Technische Universität München
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Functionalized *N*-Heterocyclic Carbene Complexes of Iridium and Ruthenium: Synthesis, Characterization and Scope towards (Tandem-) Catalysis

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Für meine Familie und Freunde

Die vorliegende Arbeit wurde am Lehrstuhl für Anorganische Chemie im Fachgebiet Molekulare Katalyse der Technischen Universität München im Zeitraum von Mai 2013 bis Mai 2016 angefertigt. Teile der Arbeit wurden im Dipartimento DI4A der Università di Udine, Italien, angefertigt.

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List of Abbreviations

cod	cyclooctadiene
DFT	Density Functional Theory
HSAB	Hard and Soft Acids and Bases
M	metal
Me	methyl
MPV	Meerwein-Ponndorf-Verley reaction
NHC	*N*-heterocyclic Carbene
NHDC	*N*-heterocyclic Dicarbene
NMR	Nuclear Magnetic Resonance
OAc	acetate
ORTEP	Oak Ridge Thermal Ellipsoid Plot Program
Ph	phenyl
ppm	parts per million
tht	tetrahydrothiophene
TH	transfer hydrogenation
TOF	turnover frequency
TON	turnover number
TUM	Technical University of Munich
VT	variable temperature

VORWORT

An dieser Stelle möchte ich die Gelegenheit nutzen, ein paar Anmerkungen zur Entstehung dieser Arbeit zu machen. Im Laufe der mehr als dreijährigen Promotionszeit kommt es durchaus vor, dass man am Sinn und der Machbarkeit einzelner Aspekte des Promotionsvorhabens zweifelt, umso erfreulicher ist es nun, die gesammelten Resultate als Gesamtwerk vor mir zu sehen. Bevor ich auf Inhaltliches zu sprechen komme, möchte ich mich ganz herzlich bei **Prof. Fritz E. Kühn** für die Möglichkeit bedanken, in seiner Arbeitsgruppe diese Arbeit anfertigen zu können. Unter seiner Führung profitierte ich nicht nur fachlich, sondern konnte mein Thema frei und eigenverantwortlich entwickeln, was sicher keine Selbstverständlichkeit im universitären Umfeld ist.

Diese Arbeit beschäftigt sich im weitesten Sinne mit der Verwendung funktionalisierter *N*-heterozyklischer Carbenliganden zur Synthese von Übergangsmetallkomplexen. Leider muss ich das Thema dermaßen allgemein halten, da sich die Schwerpunkte und Ausrichtung meiner Arbeit im Laufe der Promotionszeit mehrfach veränderten, auch wegen der zu Beginn kaum vorhersehbaren Ergebnisse. So beginnt der Ergebnisteil mit einem Thema, welches ich bereits unter Betreuung von **Korbinian Riener** in meiner Masterarbeit im Lehrstuhl von **Prof. Wolfgang A. Herrmann** begann und dann zum Start meiner Promotion im Sommer 2013 weiter bearbeitete. Konkret beschäftigten wir uns mit Stickstoff-funktionalisierten NHC-Liganden an einem Iridium-Komplex. Nicht nur war mir Korbi hier ein sehr geschätzter Kollege, sondern es entwickelte sich auch eine tiefgehende Freund- und Laborpartnerschaft, die uns half, über so manches im Raum CH37409 Geschehende hinwegzusehen. Wissenschaftlich gesehen gelang es mit unserem gemeinsam verfassten Artikel, die Interaktion des *N*-funktionalisierten Arms mit dem Ir-Zentralatom näher zu quantifizieren, was trotz der weiten Verbreitung dieses Motivs in der Literatur bisher noch nicht gelungen war.

Mit dem Abschluss der Iridium-Chemie wechselte mein thematischer Schwerpunkt zur Synthese Phosphor-funktionalisierter Ruthenium-Carbenkomplexe und deren Anwendung in der Transferhydrogenierung. Dieses Thema, welches schon seit einigen Jahren in enger Kooperation der TUM mit der Università di Udine in Italien verfolgt wird, sollte den Grundstein für die spätere Entwicklung bimetallischer Tandemkatalysatoren darstellen. Doch zu Beginn, Ende 2013, konnte davon noch keine Rede sein; vielmehr erschien es Erfolg versprechend, Modifikationen an bereits bekannten Ru-Carbenkomplexen vorzunehmen, um deren bereits sehr hohe Aktivität in der Reduktion verschiedener Ketone weiter zu steigern. Es war dies auch der Zeitpunkt, zu welchem **Prof. Walter Baratta** den Posten meines Zweitbetreuers übernahm, was sich schnell als echter Glücksfall herausstellte. Nicht nur konnte ich von seinen Kenntnissen in der Ruthenium-Chemie profitieren, darüber hinaus stand er mir sowohl vor Ort als auch über Skype jederzeit hilfsbereit zur Seite. Tatsächlich gelang es während meines ersten Aufenthalts in seiner Arbeitsgruppe im Frühjahr 2014, eine sehr interessante Modifikation eines bestehenden Ruthenium-Komplexes zu isolieren, welcher den

Grundstein für die dann folgenden Synthesen bimetallischer Silber-Ruthenium bzw. Gold-Ruthenium Verbindungen legte. Diese Ergebnisse publizierten wir in unserem ersten gemeinsam verfassten Artikel, und von den vielen kreativen und konstruktiven Tipps von Prof. Baratta bezüglich der Verschriftlichung dieser Resultate profitiere ich noch heute. Ausgehend vom Silber-Ruthenium Komplex gelang uns dann die Synthese mehrerer bimetallischer Übergangsmetallkomplexe. Hervorzuheben ist hier sicherlich das Palladium-Ruthenium Motiv, da es die sehr unterschiedlichen katalytischen Reaktivitäten des Palladiums mit denen des Rutheniums vereint. Es gelang uns, diese Verbindung als effektiven Tandemkatalysator für gleichzeitige Kreuzkupplungs- und Hydrierreaktionen zu etablieren. Mit Blick auf die günstigen Eigenschaften der Tandemkatalyse in Bezug auf Nachhaltigkeit und Umweltschutz empfinde ich den zugehörigen Artikel, welcher Anfang 2016 erschien, als zentrale Errungenschaft dieser Arbeit.

In meiner Promotionszeit hatte ich das Glück, gleichzeitig mit vielen Freunden aus meinem Studiensemester im selben Lehrstuhl arbeiten zu dürfen. Erfreulicherweise gab es hier auch fachliche Überschneidungen, so dass ich zu einem schönen Artikel meiner Studienkollegin **Manuela Hollering** beitragen konnte, der sich mit den Vorzügen tetradentater Carbenliganden beschäftigt. Darüber hinaus möchte ich mich natürlich bei den vielen Mitarbeitern und Kollegen bedanken, welche die Promotion zu der tollen und auch lustigen Zeit gemacht haben, als die ich sie empfunden habe. Namentlich zu nennen sind hier meine Freunde und Laborkollegen **Reentje Harms** und **Teresa Meister**, sowie der Rest meines Freundeskreises in- und außerhalb der anorganischen Chemie. Besonders **Stefan Haslinger, Jens Kück, Marcus Wegmann** und **Simon Meister** waren sowohl fachlich als auch privat stets wichtige Ansprechpartner.

Auch ohne wissenschaftliche Überschneidungen wäre diese Arbeit wohl kaum ohne das ein oder andere Zusammensein mit Bier oder Ähnlichem mit **Matthias Grübel**, **Dominik Höhne, Florian Groche** und allen anderen Freunden und Kollegen gelungen. Besonders die jährlichen Seminare unter Führung von **DJ Perrhenate** halfen maßgeblich, die Motivation zu erhalten.

Während diese Zeilen geschrieben wurden, trugen meine ebenfalls mit dem Verfassen ihrer Doktorarbeit beschäftigten Kollegen **Patricia Wand**, **Robert Reich** und **Jens Kück** maßgeblich zur guten Stimmung im nun zur Schreibstube umfunktionalisierten Labor bei. Auch wenn wir nur kurz das Vergnügen hatten, Laborpartner zu sein, war es mir doch eine große Freude!

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Des Weiteren entsteht wohl keine Arbeit ohne Mithilfe von Gruppenbetreuern, Kristallographen und Technikern. Hier möchte ich mich ganz herzlich bei **Alexander Pöthig** für seine Betreuung vor allem in der ersten Hälfte der Promotion bedanken. Auch **Christian Crystal Jandl, Maria Weindl, Ulrike Ammari, Bircan Dilki, Petra Ankenbauer, Jürgen**

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Natürlich gebührt der größte Dank aber denjenigen, die mir das Studium an dieser hervorragenden Universität in dieser schönen Stadt durch ihr Vertrauen, ihre Liebe und auch ihre finanzielle Unterstützung überhaupt erst ermöglicht haben: meinen Eltern **Martin und Doris Bitzer** sowie meinem Bruder **Niklas**. Ich danke euch für die viele Geduld, die ihr mit mir aufgrund dieser langen Ausbildung haben musstet und all die Unterstützung in den fast 30 Jahren meines Lebens.

Die letzte und mindestens genauso wichtige Person, der ich für alles, was ich bisher mit ihr erleben durfte danken möchte, ist meine Freundin **Tini Ott**. Ich freue mich auf viele weitere tolle Jahre mit dir!

Nachdem ich nun hoffentlich niemanden vergessen habe (ich bitte im Verzeihung, sollte dem doch so ein), möchte ich dieses Vorwort mit einem Zitat beenden:

"Ich habe fertig!"

Giovanni Trapattoni, italienischer Fußballtrainer

München, im Mai 2016

Zusammenfassung

N-heterozyklische Carbene sind durch ihre Vielseitigkeit und Stabilität aus der modernen organometallischen Chemie nicht mehr wegzudenken. Die strukturelle Vielfalt dieser Verbindungen erlaubt ihren Einsatz als Liganden in unzähligen Komplexverbindungen. Insbesondere im Falle katalytisch interessanter Übergangsmetalle haben sich NHCs als leicht modifizierbare und einfach herzustellende Liganden etabliert. Neuere Forschung zu diesem Thema befasst sich bereits mit sehr speziellen Anwendungsmöglichkeiten. So sind heute einerseits zahlreiche synthetische Möglichkeiten zur zielgerichteten Funktionalisierung bekannt, die unter anderem Zugang zu mehrzähnigen Liganden mit oder ohne Hemilabilität erlauben. Andererseits kann mittlerweile auch der Koordinationsmodus des Carbens gezielt gesteuert werden, und auch von NHCs mit der Möglichkeit der simultanen Koordination zweier verschiedener Metalle wurde berichtet. Insbesondere letztere Verbindungen zeigen hohes Potenzial für effiziente und ressourcenschonende Tandemkatalysatoren, welche mithelfen können, unnötige Arbeitsschritte, Kosten und das Anfallen chemischer Abfälle zu verringern.

Im Rahmen dieser Arbeit wurden verschieden funktionalisierte Carbenliganden an Iridium- und Ruthenium-Komplexen eingesetzt, um gezielt bestimmte Eigenschaften dieser Verbindungen zu erreichen oder zu untersuchen. Im Falle eines fluktionalen, bispyridin-funktionalisierten Ir(I)-Motivs konnte so erstmals die schwache Wechselwirkung zwischen Stickstoff und Iridium quantifiziert werden; darüber hinaus stellt dieser Komplex einen der stabilsten je berichteten Transferhydrier-Katalysatoren auf Ir-NHC Basis dar.

Tetracarbenliganden dagegen sind relativ rigide Strukturmotive, die durch ihre vierzähnige Koordination zumeist zu sehr stabilen Verbindungen führen, allerdings strukturell durch ihre geringe Beweglichkeit eingeschränkt sind. Mithilfe eines flexiblen, offenkettigen Tetraimidazoliumsalzes konnten Ruthenium(II)-Komplexe hergestellt werden, welche durch gezielte Wahl der jeweiligen Reaktionsbedingungen in ihrer Geometrie beeinflussbar sind und die darüber hinaus hohe Aktivität in der Transferhydrierung von Ketonen aufweisen.

Ausgehend von einem Phosphin-funktionaliserten Ru-NHC Komplex gelang außerdem die Synthese verschiedener bimetallischer Dicarbenkomplexe mithilfe von Metallierungs- und Transmetallierungsreaktionen. Eine besonders interessante Pd–Ru Spezies wurde dann als effektiver Tandemkatalysator für Suzuki-Miyaura/Transferhydrierungsreaktionen eingesetzt und stellt zum aktuellen Zeitpunkt das aktivste homogenkatalytische System für diese Transformation dar. Insbesondere hier sind Folgearbeiten zur Entwicklung weiterer Tandemsysteme für verwandte Anwendungen ein interessantes Forschungsbiet für die Zukunft.

Abstract

Modern organometallic chemistry is hard to imagine without versatile *N*-heterocyclic carbene ligands. Due to their outstanding stability and structural diversity these motifs are nowadays employed in countless coordination complexes. In particular, transition metal complexes bearing tailorable and readily available NHCs have been established as potent homogeneous catalysts. Current research on this field focuses on specific applications and modifications. Consequently, today's chemists can rely on manifold synthetic tools for the functionalization of carbenes, enabling access to polydentate ligand systems with or without hemilabile behavior. In addition, it is also possible to control the coordination mode of carbenes and ditopic carbenes with simultaneous binding to two different metals have been reported. These latter compounds are particularly attractive as tandem catalysts which are capable of reducing labor, costs, and chemical waste.

