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Homogeneous Catalysis and Supramolecular Chemistry: Diverse Applications of Transition Metal Complexes

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A Winner is a Dreamer Who Never Gives Up

Nelson Mandela

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Zusammenfassung

Vor dem Hintergrund der sehr speziellen Voraussetzungen für die verschiedenen Bereiche der homogenen Katalyse sind die sterischen und elektronischen Anforderungen an Übergangsmetallkomplexe immer größer geworden. Besonders die *N*-heterozyklischen Carbenliganden wurden stetig weiterentwickelt und modifiziert um den steigenden Ansprüchen gerecht zu werden. Eine der bedeutendsten Umsetzungen ist die Transferhydrierung mit Ruthenium-basierten NHC-Komplexen.

Im Kontext dieser Arbeit liegt der Hauptfokus auf der Entwicklung mehrzähliger NHC Liganden. Die Einführung von drei- oder vierzähligen, offenkettigen NHC Liganden, die über Alkylbrücken miteinander verbunden sind, kombiniert die Vorteile der Chelatisierung mit einem hohen Grad an koordinativer Variation. Die hier beschriebenen offenkettigen Ruthenium(II)-tetra-NHC Komplexe weisen sägebockartige oder äquatoriale Koordination auf. Neben der Länge der Alkylbrücken beeinflusst auch die Koordination von Nucleophilen die Koordinationsgeometrie. Beide Struktur motive wurden auf ihre katalytische Aktivität in der Transferhydrierung getestet. Besonders der Komplex in Sägebock-Konformation weist eine bemerkenswert hohe Aktivität auf. Zusätzlich wurde ein weiterer offenkettiger Ruthenium(II) Komplex mit einem normalen imidazolbasierten und zwei abnormalen triazolbasierten Carbenen beschrieben. Der Komplex weist eine meridionale Koordination auf, wobei für das verwendete Modellsystem vielversprechende Ergebnisse in der Transferhydrierung erhalten wurden.

Kohlenstoffdioxid wird in der Industrie derzeit nur sehr spärlich für die chemische Synthese verwendet. Demzufolge liegt in der konzeptionellen Studie besonderes Augenmerk auf der katalytischen Umsetzung von CO₂ zu Acrylsäure und deren Derivaten. Besonders in Bezug auf Nachhaltigkeit ist die photokatalytische Aktivierung von CO₂ von großem Interesse. Entsprechend wurden Vorstufen von Rhenium(I) Biphosphinin Komplexen synthetisiert, die möglicherweise als interessante Alternative zu bereits bestehenden Rhenium-basierten Systemen gesehen werden können.

Außerdem werden supramolekulare Koordinationskäfige als selektive Transportsysteme für Krebsmedikamente im Zuge dieser Arbeit untersucht. Biologische Bildgebungsverfahren basierend auf Fluoreszenzmikroskopie werden beschrieben, um die Aufnahme der Metallkäfige mit dem eingelagerten Krebsmedikament Cisplatin in der Zelle zu verfolgen. Nachfolgend wurden verschiedene Konzepte zur Steigerung der Lumineszenz der Käfige untersucht. Ein Käfig mit außergewöhnlich hoher Quantenausbeute von 66% wurde beschrieben.

Abstract

In the light of very specific requirements for the diverse applications in homogeneous catalysis, variation of steric and electronic characteristics of transition metal complexes become more sophisticated. In particular, *N*-heterocyclic carbene ligands have been extensively modified and tailored to increasingly delicate catalytic reactions. One of the most fundamental transformations, the transfer hydrogenation has become the center of attention especially for ruthenium-based NHC complexes.

In the context of this work, the main focus is on the development of polydentate NHC ligands. The introduction of three or four NHC moieties connected by alkyl bridges combines the advantages of chelation with a high coordinative variability, due to acyclic ligand motifs. Open-chain ruthenium(II) tetra-NHC complexes are synthesized and show either sawhorse-type or equatorial coordination. Besides the length of the alkyl linker, additional coordination of nucleophiles to the two remaining coordination sites influences the coordination geometry. Evaluation of both structural motifs in transfer hydrogenation revealed a remarkable activity of the ruthenium(II) tetra-NHC complex with sawhorse-type geometry. Another open-chain ruthenium(II) complex featuring a normal 2-imidazolyldene as well as two abnormal 1,2,3-triazolyldene carbene moieties is synthesized. The complex with the meridional coordinated tri-NHC ligand shows promising results for the transfer hydrogenation of the employed model substrate.

