

**Technische Universität München**

Fachgebiet Molekulare Katalyse

**Influence of Open Chain, Tetradentate NHC and  
NHC/Pyridine Hybrid Ligands on the Coordination and  
Electrochemistry of Late Transition Metal Complexes**

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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. L. Hintermann

Prüfer der Dissertation: 1. Univ.-Prof. Dr. F. E. Kühn

2. Hon.-Prof. Dr. R. W. Fischer

Die Dissertation wurde am 28.10.2015 bei der Technischen Universität München eingereicht und durch die Fakultät für Chemie am 23.11.2015 angenommen.



*Ausdauer wird früher oder später belohnt – meistens aber später.*

Wilhelm Busch



Die vorliegende Arbeit wurde im Fachgebiet Molekulare Katalyse der Technischen Universität München in der Zeit von Oktober 2012 bis Oktober 2015 angefertigt.

Besonders danken möchte ich meinem verehrten Lehrer und Doktorvater

**Herrn Professor Dr. Fritz E. Kühn**

für die Aufnahme in seinen Arbeitskreis, für die uneingeschränkten Forschungsmöglichkeiten, für das positive Arbeitsumfeld, für das entgegengebrachte Vertrauen in meine Arbeit, für die fortwährende Unterstützung und für all die Möglichkeiten, die sich mir dadurch in den letzten drei Jahren eröffnet haben.

## Danksagung

An dieser Stelle möchte ich die Gelegenheit nutzen und einigen Personen danken, die mich in den letzten drei Jahren unterstützt und damit einen nicht unerheblichen Beitrag zum Gelingen meiner Arbeit geleistet haben:

**Dr. Mirza Cokoja** für zahlreiche und inspirierende fachliche Gespräche und die schnelle Korrektur meiner Publikationen, vor allem aber auch für die fortwährende und ungebrochene Unterstützung seit dem ersten Tag meiner Masterarbeit,

**Dr. Alexander Pöthig** für zahllose fachliche und private Gespräche, lustige Burger-, Grill- und Spieleabende und die kompetente Hilfe zum Thema Kristallstrukturanalyse,

**Dr. Markus Drees** für unterhaltsame Nachmittage/Abende im Kaffeeraum, für hilfreiche Ratschläge zum „Leben in Giesing“ und quer durch alle Belange der Doktorarbeit,

**Dr. Gabriele Raudaschl-Sieber** für interessante und thematisch breit gefächerte Gespräche und für die Anleitung und Unterstützung im Bereich der NMR Spektroskopie,

**Prof. Jean-Marie Basset** und die Kooperationspartner der **KAUST** für die erfolgreiche Zusammenarbeit über die letzten Jahre,

**Markus Anneser** für das sehr gute Teamwork, für die geteilte Freude und das geteilte Leid über geglückte und misslungene Synthesen, für unglaublich viele und häufig geniale Vorschläge und für die vielen kulinarischen Highlights der letzten drei Jahre,

**Stefan Haslinger**, für die tolle Zusammenarbeit, für die lustigen Kurzaufenthalte an der KAUST und in Denver, für die gründliche Überarbeitung meiner Manuskripte, für viele konzeptionelle Vorschläge und für die Lösung der „ein oder anderen“ Kristallstruktur,

**Anja Lindhorst** für tagtägliche Diskussionen und konstruktive Kritik, für viel gute Laune, für ihre Ehrlichkeit und einfach dafür, dass sie es zwei Jahre mit mir in einem Labor ausgehalten hat, wenn alle anderen schreiend den Raum verlassen haben,

**Christian Jandl** für die Messung „ein paar einzelner“, weiterer Kristallstrukturen, für die vielen lustigen Spieleabende und für seine sympathisch und erfrischend ehrliche Art,

**Robert Reich** für seine gute Laune, für unzählige Dart-Partien, für die rasche Korrektur dieser Arbeit, für lange Abende auf dem Fussballplatz und für seine Hilfsbereitschaft,

**Philipp Altmann, Patricia Wand** und **Dr. Marlene Kaposi** für ihre engagierte Hilfe und für die gemeinsamen Mittagessen, Kaffeepausen oder Spieleabende und allen weiteren Mitgliedern des Arbeitskreises für die Schaffung eines äußerst angenehmen Arbeitsklimas mit vielen, wunderschönen Erinnerungen,

**Dr. Andreas Raba** und **Dr. Nidhi Grover** für ihre Unterstützung und Hilfe zu Beginn meiner Promotion,

**Dominik Reich** und **Bruno Dominelli** für ihre äußerst motivierten Forschungspraktika, den freundlichen und sehr hilfsbereiten Damen aus dem Sekretariat, **Irmgard Grötsch, Ulla Hifinger, Roswitha Kaufmann** und **Renate Schubauer-Gerl**, für die Unterstützung im täglichen Bürokratie-Dschungel und die Geduld mit uns Doktoranden,

**Jürgen Kudermann** und **Maria Weindl** für kompetente Hilfe und Ratschläge zum Thema NMR und die sehr angenehmen Wartezeiten bei Messungen oder Reparaturen,

dem technischen Personal, insbesondere **Martin Schellerer, Rodica Dumitrescu, Ulrike Ammari, Petra Ankenbauer** und **Bircan Dilki**, für die tägliche Hilfe bei der Bestellung von Chemikalien oder der Charakterisierung von Verbindungen.

Weiterhin möchte ich meinen Eltern und Großeltern danken, die mich während des gesamten Studiums unterstützt und motiviert haben. Ohne ihre Unterstützung wäre es um einiges komplizierter gewesen. Ein besonderer Dank gilt ferner meinen beiden Brüdern, auf die ich mich schon mein gesamtes Leben verlassen kann und die auch hier in München immer zur Stelle waren, wenn ich Hilfe gebraucht habe.

Abschließend möchte ich meiner Freundin Anett danken, die in den vergangenen Jahren und besonders den letzten drei Monaten das tägliche „Auf und Ab“ ertragen hat, mir immer zur Seite stand und mir dadurch dauerhaft Halt gegeben hat. Danke auch für das schönste Geschenk meines Lebens!

## Deutsches Abstract

Die vorliegende Dissertation beschäftigt sich mit der Untersuchung einer Untergruppe der rasch wachsenden Klasse der polydentaten *N*-heterocyclischen Carbene (NHC). Während der Fokus der Forschung in den letzten 20 Jahren hauptsächlich auf mono-, bi- und tridentaten NHCs und ihrem Einfluss auf die homogene Übergangsmetallkatalyse lag, wurden im Rahmen dieser Arbeit die Auswirkung offenkettiger, tetradentater NHC Liganden auf die Struktur- und Elektrochemie von Komplexen mit späten Übergangsmetallen untersucht.

Die erste Veröffentlichung beschreibt in diesem Zusammenhang die Entwicklung einer Synthese für offenkettige tetra-NHC Liganden. Der zentrale Schritt ist dabei die Isolierung eines Diimidazolium-Bausteins, dessen eine Seite durch eine Methylgruppe geschützt ist und der somit eine Makrocyclisierung oder Polymerisierung verhindert. Die erhaltenen Silberkomplexe weisen eine Stöchiometrie auf, die ideal für eine Transmetallierung der Liganden auf Metallsalze des Typs  $\text{MX}_2$  (M: Metall, X: Halogen) ist.

Die zweite Publikation beschäftigt sich folglich mit den Transmetallierungsreaktionen der entwickelten Silber-NHC Komplexe. Die Reaktion mit Münzmetallhalogeniden der Oxidationsstufe +I, Gruppe 10 Übergangsmetallhalogeniden der Oxidationsstufe +II und Eisen(II)-bromid wurde erfolgreich durchgeführt und die erhaltenen Komplexe charakterisiert. Bemerkenswert sind vor allem die Koordinationsmodi der Liganden in den oktaedrischen Eisenkomplexen. In Abhängigkeit der Flexibilität des Liganden bindet dieser in einer äquatorialen oder sägebockartigen Struktur an das Eisen.

In der dritten Publikation wurde systematisch der Einfluss untersucht, den tetradentate NHC/Pyridin-Hybridliganden auf das Oxidationspotential von Eisen(II)-Komplexen haben. Dazu wurden chelatisierende Liganden des Typs  $(\text{NHC})_n(\text{Pyridin})_{4-n}$  ( $n = 1 - 3$ ) und deren oktaedrischen Eisen(II)-Komplexe synthetisiert. Es wurde gezeigt, dass das Oxidationspotential vor allem durch die Anzahl der koordinierten NHC-Donoren bestimmt wird, wobei ein zusätzliches NHC eine Senkung des Potentials um 0,2 Volt bewirkt. Faktoren wie die Anordnung der Donoren oder die Verzerrung des Komplexes hingegen haben einen geringen Einfluss von bis zu 0,1 Volt.



## English Abstract

Within the quickly growing field of polydentate *N*-heterocyclic carbenes (NHC), especially mono-, bi-, and tridentate NHCs were often investigated as ligands in late transition metal catalysis. This thesis focuses on open chain, tetradentate NHC ligands and their influence on the coordination and electrochemistry of late transition metal complexes.

In this context, the first publication deals with the development of a synthesis for flexible, open chain tetra-NHC ligands. Central point is the introduction of a di-imidazole building block with one protected site which is inhibiting polymerization and macro cyclization. The obtained silver complexes exhibit interesting structures and feature an ideal stoichiometry for transmetalation reactions with  $\text{MX}_2$  salts (M: metal, X: halide).

The second publication consecutively deals with the use of the reported silver-NHC complexes as transmetalation agents. Reaction with coinage metal halides in the oxidation state +I, group 10 metal halides in the oxidation state +II, and iron(II) bromide were successfully performed. Besides square-planar coordinated metals of the nickel group, especially the coordination geometry of the tetra-NHC ligands within the octahedral-coordinated iron(II) complexes is interesting. Depending on the flexibility of ligand's linker, either an equatorial or a sawhorse-type coordination of the ligand with two *cis*-positioned acetonitrile ligands is obtained.

In the third publication, a systematic approach is presented in order to investigate the influence of tetradentate NHC/pyridine hybrid ligands on the oxidation potential of iron(II) complexes. Therefore, ligands of the general type  $(\text{NHC})_n(\text{pyridine})_{4-n}$  ( $n = 1 - 3$ ) and the respective iron(II) complexes were synthesized. It could be demonstrated that the oxidation potential is mainly determined by the number of NHC moieties coordinated to the metal center, whereas each additional NHC unit is found to lower the potential by 0.2 volt. However, minor influence of up to 0.1 volt could be related to structural reasons.

## List of Abbreviations

ACS	American Chemical Society
btsa	bis(trimethylsilyl)amide
CCDC	Cambridge Crystallographic Data Centre
CO	carbon monoxide
DMF	dimethylformamide
e.g.	for example
Fc	ferrocene
H <sub>2</sub> O <sub>2</sub>	hydrogen peroxide
L	ligand
M	metal
MeCN	acetonitrile
NHC	<i>N</i> -heterocyclic carbene
NMR	nuclear magnetic resonance
ppm	parts per million
THF	tetrahydrofuran
V	volt
VE	valence electrons
X	halide

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## I. Introduction

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## I.1 Current Challenges in Chemistry

Countless chemists for sure have grown up with a common German saying which claims: “*Chemie ist, wenn es knallt und stinkt!*” (translation: “*Chemistry is when it bangs and stinks!*”). Although certainly applicable for chemistry lessons in elementary and secondary school, these seven words humiliate generations of chemists and their achievements. One of the most important accomplishments – in order to feed the world’s growing population<sup>1</sup> – is certainly the synthesis and use of fertilizers,<sup>2</sup> which today is closely related to the development of a catalytic process on an industrial level converting nitrogen to ammonia.<sup>3</sup> Also crucial was the discovery and industrial production of medical products like penicillin as first antibiotic<sup>4</sup> or countless other drugs. As a result, our life expectancy increased drastically and will be further rising.<sup>5</sup> However, not only vitally important products have a strong influence on today’s life. Who could really imagine everyday life without steel, plastics, polymers, or other synthetic materials? Most of them are produced in different branches of the chemical industry and have been subject of research for a long time. Fossil organic hydrocarbons like crude oil, coal, and methane – as starting point for many of these processes – are converted into a broad range of basic chemicals like ethylene, propylene, syn-gas, or hydrogen, which give access to nearly all synthetic chemicals.<sup>6</sup> Some of the resulting final products even end up as liberating earmuffs or flavorsome products.