In the context of this work, various functionalized carbene ligands were employed to achieve or study specific properties of iridium- and ruthenium complexes. A bispyridine-functionalized Ir(I) motiv allowed for the first time to quantify of the weak interaction of an *N*-donor with the iridium atom. In addition, this species was active in transfer hydrogenation catalysis and constitutes one of the most stable Ir(I)-NHC catalysts to date.

In contrast, tetracarbene ligands are relatively rigid structures which enable comparatively stable compounds due to their chelating coordination mode. However, the structural diversity of these motifs is often limited due to the low flexibility of the ligand precursors. Utilizing an acyclic, open-chain tetraimidazolium salt, we synthesized Ru(II)-complexes whose geometry can be modified depending on the reaction conditions. In addition, these complexes showed pronounced activity in the TH of ketones.

A further topic of this thesis is the synthesis of carbene-based bimetallic compounds. Using metalation and transmetalation reactions, ditopic dicarbene complexes starting from a phosphine-functionalized Ru-NHC complex were isolated. Of particular interest is a Pd–Ru species which was subsequently employed as tandem catalyst for combined Suzuki-Miyaura/transfer hydrogenation reactions. The catalytic system presented within this work constitutes the most active homogeneous setup to date and builds the foundation for future application of bimetallic NHC complexes in related one-pot transformations.

1. INTRODUCTION

1.1 *N*-Heterocyclic Carbene Ligands

1.1.1 History and Properties

Carbenes are neutral carbon species with only six valence electrons and exhibit very high reactivity and low stability due to their electron deficiency.[1] One subclass of this motif are *N*-heterocyclic carbenes (NHCs), in which the carbene atom is electronically stabilized by adjacent nitrogen donors. NHCs were first reported in the pioneering works of Wanzlick and Öfele in the 1960's,[2-3] who almost simultaneously synthesized Hg and Cr complexes bearing NHC ligands. Although it took another two decades for NHCs to truly become established as widespread ligands in organometallic chemistry, Öfele foresaw their enormous potential in his initial article:

„Die Chemie stabiler Übergangsmetall-Carbenkomplexe, bisher nur durch Umwandlung von CO-Liganden in Carben-Liganden durch nucleophile Addition zugänglich, dürfte durch die neue Synthese eine wesentliche Erweiterung erfahren, […]"

Karl Öfele, *J. Organomet. Chem.* **1968,** *12,* P42.[3]

Regardless of these groundbreaking discoveries, the concept was not further pursued for another two decades, as at this time carbenes were considered as too instable to be isolated or applicable in organometallic chemistry.[1] This perception changed fundamentally in 1991 with the isolation of the first stable and crystalline *N*-heterocyclic carbene by Arduengo (Figure 1).[4] His structural motif not only allowed electronic stabilization by the nitrogen donors, but also used steric hindrance in order to block the access to the carbene. To this end, the nitrogen atoms were modified with bulky adamantyl substituents which effectively shielded the reactive site.

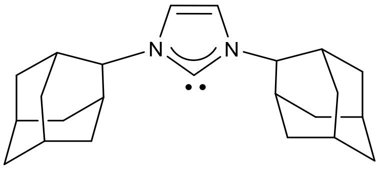


Figure 1: Arduengo's isolated *N*-heterocyclic carbene.[4]

Following this breakthrough, countless methods for the synthesis of related structural motifs were developed and the number of organometallic complexes bearing such ligands expanded quickly.[1,5] A sheer gold rush was initiated with the use of NHCs as spectator ligands for Pd-catalyzed Heck-reactions by Herrmann et al., the first reported application of this ligand class in catalysis.[6] The intrinsic ability to tailor NHCs for specific tasks as well as their high activity in manifold applications rapidly established these systems as viable alternatives for the ubiquitous phosphines,[1,7] and as a result the electronic and steric properties of NHCs and their bonds to metals were scrutinized in detail.[5,8-10]. Considering the electronic situation, NHCs have been characterized as strong σ-donors with low π-backbonding ability (Figure 2).

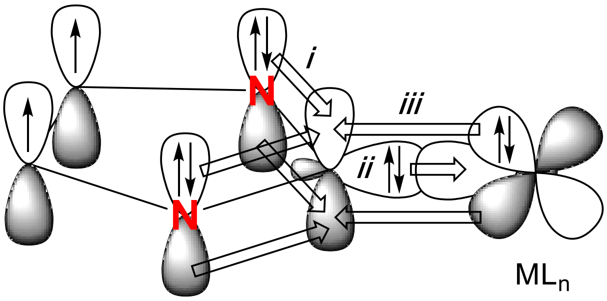


Figure 2: Electronic bonding situation in imidazolyl-based NHC ligands.[11] *(i)*: N–C p_z-p_z interaction, *(ii)*: σ-coordination of the singlet carbene, *(iii)*: π-backbonding (rarely reported).[12]

Due to the very strong σ-donation, carbene–metal bonds are exceptionally stable, rendering NHC complexes highly inert against moisture, heat and oxygen. In particular, the low oxidation reactivity is a key difference to the competing organophosphine ligands, which display pronounced oxophilic character.[13]

The steric demand of NHC ligands is predominantly determined by the so-called "wingtip"-substituents on the nitrogen atoms: in most cases the carbene ligand can rotate freely around the carbene–metal bond. Thus, these substituents occupy a space that is best described as partial sphere.[1] Nolan et al. expanded this approach and developed the "buried volume" model,[14] which in analogy to Tolman's cone angle description for phosphines[15] defines the steric situation of generic NHC systems (Figure 3).[16]

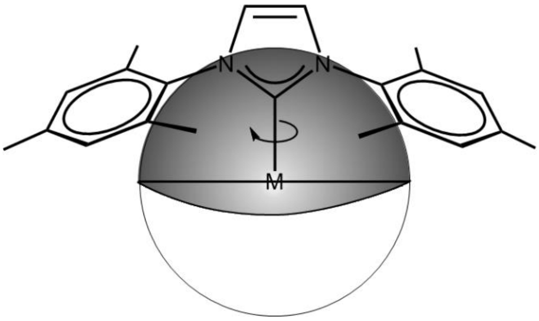
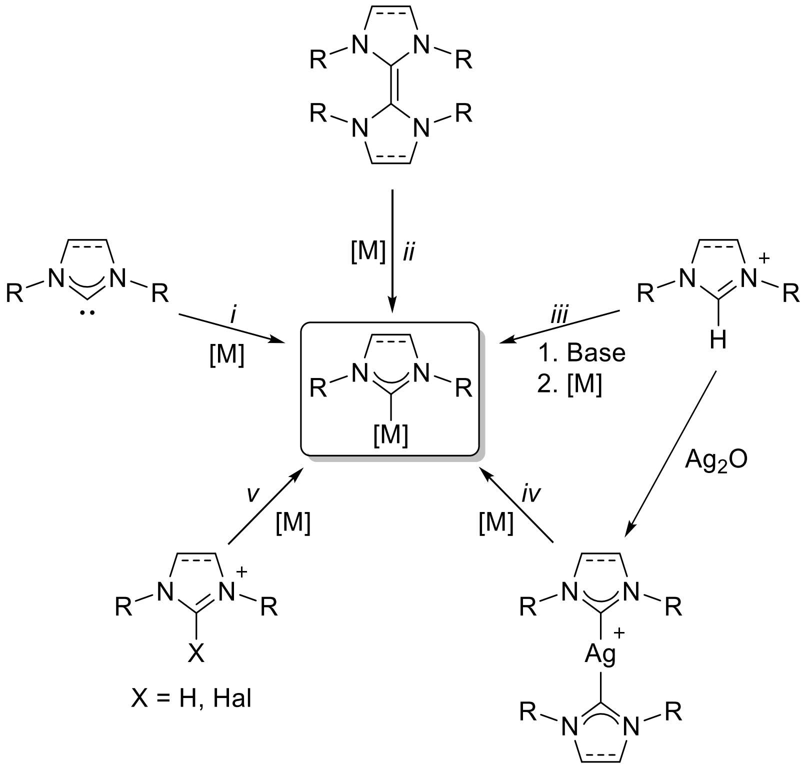


Figure 3: "Buried volume" model for NHC ligands.[12]

Today, several different approaches are employed for the synthesis of NHC complexes (Scheme 1).[8] Prominent examples are:

- *(i)* Reaction of the free carbene with metal precursors
- *(ii)* Cleavage of enetetramines with coordinatively unsaturated electrophilic metal precursors
- *(iii)* In-situ deprotonation of azolium salts and reaction with metal precursors
- *(iv)* Transmetalation of silver NHC complexes
- *(v)* Oxidative additions of metal precursors into C–X bonds



Scheme 1: Synthetic methods for NHC complexes.[8]

Methods *(iii)* and *(iv)* are related as the synthesis of Ag-NHCs using silver oxide is in fact one example of an in-situ deprotonated azolium salt, with Ag_2O acting both as base and metal source.[17] Taking the huge number of available azolium salts as well as the broad reactivity of silver carbenes in transmetalation reactions into account,[18] *(iii)* and *(iv)* are probably the most prominent approaches for the synthesis of transition metal NHC complexes and will also be applied in the context of this thesis. Imidazolium salts are the most important ligand precursors as they are relatively simple to prepare, and two methods are currently most frequently encountered:[8,11,19]

- Nucleophilic substitution of imidazoles
- Multicomponent reactions forming the substituted imidazolium ring

While the former reaction allows the facile synthesis of wingtip-substituted imidazolium salts by reaction of imidazole with alkyl halides, the latter enables access to ligand precursors with modified backbone atoms. With the availability of such powerful synthetic tools, the scope of accessible NHC ligands spans from the early and simple examples published by Arduengo, Wanzlick and Öfele to highly sophisticated, multidentate systems with very specific properties. Consequently, application-specific tailoring of ligand structures is key in order to obtain organometallic complexes with high efficiency in catalysis.[11,20]

1.1.2 Tailoring *N*-Heterocyclic Carbenes

Almost 30 years after their first application in catalysis,[6] countless variations of the NHC motif are known. The ways in which these ligand motifs can be modified are manifold, and only some of them can be discussed in the frame of this work. For the sake of clarity, emphasis will be put on systems with 5-membered heterocycles such as imidazoles, triazoles and related molecules. For such structures, Figure 4 summarizes potential approaches towards functionalized NHC ligands.[10]

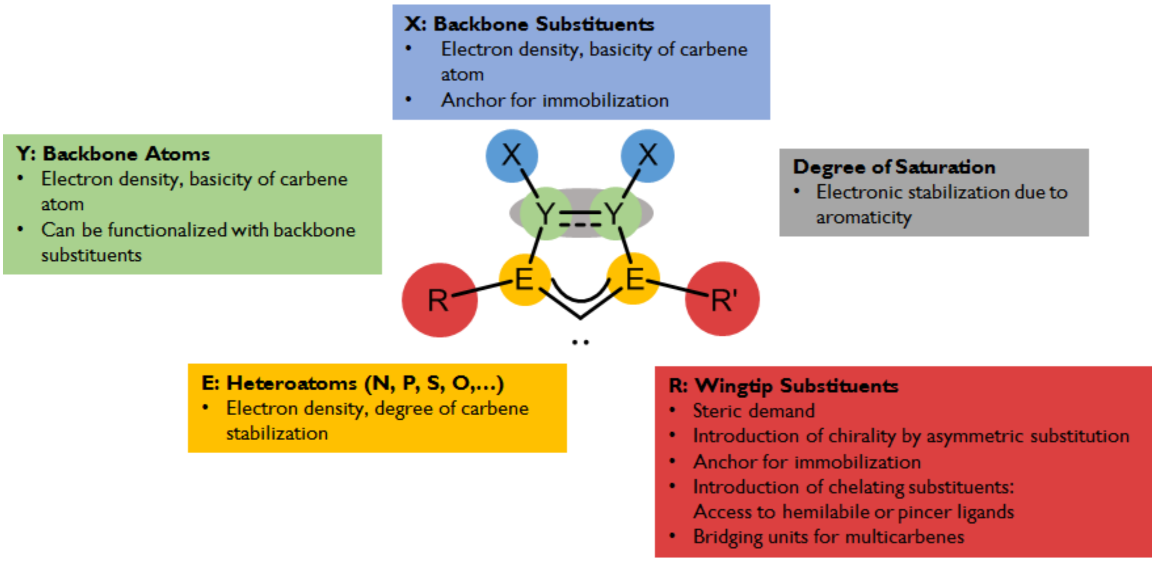


Figure 4: Possible starting points for modifications of NHC ligands.

The most fundamental question in the design of NHC ligands is the type of cyclic system constituting the foundation for the molecular structure. Although imidazoles are the most widely used motifs, related derivatives like triazolyls have also been reported,[5,8,10] albeit in much smaller extent (Figure 5). However, especially for the synthesis of hetero-bimetallic *N*-

heterocyclic dicarbene complexes (*vide infra*), triazolyl-derived systems have found a niche in which they are a prominent species.[21] Also known are examples where one or both nitrogen atoms of the imidazole are replaced by other heteroatoms like phosphorous, sulfur or oxygen.[7-9] Such modifications significantly influence the reactivity of the free carbene due to the altered orbital interactions and geometries. Despite their undoubtedly interesting characteristics, these uncommon systems cover fields of academic interest but have not gathered significant prevalence in applications yet due to their low stability.