Carbon dioxide is currently only rarely used for chemical synthesis in industry. Consequently, attention is drawn to the catalytical transformation of CO₂ to acrylic acid and its derivatives in a conceptual study. Photocatalytic activation of carbon dioxide is highly interesting in terms of sustainability. Herein, precursors for potentially active rhenium(I) biphosphinine photocatalysts are described with the aim to vary the chromophoric system of already established rhenium(I)-based systems.

Furthermore, supramolecular coordination cages and their applicability as selective drug carriers for anticancer medication are examined in this work. Biological imaging using fluorescence microscopy of the uptake of the metallocages with the encapsulated drug cisplatin into the cells is attempted. Subsequently, rational approaches to highly luminescent cage compounds are discussed leading to an exceptionally high quantum yield of 66%.

List of Abbreviations

5c-6e	five-center six-electron
aNHC	abnormal <i>N</i> -heterocyclic carbene
B3LYP	Becke, three parameter, Lee-Yang-Parr exchange-correlation functional
CuAAC	Cu(I)-catalyzed azide-alkyne 1,3-cycloaddition
DFT	density functional theory
DMSO	dimethyl sulfoxide
equiv.	equivalent
ESI	electrospray ionization
GC	gas chromatography
HOMO	highest occupied molecular orbital
<i>i</i> PrOH	<i>iso</i> -propanol, 2-propanol
IR	infrared
L	ligand
LUMO	lowest unoccupied molecular orbital
M	metal
Me	methyl
Mes	mesityl
MIC	mesoionic carbene
MO	molecular orbital
MOF	metal-organic framework
MS	mass spectrometry
MPV	Meerwein-Ponndorf-Verley
NHC	<i>N</i> -heterocyclic carbene
NMR	nuclear magnetic resonance
ORTEP	Oak Ridge Thermal Ellipsoid Plot
P	protective group
Ph	phenyl
PHC	<i>P</i> -heterocyclic carbene
ppm	parts per million
r.t.	room temperature
rNHC	remote <i>N</i> -heterocyclic carbene

SC-XRD	single crystal X-ray diffraction
SCC	supramolecular coordination complex
<i>t</i> Bu	<i>tert</i> -butyl
TEP	Tolman electronic parameter
TD	time-dependent
<i>tert</i> -BuNC	<i>tert</i> -butyl isocyanide
TH	transfer hydrogenation
THF	tetrahydrofuran
TOF	turnover frequency
TON	turnover number
VT	variable temperature
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Table of Contents

1	Introduction	1
1.1	Homogeneous Catalysis	2
1.2	<i>N</i> -heterocyclic Carbene Complexes and their Application in Transfer Hydrogenation Catalysis	4
1.2.1	Development of <i>N</i> -heterocyclic Carbene Ligands	4
1.2.2	Synthetic Access Routes to NHC Metal Complexes	6
1.2.3	Efficient Variation of Steric and Electronic Properties of NHC Precursors	9
1.2.4	Advances to Abnormal Coordination Modes	12
1.2.5	Polydentate <i>N</i> -heterocyclic Carbenes	16
1.2.6	Transfer Hydrogenation Catalysis	19
1.3	Transition Metal Mediated Transformation of Carbon Dioxide	22
1.4	From Homogeneous Catalysis to Novel Applications in Supramolecular Chemistry	23
2	Objective	25
3	Results – Publication Summaries	28
3.1	Controlling Coordination Geometries: Ru–Carbene Complexes with Tetra-NHC Ligands	30
3.2	Bonding and Catalytic Application of Ruthenium <i>N</i> -Heterocyclic Carbene Complexes Featuring Triazole, Triazolylidene and Imidazolylidene Ligands	32
3.3	Transition metal mediated coupling of carbon dioxide and ethene to acrylic acid/acrylates	34
3.4	[Re(CO) ₃ Cl(C ₅ H ₄ CIP) ₂] and [Re(CO) ₂ Cl(C ₅ H ₄ CIP) ₃]: synthesis and characterization of two novel rhenium(I) phosphinine complexes	36
3.5	Evaluation of New Palladium Cages as Potential Delivery Systems for the Anticancer Drug Cisplatin	38
3.6	Supramolecular <i>exo</i> -functionalized palladium cages: fluorescent properties and biological activity	40
3.7	Self-assembly of highly luminescent heteronuclear coordination cages	42
4	Conclusion and Outlook	44
5	Reprint Permissions	48
5.1	Controlling Coordination Geometries: Ru–Carbene Complexes with Tetra-NHC Ligands	49