Current challenges are closely related to some of the aforementioned topics. In fact, replacements of crude oil as exhaustible resource are yet to be discovered. In this context, the carbon management in total has to be object of further research.<sup>7</sup> PAUL ANASTAS has summarized some of the most basic demands of current chemistry within his “*Twelve Principles of Green Chemistry*”.<sup>8-9</sup> In general, these cover the fields of safety issues, pollution problems, and waste avoidance. Point 9 out of 12 demands the use of catalysts in chemical reactions instead of stoichiometric amounts of reagents. In addition to avoidance of waste, catalysts decrease the activation energy and accordingly the necessary reaction temperature.<sup>10</sup> A most desirable application is the current methanol

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production: Although catalyzed in both steps, methanol is synthesized from syn-gas at around 275 °C which itself is often generated from methane and water vapor at around 900 °C.<sup>11</sup> Huge amounts of energy could be saved, if mankind was able to mimic nature's direct, enzymatic oxidation of methane or light alkanes with molecular oxygen.<sup>12-13</sup> Therefore, numerous scientists work on understanding or employing enzymatic C–H bond functionalization processes.<sup>14</sup> Other approaches focus on the preparation of artificial, molecular catalysts for C–H bond oxidation with dioxygen.<sup>15</sup> Often these model compounds are designed as mimicry of active centers in enzymes – like the group of metalloporphyrins<sup>16</sup> – in order to achieve similar reactivity. As for enzymatic reactions, high-valent and oxygen containing iron species could be proven as integral part in artificial oxidation reactions.<sup>17</sup>

However, NHC ligands as directing ligands in catalysis,<sup>18</sup> which have revolutionized olefin metathesis and cross-coupling reactions,<sup>19-20</sup> have only recently been introduced in iron-catalyzed oxidation reactions<sup>21-22</sup> or the isolation of high-valent iron oxo species.<sup>23</sup> Therefore, further investigations on NHCs in general and iron NHC complexes in special are necessary.

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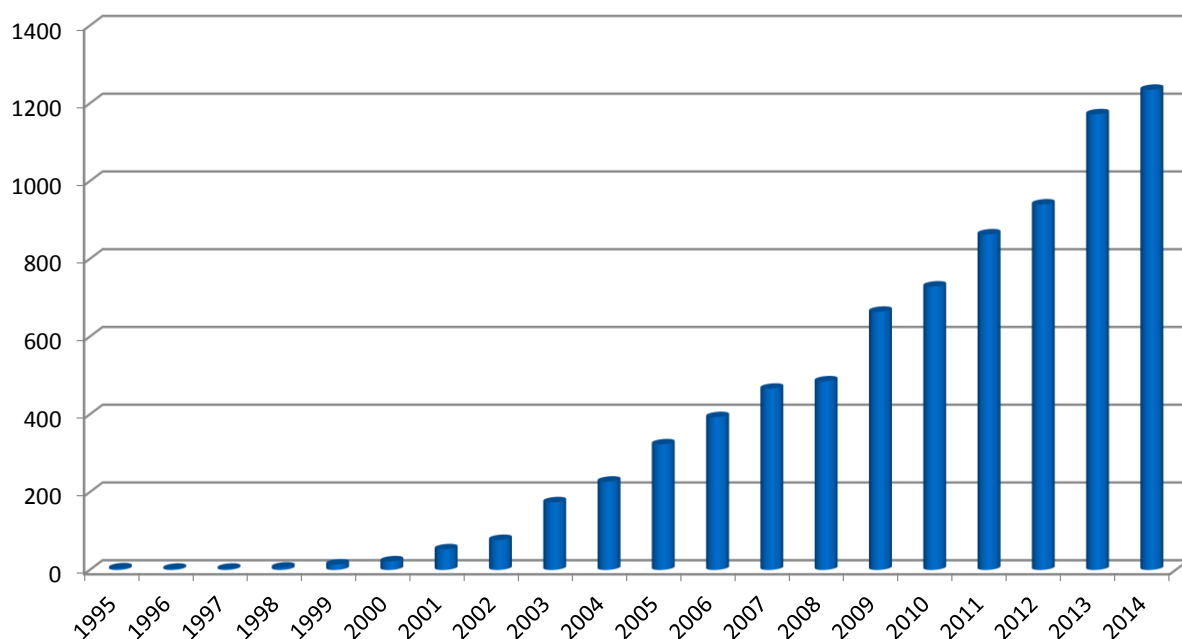
### I.2 N-Heterocyclic Carbene Ligands

#### I.2.1 Free Carbenes to NHC Ligands – an Overview

Carbenes are divalent carbon atoms with two unshared electrons and generally considered unstable and short-lived. However, already in the middle of the 19<sup>th</sup> century, observations on the decomposition of chloroform suggested the existence of dichlorocarbene.<sup>24</sup> In the beginning of the 20<sup>th</sup> century, investigations on the reactivity of diazomethane showed its carbene-like reactivity and potential to act as methylene-precursor.<sup>25</sup> Addition of diazomethane derivatives to arenes were found to lead to an insertion of a carbon atom into the aromatic ring and were claimed to proceed via cyclopropanation of a double bond.<sup>26-27</sup> The same reactivity was obtained for *in situ* generated dichlorocarbene.<sup>28</sup> Although these results delivered sufficient evidence to postulate the existence of simple carbenes derived from methylene, it was not possible to isolate them.

In contrast to free carbenes, metal complexes with coordinated carbenes have been isolated and characterized early. FISCHER,<sup>29</sup> WANZLICK/ÖFELE,<sup>30-31</sup> and SCHROCK<sup>32</sup> were able to synthesize and successfully characterize three different types of carbene complexes. In this context, it was noted that the first carbene complex was already isolated in 1925,<sup>33</sup> however incorrectly characterized as isonitrile/hydrazine complex.<sup>34</sup> Today, complexes with *N*-heterocyclic carbenes (NHC) as described by WANZLICK and ÖFELE outnumber all other carbene type complexes. Still, it took more than 20 years after their initial discovery, until NHC chemistry shifted into the focus of research. The isolation of the first free *N*-heterocyclic carbene in 1991 by ARDUENGO *et al.*<sup>35</sup> was the trigger for following work that elevated them “*from mere laboratory curiosities to compounds of enormous practical significance*”.<sup>36</sup> Over the last 20 years, a continuously increasing number of scientific publications dealing with NHCs and their chemistry could be noted (Figure I.1).

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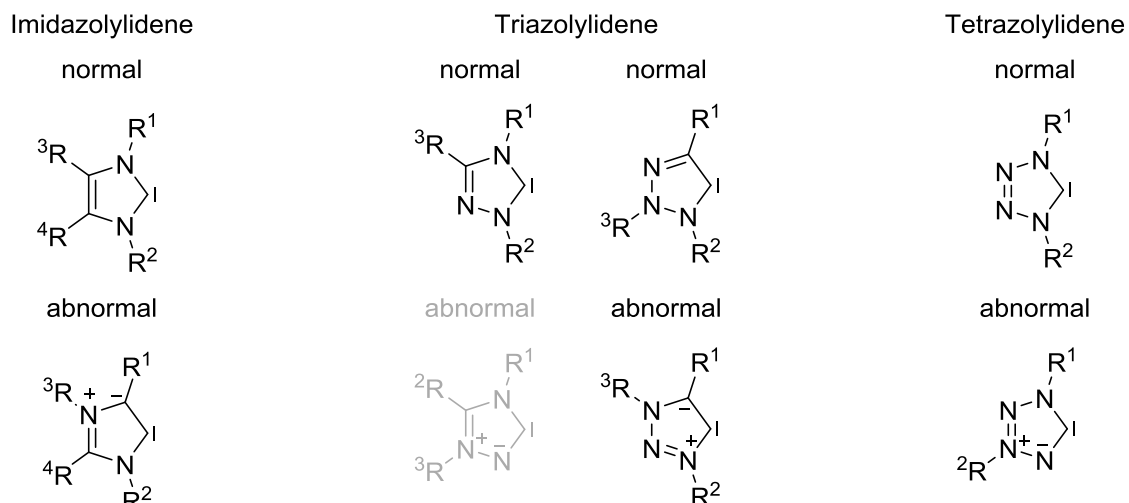
**Figure I.1** Number of publications with the topic “N-heterocyclic carbene”. Accessed via CAS SciFinder on September 01, 2015.

This trend continues in 2015 with another 945 recorded publications during the first eight months. The huge majority of NHC-based research is focusing on the coordination chemistry of transition metals and the application of the respective complexes,<sup>36</sup> with catalysis being the main focus.<sup>37</sup> However, uses in medicine and as luminescent or functional material are reported as well.<sup>38-42</sup> Interestingly, besides the use as transition metal complexes, NHCs are also applied as organocatalysts<sup>43-44</sup> and ligands to main group<sup>45-46</sup> or f-block elements.<sup>47</sup>

Although by definition NHCs may be based on any nitrogen-containing heterocycle, the most common building blocks are the 5-membered imidazole and its hydrogenated derivative imidazoline. Other platforms like triazoles<sup>48</sup> and tetrazoles<sup>49</sup> are less common but also known (Figure I.2, top). In addition to the position and number of nitrogen atoms, NHCs may also vary in the position of substituents and/or the position of the carbene carbon.<sup>50-52</sup> As a result, compounds for which no mesomeric structure without zwitterionic character can be drawn are found. Those are called abnormal or mesoionic NHCs (Figure I.2, bottom).

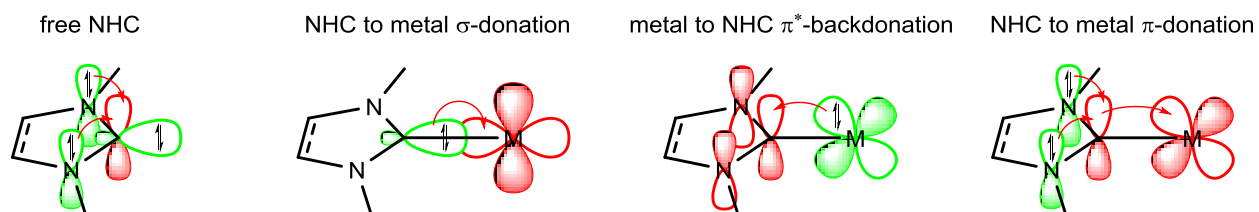


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**Figure I.2** Selection of normal and abnormal NHCs based on only nitrogen-containing 5-membered heterocycles.

In contrast to methylene (“:CH<sub>2</sub>”) as simplest carbene, which is considered exhibiting a triplet ground state, free NHCs show a singlet ground state. A populated sp<sup>2</sup>-hybridized orbital and an empty p<sub>z</sub>-orbital, which is stabilized by interaction with free electron pairs at the neighboring nitrogen atoms, are located at the C2 carbon (Figure I.3, left).<sup>53</sup> As a consequence of the electronic and steric situation, WANZLICK early observed dimerization of *in situ* formed free NHCs with sterically non-demanding substituents.<sup>54-56</sup> However, the mechanism and motivations to form dimers are more complicated than they appear and do not only rely on the substituents but also on other factors.<sup>57</sup>



**Figure I.3** General electronic structure of free NHCs (left) and the three bonding contributions to NHC metal complexes (green: populated orbitals, red: empty orbitals).<sup>58</sup>

When coordinated to a metal center, NHCs act as strong σ-donors in which the sp<sup>2</sup> orbital interacts with an unoccupied transition metal d-orbital. In addition to the strong σ-bonding, also π-interactions between the empty C2-p<sub>z</sub> orbital and metal d-orbitals occur. Depending on the electronic structure of the metal (oxidation state, further donors) and

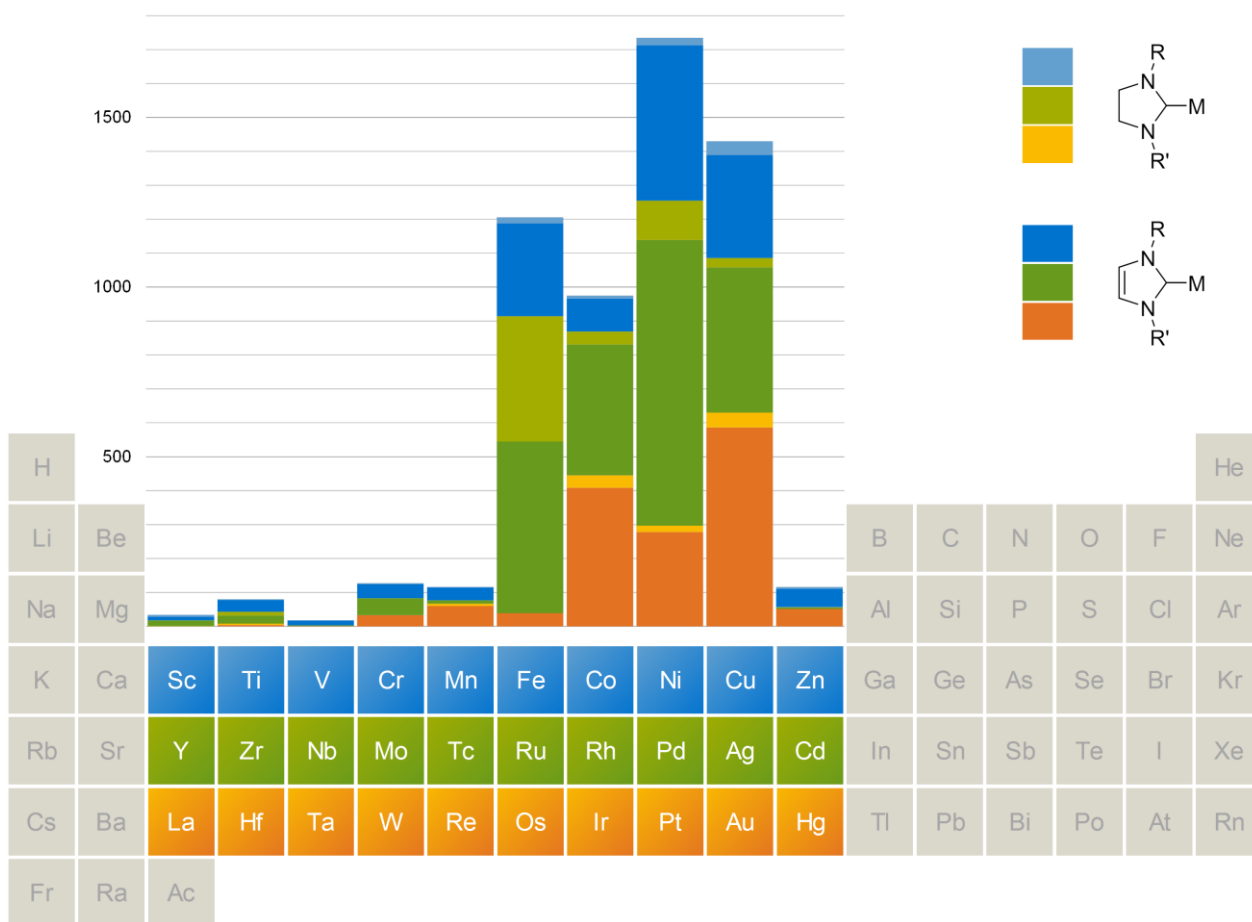
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the ligand (substitution, backbone saturation), back bonding or further  $\pi$ -donative contributions are strengthened.<sup>58</sup>