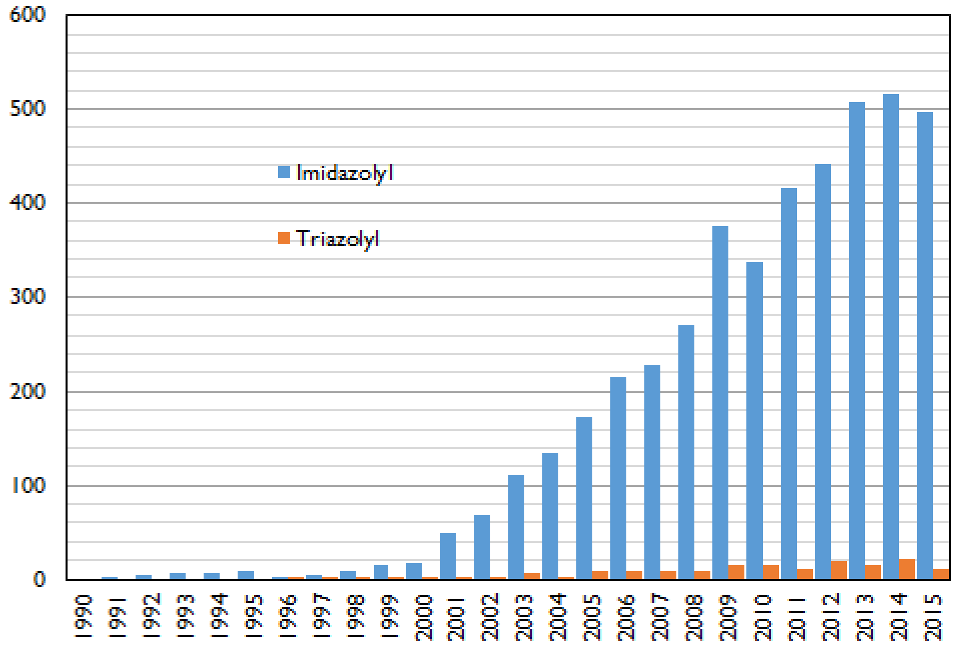


Figure 5: Literature reports on imidazolyl-derived (blue) and triazolyl-derived (orange) NHC complexes as determined from a SciFinder® structure search.

Accordingly, the vast majority of reports on NHC-based complexes employs imidazolium-derived ligands. Despite the common structural feature, a plethora of modifications can be achieved by introduction of substituents either at the backbone or at the nitrogen atoms. With the substituents of the backbone atoms pointing away from the metal center, such modifications allow influencing of the electron density of the carbene ligand with only small impact on the buried volume and sterics of the NHC.[20] Besides electronic parameters, backbone functionalization also enables immobilization on solid supports (Figure 6)[22] or solubility control.[23] As a drawback, backbone functionalization is synthetically difficult to achieve due to the low reactivity of the CH groups in the imidazolium ring. Therefore, synthetic methodologies are based on multicomponent-reactions where the substituted imidazole is formed from carbon- and nitrogen building blocks.[8]

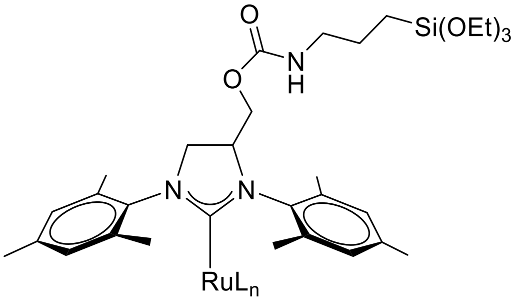
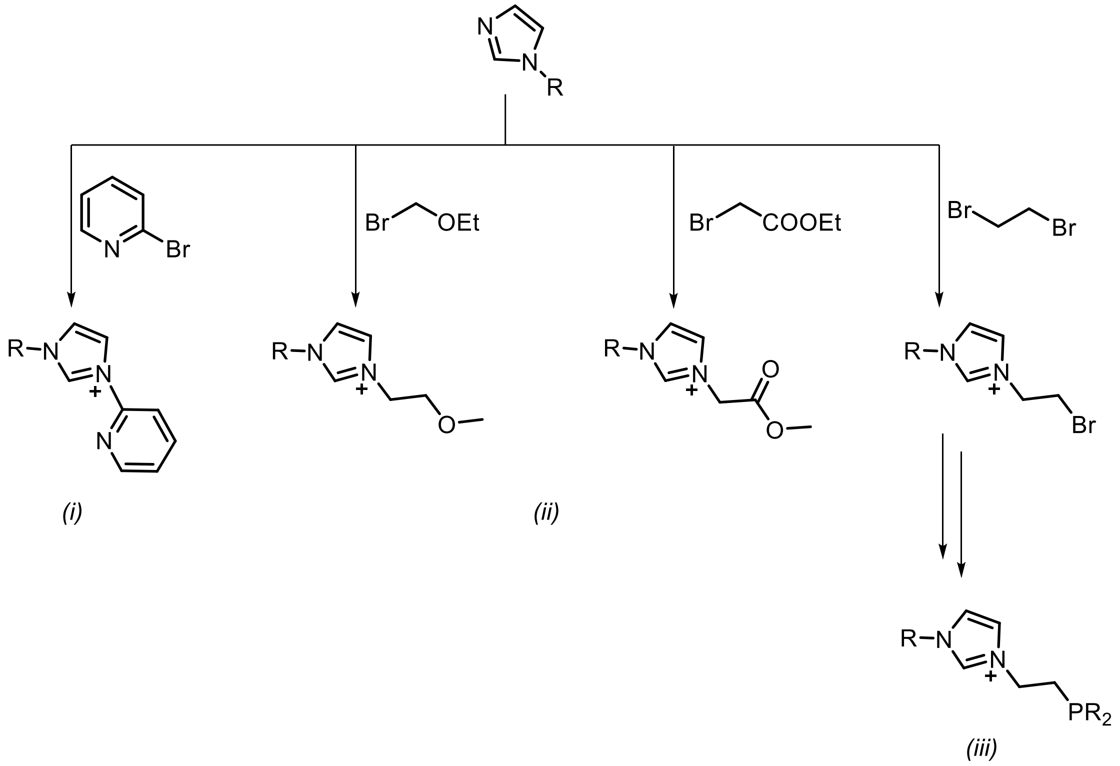


Figure 6: Example of a backbone-functionalized dihydro-imidazolyl Ru-NHC complex.[22]

Conversely, functionalization of the nitrogen atoms is comparatively simple using standard nucleophilic substitution reaction protocols.[24] Considering the large amount of available wingtip-substituents, *N*-functionalization is by far the most prominent way to design NHC ligands for specific purposes.[11,24] Due to their orientation, the size and shape of these substituents directly influence the buried volume of the NHC ligand, which in turn affects the stability and activity of a NHC complex in a given catalytic application. Besides steric parameters, wingtip substituents can also impair the electronic situation at the carbene atom, although their influence is relatively minor.[20,25] Similar to backbone substituents, *N*-functionalization is also employed to control the solubility of either the imidazolium salt or the resulting carbene complex.[25] Immobilization of NHCs via *N*-substituents has been reported and is a topic of continuous research.[20,26-27] Due to the proximity of wingtip-substituents to the metal center, asymmetric functionalization is a useful tool to induce chirality in a NHC complex, a property being particularly attractive for asymmetric catalysis.[28] In addition to this broad spectrum of potential ways to functionalize NHCs, the nitrogen atoms also constitute anchoring points for the synthesis of polydentate ligands: by introduction of substituents bearing nucleophilic functional groups like heteroatoms, olefins, other carbenes or arenes, synthetic access to chelating ligands – including hemilabile and pincer structures – is provided.[11,24]

1.1.3 Polydentate NHC Ligands

With *N*-heterocyclic carbenes gaining ever-increasing attention as ligands in homogeneous catalysis, also their limitations move into focus: in contrast to the ubiquitous phosphine ligands, NHCs are prone to reductive elimination at certain conditions, leading to ligand loss and thus catalyst deactivation.[29-30] Therefore, and due to the synthetic ease enabling wingtip-functionalization, myriads of NHC-ligands bearing one or more additional moieties with ability to coordinate metal centers have been developed.[11,24,30-32] (Scheme 2).



Scheme 2: Introduction of chelating moieties by wingtip functionalization (selected examples).[24]

Chelating moieties may include, but are not limited to, *N*-donors like amines or pyridines *(i)*, *O*-donors *(ii)* or phosphines *(iii)*. The latter are easily introduced by nucleophilic substitution reactions of bromide-functionalized NHC wingtips. Depending on their design, functionalized NHCs can induce the following effects on carbene complexes:[11,30]

- Stabilization against ligand separation by reductive elimination, as the required orbital interactions are prevented by steric fixation
- Stabilization of free coordination sites
- Introduction of hemilability
- Expansion of structural diversity, as the additional moiety itself can be modified depending on the intended application

While the number of available functionalized carbene ligands is almost unlimited, the focus on this thesis will be on bidentate, hemilabile and tetradentate variations of NHC ligands and their impact on the catalytic activity, especially in transfer hydrogenation reactions. Also, this work will concentrate on *P*, *N* and *C*-donors as they are most widely encountered in catalysis.[30,32-34]

While many multidentate ligands display hemilabile behavior (*vide infra*), bidentate carbene-phosphine ligands are usually strongly bound to metal centers, as both coordinating groups show pronounced donor properties. This particular ligand motif is very popular as its electronic and steric characteristics can be tailored by the introduction of substituents to either the carbene or phosphine moiety.[35] Additionally, this ligand system mimics bisphosphine ligands, which are a prominent structural feature of highly active transition metal catalysts,[11] for example in transfer hydrogenation reactions.[36] Consequently, our groups recently synthesized a phosphine-functionalized Ru-aNHC complex (Figure 7), which was applied in the TH of ketones and exhibited outstanding TOFs of up to 140 000 h^{-1} in the presence of a diamine base.[37]

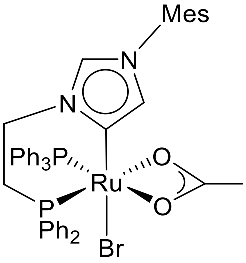


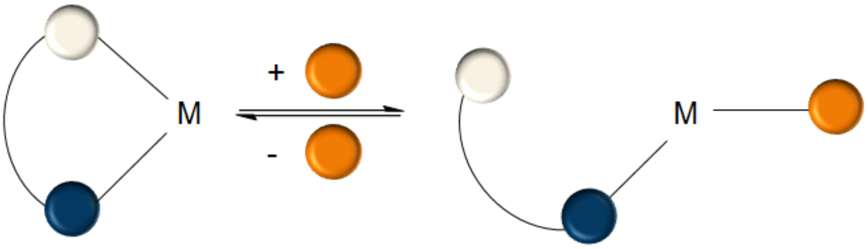
Figure 7: Phosphine-functionalized Ru-aNHC complex as highly active TH catalyst for the reduction of ketones.[37]

Regarding this particular ligand fragment, the thesis includes follow-up work with a shortened alkyl bridge, resulting in unexpected coordination properties.

In contrast, *O*- and *N*-functionalized NHCs often exhibit pronounced hemilability: while one of the coordinating moieties is permanently attached to the metal center, the interaction with the remaining coordination groups is rather weak. Hemilabile ligand systems offer some important advantages which render them as interesting ligand candidates in catalysis (Scheme 3):[38-41]

- The labile fragments of the ligand can easily be displaced by substrates, providing free coordination sites.
- If the labile group gets displaced by a substrate molecule, it is kept in close proximity to the metal center as it is linked to the strongly binding atom. Thus, when the substrate leaves the catalytic species, the resulting coordination site can be stabilized by the dangling donor.

- In addition to the ability to coordinate metals, the heteroatom of the labile group can adopt additional functions like (de-)protonation of reactants (bifunctional catalysis).[42]



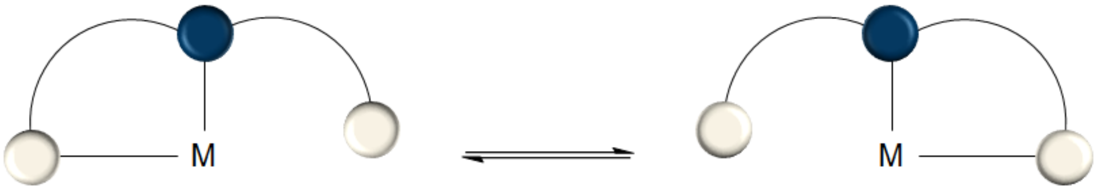
Scheme 3: Reactivity of hemilabile ligands. Blue: strongly bound donor, white: labile donor, orange: external ligand or substrate.