5.2	Bonding and Catalytic Application of Ruthenium <i>N</i> -Heterocyclic Carbene Complexes Featuring Triazole, Triazolylidene and Imidazolylidene Ligands ..	50
5.3	Transition metal mediated coupling of carbon dioxide and ethene to acrylic acid/acrylates ..	51
5.4	[Re(CO) ₃ Cl(C ₅ H ₄ CIP) ₂] and [Re(CO) ₂ Cl(C ₅ H ₄ CIP) ₃]: synthesis and characterization of two novel rhenium(I) phosphinine complexes ..	56
5.5	Evaluation of New Palladium Cages as Potential Delivery Systems for the Anticancer Drug Cisplatin ..	57
5.6	Supramolecular <i>exo</i> -functionalized palladium cages: fluorescent properties and biological activity ..	61
5.7	Self-assembly of highly luminescent heteronuclear coordination cages ..	62
5.8	Figures and Schemes ..	63
6	Bibliographic Data of Complete List of Publications ..	64
7	References ..	72
8	Complete List of Publications ..	83
9	Appendix ..	85

1 INTRODUCTION

1.1 Homogeneous Catalysis

The chemical industry is one of the most international and competitive industries, which is also connected to a wide field of processing and manufacturing activities. Consequently, it supplies virtually all sectors of the economy and provides a significant contribution to net exports. In Figure 1, the scope of the world chemicals sales and trade flows by region is depicted. While Europe is still one of the largest contributors, world sales were largely driven by China in 2014.¹

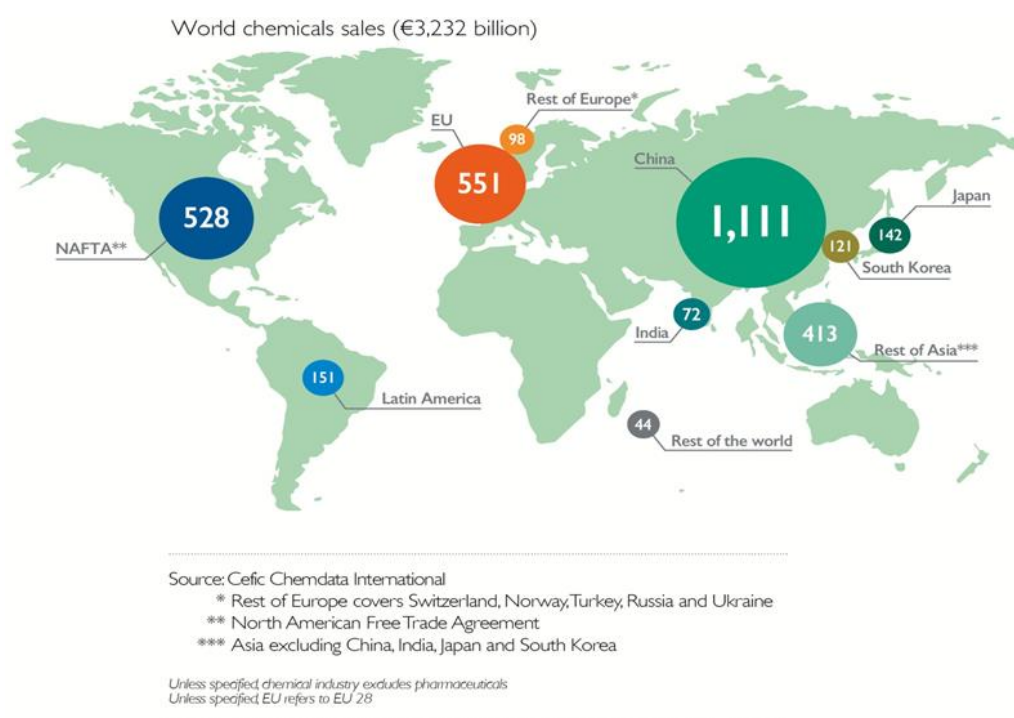


Figure 1. Worldwide chemicals sales in 2014, which amount to a total of €3,232 billion. Noteworthy, Asia chemicals production outpaces other regions, even when global sales grew only 2.6% in 2014. Reprinted with permission from Cefic Chemdata International 2016. Copyright 2016 Cefic.