Due to their electronic and steric situation, NHCs are often compared to phosphane ligands and presumed to replace or at least supplement them as ubiquitous ligands in transition metal catalysis.<sup>59-60</sup> In order to rank the donor strengths of different NHC and phosphane ligands, NOLAN and co-workers measured the C–O stretching band frequencies of similar (L)–Ir<sup>I</sup>–(CO) complexes with different ligands L.<sup>61</sup> They found that phosphanes in general are much weaker donors than NHC ligands. On comparison of the imidazol(in)-2-ylidene types, those with an unsaturated backbone showed a little stronger donor capability. When taking a closer look at other NHC platforms (Figure I.2), especially abnormal-bound imidazolylidene and tetrazolylidene ligands proved to be noticeably stronger donors than their ‘normal’ derivatives.<sup>49-50</sup> However, 1,2,3-triazolylidenes show only small differences concerning the donor strength in dependence of the carbene position.<sup>48,62-63</sup>

In general, various synthetic routes towards NHC complexes<sup>53</sup> and their precursors exist,<sup>64</sup> giving rise to a myriad of known compounds. In the further framework of this thesis, the focus will be on NHCs of the imidazolylidene type, which was not only the first reported type, but is also by far the most common platform. As mentioned before, transition metal complexes are the dominant use for NHCs, however, huge discrepancies between the commonness of different metal complexes exist. While complexes with late transition metals of groups 8 to 11 are known in large numbers and widely applied, complexes with early transition metals of groups 3 to 7 are relatively rare as indicated by the number of entries in the database of the Cambridge Crystallographic Data Centre (CCDC) for transition metal complexes with NHCs of the imidazol(in)ylidene types (Figure I.4).

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**Figure I.4** 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.

As seen in Figure I.4, palladium NHC complexes account for the largest group with around 1000 reported crystal structures of the imidazol-2- and imidazolin-2-ylidene types whereas almost 90% of these are based on an unsaturated backbone. The complexes are often applied as catalyst for C–C cross-coupling reactions,<sup>20,65-68</sup> although uses in oxidation catalysis, oligo- and polymerization, or as anticancer drugs are reported as well.<sup>69</sup> As for palladium, the research focus for nickel NHC complexes lies on the C–C bond formation.<sup>70</sup> Ruthenium NHC complexes with around 900 reported crystal structures of the imidazol(in)ylidene types represent the second largest fraction. However, compared to 10% for palladium, an enormous fraction of more than 40% is built upon a saturated backbone going back to the initial finding of GRUBBS *et al.* that

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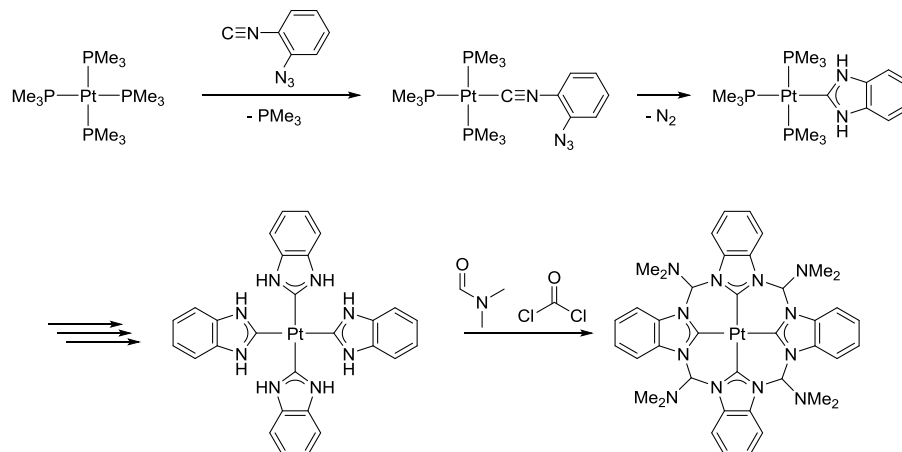
ruthenium imidazolidin-2-ylidene complexes are more active in olefin metathesis than their unsaturated derivatives.<sup>19,71-72</sup> In addition to the ubiquitous use of ruthenium NHCs as catalysts in olefin metathesis,<sup>73</sup> they are also widely applied in (transfer-) hydrogenation, hydrosilylation, arylations, isomerizations, and other applications.<sup>74-75</sup> Gold NHC complexes represent the third largest fraction (Figure I.4) with more than 600 reported crystal structures. Several applications are known<sup>76</sup> with a focus on catalysis<sup>77-78</sup> and medical applications.<sup>79-80</sup> For silver complexes, most applications are limited to carbene transfer on other metals; however, uses as catalysts<sup>76,81-82</sup> and antibiotics are known.<sup>83-84</sup> Copper NHCs again are widely used in catalysis<sup>76,85</sup> and medical applications.<sup>80</sup> Recently, some focus was put on the highly topical activation of carbon dioxide.<sup>86</sup> The uses of rhodium and iridium NHC complexes are highly similar,<sup>37,87</sup> with a strong focus on hydrogenation, -silylation, -formylation and related reactions.<sup>88-89</sup> Iron as number 10 with around 300 known NHC complex crystal structures (Figure I.4) is dramatically underrepresented compared to its higher homologues ruthenium (around 900 NHC structures). Given the high potential and manifold uses that are known in non-NHC catalysis,<sup>90-91</sup> iron will be in the focus of upcoming research.

In addition to metal-specific research, general “hot topics” in NHC development are e.g. the introduction of water-soluble ligands<sup>92</sup> in order to do catalysis in aqueous media,<sup>93</sup> NHC ligands for asymmetric catalysis,<sup>94</sup> or multidentate NHC ligands with chelating abilities.<sup>95-97</sup> Especially the last group has been examined thoroughly and found to have huge impact on catalytic applications.

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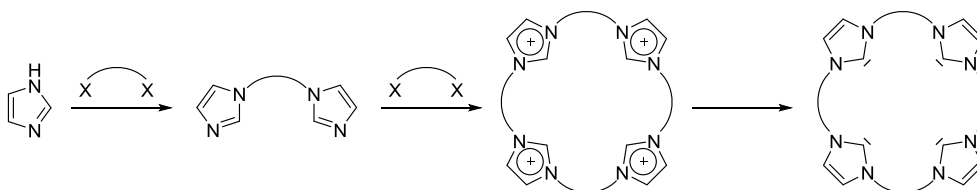
### I.2.2 Tetra-NHC Ligands and their Complexes

While scorpionato type tri-NHC ligands were first reported in 1996,<sup>98-99</sup> tetra-NHC ligands are still a decade younger. The initial work by HAHN *et al.*<sup>100</sup> presented a template synthesis starting from isocyanides and building up 1,3-diprotonated benzimidazol-2-ylidenes *in situ* (Scheme I.1).



**Scheme I.1** Template synthesis of the first tetra-NHC ligand.

In a second step, the coordinated and unsubstituted benzimidazol-2-ylidenes are linked by reaction with phosgene and DMF to yield the macrocyclic framework of the ligand. Two years later, MURPHY *et al.*<sup>101</sup> presented a new synthetic access of macrocyclic tetra-NHC ligands which has become today's standard pathway (Scheme I.2).

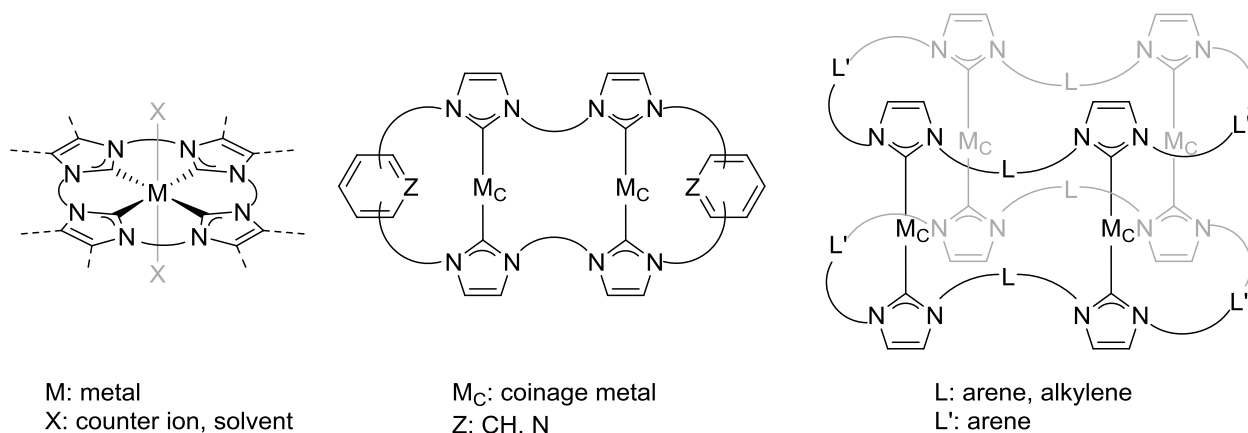


**Scheme I.2** Today's most common route to access macrocyclic tetra-NHC ligands.

The approach includes the assembly and use of tetraimidazolium salts as ligand precursors and was strongly influenced by previous studies on imidazolium-based anion receptors.<sup>102-104</sup> Until today, various macrocyclic tetra-NHC ligands have been prepared by following that specific sequence.<sup>105-110</sup> Although based on a similar synthesis, their

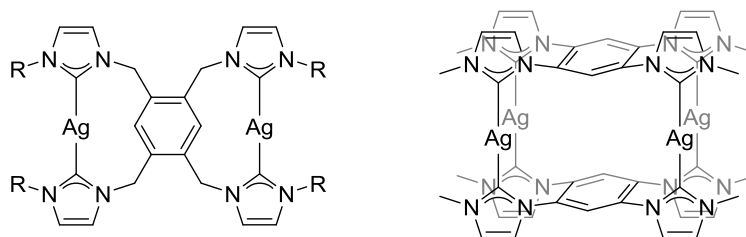
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coordination chemistry varies strongly. While single atom-bridged or flexible alkyl-linked tetra-NHC ligands are mostly used to prepare mononuclear transition metal complexes (Figure I.5, left),<sup>100-101,105-106,108,111-115</sup> their aryl-bridged relatives are mainly used to synthesize polynuclear coinage metal cages (Figure I.5, mid and right).<sup>109-110,116-117</sup>



**Figure I.5** Overview on macrocyclic tetra-NHC ligands and their most prominent metal complexes.

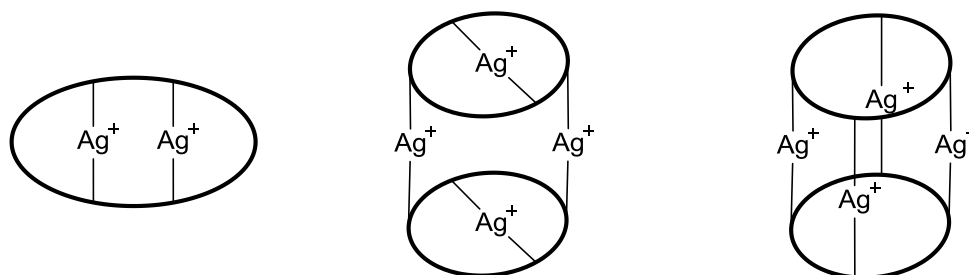
Recent developments were found to weaken the borders between the above mentioned types by presenting compositions of both classes. A flexible and arene linked ligand was presented by the group of HAHN,<sup>118</sup> consequently both types of complexes are reported as well. A different conceptual approach was followed by PÖTHIG *et al.*<sup>119</sup> who evolved classical pyrazole-bridged di-NHC ligands to their dimerized, macrocyclic tetra-NHC analogs. As a result, a nickel complex with two square planar-coordinated metal ions within the ligand's cavity could be accessed. In addition to macrocyclic ligands, a small number of acyclic tetra-NHC ligands is known as well. These ligands are based on a two- or fourfold substituted arene platform and – due to the rather rigid centered unit – not a single mononuclear complex is reported.<sup>120-125</sup> In most cases, silver complexes were the focus of the study (Figure I.6).