For *O*- and *N*-functionalized NHCs the question which moiety is permanently bound depends on the metal and can be predicted using the HSAB concept: while s-block and early transition metals firmly coordinate hard donors like oxides or amides, they display only weak interactions with carbenes.[43-44] An inverse situation is found for late (soft) transition metals like Ru, Ir or Pd, which strongly bind to carbenes and only weakly coordinate hard donors.[11]

Oxygen- or nitrogen functionalized NHCs can be considered as carbene analogues of the highly successful P–O and P–N ligands and have thus been in the focus of recent research.[45] Although examples of such ligands are known to form complexes with many transition metals, the discussion concentrates on Ir-based systems to limit the scope of this work. *O*- or *N*-functionalized Ir-NHC complexes have been reported to a great extent,[42,46-57] and in many cases hemilabile behavior was experimentally verified.[48,50,53,56-57] Some of these compounds were employed in catalytic applications, also including transfer hydrogenation reactions.[47,50,52,55-56,58] One particularly interesting study was performed by the group of Oro,[50] who directly compared methoxy-functionalized Ir(I)-NHC catalysts with their pyridine-bearing analogues. Using both for the catalytic reduction of cyclohexanone, it was determined that the significantly harder *O*-donor allowed much higher activity as the more strongly interacting *N*-donor. It should be noted that the observed catalytic activity does not match the values reported for the most active non-functionalized Ir-NHC systems.[59] In light of these results, the use of functionalized Ir-NHCs for TH catalysis appears questionable despite their promising and unique properties and relative abundance, indicating the lack of reliable data in this field.

Besides functionalized NHCs bearing only one additional donor-atom, tridentate ligand precursors can be obtained if both wingtips are equipped with suitable substituents. The resulting “pincer” coordination mode has gathered significant relevance and can be considered as an entire ligand class with manifold applications. Therefore, a complete discussion of its characteristics is far beyond the scope of this work, but thorough reviews on this topic are available in the literature.[29,32,60-61]

It has been reported for sterically constrained structures that such potentially tridentate ligands can form highly fluxional systems, where the substituents constantly replace each other in a bidentate coordination mode (Scheme 4).



Scheme 4: Fluxional behavior of potential terdentate NHC ligands. Blue: NHC moiety, white: dangling donor-functionalized wingtip substituent.

Such fluxionality is a comparatively rare phenomenon, and only few mechanistic and catalytic studies thereof have been published.[62-63] Utilizing modern analytical techniques like variable-temperature NMR spectrometry and DFT calculations, further insights into the involved mechanisms appear feasible and could help to understand hemilabile behavior of donor-functionalized wingtip-substituents in more detail.

A different type of chelating ligand systems can be achieved by linking multiple carbene moieties with alkyl bridges. These ligands generally do not display hemilabile or fluxional behavior due to the strong bonding between carbenes and the metal center.[33-34,64] Depending on the nature and length of the linker, a broad structural diversity of multicarbene ligands ranging from biscarbenes to tetracarbenes is available to date. Especially tetracarbenes are a comparatively rare species which is attracting current interest due to their strong chelating properties and ability to stabilize reactive intermediates.

Many complexes bearing these ligands are synthesized from macrocyclic precursors with high structural rigidity.[33-34,65-66] Accordingly, tetracarbenes usually coordinate in the equatorial plain of the metal, and only two exceptions are known.[67-68] This behavior limits the possibility to specifically design the coordination environment. More flexible, open-chain tetra-NHC ligands are reported, but do often not allow the synthesis of mononuclear complexes.[69-71] Conversely, our group recently presented acyclic tetraimidazoles with variable alkyl linkers, which were applied as ligands for mononuclear transition metal NHC complexes.[72-73] The versatility of this ligand motifs considering possible coordination geometries is underpinned by the formation of octahedral Fe complexes with either equatorial or sawhorse-orientation of the tetradentate ligand.[73] The placement thereby depends on the length of the alkyl bridges and the remaining ligands coordinating to the metal (Figure 8).

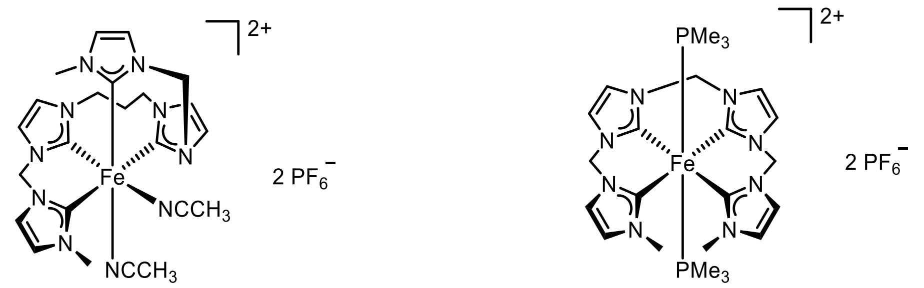


Figure 8: Variable coordination modes of acyclic alkyl-bridged tetracarbene ligands.[73]

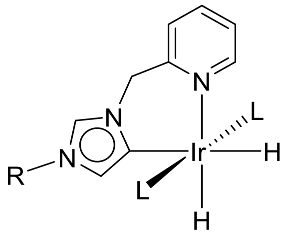
Keeping in mind the strong interaction of chelating tetracarbenes with the metal center, their use as highly stable ligands for diverse applications seems to be an interesting field for future research.

1.1.4 Abnormal Coordination Modes

In the vast majority of NHC complexes, the metal is bound to the ligand via the carbene atom in C2-position of the imidazolium ring (nNHC).[5] Two rather obvious explanations for the prevalence of nNHCs can be stated:

- The synthesis of NHC complexes mostly proceeds via deprotonation of imidazolium salts in presence of metal precursors (*vide supra*). As the proton at the C2-carbon atom is the most acidic site, deprotonation preferentially occurs at this position.
- The stabilization of the electron-deficient carbene is maximized at the NCN-position, where two adjacent nitrogen atoms can donate electron density.

However, in 2001 Crabtree et al. reported for the first time an unusual NHC complex in which the metal binds via the C5-atom of the imidazolium backbone (Figure 9).[74]



R = *n*Bu or ^{i}Pr, L = PPh$_3$

Figure 9: Crabtree's first example of an abnormal NHC complex (aNHC).[74]

Due to their electronic properties, these so-called abnormal carbenes (aNHCs) are considered as even stronger donors compared to their normal counterparts, which was proven to be beneficial for catalytic applications like transfer hydrogenation[75] or Suzuki-Miyaura coupling,[76] which in general require highly basic ligands.

As more examples of aNHCs emerged in the following years, several pathways for their synthesis were established.[77-79] Selective abnormal coordination can for example be achieved by substitution of the C2-proton with alkyl groups, leaving solely the backbone carbon atoms available for metal binding. Another possibility is the introduction of halide substituents into the backbone of imidazolium salts, followed by oxidative addition of a metal precursor in the corresponding C–X bond. In addition to imidazolium salts which have been specifically modified in order to selectively yield aNHC metal complexes, in some cases the formation of abnormally coordinated carbene ligands is also observed due to steric constraints: metal binding via the C4- or C5-atom leads to an inverse orientation of the wingtip substituents, which are now pointing away from the metal center (Figure 10). Thus, if the complex bears other sterically demanding ligands, the abnormal coordination mode can lead to a more stable product. From a synthetic point of view this indicates that the preferred coordination mode of a carbene ligand can be controlled by the size of the wingtip-substituents.[79]

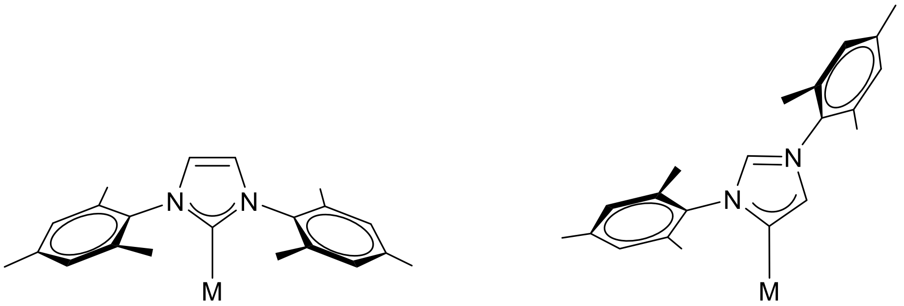


Figure 10: Comparison of steric orientation of wingtip substituents in nNHCs (left) and aNHCs (right).

A third coordination mode was reported in 2006 by the group of Arnold et al.[80] and allows for the formation of bimetallic carbene complexes as depicted in Figure 11. Formally, this can be achieved by deprotonation of the carbene ligand in a NHC complex, resulting in a negatively charged (anionic) moiety, which due to its delocalized electron system exhibits two carbon atoms with partially carbenoid character. Subsequent metalation leads to bimetallic complexes bearing so-called anionic dicarbenes or *N*-heterocyclic dicarbenes (NHDCs).[81] This very uncommon ligand motif offers some interesting structural features:[21]

- Synthetic access to bimetallic complexes with fixed metal-to-metal separation
- Possible electronic interaction across π-system
- Large structural diversity due to widespread availability of NHCs

- High potential for application in tandem catalysis

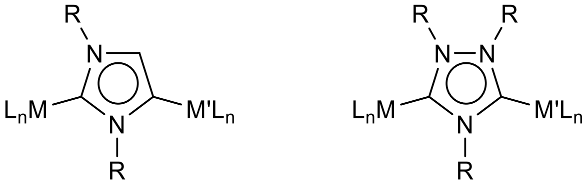


Figure 11: Structure of imidazolyl- (left) and triazolyl- (right) derived NHDC complexes.

Despite these promising characteristics, the number of reported NHDC compounds is still comparatively small. In contrast to monometallic NHC complexes, both imidazolyl and triazolyl-derived structures are almost evenly distributed. Synthetically, two major pathways have been established in the previous reports:[81]

- Chemical reduction using elemental Li or organometallic reducing agents like KC_8. Although a variety of NHDC complexes could be obtained following this protocol, the harsh reaction conditions constitute a significant limitation of this pathway.
- Deprotonation of existing carbenes using strong alkali-metal bases or basic metal alkyls like $ZnEt_2$ or Me_3SiCl. In addition for the necessity of such highly reactive compounds, the synthetic scope of this method in limited as the respective reagents determine the nature of the metal that is introduced into the structure.

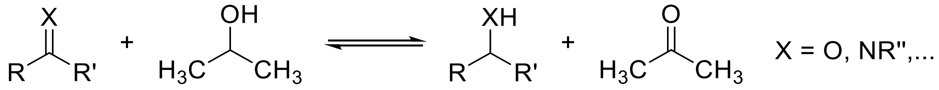
Regarding imidazolyl-derived structures, the limitations of these methods result in the fact that most examples are based on main group elements which display restricted applicability in catalysis.[81] Only in some cases structures bearing at least one transition metal could be obtained,[80,82-88] and examples for imidazolyl-derived NHDC complexes bearing two transition metals are exclusively homo-bimetallic[82-83,85,89-90] and thus of low interest for application in tandem procedures.

Interestingly, the situation is quite different for triazolyl-derived systems, where a number of hetero-bimetallic NHDC complexes with transition metals have been reported in particular by Peris et al.[21,91-101] Due to the increased acidity of triazolyls, the deprotonation of these ligands is facilitated and can be achieved by relatively mild reagents like sodium acetate, potassium carbonate or internal bases. Accordingly, various triazolyl-NHC complexes bearing diverse transition metals react with metal precursors in the presence of a base, resulting in bimetallic species comprising Ru, Ir, Pd and other metals.

Consequently, some of these systems have successfully been employed for tandem reactions and it could be shown that such bimetallic compounds exhibit better performance than the combination of different monometallic species with similar stereoelectronic properties.[21,92-93,95-96,99-100] The high activity of triazolyl-derived NHDCs is considered as an incentive to develop synthetic protocols towards related imidazolyl-based systems, for which only one catalytic application – the skeletal rearrangement of enynes – was reported prior to this thesis.[82]

1.2 Transfer Hydrogenation Catalysis

Hydrogenation reactions play an important role in synthetic chemistry with main applications in hydrocracking, hydrotreating (sulfur removal) or the solidification of fatty acids (margarine production).[102] While these processes are almost exclusively heterogeneously catalyzed, homogeneous catalysts are mainly employed for the synthesis of fine chemicals with high demands on selectivity. In the context of this thesis, particular focus will be on the field of transfer hydrogenation (TH) reactions, using chemical hydrogen donors like 2-propanol rather than dihydrogen gas (Scheme 5).[103]



Scheme 5: Transfer hydrogenation reaction using 2-propanol as hydrogen donor.