Figure 2 illustrates the segments of the chemical industry in Europe in 2014.¹ The three main sectors are base chemicals, specialty chemicals and consumer chemicals. Base chemicals are considered commodity goods and are manufactured at a high volume. Specialty chemicals are produced in smaller volumes and consist of a very heterogeneous product portfolio. Consumer chemicals are all products that are sold to the final customer and make up for only 12.6%. The development and production of chemical products on this scale is only possible with the use of catalysts.²

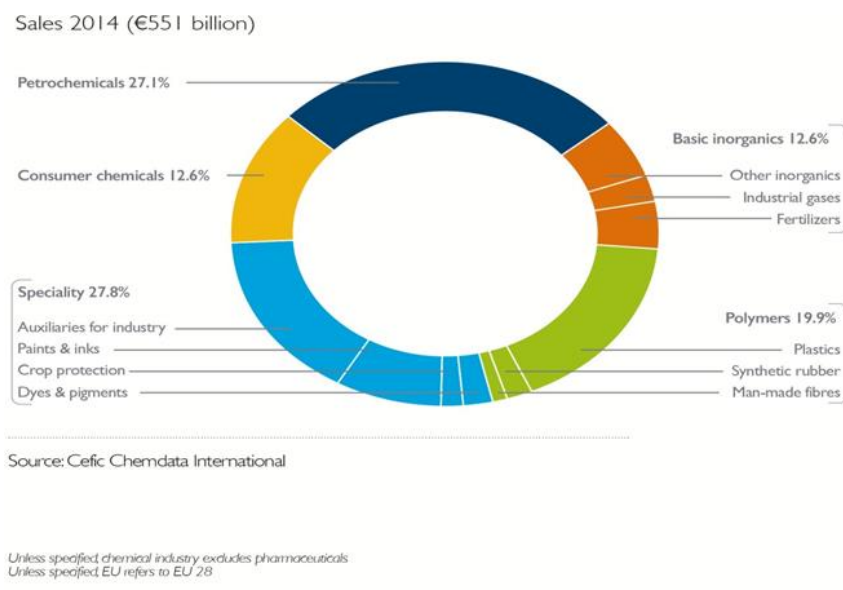


Figure 2. EU chemicals sales by sector (excluding pharmaceuticals) amounting to a total of €551 billion in 2014.¹ Reprinted with permission from Cefic Chemdata International 2016. Copyright 2016 Cefic.

Taking into account economical and ecological aspects, the use of catalysts is imperative, since catalysts reduce the energy demand and can alter the reaction pathways and products to higher selectivities. Undesired products are avoided and waste is minimized. Consequently, “greener” pathways in the synthesis of both bulk and fine chemicals are developed.²⁻⁵ Heterogeneous processes are still state-of-the-art for large scale chemical transformations in industry, taking up around 80% of all catalytic processes, due to easier separation of catalyst and product.^{2,4} Homogeneous systems amount to roughly 15%, and biocatalysts to the remaining 5%. However, during the last decades, homogeneous catalysis has grown significantly and the development of new transition metal complexes established homogeneous catalysis in various fields. Industrially applied homogeneous transition metal mediated catalysis includes hydrogenation, oxidation (e.g. hydrocarbons), polymerization, isomerization, metathesis, oligomerization, hydrosilylation and hydrocyanation among others.^{2,4}

The economic significance of hydrogenation and transformation reactions provides the rationale for the main focus of this work. In addition, to a close examination of transfer hydrogenation reactions, the concept of goal-oriented design will be explored with respect to the development of new catalyst structural motifs. Transformation of carbon dioxide and its utilization in synthetic chemistry will be investigated on a conceptual as well as a synthetic level. The third part will be focusing on the transition of homogeneous catalysts to novel applications of supramolecular systems.

1.2 *N*-heterocyclic Carbene Complexes and their Application in Transfer Hydrogenation Catalysis

In this section, an extensive account of *N*-heterocyclic carbene chemistry will be presented, focusing on the early history of NHC ligands, synthetic advantages and challenges, complex formation, electronic as well as steric characteristics and recent developments in NHC chemistry. Coupled with reports on interesting applications in homogeneous catalysis, this will provide a contextual basis for the NHC based research presented in this work.

1.2.1 Development of *N*-heterocyclic Carbene Ligands

Ever since the first evidence of their existence, carbenes have played an important role in organometallic chemistry. Carbenes are rarely stable in the free state due to their thermodynamic as well as kinetic instability and resulting high reactivity.^{4,6} In general, the derived metal carbene complexes are divided in two groups, the Fischer⁷ (singlet carbene) and the Schrock⁸ (triplet carbene) type carbene complexes. In case of the Fischer type carbene, direct carbon to metal donation dominates and the carbon acts as a 2 e⁻ lone-pair donor, resulting in preferred coordination to late transition metals in low oxidation states. Schrock carbenes, however; are usually bound to early transition metals with high oxidation states, resulting in a formal double bond due to strong back-bonding.⁴ One of the most prominent class derived of Fischer-type carbenes are without doubt *N*-heterocyclic carbenes with countless reports within the last two decades.^{6,9-11} Just a couple of years after the first real metal carbene complex was reported by Fischer^{7,12} *et al.*, Öfele¹³⁻¹⁴ and Wanzlick¹⁵ *et al.* independently described chromium and mercury transition metal complexes with *N*-heterocyclic carbene ligands (Figure 3).