**Figure I.6** Different types of complexes with acyclic tetra-NHC ligands.

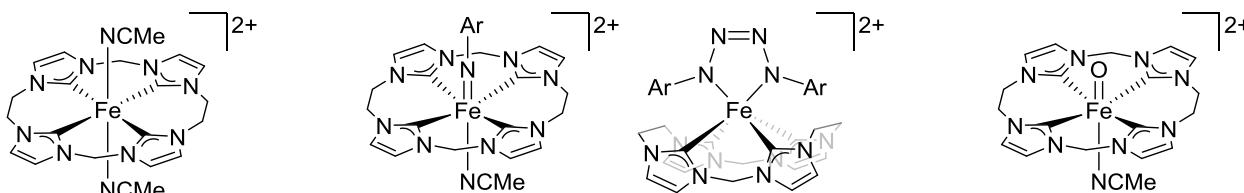
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Although complexes with tetra-NHC ligands feature a variety of coordinated metals, in terms of the sheer number of known complexes, silver is outperforming all other metals. Three different types of silver tetracarbene complexes are known in literature. The first type features two linearly coordinated silver ions inside the internal cavity of the ligand (Figure I.7, left).<sup>109-110,123</sup> If the cavity is not large enough for two neighboring silver ions, one of them is located inside each cavity and two additional silver ions are bridging the ligands. As a result, a dimeric complex is formed.<sup>110,114</sup> The third type (molecular box structure) is encountered for nearly all acyclic and a few macrocyclic systems with rigid arene linkers: All four silver ions act as bridge between two ligands.<sup>116,118,120-121,123</sup>



**Figure I.7** Possible conformations of silver tetra-NHC complexes: monomeric complexes with the silver located in the internal cavity (left), dimeric complexes with the silver located in the cavity and bridging two ligands (middle), and molecular box structure with the silver coordinated between two ligands (right).

While silver complexes clearly outnumber all other metal complexes with tetra-NHC ligands, the true highlights are certainly iron complexes with their highly interesting reactivity. In 2011, the group of JENKINS was able to present the first iron complex with a tetra-NHC ligand and studied it as catalyst for aziridations.<sup>113</sup> Their mechanistic investigations resulted in the evidence for the presence of an iron(IV) imide<sup>113</sup> as well as an iron(IV) tetrazene<sup>126</sup> species during reaction. Inspired by these results, MEYER *et al.*<sup>23</sup> synthesized an iron(IV) oxo complex (Figure I.8). These species are often considered as active intermediates in catalytic oxidations and are therefore in the focus of research.<sup>17</sup>



**Figure I.8** Highlight structures of the iron tetra-NHC chapter.

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Besides iron, especially cobalt and nickel complexes with tetra-NHC ligands show interesting redox behavior and were applied for reduction reactions.<sup>111-112</sup> In addition, a recent publication by JENKINS *et al.*<sup>115</sup> introduced borane-bridged tetra-NHCs which are no longer neutral ligands but anionic. As a result, the first main group complexes of aluminum, indium, and tin were obtained featuring a tetra-NHC ligand.

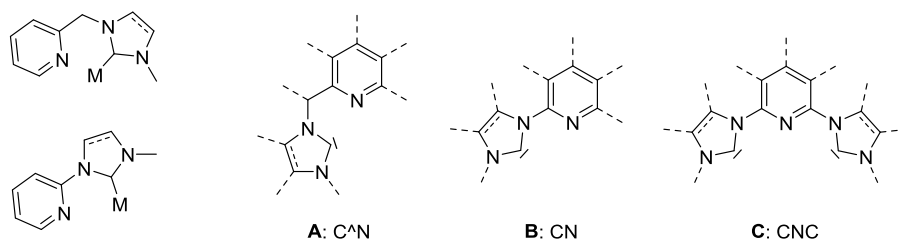
As shown in this chapter, different types of tetra-NHC ligands are known. However, especially flexible ligands, which do not only coordinate in an equatorial position, are lacking. An approach to overcome these limitations would be the break-up of the macrocyclic framework without falling back on a centered arene platform.



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### I.2.3 NHC/Pyridine Hybrid Ligands

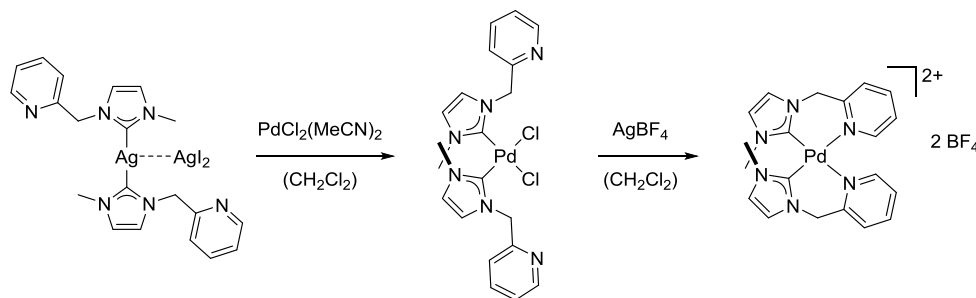
One of the earliest modifications applied to NHCs were reported soon after ARDUENGO'S breakthrough in 1991<sup>35</sup> and included the synthesis of multidentate, chelating NHC ligands.<sup>96-97,127-128</sup> In addition to purely NHC containing ligands also mixed donor ligands became target of investigations. Such hybrid ligands were first presented in 1993 and featured additional sulfur and phosphorus atoms or alkene groups which were able to coordinate to a metal center.<sup>129-130</sup> A first application for these hemilabile NHC ligands was cyclopropanation catalysis, as shown for ruthenium complexes in 1997.<sup>131</sup> But it was not until 2000 that NHC/pyridine hybrid ligands were reported.<sup>132-136</sup> Then however, several groups simultaneously reported on different structural motifs for such ligands. Until today, more than 300 scientific non-patent publications deal with the synthesis, application or general investigation of metal complexes with NHC/pyridine hybrid ligands (accessed via CAS Scifinder on September 02, 2015 as shown in Figure I.9, left). These ligands feature between two and eight donor moieties with varying compositions. Types **A** – **C** are by far the most prominent structural motifs with around 80 publications for each.



**Figure I.9** Search entries in CAS Scifinder (left) and the three most widely used NHC/pyridine hybrid ligand types **A**, **B**, and **C** (right).

The first report on an NHC/pyridine hybrid ligand was published in 2000 by the group of CAVELL and included the synthesis of the imidazolium precursor for a type **A** ligand from methylimidazole and picolyl chloride.<sup>132</sup> The ligand was shown to form a linearly coordinated silver di-NHC complex which was used as transmetalation agent to access palladium complexes (Scheme I.3).

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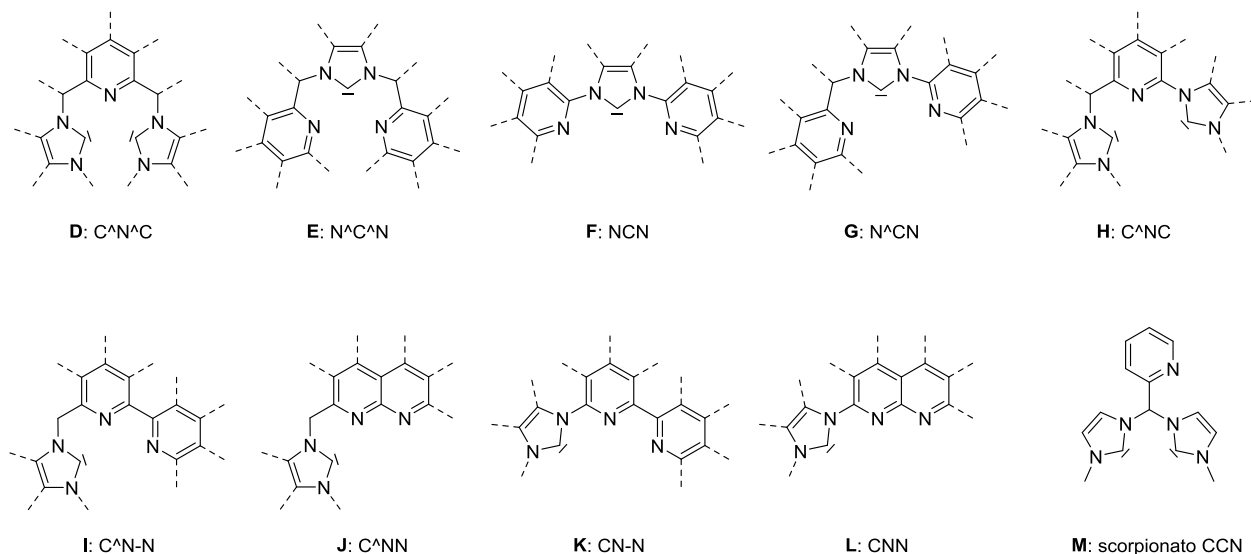
**Scheme I.3** First report on a complex with type **A** ligand and subsequent demonstration of the hemilabile character.

Within their work, the group focused on the hemilabile character of the ligand and presented an example for the *on-off* switch capability of the pyridyl moieties. In addition, studies for HECK, SONOGASHIRA, and SUZUKI coupling reactions were performed using various palladium complexes as precatalysts. Similar type **A** and **B** ligands, metal complexes, and reactivates as well as isolation of copper(I) complexes were reported within the following year by the group of DANOPOULOS.<sup>133-134,137</sup> A highly interesting observation was described in 2001 by CRABTREE *et al.*,<sup>138</sup> who noticed the formation of C-4 bound instead of type **A** coordinated iridium complexes and further investigated the class of these abnormal NHCs.<sup>139-141</sup> Following a similar approach, DANOPOULOS reported on an abnormal coordinated type **B** ligand in a rhodium NHC complex.<sup>142</sup> This time however, C–H activation did not occur in the backbone of the imidazolium moiety but in the pyridine ring. As a result, the formation of a cyclometalated rhodium complex with a carbene ligand and a carbometalated pyridine was observed.

Besides bidentate ligands, the early years of this research field were characterized by pincer ligands of types **C**, **D**, **E**, and **F** (Figure I.10, top). Starting in 2000, the group of LIN presented the first CNC (**C**) ligand with a double helical mercury complex.<sup>135</sup> Only months later, an NCN (**F**) palladium complex, with special focus on the hemilability of these hybrid ligands, was presented.<sup>136</sup> After initial, structural investigations,<sup>143-146</sup> the focus soon shifted towards catalytic applications in palladium catalyzed cross-coupling reactions,<sup>147-149</sup> reactivity studies of these palladium complexes,<sup>150-151</sup> and ruthenium catalyzed transfer hydrogenations.<sup>152</sup> In 2004, a study on early first-row transition metal complexes with type **C** ligands was presented.<sup>153</sup> The authors successfully used the chromium complexes for ethylene oligomerization and titanium and vanadium

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complexes for ethylene polymerization. Interestingly, especially the iron complex was found to be inactive in catalysis what was related to the coordinatively saturated form in which iron is present.



**Figure I.10** Schematic presentation of NHC/pyridine pincer ligand types **D – L** and scorpionato type **M**.

In 2003, CATALANO presented a new application for NHC/pyridine hybrid ligands.<sup>154</sup> A trinuclear silver complex with type **E** ligand and very short silver-silver distances of less than 3 Å showed luminescent behavior. During the following decade, the group investigated numerous coinage metal complexes with ligands of type **A**, **B**, **E**, and **F**.<sup>155-165</sup> Their findings included some highly interesting complexes and metal-organic polymers with mixed-metal composition and luminescent properties.

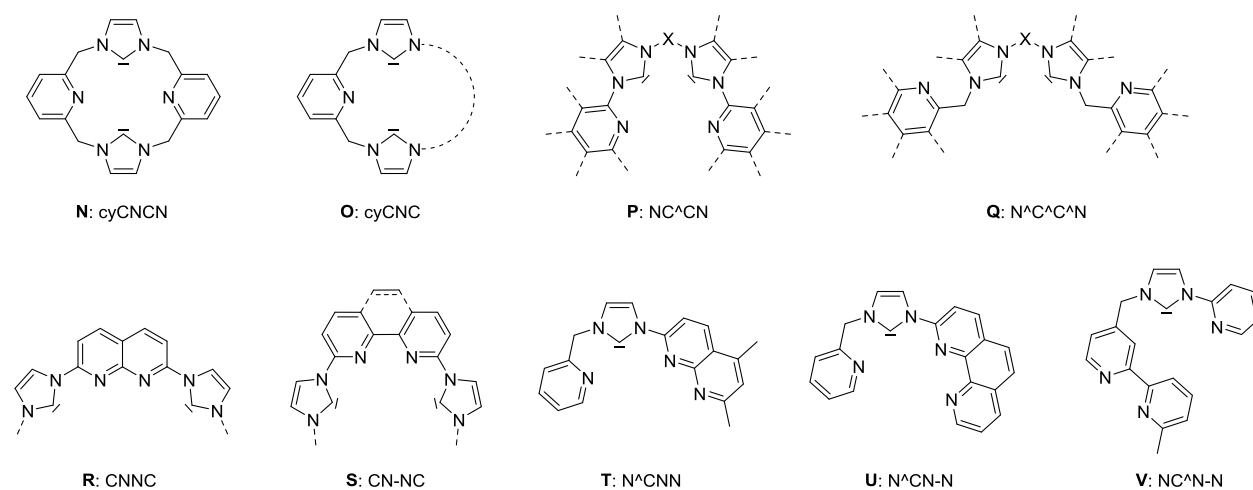
In addition to further development of known uses, additional applications for metal complexes with ligands of type **A – F** were introduced within the last decade. These included reports on antimicrobial agents,<sup>166-167</sup> photoluminescent ruthenium complexes,<sup>168</sup> their application as photosensitizers,<sup>169</sup> the general investigation of the manifold ruthenium redox chemistry,<sup>170</sup> synthesis of uranium pincer complexes,<sup>171</sup> active site models for hydrogenase and the use as catalysts for the electrochemical reduction of protons,<sup>172</sup> in Umpolung reactions,<sup>173</sup> the diboration of alkenes,<sup>174</sup> reduction of nitroarenes,<sup>175</sup> hydrovinylation reactions,<sup>176</sup> aerobic oxidations in sustainable media,<sup>177</sup> hydroamination of unactivated alkenes,<sup>178</sup> hydrogenation of hindered and

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unfunctionalized Alkenes,<sup>179</sup> or catalytic cycloisomerizations.<sup>180</sup> Chiral type **A** ligands were used for the iridium-catalyzed asymmetric hydrogenation of olefins.<sup>181</sup> In addition, manganese type **A**<sup>182</sup> as well as palladium type **C** and **D**<sup>183</sup> complexes were tested in the electrocatalytic reduction of carbon dioxide.