Despite of creating a side product in stoichiometric amount the TH methodology offers several advantages:[36,104]

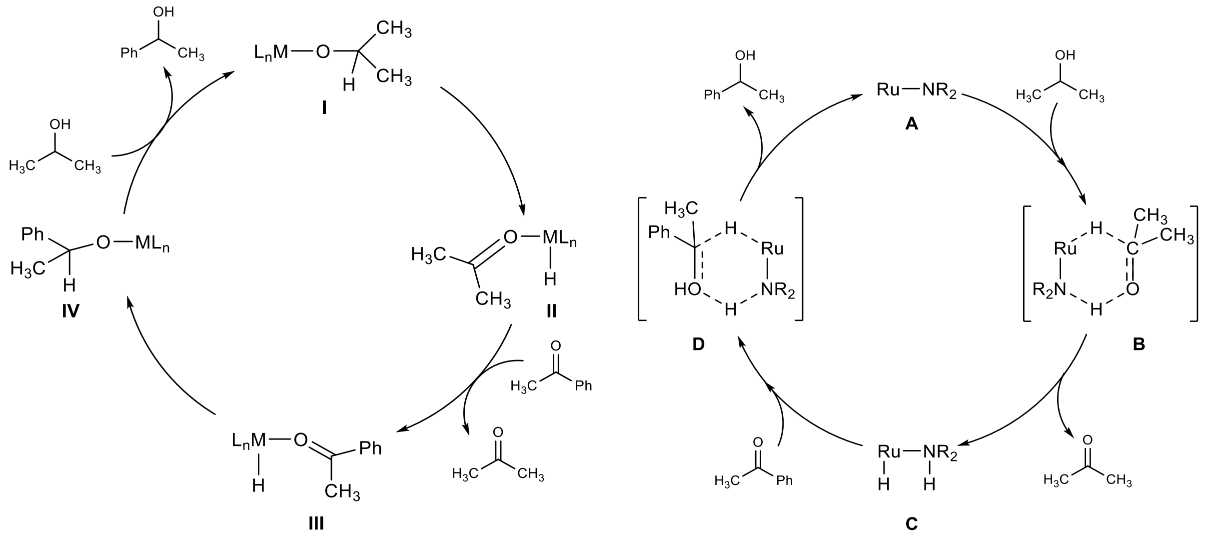
- No pressurized or flammable gas is necessary, avoiding explosion hazards
- Significantly simpler reaction setup as transformations can be performed at atmospheric pressure
- Common hydrogen donors like 2-propanol are easily accessible, display low toxicity and are facile to handle
- The side product as well as excess hydrogen donor are easy to separate from the reaction mixture and can be recycled

The first reports indicating such reactivity were published more than 115 years ago[105-106] but remained neglected by synthetic chemists until Meerwein, Ponndorf and Verley independently developed the aluminum oxide promoted hydrogen transfer of alcohols to aldehydes and ketones in 1925 (Meerwein-Pondorf-Verley reaction, MPV):[107-109]

> *"Durch Ersatz der Alkali-alkoholate durch die Aluminiumalkoholate können alle diese Nebenreaktionen ausgeschaltet werden und man gelangt so zu einem überaus einfachen und glatt verlaufenden Reduktionsverfahren für Aldehyde und in beschränktem Maße auch für Ketone, […]"*
>
> Hans Meerwein, *Ann. Chem.* **1925**, *444*, 223.[107]

The great advantage of this methodology is its high chemoselectivity: aldehydes can be reduced more quickly than ketones, and alkenes and alkynes which readily react with dihydrogen display no reactivity under MPV conditions.[110] However, the high consumption of aluminum alkoxides (up to stoichiometric amounts) constitutes the major drawback of the MPV procedure, stimulating the development of alternative, more economic systems.

Thus, four decades later, transition metal catalyzed processes appeared in the literature[111-113] and became more widespread in the course of the subsequent years.[103,114] Following these early contributions to the field, a plethora of homogeneous catalysts for TH processes have been established,[36,115] and in particular the group of Noyori succeeded in developing asymmetric reaction protocols, enabling the stereoselective synthesis of alcohols and amines.[36,116-117] Due to their high activity, these catalysts can be employed in very low loadings, rendering their use highly efficient despite the relatively high costs of the involved transition metals. Today, the most effective systems are based on Ru, Ir and Rh;[36] and two mechanistic pathways have been determined (Scheme 6):[104,118]



Scheme 6: Proposed mechanisms for transition-metal catalyzed transfer hydrogenation reactions.[104] Left: Hydric route ("inner-sphere"-mechanism), right: Dihydride mechanism ("outer-sphere").[117]

The "inner-sphere" mechanism involves a direct interaction of substrate and hydrogen donor with the metal center and is most commonly observed. The reaction proceeds via the alkoxycomplex **I** which is formed by deprotonation of 2-propanol in presence of a base.[119-120] Subsequently, a metal-hydride species (**II**) is formed by β-H-elimination, resulting in the formation of acetone, which is released from the catalytic species by a ligand exchange reaction with the substrate (here: acetophenone) (**III**). The reduction of the carbonyl atom is achieved by migratory insertion of the ketone into the metal-hydrogen bond, resulting in the metal alkoxide **IV**. Finally, the product 1-phenylethanol is displaced by a new 2-propanol molecule.[104,120]

Noyori et al. proposed an alternative pathway which has become known as the "outer-sphere" mechanism involving a hydride and a proton.[117] This reaction sequence is observed for Ru-complexes bearing a chelating ligand with amino groups, enabling a *syn*-periplanar arrangement of the hydrogen donor with the Ru-NR_2 fragment (**B**). In this pericyclic transition state, 2-propanol is converted to acetone by simultaneous release of both hydrogen atoms, forming the Ru hydride species **C**. This intermediate in turn enables another pericyclic transition state (**D**) where the substrate and both hydrogens are immediately transferred, without direct interaction of the substrate and the metal center. As two active centers (Ru and NR_2) are involved in this sequence it can be considered as an example of bifunctional catalysis.[104] Along with the mechanistic concept, Noyori et al. developed a series of highly efficient TH and hydrogenation catalysts which still inspire the development of novel variations thereof.[36]

Today, a variety of catalysts for (asymmetric) transfer hydrogenation reactions following either (or both) of these mechanisms have been reported,[36,120] and some have gained commercial success for the production of fine chemicals, pharmaceuticals and cosmetics.[102,121-123]

With their increasing popularity in the beginning of the 21st century, *N*-heterocyclic carbenes also emerged as ligand systems for transition-metal based TH catalysts. In 2001, Nolan et al. reported the first example of an Ir-complex bearing aryl- and alkyl-functionalized carbene ligands,[124] and many more examples containing Ir or Rh centers followed quickly,[29,36,125-126] also containing hemilabile ligand systems.[50,52,58,127-130] The most active Ir-NHC catalyst reaches TOFs of up to 24 000 h^{-1} for the conversion of acetophenone to 1-phenylethanol. For Ru-based catalysts, pioneering work was done by the groups of Peris[131] and Danopoulos[132] using tridentate CNC pincer ligands. Due to their extraordinarily high activities, Ru-based compounds became the most popular NHC-ligand bearing catalysts for TH applications.[36,133-135]. In 2011, Baratta and Kühn showed that the catalytic activity of Ru-NHCs can even further be improved if abnormally coordinated aNHC ligands are employed (Figure 7),[37] enabling turnover frequencies of up to 140 000 h^{-1} for the reduction of acetophenone in the presence of a diamine base (bifunctional catalysis).

1.3 Tandem Catalysis

With today's availability of myriads of potential catalysts for almost every desired chemical transformation, chemists strive for streamlined, ecological and economical synthetic solutions in order to minimize waste, labor, costs, and safety hazards. Thus, the development of catalytic systems promoting more than one chemical process without isolation of intermediates has gained significant interest in recent years.[136-138] Many of these "one-pot" methodologies have been reported in order to achieve this goal, therefore it is by now necessary to differentiate between these various approaches in order to establish concise definitions. Lately, conventions as depicted in Figure 12 are the mutual consent of synthetic chemists:[138-139]

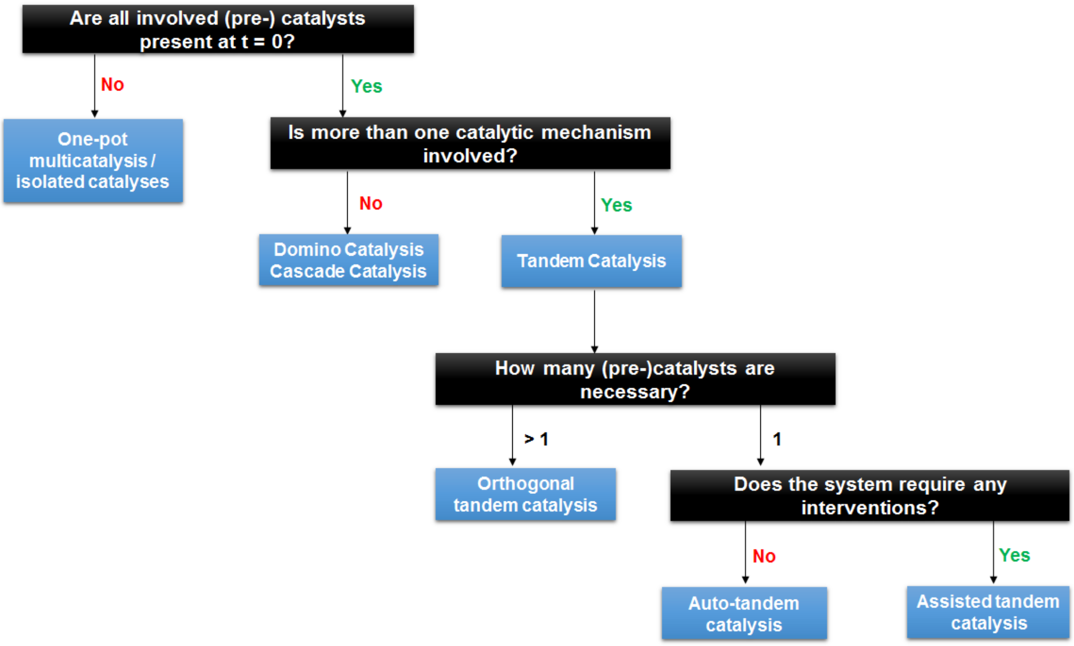


Figure 12: Definitions of multi-step one-pot reactions according to literature consensus.[138-139]

Common feature of one-pot reactions is the presence of a multi-step chemical transformation of a substrate without isolation of intermediates. It must be distinguished between systems where a second catalyst is added after the first catalytic sequence has been completed and those where all catalysts are present in the reaction mixture at the time of initiation. In the latter case the common terminology is domino or cascade catalysis if only one catalytic mechanism is involved (e.g. two subsequent C–C bond formations) and tandem catalysis if two independent catalytic transformations (e.g. a C–C bond formation followed by a hydrogenation reaction) are performed. For tandem catalysis one can discriminate systems where more than one (pre-)catalyst is required to accomplish the one-pot sequence (orthogonal tandem catalysis) or if a single compound can catalyze all required steps. Multiple transformations using a single catalyst and occurring under identical conditions are referred to as auto-tandem reactions, while procedures requiring a change in the reaction conditions (e.g. solvent addition, temperature variation etc.) in order to initiate the second transformation are called assisted tandem catalysis. Whichever of the above mentioned methods is applicable for a given task, all procedures reduce the amount of energy and solvents necessary for workup and purification of intermediates, with concomitant increase in overall yields.[136-138,140]

As for almost every other major catalytic application, *N*-heterocyclic carbenes have been employed for such one-pot reactions. In particular, NHCs are used as organocatalysts for tandem Umpolung reactions,[139] while application of transition-metal NHC complexes is still comparably rare. However, the synthetic access to ditopic *N*-heterocyclic dicarbenes[81] allowed the development of a new class of bimetallic tandem catalysts (Figure 13),[21] and it was shown that the combination of such bimetallic species is beneficial as compared to the combination of monometallic species.[21,141] These so-called "cooperative effects" are not only observed for bimetallic carbene catalysts, but for manifold multi-metal systems with fixed metal-to-metal separation and can be attributed to the spatial proximity, electronic contact and hampered chemical interactions among the involved metal centers.[21,142-145] As the development of bimetallic NHDC complexes is a very recent progress in coordination chemistry, major contributions to the field of carbene-based bimetallic tandem catalysis can be expected in the near future. In the context of this thesis, a novel Pd–Ru catalyst for a tandem Suzuki-Miyaura/transfer hydrogenation reaction is presented, constituting a highly attractive homogeneous system for this transformation.

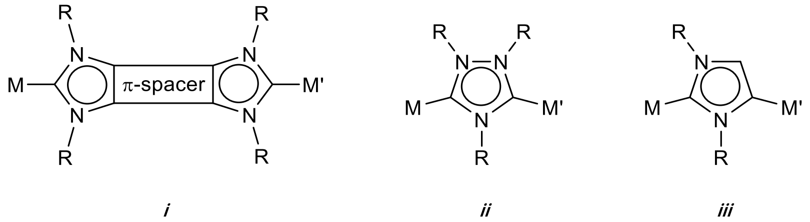


Figure 13: Examples of ditopic NHC-based complex structures with potential applicability in tandem catalysis. *(i)*: Janus-type NHC ligand, *(ii)*: 1,2,4-triazolyl-3,5-diylidene ligand, *(iii)*: 1,3-imidazolyl-2,4-diylidene ligand.

2. OBJECTIVE

Inspired by the outstanding amount of potential applications, functionalized *N*-heterocyclic carbene ligands of different nature are the subject of this thesis.

The first section takes the large number of Ir(I)-NHC complexes bearing *N*-functionalized carbenes as an incentive to study the weak interactions between the Ir and nitrogen atoms in more detail. Despite being frequently reported, hemilabile behavior of such motifs is not thoroughly supported by experimental and theoretical data yet. Therefore, a bispyridine-functionalized imidazolium salt was chosen as a suitable candidate for detailed studies (Figure 14).

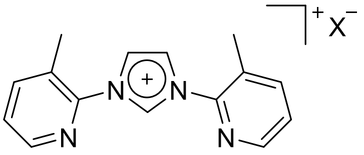


Figure 14: Bis-pyridine functionalized imidazolium salt as suitable ligand precursor for studies on hemilabile systems.

