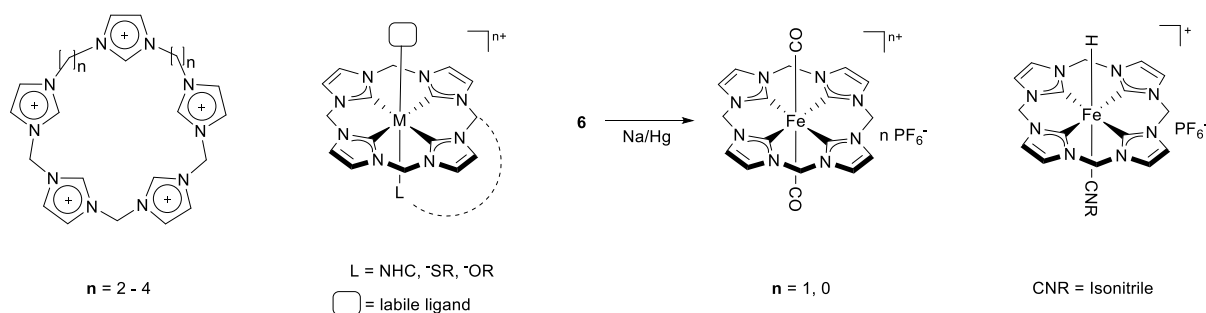
6. Summary and Outlook

The central idea of this thesis was the creation of bioinspired iron NHC complexes and to fathom their structure and reactivity. A secondary goal in this project was to employ the knowledge gained for the utilization of those PF₆⁻ compounds in biomimetic catalytic applications. Under this premise a broad spectrum of ligands and iron complexes was synthesized and underwent a thorough investigation. As an intermediate result of this endeavour the novel cyclic tetra(NHC) iron complex **1** was selected for an extensive investigation due to its remarkable stability and its close structural relation to the naturally occurring heme systems. Like its natural counterpart, the “handcrafted” complex **1** displays a high affinity for a large number of biologically important small molecules such as carbon-



Scheme 17: Summary of the key features of complex **1**: *Synthesis, reactivity and application in epoxidation catalysis of olefins.*

and nitrogen monoxide and sulfoxides as well as molecular oxygen and peroxides, which are the fuel and the bane for all higher biological life (Scheme 17). These analogies, supporting our previous theoretical considerations, yielded its application the most active epoxidation catalyst known to date (TOFs up to 183,000 h⁻¹). Its high activity, however, comes at the cost of incompatibility with some functional groups e.g. halides. For unfunctionalized terminal and internal olefins **1** shows an outstanding performance concerning both conversion and selectivity at simple room temperature conditions. Thus, combined with its relatively cheap and straightforward preparation even in a multigram scale, **1** will surely find its use, be it in synthetic or even technical applications. For future developments, an endless field of new possibilities stands open. Besides the obvious choice of using other transition metals such as cobalt, manganese or the “usual suspects” for catalytic applications (Ru, Rh, Pd, Pt,... etc.), even if purely focused on iron, manifold structural modifications or new catalytic applications come into mind. On the side of structural modifications the exchange of labile acetonitrile ligands by further NHCs - free or covalently connected to the tetra(NHC) - could further enhance the ligand’s donor capability. First approaches in this direction were already undertaken for similar systems, revealing a significant change in complex behaviour. A possible variation of the number of NHC moieties embedded in the macrocyclic ring to five, six or even eight could lead to interesting new structures, be it mono- or bimetallic complexes with even heterobimetallic compounds imaginable (Scheme 18).



Scheme 18: *Theoretical* concepts for ongoing development of cyclic tetra(NHC) ligands and their complexes.

Although the reactivity of **1** towards oxidizing agents is well investigated with reducing agents little is known. Suitable acceptor ligands (CO, CNR, etc.) might stabilize lower oxidation states (1, (0)?) or stabilize possible hydrides of **1**. On the non structural side of modifications a further expansion in the scope of catalytic applications come to mind, again already known for closely related compounds. The applications of **1** or its derivatives for

aziridination, aromatic hydroxylation and even C-H oxidation are easy to comprehend, but more exotic possibilities like hydrogenation do not appear inconceivable.