Although the huge majority of reported research dealt with bidentate or symmetrical pincer ligands (**A** – **F**), a small fraction also covers non-symmetrically linked pincer ligands of types **G**,<sup>184</sup> **H**,<sup>185</sup> **I**,<sup>186-187</sup> **J**,<sup>188-189</sup> **K**,<sup>190-196</sup> and **L**.<sup>188,197-203</sup> In addition, one ligand of scorpionato type **M** is reported;<sup>204</sup> however, it only exhibits a  $\kappa^{2(C,C)}$  coordination with the pyridyl moiety not attached to the rhodium center. But not only the linkage of the ligands can be altered, also incorporation of further donor moieties apart from NHC and pyridine was investigated early. First reported to prepare water-soluble pincer complexes<sup>166</sup> or allow linkage to a target group (e.g. peptide or receptor ligand),<sup>205</sup> it can also be used to provide different chelating groups in order to influence the coordinated metal center.<sup>206-207</sup>

As mentioned, bi- and tridentate ligands have been the central focus of NHC/pyridine hybrid ligands; however, already in 2001, the group of YOUNGS presented an exciting macrocyclic, tetradentate di-NHC di-pyridine ligand (Figure I.11, **N**).<sup>208</sup> Several publications concerning its structure chemistry with various metals soon followed,<sup>209-212</sup> until recently in 2015 the octahedral iron(II) complex was reported.<sup>213</sup>



**Figure I.11** Macrocyclic tetra- and polydentate (**N,O**) and open-chain, tetradentate NHC/pyridine hybrid ligands and (**P – V**).

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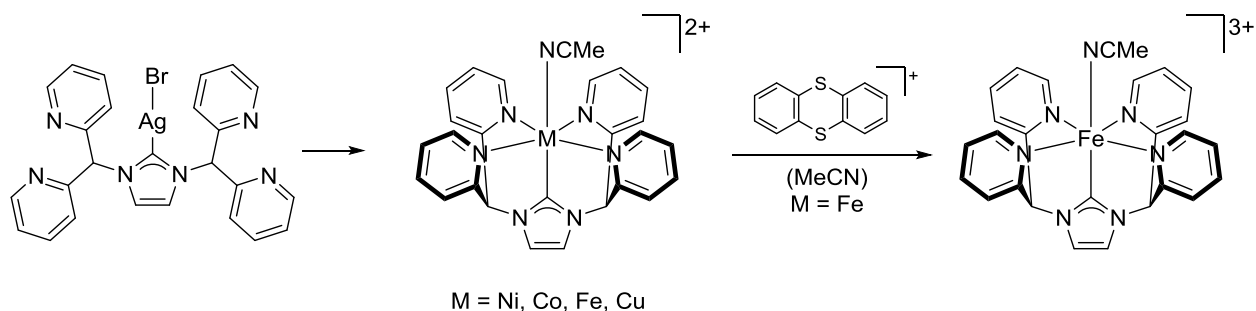
Not only the ligand, but also the synthesis of a macrocyclic polyimidazolium salt itself was highly interesting and inspired several reports on similar compounds (**O**) with varying linkers (e.g. coordinating groups, alkyl groups, aryl groups).<sup>116,167,214-220</sup> Although younger, reports on open chain and tetradentate ligands of types **P** and **Q** outnumber such of their macrocyclic relatives easily. Besides purely synthetic work,<sup>221-228</sup> these also include catalytic applications (cross-coupling with group 10 metals,<sup>229-233</sup> hydrosilylation with platinum,<sup>193</sup> rhodium,<sup>234</sup> or iridium,<sup>235</sup> water oxidation with ruthenium,<sup>236</sup> electrocatalytic reduction of carbon dioxide with nickel<sup>237-238</sup>) or luminescence investigations.<sup>239-241</sup> Recently, investigation of the iron complexes gained particular interest especially within our group,<sup>227</sup> as it could be shown that these complexes are precatalysts for olefin epoxidation<sup>21</sup> and arene hydroxylation.<sup>22</sup> These reports were the first examples for oxidation catalysis with iron NHC compounds.<sup>242</sup> Somewhat younger and less applied are reports that focus on ligands with inverted NCCN donor sequence. The resulting CNNC ligands of type **R** were initially presented by CHEN *et al.*<sup>243</sup> and soon after modified by the group of KUNZ to give the more flexible **S** type.<sup>244</sup> These were able to form mononuclear silver and palladium complexes – although the latter was arranged in a strongly distorted square-planar geometry. In contrast, type **R** ligands were proven to form dinuclear palladium complexes.<sup>245</sup> Later, CHEN *et al.*<sup>196,246</sup> also reported on polynuclear copper and silver complexes for type **S** ligands.

Parallel to the development of **K** type CNN ligands, the group of CHEN presented a first NNCN ligand (**T**) and its silver and palladium complex.<sup>247</sup> Due to the ligand's rigidity, the formed palladium complex contains two  $\kappa^{2(\text{C,N})}$ -coordinated ligands to build up the distorted square-planar metal coordination geometry. Cross-coupling studies were included within the first work and extended in a following publication.<sup>248</sup> In a follow-up work, additional flexibility within the NNCN ligand was achieved by replacing the fundamental naphthyridine (**T**) with a phenanthroline unit (**U**).<sup>194,249</sup> However, within the comprehensive description of silver, nickel, palladium, platinum, cobalt, copper, and ruthenium complexes, not a single mononuclear  $\kappa^{4(\text{N,N,C,N})}$ -coordinated complex is reported as the ligand's linkage is still too rigid. In contrast to these investigations, NNCN ligand **V** was designed by the group of MEYER in order to form dinuclear

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ruthenium complexes with two chemically differing ruthenium centers,<sup>250-251</sup> which were used in water oxidation catalysis.

Besides the discussed multidentate ligand structures of types **A – V**, single examples for higher denticity with 5 up to 8 donor moieties are known as well.<sup>109,116,125,239,246,252-253</sup> They are mostly utilized to form polynuclear coinage metal complexes regardless of the ligand's macrocyclic or acyclic structure. The only work which is not fitting in this scheme was published by SMITH and LONG in 2010.<sup>254</sup> They presented a chelating, pentadentate Py<sub>4</sub>NHC ligand precursor which formed octahedral iron(II), cobalt(II), nickel(II), manganese(II), and copper(II) complexes via transmetalation starting from the silver complex (Scheme I.4).



**Scheme I.4** Coordination chemistry of first row transition metals with a Py<sub>4</sub>NHC ligand as presented by SMITH and LONG.<sup>254</sup>

Except for the manganese complex, which is coordinated in a tripodal fashion by the ligand, all complexes contain a single coordinated acetonitrile ligand. It was shown that the iron(II) complex could be oxidized to its iron(III) species by the use of thianthrenyl hexafluorophosphate.

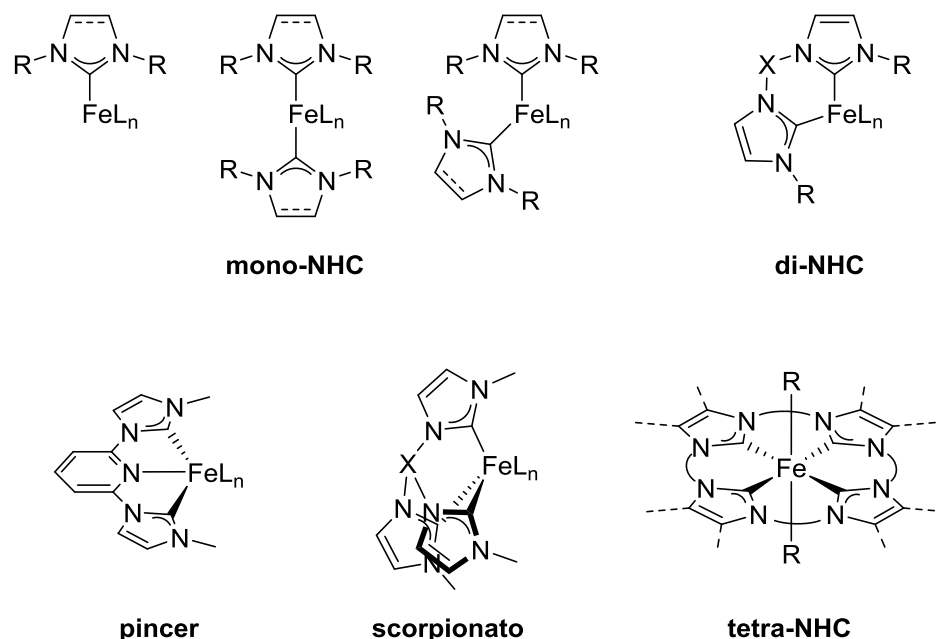
In conclusion, countless NHC/pyridine hybrid ligands exist. Recently, the focus shifts towards higher denticity with up to 4 donor moieties. However, no systematic studies are reported, dealing with the influence of differently composed tetradentate ligands on the oxidation potential of a metal center. In addition, no example for the link between NN CN, NCCN, and CCCC ligands – namely a tetradentate NCCC ligand – has been published yet.

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### I.2.4 Iron NHC Complexes

Iron as non-toxic, highly abundant, and cheap first row transition metal is recently attracting increasing attention in countless catalytic applications.<sup>90-91,255-256</sup> With a growing interest in iron as such, also Iron NHC complexes gain additional attention, leading to the development of a rich coordination chemistry and numerous applications. Although initially reported in 1969,<sup>257</sup> the majority of iron NHC related research was performed since 2000 and has recently been reviewed several times.<sup>242,258-259</sup> Therefore, this chapter does not comprehensively cover the complete chemistry, but rather sticks to giving a brief overview and highlighting selected compounds and applications.

Iron NHC complexes in general can be accessed via a variety of different approaches starting from imidazolium salts and basic iron precursors,<sup>257,260</sup> imidazolium salts, neutral iron precursors and external bases,<sup>98</sup> insertion of an iron precursor into an NHC dimer,<sup>261</sup> *in situ* formation of the NHCs from diamines,<sup>262</sup> or transmetalation from pre-formed metal NHC complexes.<sup>263</sup> In addition to those few complexes described in Chapter I.2.2 and I.2.3, a plethora of iron NHC complexes exists. Some of the general types, concerning ligand structure and metal complexes, are summarized in Figure I.12.