Despite bearing three possible coordination groups, the steric strain in this ligand motif only allows for a bidentate binding mode, leaving the remaining pyridine moiety in a dangling position. This in turn enables a fluxional system where both pyridine arms continuously replace each other (Scheme 4) – a phenomenon which is to be studied by DFT and VT NMR experiments. In addition, the impact of this hemilabile system on the catalytic stability as well as on the reactivity of the involved Ir(I)-NHC is to be determined.

While *N*-functionalized NHCs often enable the dynamic behavior observed for the aforementioned Ir-complex, tetracarbenes are a generally rigid and voluminous ligand species that have been rarely employed for transition metal complexes. However, open-chain tetraimidazolium salts offer high flexibility due to their acyclic nature, and reaction of this salt with a suitable Ru-precursor is an interesting addition to previously published reports on such ligand systems for Fe- and Ag systems.[72-73] With Ru(II) offering six available coordination sites, the influence of the remaining two ligands on the geometry of the tetracarbene chain is an particularly compelling question that needs to be addressed in this thesis.

Finally, modification of the phosphine-functionalized NHC ligand in the Ru-complex depicted in Figure 7 appears to be attractive in order to obtain even more active transfer hydrogenation catalysts. Therefore, an imidazolium salt with a shortened linker length (Figure 15) is to be employed as ligand precursor for related Ru(II) compounds.

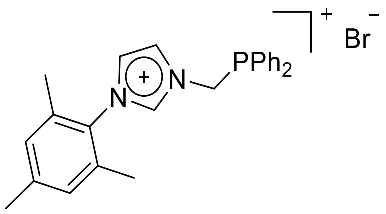


Figure 15: Modified phosphine-functionalized imidazolium salt.

The resulting abnormal Ru complex offers an interesting and versatile approach towards the synthesis of hetero-bimetallic, imidazolyl-based transition metal NHDC complexes, which have not been reported prior to this thesis. Taking the applicability of triazolyl-derived NHDCs in tandem catalysis as a role model, a Pd–Ru system is to be isolated and employed for tandem Suzuki-Miyaura/transfer hydrogenation reactions. In addition, experimental evaluation of cooperative effects is feasible by comparison of the bimetallic system with monometallic derivatives.

3. RESULTS – PUBLICATION SUMMARIES

3.1 On The Concept of Hemilability: Insights into a Donor Functionalized Iridium(I) NHC Motif and Its Impact on Reactivity

Korbinian Riener,# **Mario J. Bitzer**,# Alexander Pöthig, Andreas Raba, Mirza Cokoja, Wolfgang A Herrmann, Fritz E. Kühn

#Korbinian Riener and Mario J. Bitzer contributed equally to this work.

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In this article, we synthesized a pyridine-functionalized Ir(I)Cl NHC complex (**1a**) with pronounced fluxional hemilabile behavior. For the first time, crystal structures of both the open- and closed modification are described (Figure 16).

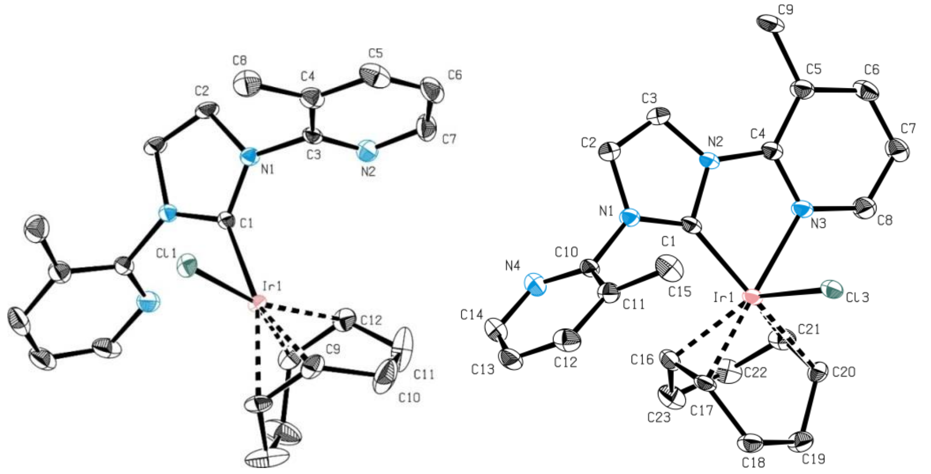

Figure 16: ORTEP-style molecular structure of κ^1C-**1a** (left) and κ^2C,N-**1a** (right). Hydrogen atoms as well as co-crystallized solvent molecules are omitted for clarity. Selected bond lengths (Å), angles (°), and torsion angles (°): κ^1C-**1a**: Ir1–Cl1 2.358(2), Ir1–C1 2.049(4), Ir1–C9 2.174(3), Ir1–C12 2.105(4), C1–Ir1–Cl1 86.9(2), N1–C1–N1a 103.6(4), C1–N1–C3–N2 72.2(4). Symmetry code: x, -y + ½, z. κ^2C,N-**1a**: Ir1–Cl3 2.5759(9), Ir1–C1 2.000(4), Ir1–N3 2.117(3), Ir1–C16 2.142(4), Ir1–C17 2.117(3), Ir1–C20 2.189(4), Ir1–C21 2.163(4), C1–Ir1–Cl3 96.31(11), C1–Ir1–N3 76.37(13), N3–Ir1–Cl3 82.28(9), C1–N2–C4–N3 5.5(5), C1–N1–C10–N4 -111.5(4).

VT NMR studies reveal a dynamic system in CH_2Cl_2 solution that cannot be halted even at the low temperature limit of the solvent (-90 °C), indicating the weak interaction of the *N*-donor with the Ir atom. DFT calculations underpin these observations and quantify the energy barrier for the *N*-coordination at only 10 kcal/mol. Based on the experimental and theoretical data, a κ^1–κ^2 mechanism is assumed rather than a κ^2–κ^2 process. A bromo-derivative of this complex (**1b**) with better solubility and stability was synthesized and evaluated in transfer hydrogenation catalysis. Although functionalization of the NHC in Ir(I) motifs does not positively influence the catalytic activity in TH reactions with regards to TOFs, **1b** exhibits outstanding catalytic stability, permitting up to 9000 turnovers for the reduction of acetophenone at a catalyst loading of only 0.01 mol%. In further experiments, the reactivity of

1b in various reactions was examined. While ligand addition (PMe_3 and PPh_3) and halide abstraction resulted in the formation of fluxional hemilabile derivatives, substitution of the cod ligand by carbon monoxide enabled the formation of the unexpected monocarbonyl motif **2** with no hemilability.

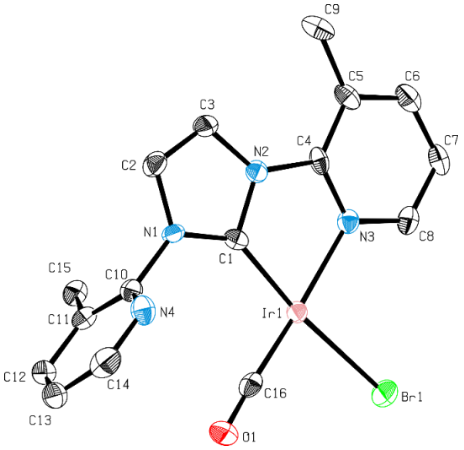

Figure 17: ORTEP-style molecular structure of **2**. Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å), angles (°), and torsion angles (°): Ir1–Br1 2.35049(11), Ir1–C1 1.921(4), Ir1–N3 2.109(4), Ir1–C16 1.806(6), C1–Ir1–Br1 171.7(2), C1–Ir1–N3 77.2(2), C16–Ir1–N3 174.3(2), N3–Ir1–Br1 94.7(2), C1–N2–C4–N3 0.2(6), C1–N1–C10–N4 89.8(6).

Finally, oxidative addition of dihydrogen resulted in a rare non-fluxional Ir(III) species which remains stable for days at -30 °C without hydrogenation of the coordinated cod ligand (Figure 18).

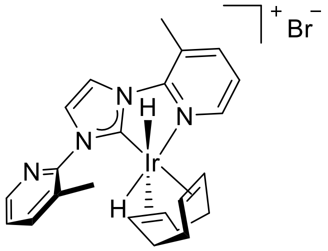

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Figure 18: Ir(III)-dihydride **3** obtained by reaction of **1a** with molecular hydrogen.

3.2 Controlling Coordination Geometries: Ru-Carbene Complexes with Tetra-NHC Ligands

Manuela Hollering, Daniel T. Weiss, **Mario J. Bitzer**, Christian Jandl, Fritz E. Kühn

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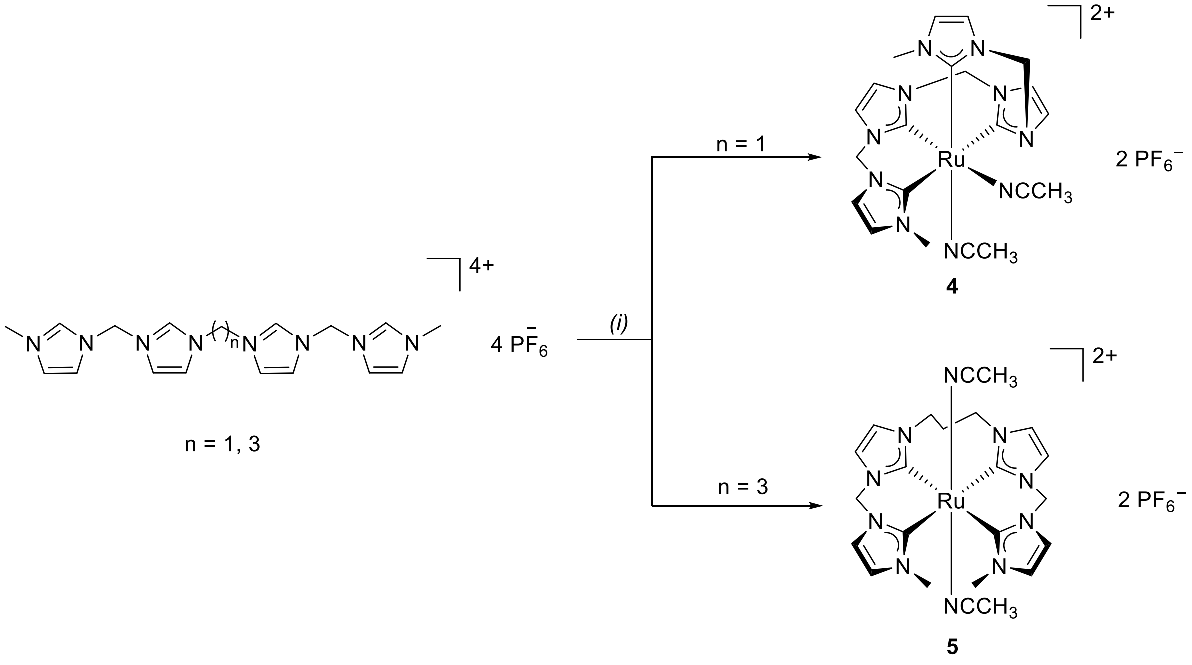
Flexible multidentate NHC ligands offer the possibility to control the coordination geometry of transition metal complexes. Here the synthesis of tetradentate Ru-NHC complexes is described, and examples displaying either equatorial or sawhorse-type orientation are obtained as a function of the alkyl linkers in the ligand precursors.



Scheme 7: Synthesis of tetradentate sawhorse (**4**) or equatorial (**5**) Ru-NHC complexes. *(i)*: Microwave, Ag_2O, $[RuCl_2(p\text{-cymene})]_2$, 100 °C, 1 h, 100 W.

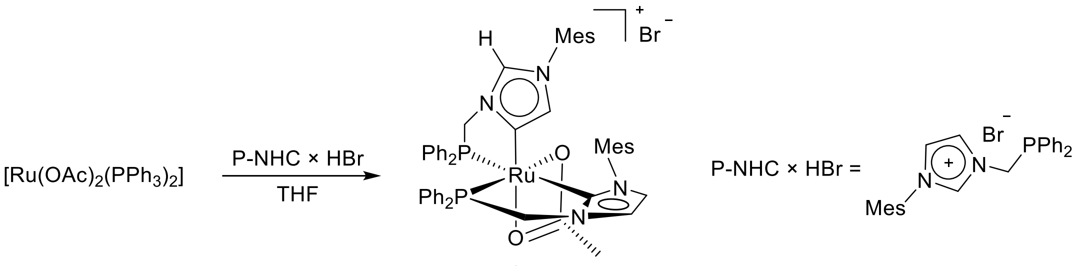
Compounds **4** and **5** constitute the first examples of acyclic Ru tetracarbene complexes. Remarkably, the sawhorse-type **4** can easily be converted to an equatorial derivative by reaction with excess trimethylphosphine, replacing the labile acetonitrile ligands. In contrast, reaction of **4** with *tert*-butyl isocyanide results in substitution of the acetonitrile ligands under preservation of the sawhorse orientation. These results show that the coordination geometry can not only be controlled by the design of the tetradentate ligand precursor, but also by the substituents on the remaining vacant coordination sites. In consequence, these Ru-NHC complexes can be tailored towards specific applications. Exemplarily, both **4** and **5** were employed in the catalytic transfer hydrogenation of acetophenone at a catalyst loading of 0.1 mol%. While the sawhorse-type **4** exhibits outstanding activity for the conversion of the ketone to 1-phenylethanol (TOF: 110 000 h^{-1}, 98% conversion after 1 min), the equatorial-type catalyst **5** displays much lower reactivity, yielding 97% 1-phenylethanol after 30 min (TOF: 4500 h^{-1}). The observed activity of **4** is among the highest reported values for Ru-NHC complexes reported to date, especially as no amine function is necessary which is usually employed to obtain such high activities (bifunctional catalysis). The reported data thus establish sawhorse-type acyclic tetradentate Ru catalysts as viable alternatives to existing catalytic systems.