7. List of Publication and Curriculum Vitae

7.1. Journal Contributions

1.) "Synthesis and Characterization of an Iron Complex Bearing a Cyclic Tetra-N-heterocyclic Carbene Ligand: An Artificial Heme Analogue?"

Markus R. Anneser, Stefan Haslinger, Alexander Pöthig, Mirza Cokoja, Jean-Marie Basset, Fritz E. Kühn, *Inorg. Chem.* **2015**, *54*, 3797-3804.

2.) "Binding of Molecular Oxygen by an Artificial Heme Analogue: Investigation on the Formation of an Fe-Tetracarbene Superoxo Complex"

Markus R. Anneser, Stefan Haslinger, Alexander Pöthig, Mirza Cokoja, Valerio D'Elia, Manuel P. Högerl, Jean-Marie Basset, Fritz E. Kühn, *Dalton Trans.* **2016**, *45*, 6449-6455.

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

Jens W Kück, **Markus R Anneser**, Benjamin Hofmann, Alexander Pöthig, Mirza Cokoja, Fritz E Kühn, *ChemSusChem* **2015**, *8*, 4056-4063.

4.) "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, Fritz E. Kühn, *Organometallics* **2015**, *34*, 5155-5166.

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, Fritz E Kühn, *Chem. Eur. J.* **2015**, *21*, 17860-17869.

6.) "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, Franc Meyer *Organometallics* **2015**, *34*, 2819-2825.

7.) "Facile and scalable preparation of 2-imidazolylpyridines"

Andreas Raba, **Markus R Anneser**, Dominik Jantke, Mirza Cokoja, Wolfgang A Herrmann, Fritz E Kühn, *Tetrahedron Lett.* **2013**, *54*, 3384-3387.

8.) "Iron(II) N-Heterocyclic Carbene Complexes in Catalytic One-Pot Wittig Reactions: Mechanistic Insights"

Özden Karaca, **Markus R Anneser**, Jens W. Kück, Anja C Lindhorst, Mirza Cokoja, Fritz E Kühn, *J. Catal.* **2016**, *344*, 213-220.

9.) “Cyclization of ortho-hydroxycinnamates to coumarins under mild conditions: A nucleophilic organocatalysis approach“

Florian Boeck, Max Blazejak, **Markus R Anneser**, Lukas Hintermann, *Beilstein J. Org. Chem.* **2012**, *8*, 1630–1636.

7.2. Curriculum Vitae



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First name	Markus
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Education

04/2016 – 09/2016	ATV München „Life Science Management“
12/2012 – 12/2016	Technical University Munich (TUM) Chair of Inorganic Chemistry/Molecular Catalysis Catalysis Research Center (CRC) Ph.D. in Chemistry (Dr. rer. nat.) Supervisor: Prof. Dr. Fritz E. Kühn Dissertation: <i>“A Bioinspired Tetra(NHC) Iron Complex: Synthesis, Characterization and Catalytic Application of an Organometallic Heme Analogue.”</i> <ul style="list-style-type: none">▪ Synthesis and characterization of novel organic and inorganic compounds▪ Handling of highly sensitive organometallic compounds▪ Mechanistic investigations▪ Writing of four first author publications▪ Assistant for the lab course „Anorganisch chemisches Grundpraktikum II“
10/2010 – 10/2012	Technical University Munich (TUM) Master of Science, Chemistry Major subject: Inorganic chemistry Minor subject: Organic chemistry Master-thesis: <i>“Synthesis and Characterization of Polydentate N-Heterocyclic Carbenes of Manganese(II) and Cobalt(II)”</i>
10/2007 – 08/2010	Technical University Munich (TUM) Bachelor of Science, Chemistry Bachelor-thesis: <i>„Synthesis and characterization of dodecaphenylporphyrine and reaction with fullerides“</i>
08/1998 – 08/2007	Dom-Gymnasium, Freising, Germany Abitur

International Experience

11/2013 – 12/2013 King Abdullah University of Science and Technology (KAUST),
TUM Cooperation, Saudi Arabia

Skills

Language German (native), English (business fluent)

Analytical methods NMR, IR, UV/Vis, FAB-MS, ESI-MS, GC, CV

Computer MS Office, Origin, SciFinder, Reaxys, ChemDraw, MestreNova

Student supervision Two Master-Thesis, four research internships, four times
„Anorganisch chemisches Grundpraktikum II“

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