**Figure I.12** Different types of iron-NHC complexes with up to tetradentate NHC ligands.

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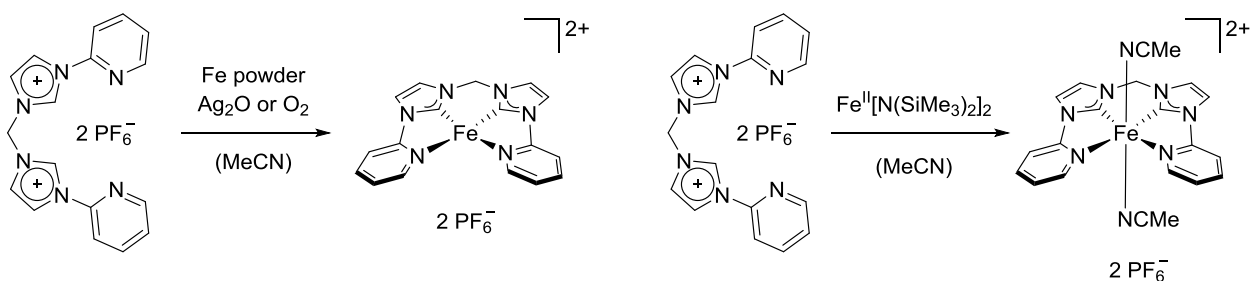
A huge number of iron complexes in several oxidation states (0, +I, +II) with one or two mono-NHC ligands are known. Starting from an imidazolium salt and HIEBER's<sup>264</sup> iron carbonyl hydride,<sup>257</sup> a free NHC and iron pentacarbonyl,<sup>265</sup> or a WANZLIK dimer and iron carbonyls,<sup>266</sup> the trigonal bipyramidal iron(0) complexes with one or two mono-NHC ligands and three or four carbonyl ligands are available. These can be further manipulated by ligand substitution reactions or oxidization to their iron(I) analogs with silver(I) salts.<sup>267</sup> Similar to the iron carbonyl chemistry, also research with nitrosyl ligands has been performed.<sup>268</sup> Tetrahedral iron(II) halide complexes with two mono-NHC ligands can be accessed from the respective iron(II) halides and free NHCs.<sup>269</sup> Exchange of the halide ligands leads to a manifold coordination chemistry.<sup>270</sup> Another promising access to iron(II) NHC complexes was presented by DANOPOULOS in 2011 and introduced the use of an iron bisamide as precursor with internal base to access three-coordinated iron(II) complexes.<sup>260</sup> Further subclasses of iron mono-NHC complexes are e.g. the large group of piano stool complexes, which contain a roofing cyclopentadienyl ligand,<sup>242,268</sup> or iron-sulfur clusters with NHC ligands,<sup>242,271</sup> which are mostly used as model for the active center in [FeFe] hydrogenase.<sup>272</sup>

Besides monodentate NHC ligands, especially the use of chelating, multidentate ligands had a strong influence on recent iron NHC chemistry. Di-NHC ligands,<sup>273-274</sup> CNC pincer ligands,<sup>153,275-276</sup> and scorpionato-type tri-NHC ligands have been thoroughly investigated and shown some highly interesting reactivities. Pincer-type iron(II) complexes were already reduced to their iron(0) form in 2005.<sup>277</sup> When not exposed to carbon monoxide, these were found to form N<sub>2</sub> complexes. Denying nitrogen as ligand, by preparing the complex under argon, causes the decomposition of the iron(0) complex and formation of product mixtures.<sup>275</sup> In addition, it could be proven, that these iron(0) dinitrogen complexes are able to form addition products with hydrogen and silanes<sup>278</sup> or work as catalyst in the hydrogenation of hindered and unfunctionalized arenes.<sup>179</sup>

A related hybrid ligand class was developed by CHEN *et al.*<sup>229-230</sup> (see Chapter I.2.3) and featured an additional pyridine donor moiety. Their report of an iron(II) NCCN complex was published in 2009 and claimed the direct synthesis starting from the imidazolium salt, iron powder, and silver oxide or oxygen (Scheme I.5, left).<sup>221</sup>



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**Scheme I.5** Postulated synthesis of a square-planar 14 VE iron NCCN complex and report of the analog octahedral-coordinated 18 VE complex.

This report of a square-planar coordinated 14 VE iron(II) complex was heavily questioned three years later,<sup>227</sup> when our group presented a synthesis starting from the imidazolium salt and a basic iron amide precursor (Scheme I.5, right). In addition to the two axial acetonitrile ligands, which have not been found by CHEN and co-workers (although working in acetonitrile as well), also huge discrepancies in <sup>13</sup>C NMR spectra are present. The shift of the carbene-carbon, according to CHEN *et al.* at 159.1 ppm, was found at 216.2 ppm. Nevertheless, the complex itself was found to be highly interesting and showed potential in both, the catalytic epoxidation of olefins and the hydroxylation of arenes.<sup>21-22</sup>

When changing the ligand system from meridional coordinating CNC pincer ligands to facial coordinating scorpionato-type tri-NHC ligands, a different class of “nitrogen-chemistry” becomes accessible. After the initial report of a hexacarbene complex with two tri-NHC ligands, which was interestingly oxidized *in situ* from iron(II) to iron(III) without being exposed to a definite oxidation agent,<sup>98</sup> electrochemical investigations showed even the reversible accessibility of the iron(IV) form due to the strongly donating ligand sphere.<sup>279</sup> As a result from this finding, several iron species in oxidation states +III, +IV, and +V with imido and nitrido ligands were isolated by reaction with azides under nitrogen evolution.<sup>280-285</sup> Reactivity studies could show that these iron species are able to transfer nitrogen or form ammonia.<sup>282,284</sup>

In agreement with these results, the recent development of iron complexes with tetra-NHC ligands was promptly followed or even accompanied by reports on iron(IV) imido

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and oxo species with the imido species claimed as intermediate in aziridation reactions (see chapter I.2.2).<sup>23,113</sup>

As in parts mentioned before, catalysis is the main application for iron NHC complexes.<sup>242</sup> The first reported use, as catalyst for radical polymerizations, was presented in 2000 by GRUBBS.<sup>269</sup> Since then, interesting reports on the use of iron NHCs in C–C<sup>286-288</sup> or C–X (X = B,<sup>289</sup> N,<sup>113,290</sup> Mg,<sup>291</sup> S<sup>292</sup>) bond formation, hydrosilylation,<sup>293</sup> different types of hydrogenation,<sup>179,293</sup> and other applications have been published.<sup>242</sup> The most recent reports by our group extend the range of applications towards oxidation catalysis with H<sub>2</sub>O<sub>2</sub>.<sup>21-22</sup>

Although a variety of different reactions is catalyzed by iron NHC complexes, especially mechanistic studies – in order to understand the molecular steps – are still lacking.<sup>242</sup> These would not only include spectroscopic investigations but also the isolation of highly reactive intermediates, which are, intrinsically, hard to trap. As shown in this chapter, especially polydentate NHC ligands are used to stabilize iron in unusually high oxidation states like iron(IV/V). Accordingly, these could be tools to get a grip on reactive compounds. However, a ligand which e.g. combines the donor strength of tetra-NHCs with the availability of *cis*-positioned free coordination sites (e.g. scorpionato-type ligands) has not yet been reported and could show interesting results when attached to iron.

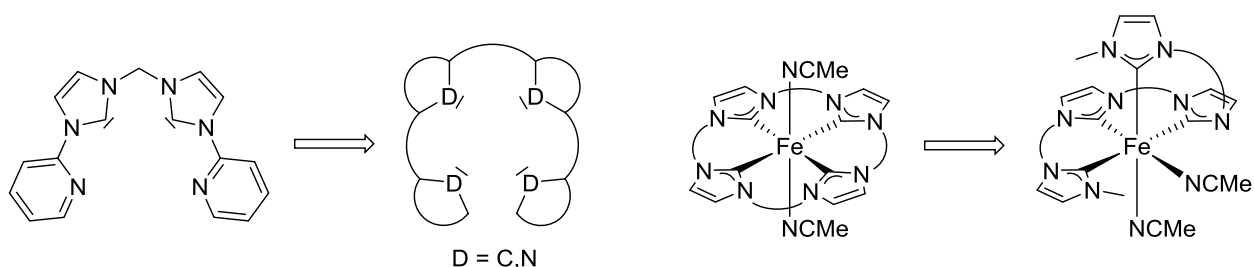
## II. Objective

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Bearing in mind, that iron as non-toxic, highly abundant metal can be used as catalyst for C–H bond oxidation, investigations of the mechanism are of high interest. One of the most commonly applied approaches includes the synthesis of iron model complexes which are used as precatalyst or in order to prepare oxygen-containing intermediates.

This particular thesis was executed as part of a collaboration with the “King-Abdullah-University of Science and Technology” in the aforementioned context. Several approaches towards understanding C–H bond activation from heterogeneous catalysis, homogeneous catalysis, and physical chemistry were combined. The organometallic part focused on iron NHC complexes that were found to be active catalysts in cyclohexane oxidation. Throughout this collaboration, a series of studies were published including the syntheses of novel iron complexes, their electronic modification, application in oxidation catalysis, and decomposition pathways.<sup>108,294-297</sup>

Within this work the focus lies on the modification of the NCCN ligand system in order to understand its influence on a catalytically active iron complex. Therefore, syntheses for tetradentate NHC/pyridine hybrid ligands with varying compositions and the respective iron complexes are targeted (Scheme II.1, left). In addition, a flexible tetra-NHC ligand is aimed at, in order to break up the macrocyclic framework of the previously reported structures and to overcome limitations which cause an equatorial ligand-formation for all octahedral iron complexes so far (Scheme II.1, right). In this context, the general coordination chemistry of the ligand system is to be investigated.



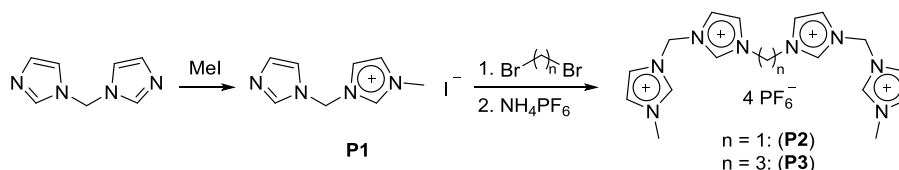
**Scheme II.1** Synthetic goals of this work: A series of tetradentate NHC/pyridine hybrid ligands (left) and a flexible, open chain tetra-NHC ligand.

### III. Results – Publication Summaries

This chapter summarizes publications which originated from the present dissertation. The original manuscripts are attached to this thesis and can be found in its appendix.

#### III.1 Application of Open Chain Tetraimidazolium Salts as Precursors for the Synthesis of Silver Tetra(NHC) Complexes

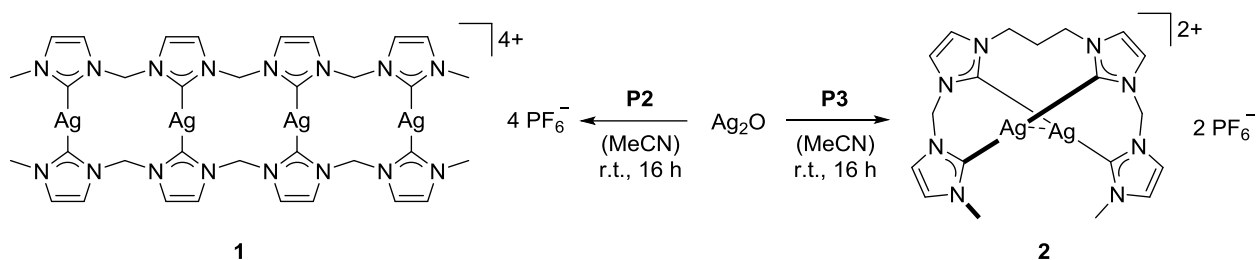
As mentioned before, literature-known tetra-NHC ligands are either based on a macrocyclic framework or a centered arene platform. While macrocyclic ligands in monomeric complexes generally coordinate in an equatorial fashion to a metal center, no mononuclear complexes for acyclic tetra-NHC ligands are known at all. For this reason and in order to access new coordination modes for tetra-NHC ligands in general, the synthesis of a new type of tetra-NHC ligand was developed within this work. Mono-methylation of methylene bisimidazole gave access to poly-NHC building block **P1**, which can easily be utilized for the synthesis of differently linked ligand precursors **P2** and **P3** (Scheme III.1).



**Scheme III.1** Synthesis of poly-NHC building block **P1** and subsequent formation of tetraimidazolium salts **P2** and **P3**.

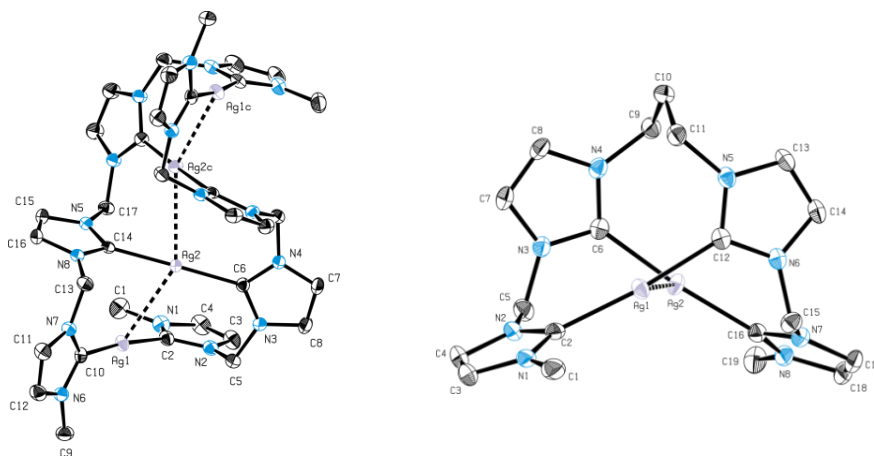
Isolation and purification of **P1** was found to be the crucial step, as the reaction yielded a mixture of reactant, **P1** and the di-methylated diimidazolium salt. Reaction of **P1** with an excess of dibromomethane or half an equivalent 1,3-dibromopropane in acetonitrile gave **P2** and **P3** in high yields after anion exchange with ammonium hexafluorophosphate. To prove that these imidazolium salts can act as precursors for tetra-NHC ligands, they were reacted with an excess of silver oxide in acetonitrile (Scheme III.2).

### III. Results – Publication Summaries



**Scheme III.2** Synthesis of silver tetra-NHC complexes **1** and **2**.

The formation of NHC complexes was demonstrated by the disappearance of the imidazolium proton signals in <sup>1</sup>H NMR spectroscopy according to which **1** is arranged in a flexible, dimeric form while **2** exhibits a frozen, monomeric coordination. All compounds were analyzed by NMR spectroscopy, elemental analysis, and mass spectrometry. The silver complexes were additionally characterized by single crystal X-ray diffraction (Figure III.1).