3.3 Ru–Ag and Ru–Au Dicarbene Complexes from an Abnormal Carbene Ruthenium System

Mario J. Bitzer, Alexander Pöthig, Christian Jandl, Fritz E. Kühn, Walter Baratta

published as Communication in *DALTON TRANSACTIONS* **2015**, *44*, 11686-11689

Reaction of [Ru(OAc)(PPh$_3$)$_2$] with a functionalized imidazolium bromide containing a CH$_2$-bridged phosphine-arm (P-NHC × HBr) yields Ru-NHC complex **6** as a bright yellow solid (Scheme 8). This compound is the first example of a Ru carbene complex bearing both normal and abnormal NHC ligands. Complex **6** was used for the catalytic transfer hydrogenation of acetophenone, benzophenone and cyclohexanone in the presence of 2-propanol and sodium isopropoxide. It exhibits very high activity with a TOF of up to 49 000 h^{-1} at a catalyst loading of 0.1 mol%.



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Scheme 8: Reaction of [Ru(OAc)(PPh$_3$)$_2$] with P-NHC × HBr yielding Ru-aNHC complex **6**.

The NCHN proton of the abnormal carbene moiety displays an exceptionally low-field shifted signal in the ^{1}H NMR at 9.75 ppm. Since this chemical shift is very similar to the one of P-NHC × HBr (10.33 ppm), Ru-NHC complex **6** was considered as an "imidazolium salt" and exposed to silver(I) oxide to examine possible metalation reactivity. After stirring at room temperature in CH$_2$Cl$_2$ suspension for 7 days, Ag–Ru NHDC complex **7** was isolated as a trinuclear compound with a silver atom that almost linearly coordinates two Ru-NHC fragments (Figure 19).

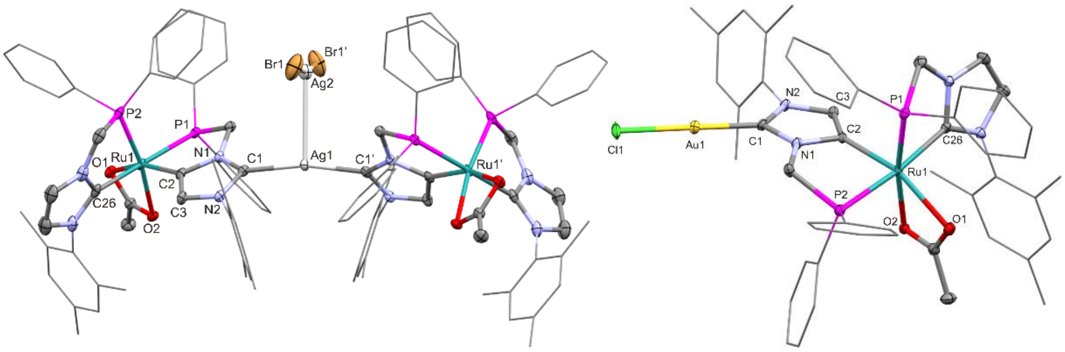


Figure 19: ORTEP-style molecular structure of **7** (left) and **8** (right). Ellipsoids are shown at 50% probability. For the sake of clarity, hydrogen atoms as well as co-crystallized solvent molecules are omitted and the aromatic substituents are shown as wireframe representation. Selected bond lengths (Å) and angles (°):
Ag–Ru NHDC **7**: Ag1–C1 2.112(5), Ag1–Ag2 3.1211(8), Ru1–C2 2.022(5), C1–Ag1–C1‘ 167.8(3), C1–Ag1–Ag2 96.09(13), C2–Ru1–P1 80.83(14). Symmetry code: 1/2-x, +y, -z.
Au–Ru NHDC **8**: Au1–C1 1.984(4), Au1–Cl1 2.3026(1), Ru1–C2 2.018(4), C1–Au1–Cl1 178.74(12), C2–Ru1–P1 88.70(11).

As compared to **6**, the coordination environment around the Ru atoms remains almost unaffected by the metalation reaction. Complex **7** is the first example of an imidazolyl-derived NHDC compound bearing two different d-block elements. This complex was then used as starting material in a transmetalation reaction with [AuCl(tht)], resulting in the formation of two dinuclear Au–Ru derivatives (**8**). Here the gold atom bears only one Ru-NHC fragment and one chloro-ligand in a linear arrangement. The synthetic methodology shows that Ru-NHC complexes bearing abnormal carbene ligands can be used as starting materials for the synthesis of bimetallic NHDC complexes with potential applicability in (tandem-)catalysis, especially if the high transfer hydrogenation activity of the Ru fragment is taken into account.

3.4 Tandem Suzuki-Miyaura/Transfer Hydrogenation Reaction Catalyzed by a Pd–Ru Complex Bearing an Anionic Dicarbene

Mario J. Bitzer, Fritz E. Kühn, Walter Baratta

published as Article in *Journal of Catalysis* **2016**, 338, 222-226

Transmetalation of the previously described Ag–Ru NHDC complex **7** with [PdCl$_2$(cod)] in toluene yields the trinuclear Pd–Ru species **9** as a yellow solid in good yield. In solution, up to four different isomers of the compound are indicated by ^{31}P {^{1}H} NMR spectroscopy and most likely caused by different conformations of the five-membered P–NHC-metallacycles. Bearing both Pd and Ru atoms, **9** was applied in a tandem reaction comprising Pd-catalyzed C–C cross-coupling and Ru-catalyzed C=O reduction (Figure 20). For this combined Suzuki-Miyaura/transfer hydrogenation reaction protocol, **9** was established as a highly active tandem catalyst with broad substrate scope, converting diverse bromoacetophenones and phenylboronic acids to the respective biphenyl alcohols (Figure 20).

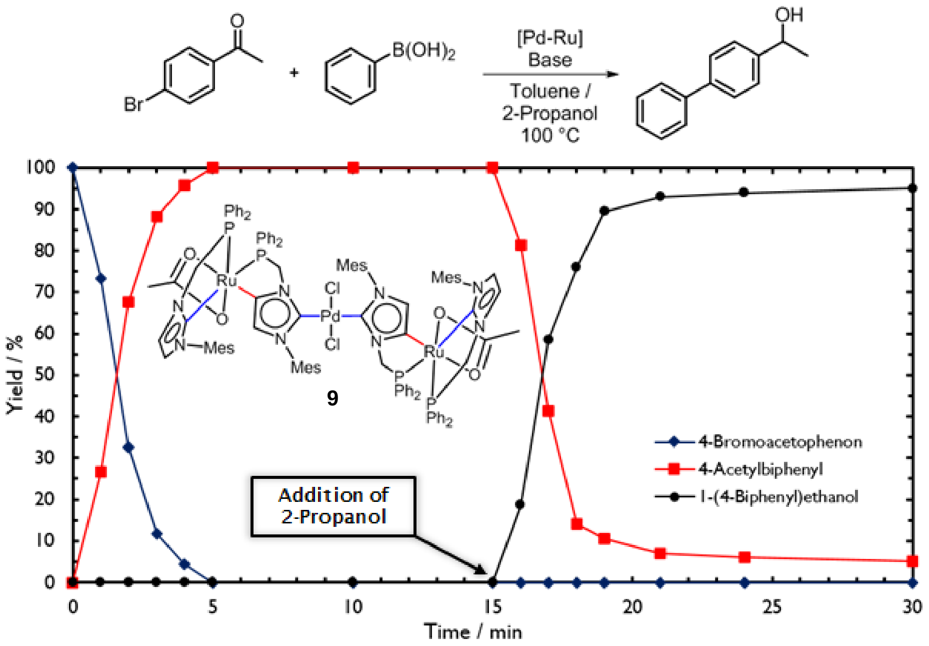


Figure 20: Tandem Suzuki-Miyaura/transfer hydrogenation process using Pd–Ru NHDC complex **9** as catalyst.

It was determined that the reaction follows a consecutive course, with the cross-coupling being the first step followed by reduction of the resulting biphenyl ketones. A competing reaction pathway involves Pd-catalyzed dehalogenation of the applied bromoacetophenones and subsequent hydrogenation to 1-phenylethanol. The product distribution can be influenced by the nature and concentration of the base mediating the catalytic process: while alkoxides promote dehalogenation reactions, the selectivity towards the desired biphenyl alcohols is enhanced by the usage of potassium hydroxide. However, due to in-situ formation of alkoxides in the applied reaction medium (toluene/2-propanol), significant amounts of undesired dehalogenation products were formed. Taking advantage of the consecutive course of the reaction, the cross-coupling step was thus performed in absence of 2-propanol until the bromoacetophenones were fully consumed, and transfer hydrogenation was then initiated by addition of 2-propanol (Figure 20), yielding up to 98% of the desired product. The combination of this reaction protocol with Pd–Ru complex **9** as catalyst constitutes a major improvement regarding catalyst loadings and reaction times as compared to existing homogeneous catalytic systems for this tandem transformation. Furthermore, it was established that the bimetallic Pd–Ru NHDC complex displays superior performance over the combination of monometallic species with stereoelectronic properties similar to **9**, indicating the ample potential of multinuclear NHDC complexes for further applications in tandem catalysis.

4. CONCLUSION AND OUTLOOK

In this work different aspects of functionalized *N*-heterocyclic carbene ligands have been investigated. The research topic covers various concepts employed for Ir and Ru metals, and due to the specific properties of one phosphine-functionalized NHC, even access to Ru-based heterobimetallic systems is permitted.

Using a bispyridine-functionalized carbene ligand, dynamic Ir(I)-NHC complexes were synthesized and allowed both experimental and theoretical studies which shed light into the so far neglected phenomenon of fluxional hemilability. The results add important insights to previously reported concepts[62-63] and provide quantitative data for the bond strength of *N*-donors to Ir centers. It was established that in this specific motif, the interaction falls in the range of ca. 10 kcal/mol, a value that might be similar for related widespread *N*-donor functionalized Ir(I)-NHC complexes. In addition, unexpected reactivity of the involved complexes was observed, leading to a monocarbonyl Ir species as well as a comparatively stable Ir(III) dihydride, two species which are rarely reported in the literature. Finally, the impact of fluxional hemilability on the catalytic stability was examined and revealed that the investigated system is among the most stable Ir-carbene catalysts reported so far, with more than 9000 turnovers for the transfer hydrogenation of acetophenone. Consequently, the presented work will allow the synthesis of highly active and stable hemilabile TH catalysts in the future.

A flexible, alkyl-bridged tetraimidazolium salt was used as ligand precursor for the synthesis of the first Ru(II) tetracarbenes bearing open-chain ligands, and viable additions to the coordination behavior of this ligand structure were enabled by the use of different alkyl linkers. The orientation of the chelating ligand (equatorial vs. sawhorse) can selectively be controlled by reaction with further reagents like phosphines and nitriles, resulting in a versatile system which can be specifically tailored for the desired application. Accordingly, both an equatorially and sawhorse-type structure were employed in TH catalysis, and in particular the latter motif achieved remarkable turnover frequencies, rendering Ru-tetracarbenes as promising alternatives to existing Ru-NHC based TH catalysts. Future work in this field should examine the beneficial properties of tetracarbenes regarding catalyst stability in order to obtain catalytic systems which can be used in very low amounts.

A completely unexpected reactivity was observed when the synthesis of a phosphine-functionalized abnormal Ru(II) carbene complex was attempted: instead of the expected monocarbene complex, a system bearing both an abnormal and a normal carbene ligand was obtained, constituting a novelty in Ru chemistry. Even more important, this species allowed synthetic access to bimetallic NHDC compounds via simple metalation and transmetalation protocols, enabling the formation of formerly unknown imidazolyl-based NHDC complexes bearing two different transition metals.