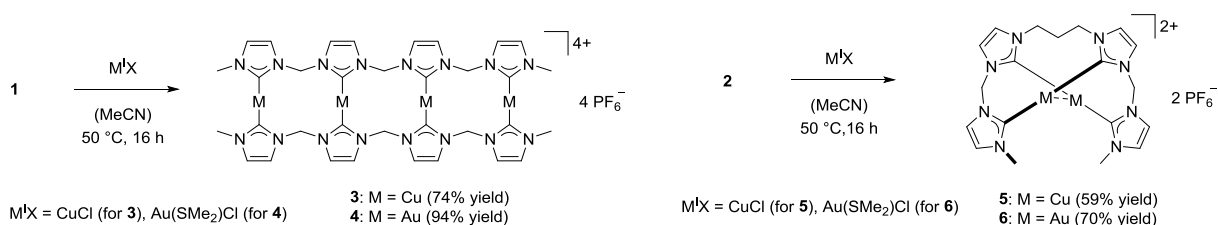
**Figure III.1** ORTEP view of the cationic fragment of **1** (left) and **2** (right) with thermal ellipsoids shown at a 50% probability level. Hydrogen atoms are omitted for clarity.

The obtained results confirmed the findings spectroscopic in solution: Complex **1** exhibits a dimeric structure with double helix character while **2** forms a monomeric complex with twisted ligand. All silver ions are coordinated linearly by two NHC moieties with the general formula of [Ag<sub>n</sub>(NHC)<sub>2n</sub>]<sup>n+</sup> rendering both complexes promising candidates for transmetalation reactions with salts of the general type M<sup>II</sup>X<sub>2</sub> (M: metal, X: halide).

### III. Results – Publication Summaries

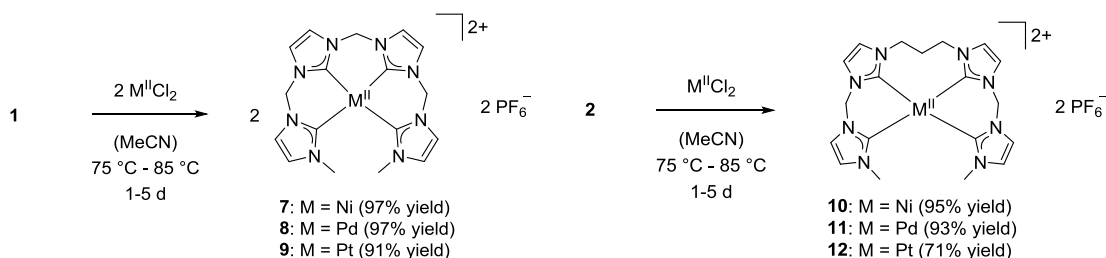
#### III.2 Structural diversity of late transition metal complexes with flexible tetra-NHC ligands

The introduction of flexible, open chain tetra-NHC ligands and their silver complexes was essential requirement to achieve new coordination modes for tetra-NHC ligands.<sup>298</sup> In analogy to the work of JENKINS *et al.*,<sup>114</sup> reactions of silver tetra-NHC complexes **1** and **2** (see Chapter III.1) with metal halides were carried out. Transmetalation with coinage metal chlorides in the oxidation state +I yielded silver-analog complexes **3–6** (Scheme III.3).



**Scheme III.3** Synthesis of coinage metal tetra-NHC complexes **3–4** (left) and **5–6** (right).

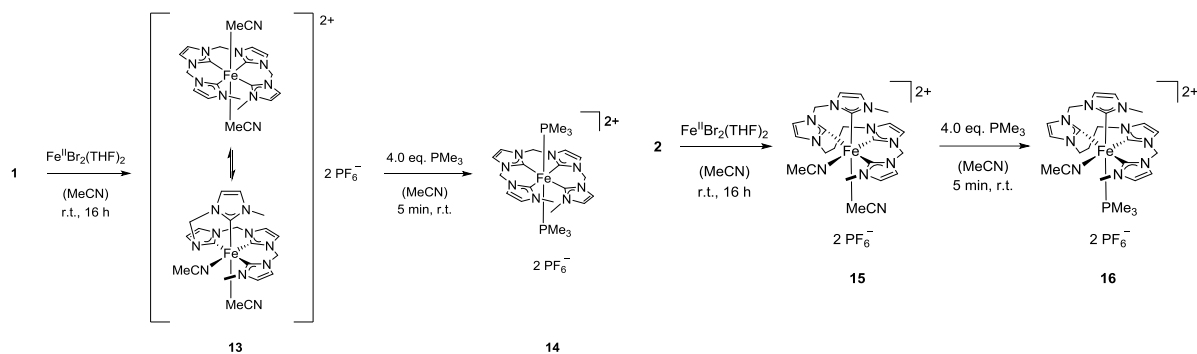
In a second step, transmetalation reactions with  $M^{II}Cl_2$  salts of group 10 metals were performed. It could be demonstrated that all complexes exhibit a distorted square-planar coordination of the metal center (Scheme III.4).



**Scheme III.4** Synthesis of group 10 metal tetra-NHC complexes **7–9** (left) and **10–12** (right).

Although harsh reaction conditions of 85 °C for up to 5 days were necessary, the yields were excellent. In contrast to this finding, reaction of silver tetra-NHC complexes with  $FeBr_2(THF)_2$  already occurred at room temperature (Scheme III.5).

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**Scheme III.5** Synthesis of iron(II) tetra-NHC complexes **13–14** (left) and **15–16** (right).

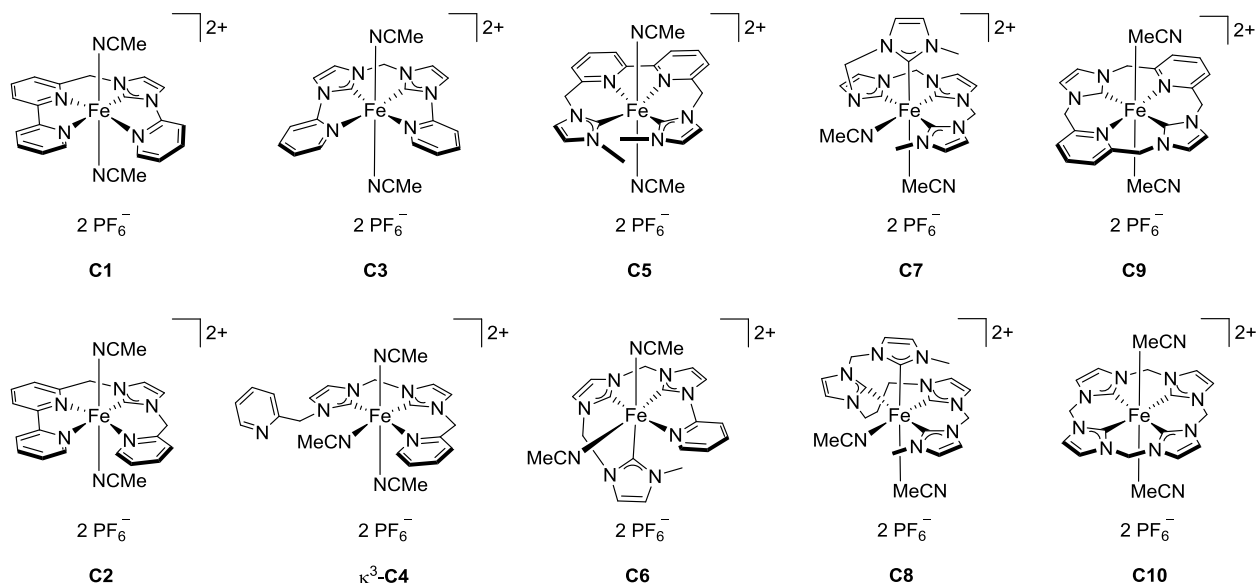
Octahedral iron(II) complexes **13** and **15** were obtained as orange powders in high yields. While **13** showed fluxionality in acetonitrile solution with the tetra-NHC ligand being either coordinated in an equatorial fashion or in a sawhorse-type coordination, complex **15** is frozen in a sawhorse-type coordination of the ligand with two additional acetonitrile ligands *cis*-coordinated. Both complexes were reacted with an excess of  $\text{PMe}_3$  giving di-substituted complex **14** and mono-substituted complex **16** in high yields.

In general, it was demonstrated that silver NHC complexes **1** and **2** can act as versatile transmetalation agents to access a broad range of transition metal complexes. Especially the iron complexes are highly interesting as they exhibit a sawhorse-type coordination of a tetra-NHC ligand for the first time with *cis*-labile binding sites being prone to ligand exchange reactions.

All complexes were analyzed by NMR spectroscopy, mass spectrometry and elemental analysis. In addition, complexes **3**, **5**, **6**, **7**, **9**, **10**, **11**, **14**, and **16** were also characterized by single crystal X-ray diffraction.

### III.3 NHC Versus Pyridine: How "Teeth" Change the Redox Behavior of Iron(II) Complexes

Although several NHC/pyridine hybrid ligands are known in literature, no extensive studies on the influence of NHC/pyridyl ratios on the oxidation potential of the metal center are reported. The iron(II) NCCN complex **C3** is an interesting system that is well investigated concerning its electronic structure.<sup>294</sup> In order to get further insights into the electronic effect of the di-NHC/di-pyridine hybrid ligand, a series of structurally similar tetradentate NHC/pyridine hybrid ligands with differing NHC/pyridyl ratios were developed. For all newly designed as well as a row of literature known ligands, the iron(II) complexes were successfully synthesized and isolated (Figure III.2).



**Figure III.2** Overview of newly developed and literature-known iron(II) complexes with tetradentate NHC and NHC/pyridine hybrid ligands whose oxidation potentials were studied and compared within this work.

All new complexes were characterized by NMR spectroscopy and elemental analysis. Single crystal X-ray diffraction revealing the absolute structure was successfully performed for complexes **C2**, **C4**, **C5**, and **C6**. Following the structural investigation, electronic studies of the iron complexes were conducted using cyclic voltammetry. The results show a linear correlation between number of NHC donors coordinated to the metal center and the oxidation potentials which are given relative to the half-cell



### III. Results – Publication Summaries

potential of the  $\text{Fc}/\text{Fc}^+$  redox couple (Table III.1). In addition, all obtained potentials were compared to those of literature-known complexes.<sup>108,213,227,299</sup>

**Table III.1** Half-cell potentials for C1 to C10 in dependence of the NHC/pyridyl ratio (1-4 NHC donors).

	Ligand	$E_{1/2}$ [V]	$\Delta E$ [mV]
<b>C1</b>	NN^CN	0.68	100
<b>C2</b>	NN^C^N	0.58	100
<b>C3</b>	NC^CN	0.42	80
<b>C4</b>	N^C^C^N	0.36	80
<b>C5</b>	C^NN^C	0.35	80
<b>C6</b>	NC^C^C	0.25	100
<b>C7</b>	C^C^C^C	0.08	90
<b>C8</b>	C^C^C^C	0.02	100
<b>C9</b>	Cyclic NCNC	0.46	110
<b>C10</b>	Cyclic CCCC	0.15	90

On average, an additional NHC instead of a pyridine donor lowers the oxidation potential of the iron(II) complex by approximately 0.2 V. Minor effects on the potentials originate from structural reasons. *Vice versa*, *trans*-standing NHC donors as well as steric strain in complexes were found to increase the oxidation potentials by up to 0.1 V.

Complex **C4** as unique example showed interesting coordination behavior. In solution, the iron center within the octahedral complex is three-coordinated by the ligand. However, in solid state after drying under high vacuum and in solution after oxidation to the iron(III) complex, the metal is four-coordinated by the tetradentate ligand with only two additional acetonitrile ligands. This on-off behavior showed to be reversible in both cases.

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**Author:** Daniel T. Weiss, Stefan Haslinger, Christian Jandl, et al

**Publication:** Inorganic Chemistry

**Publisher:** American Chemical Society

**Date:** Jan 1, 2015

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### IV.1 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\**

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*Originally published in: Inorg. Chem.* **2015**, *54*, 415–417.

DOI: 10.1021/ic502838x

Hyperlink: <http://pubs.acs.org/doi/abs/10.1021/ic502838x>

### IV.2 Structural diversity of late transition metal complexes with flexible tetra-NHC ligands

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*Originally published in: Dalton Trans.* **2015**, *44*, 18329-18339.

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### IV.3 NHC Versus Pyridine: How "Teeth" Change the Redox Behavior of Iron(II) Complexes

*Daniel T. Weiss,<sup>a,‡</sup> Markus R. Anneser,<sup>a,‡</sup> Stefan Haslinger,<sup>a</sup> Alexander Pöthig,<sup>b</sup> Mirza Cokoja,<sup>c</sup> Jean-Marie Basset,<sup>d</sup> Fritz E. Kühn<sup>a,\*</sup>*

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*Originally published in: Organometallics* **2015**, *34*, 5155-5166.