While Ag–Ru, Au–Ru and Pd–Ru systems were successfully isolated and characterized, the methodology is certainly not yet fully exploited and should provide further bimetallic NHDC compounds in due course. As all NHDC compounds reported in this thesis are derived from a single Ru-aNHC precursor, particular attention should be on the development of related aNHC motifs with similar reactivity. Especially systems comprising different metals might be viable additions to the synthetic approach presented within this work, and based on their structural and electronic properties, utilization of Crabtree's abnormal carbene complexes (Figure 21) as precursor for analogous reactions might be feasible.[146]

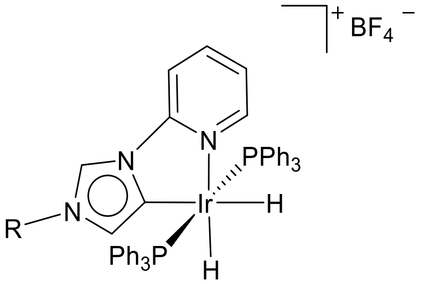
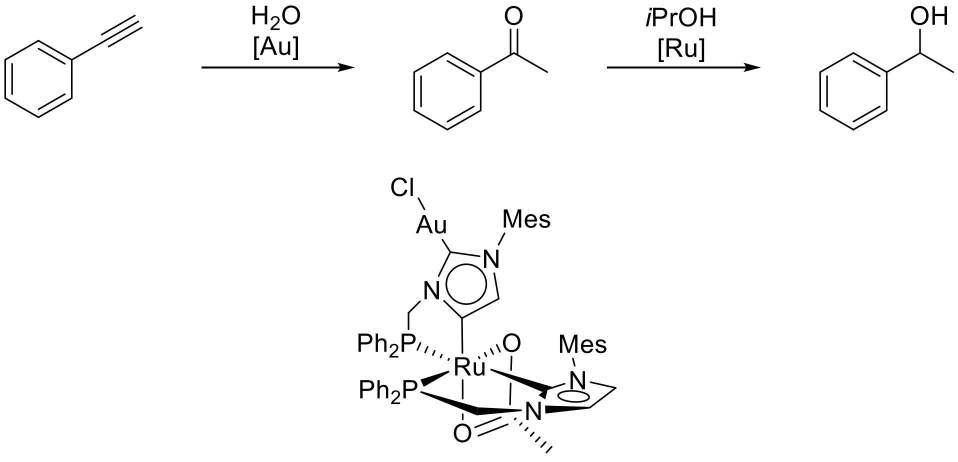


Figure 21: Ir-aNHC complex reported by Crabtree et al. with similar structural and electronic properties as Ru-NHC complex **6**.[146]

This work further shows that NHDC complexes are highly interesting for application in tandem catalysis, as the Pd–Ru complex was established as efficient catalyst for one-pot Suzuki-Miyaura/transfer hydrogenation reactions for a variety of organic substrates. In fact, after optimization of the reaction conditions including the order of solvent addition, the presented method is the most active homogeneous system for this transformation reported to date and indicates the potential of imidazolyl-derived NHDCs in the growing field of tandem catalysis. Therefore, it should be the focus of future research to establish further protocols involving the related NHDC compounds presented within this work. For example, the Au–Ru derivative **8** could be an attractive candidate for a combined alkyne hydration/transfer hydrogenation procedure as depicted in Scheme 9.



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Scheme 9: Possible tandem alkyne-hydration/TH procedure using Au–Ru complex **8** as catalyst.

For the implementation of this system it will be crucial to achieve compatible reaction conditions, as so far the former step usually proceeds in acidic media,[147-148] while the latter requires the presence of a base in order to operate efficiently.[36] However, interesting contributions to the field of alkyne hydration were published by Nolan et al., who successfully performed hydration reactions in absence of acid.[149]

Of course the applicability of bimetallic NHDCs is not limited to this specific example, as almost unlimited applications for transition metal NHC complexes have been reported in the past.[25,126,150] However, so far the synthesis of NHDC complexes is still comparatively complicated and should be simplified in order to increase the attractiveness for these systems in industrial applications. A further long-term goal should be the development of asymmetric variations of NHDC catalysts with the ability to induce enantioselectivity to the catalytic transformation. In combination with the attractive and beneficial properties of tandem procedures – i.e. cost, time and waste reduction – the application of such highly sophisticated systems would be a major breakthrough in order to achieve sustainable and economic catalysts for the synthesis of fine chemicals, cosmetics and pharmaceuticals.

In summary, this work contributes novel aspects to the already extensively studied field of *N*-heterocyclic carbenes. Although so many variations of this most widespread motif have been reported in the past decades, highly specific variations can still enable unknown reactivity or unique coordination properties, disclosing novel pathways to formerly unidentified phenomena and applications. Thus, despite their abundance, the future of functionalized NHCs appears to be bright.

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5.2 Controlling Coordination Geometries: Ru-Carbene Complexes with Tetra-NHC Ligands

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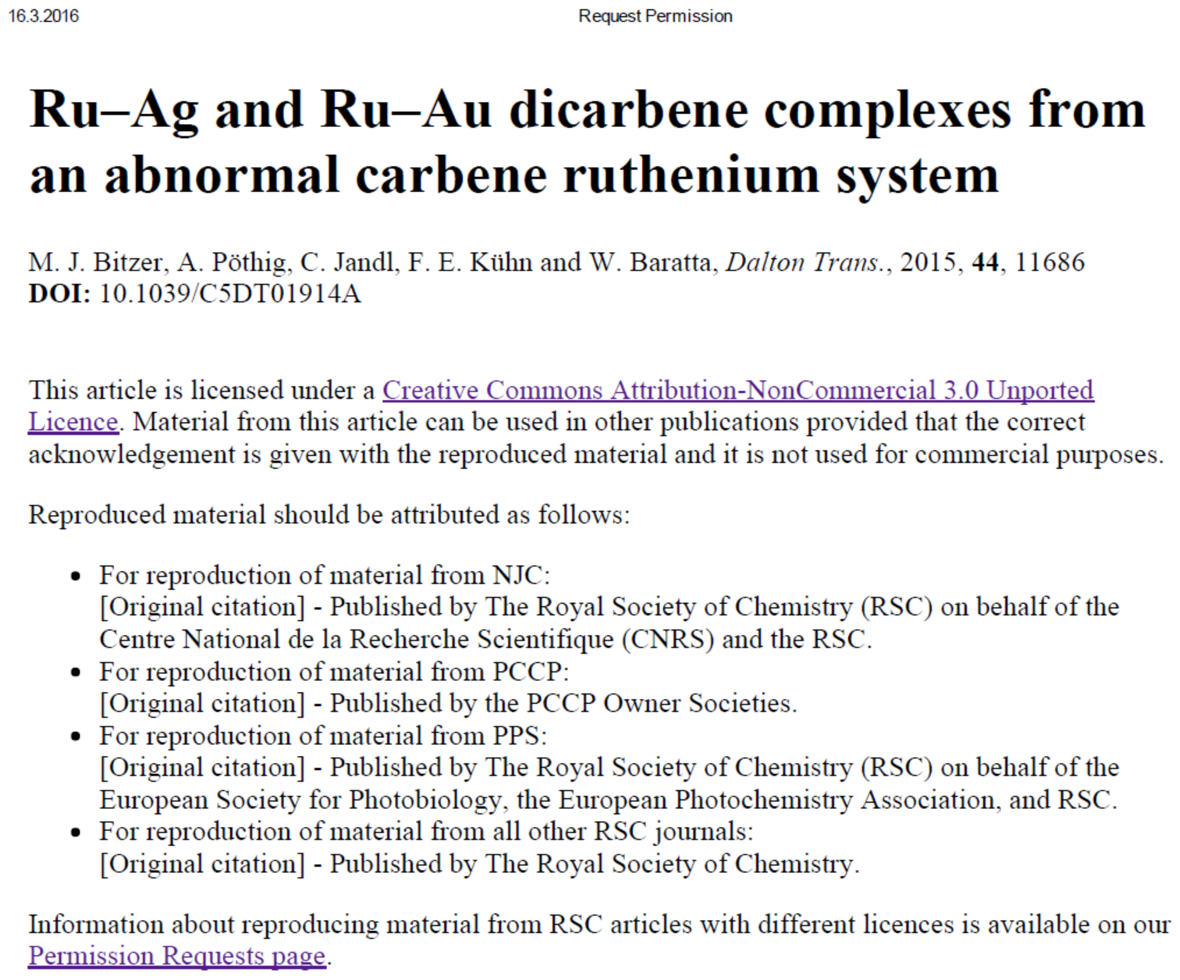

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M. J. Bitzer, A. Pöthig, C. Jandl, F. E. Kühn and W. Baratta, *Dalton Trans.*, 2015, **44**, 11686
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6. BIBLIOGRAPHIC DATA OF COMPLETE PUBLICATIONS

6.1 On The Concept of Hemilability: Insights into a Donor Functionalized Iridium(I) NHC Motif and Its Impact on Reactivity

Korbinian Riener,[†#] **Mario J. Bitzer**,[†#] Alexander Pöthig,[†] Andreas Raba,[†] Mirza Cokoja,[†] Wolfgang A. Herrmann,[†] and Fritz E. Kühn[†]

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INORGANIC CHEMISTRY **2014**, *53*, 12767-12777

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Direct link: DOI 10.1021/ic5016324

6.2 Controlling Coordination Geometries: Ru-Carbene Complexes with Tetra-NHC Ligands

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INORGANIC CHEMISTRY **2016**, *55*, 6010-6017

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6.3 Ru-Ag and Ru-Au Dicarbene Complexes from an Abnormal Carbene Ruthenium System

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6.4 Tandem Suzuki-Miyaura/Transfer Hydrogenation Reaction Catalyzed by a Pd-Ru Complex Bearing an Anionic Dicarbene

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8. COMPLETE LIST OF PUBLICATIONS

[1] *On the Concept of Hemilability: Insights into a Donor-Functionalized Iridium(I) NHC Motif and Its Impact on Reactivity*
K. Riener,* M. J. Bitzer,* A. Pöthig, A. Raba, M. Cokoja, W. A. Herrmann, F. E. Kühn, *Inorganic Chemistry* **2014**, *53*, 12767-12777. (*: equally contributing first authors)

[2] *Controlling Coordination Geometries: Ru-Carbene Complexes with Tetra-NHC Ligands*
M. Hollering, D. T. Weiss, M. J. Bitzer, C. Jandl, F. E. Kühn, *Inorganic Chemistry* **2016**, *55*, 6010-6017.

[3] *Ru-Ag and Ru-Au Dicarbene Complexes from an Abnormal Carbene Ruthenium System*
M. J. Bitzer, A. Pöthig, C. Jandl, F. E. Kühn, W. Baratta, *Dalton Transactions* **2015**, *44*, 11686-11689.

[4] *Tandem Suzuki-Miyaura / Transfer Hydrogenation Reaction Catalyzed by a Pd-Ru Complex Bearing an Anionic Dicarbene*
M. J. Bitzer, F. E. Kühn, W. Baratta, *Journal of Catalysis* **2016**, *338*, 222-226.

9. CURRICULUM VITAE

CURRICULUM VITAE

Mario Johannes Bitzer

* 03.10.1986

EDUCATION

05/2013 – present **Ph. D. Studies (Catalysis Research Center/Molecular Catalysis, TUM)**

- Cooperative project between TUM and Università di Udine, Italy
- Research and teaching assignments in Udine
- Research topic: Novel coordination modes of carbene ligands and their application in (tandem-)catalysis

10/2010 – 04/2013 **Master of Science, Chemistry (TUM, Germany)**

- Main focus: Organic Chemistry and Catalysis
- Master's Thesis: *Synthesis, Characterization and Reactivity of Hemilabile Iridium NHC Complexes*

10/2007 – 08/2010 **Bachelor of Science, Chemistry (TUM, Germany)**

- Bachelor's Thesis: *Synthesis of Lipophilic Photosensitizers for Photocatalytic Reduction of* CO_2 *in Micelles*

08/1997 - 06/2006 **Abitur (Albertus-Magnus-Schule, Viernheim, Germany)**

- Best graduate in the chemistry Abitur examination

FOREIGN EXPERIENCE

09/2015 – 11/2015 **Università di Udine, Dipartimento DI4A, Chimica, Udine, Italy**
and Erasmus-STA
02/2014 – 03/2014 Research- and teaching assignment in the group of Prof. W. Baratta

04/2011 – 09/2011 **Bayer (South East Asia) Pte Ltd, Singapore**
Research Assistant, Functional Films Research Center
Developed transparent composite materials for display fabrication

FURTHER PROFESSIONAL EXPERIENCE

05/2009 – 04/2013 **Technical University of Munich, Germany**
Tutored students in practical courses and seminars

06/2007 – 09/2007 **Dr. Franz Köhler Chemie, Bensheim, Germany**
Internship, Analytical Laboratory, Quality Assurance
Analyzed raw materials and finished products

04/2007 – 05/2007 **ALSTOM Power Generation, Mannheim, Germany**
Internship, Power Plant Chemistry Competence Center
Analyzed boiler residues of power plants;
Acquired, assembled and documented parts for analytical instruments

AWARDS AND STIPENDS

2015	GDCh (German Chemical Society) travelling scholarship
since 2013	careerloft
since 2012	e-fellows.net
2006	GDCh (German Chemical Society) award for best Abitur examination in Chemistry

FURTHER EDUCATION

2016	*Project Management - compact* TUM Graduate School, 3-day seminar
2016	*Team Leadership* TUM Graduate School, 2-day seminar
2015	*Development of Leadership Skills* TUM Graduate School, 2-day seminar
2015	*Business Idea and Market: Business Plan Basic Course* Unternehmertum GmbH, Garching, Germany Draft of a business plan for an own business idea

LANGUAGES

German	first language
English	business fluent
Italian	good knowledge
French	basic knowledge
Russian	basic knowledge

PERSONAL INTERESTS & COMMITMENT

Sports	Football, Squash
09/2009 – 10/2012	Member of the student union („Fachschaft”) • Section supervisor • Mentoring of younger students

CIVILIAN SERVICE

07/2006 – 02/2007	**Arbeiterwohlfahrt** Worker's Welfare Association, Viernheim, Germany

Munich, July 8, 2016

Mario Bitzer