DOI: 10.1021/acs.organomet.5b00732

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## V. Summary and Outlook

After the discovery that iron(II) complexes with tetradentate NHC/pyridine hybrid ligands can act as precatalyst for oxidation catalysis with hydrogen peroxide, systematic investigation on the influence of the ligand sphere on the metal center was required. Therefore, the aim of this work was the introduction of synthetic paths giving access to a variety of tetradentate poly-NHC ligands and their corresponding iron(II) complexes. As the accessed tetra-NHC ligands were the first examples for flexible, open chain structures of this type, their general coordination chemistry in transition metal complexes was studied.

The first part of the work deals with the synthesis of linearly linked tetraimidazolium salts, which can act as precursor to flexible and open chain tetra-NHC ligands. The main challenge was preventing oligo- and polymerization of the commonly applied building block methylene bisimidazole which is providing two reactive sites. Therefore, protection of one imidazole moiety was conducted by reaction with methyl iodide. The isolated imidazolium salt was found to be a promising building block for polyimidazolium structures and specifically tetraimidazolium salts. The reaction of these with silver oxide yielded the respective silver tetra-NHC complexes with a general stoichiometry of  $\text{Ag}_n(\text{NHC})_{2n}(\text{PF}_6)_n$  rendering them an ideal candidate for transmetalation experiments. Characterization via single crystal X-ray diffraction revealed different structural motifs: A dimeric complex with double-helix character and four centered silver ions compared to a monomeric complex with a twisted ligand encasing two silver ions are found. In both cases short distances of around 3 Å indicate silver-silver interactions.

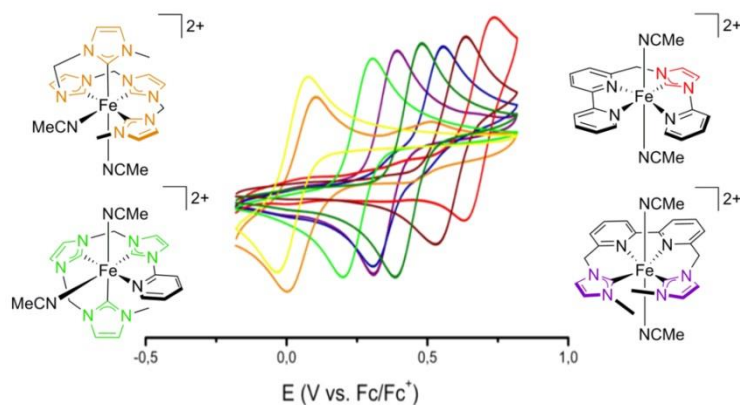
The second part of this thesis consecutively deals with transmetalation reactions of the silver tetra-NHC complexes giving access to a series of late transition metal complexes. It could be demonstrated that coinage metal and group 10 metal chlorides react with the silver complexes under precipitation of silver chloride. The resulting metal tetra-NHC complexes were filtered and precipitated by addition of diethyl ether. In contrast to high temperatures which are required for these transformations, reaction with  $\text{FeBr}_2(\text{THF})_2$  proceeded at room temperature within minutes. Filtration and precipitation yielded pure

## V. Summary and Outlook

iron NHC complexes. The flexible character of the ligands is demonstrated by the structural diversity of the obtained complexes. As for similar macrocyclic ligands, all nickel group metals were coordinated in a square-planar coordination mode. Likewise, all three coinage metal complexes (Cu, Ag, Au) feature similar structures with the length of the alkyl bridge determining the complex structure. For the less flexible methylene bridge, dimeric, tetranuclear complexes are obtained, while a longer propylene bridge leads to monomeric, dinuclear complexes. Iron complexes were found to be typically octahedral-coordinated with two additional acetonitrile ligands; however, for the first time in literature, a sawhorse-type coordination of a tetra-NHC ligand within an octahedral metal complex could be proven. The iron complex with the methylene-bridged ligand shows fluxional behavior in acetonitrile solution; sawhorse-type as well as equatorial coordination by the ligand is observed and at room temperature interconversion proceeds rapidly. The acetonitrile ligands cannot be removed under high vacuum, whereas in solution they exchange rapidly. Accordingly, ligand exchange reactions with trimethylphosphane proceed fast.

The third part of this work summarizes the efforts to understand the electronic influence of NHC/pyridine hybrid ligands on a metal center. Tetradentate NHC ligand precursors with one up to four imidazolium moieties were utilized to synthesize iron(II) NHC complexes. Mono-, di-, and tri-NHC complexes were accessed by reaction of the imidazolium salt with  $\text{Fe}^{\text{II}}(\text{btsa})_2\text{THF}$  in acetonitrile, tetra-NHC complexes as shown before by transmetalation. All obtained complexes are coordinated octahedrally with the open coordination sites occupied by acetonitrile ligands. The hybrid ligand's coordination modes are mainly determined by the length of the applied alkyl linkers. Overall, a direct and linear correlation between the number of NHC units coordinated to the iron center and the oxidation potential was revealed. Each additional carbene donor lowers the oxidation potential by 0.2 V, whereas steric strain and arrangement of the donors only show a minor influence of up to 0.1 V (Figure V.1).

## V. Summary and Outlook



**Figure V.1** Selection of iron(II) complexes with tetradentate NHC/pyridine hybrid ligands and their redox-behavior in cyclic voltammetry.<sup>300</sup>

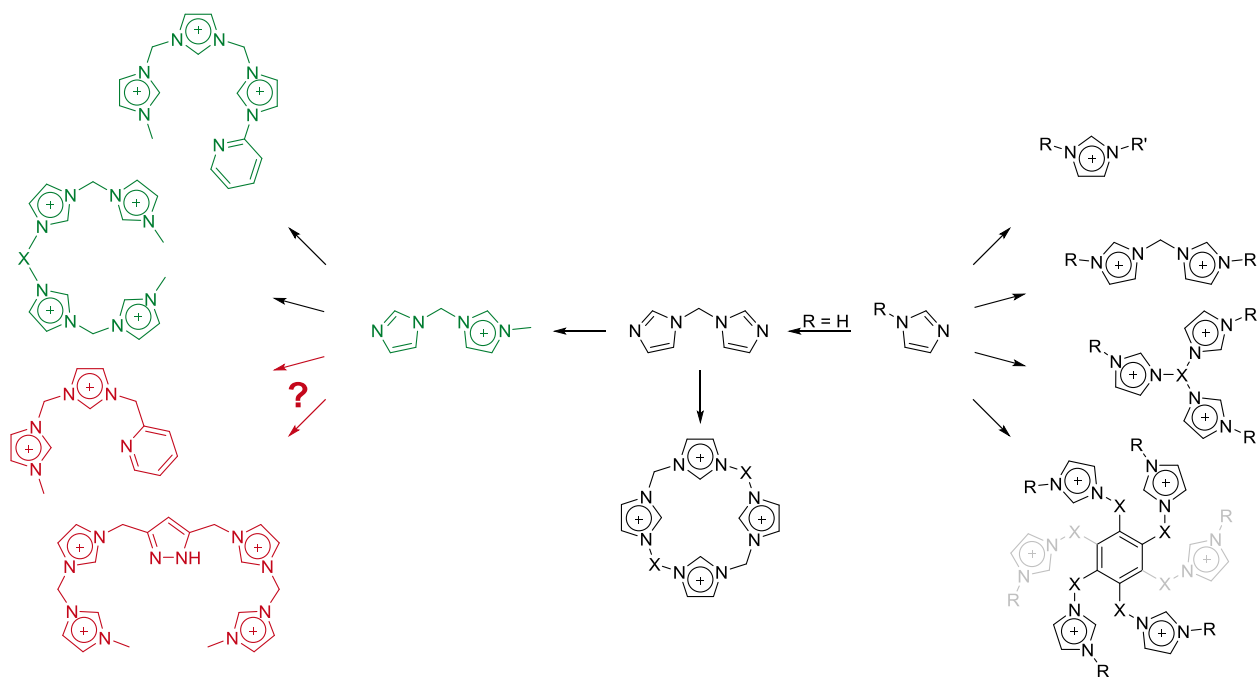
These results offer possible applications that could be further investigated. First of all, iron(II) complexes could be studied as precatalyst in oxidation reactions. Preliminary results in cyclohexane oxidation catalysis indicate that a higher number of NHC donors within the ligand leads to enhanced conversion and product yield. Furthermore, the selectivity towards the alcohol formation is increased. However, iron complexes with flexible, open chain ligands seem to be inactive for epoxidation catalysis. These findings may give useful hints for mechanistic investigations: Due to different structural situations, reactive intermediates for one of the reactions may be stable. In this context, the isolation and characterization of high valent iron oxo species with similar ligands which are only differing in donor strength could help understand oxidation processes.

A second interesting topic concerns group 10 metal complexes as these metals are known to be highly active catalysts in cross-coupling reactions. Although a huge variety of NHC complexes has been studied for such reactions, no investigations with tetra-NHC complexes are reported. This could be due to the fixed, macrocyclic framework of the ligands which is possibly prohibiting one of the key steps – the reductive elimination. Flexible ligands, which were presented in this thesis, have shown the potential to bind in an equatorial as well as a sawhorse-type coordination to a metal center. Therefore catalytic cycles which require structural re-orientation during reaction could be enabled.

Last but not least, newly designed polyimidazolium structures with interesting properties can be accessed as indicated in Scheme V.1. Pincer type C<sup>^</sup>C<sup>^</sup>N ligands as well as

## V. Summary and Outlook

poly-NHC ligands which possibly chelate two transition metal ions with free coordination site in close proximity are imaginable.



**Scheme V.1** Literature-known (poly-)imidazolium salts and their synthetic access (black), synthetic developments of this thesis (green), and potentially interesting and available structures (red).

## VI. References

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## VII. List of Publications and Curriculum Vitae

### VII.1 Journal

- 1) “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, Fritz E. Kühn *Inorg. Chem.* **2015**, *54*, 415-417.

- 2) “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, Fritz E. Kühn *Dalton Trans.* **2015**, *44*, 18329-18339.

- 3) “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.

## VII. List of Publications and Curriculum Vitae

### VII.2 Talks and Poster Presentations

03/2015 48. Jahrestreffen Deutscher Katalytiker

Weimar, Deutschland

**Poster Presentation** *“Influence of ligand design on catalytic C–H bond oxidation using molecular iron complexes”*

03/2015 249<sup>th</sup> ACS National Meeting

Denver, United States of America

**Talk** *“Flexible, Open Chain Tetracarbene Ligands: Diversity in Structural Motifs depending on Ligand Structure and Metal Center”*

## VII.3 Curriculum Vitae

### Personal information

Surname                    Weiß  
First name                 Daniel  
Nationality                German  
Date of birth              09/11/1988  
Place of birth             Berlin, Germany  
E-Mail                     daniel.t.weiss@gmx.de



### Education

10/2012 – today        Technische Universität München (TUM), Catalysis Research Center (CRC), Chair of Inorganic Chemistry/Molecular Catalysis

#### **PhD in Chemistry (Dr. rer. nat.)**

Supervisor: Prof. Dr. F. E. Kühn

Dissertation "*Influence of Open Chain, Tetradentate NHC and NHC/Pyridine Hybrid Ligands on the Coordination and Electrochemistry of Late Transition Metal Complexes*"

10/2010 – 09/2012    Technische Universität München (TUM)

#### **Master of Science in Chemistry (M.Sc.)**

Major subject: Organic Chemistry

Minor subject: Catalysis and Reaction Processing

Master's Thesis "*Dihydroxylation of technical grade oleic acid*"

10/2007 – 09/2010    Technische Universität München (TUM)

#### **Bachelor of Science in Chemistry (B.Sc.)**

Bachelor's Thesis "*Isobutane / 2-butene alkylation over base leached and lanthanum exchanged USY zeolites*"

08/1999 – 07/2007    Freiherr-vom-Stein-Oberschule, Berlin, Germany

#### **Abitur**

### Work experience

10/2012 – 09/2015    Technische Universität München (TUM), Garching, Germany

#### **Scientific employee**

- Guidance of undergraduate students
- Supervision of chair equipment (NMR, Glovebox, SPS)
- Evaluation and preparation of scientific publications

## VII. List of Publications and Curriculum Vitae

03/2012 – 08/2012 Technische Universität München (TUM), Garching, Germany (in cooperation with Vinnolit GmbH & Co. KG, Gendorf, Germany)

### Master's Thesis

- Characterization of a product mixture
- Development and scale-up of a synthesis

03/2011 – 04/2011 Süd-Chemie AG, Heufeld, Germany

### Internship

- Synthesis of heterogeneous oxidation catalysts
- Setup of a UV/Vis spectrometer and UV/Vis analytic

## Skills

Language German (mother tongue), English (business fluent), French (school knowledge)

Computer MS Excel, MS Word, MS Powerpoint, MestreNova, ChemDraw, SciFinder, EndNote, Mercury, Delphi (Object Pascal)

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

Courses Agilent Technologies  
"Einführung in die Flüssigkeitschromatographie" (2 days)

TUM Graduate School  
"Scientific Paper Writing" (2 days)

## Conferences, Scholarship

03/2015 249<sup>th</sup> ACS National Meeting  
**Talk** "Flexible, Open Chain Tetracarbene Ligands: Diversity in Structural Motifs depending on Ligand Structure and Metal Center"

03/2015 48. Jahrestreffen Deutscher Katalytiker  
**Poster presentation** "Influence of ligand design on catalytic C–H bond oxidation using molecular iron complexes"

01/2008 – 09/2012 Studienstiftung des Deutschen Volkes  
**Scholarship**