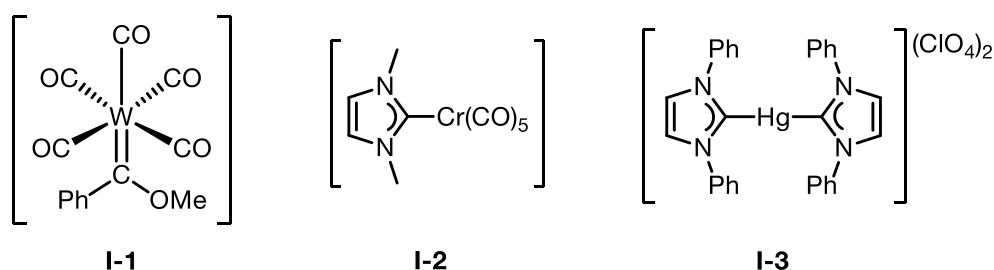


Figure 3. Early metal carbene complex **I-1** described by Fischer *et al.*⁷ Öfele and Wanzlick *et al.* reported the first *N*-heterocyclic transition metal complexes **I-2** and **I-3** over half a century ago in 1968.^{13,15}

Following these initial reports, Lappert and coworkers described compounds derived from electron rich olefins, however, attempts to isolate a stable free *N*-heterocyclic carbene remained unsuccessful for two more decades.¹⁶⁻²⁰

In 1991, the common scientific perspective of carbene related chemistry drastically changed, when Arduengo and coworkers presented one of the first examples of stable free carbenes (Figure 4). Bulky adamantyl wingtip groups at the nitrogen atoms effectively shielded the reactive, electron deficient carbene carbon due to steric hindrance in addition to the electronic stabilization effect of the nitrogen donors in the imidazolylidene moiety.

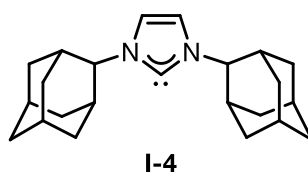


Figure 4. Arduengo's stable crystalline *N*-heterocyclic carbene, the isolable 1,3-di-1-adamantyl-imidazol-2-ylidene.²¹

The tipping point that finally started the golden age of NHC complexes was initiated by the first catalytic application described by Hermann *et al.* in 1995.²² Consequently, this previously intangible intermediary, highly reactive species of NHCs rapidly transformed into a convenient, easily tunable spectator ligand class in organometallic chemistry and homogeneous catalysis.^{6,23-26} Following these discoveries, a third type of carbenes was introduced, the Wanzlick-Arduengo carbenes. This distinction was necessary, since NHC complexes are different from both extremes, the Fischer and the Schrock carbenes and their opposing reactivities.¹¹ Contrary to the high reactivity towards Lewis bases (Fischer carbenes) or Lewis acids (Schrock carbenes), NHC transition metal complexes show generally a high stability and metal carbene bonds are exceptionally robust, often almost inert against moisture, heat and oxygen.¹¹ Considering the electronic situation, these properties are due to a strong σ -donor and low π -backbonding ability, which are derived from their intrinsic stabilization caused by an N-C p_{π} - p_{π} bonding interaction of the nitrogen atoms next to the carbene carbon atom. Consequently, nucleophilic attack on the carbon is hindered since the p -orbital is already partially filled.^{11,27}

Although NHCs started out as phosphine mimics, the stability of the transition metal complexes of *N*-heterocyclic carbenes especially the low oxidation reactivity combined with

convenient synthetic protocols is often cited as one of the key advantages of these ligands versus their organophosphine counterparts.²⁸ In addition, typically NHCs show stronger σ -donor character than even the most donating phosphines PR_3 .^{4,29} The wingtip groups R influence the steric effect on NHCs, but due to the fan shape, compared to cone shaped PR_3 ligands, freely rotating NHC ligands are less bulky than phosphines and the largest effect on the Tolman electronic parameter (TEP) is caused by the nature of the ring (Figure 5).^{4,30-31}

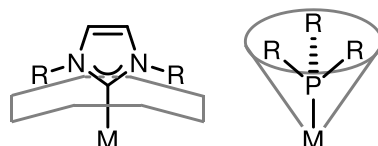
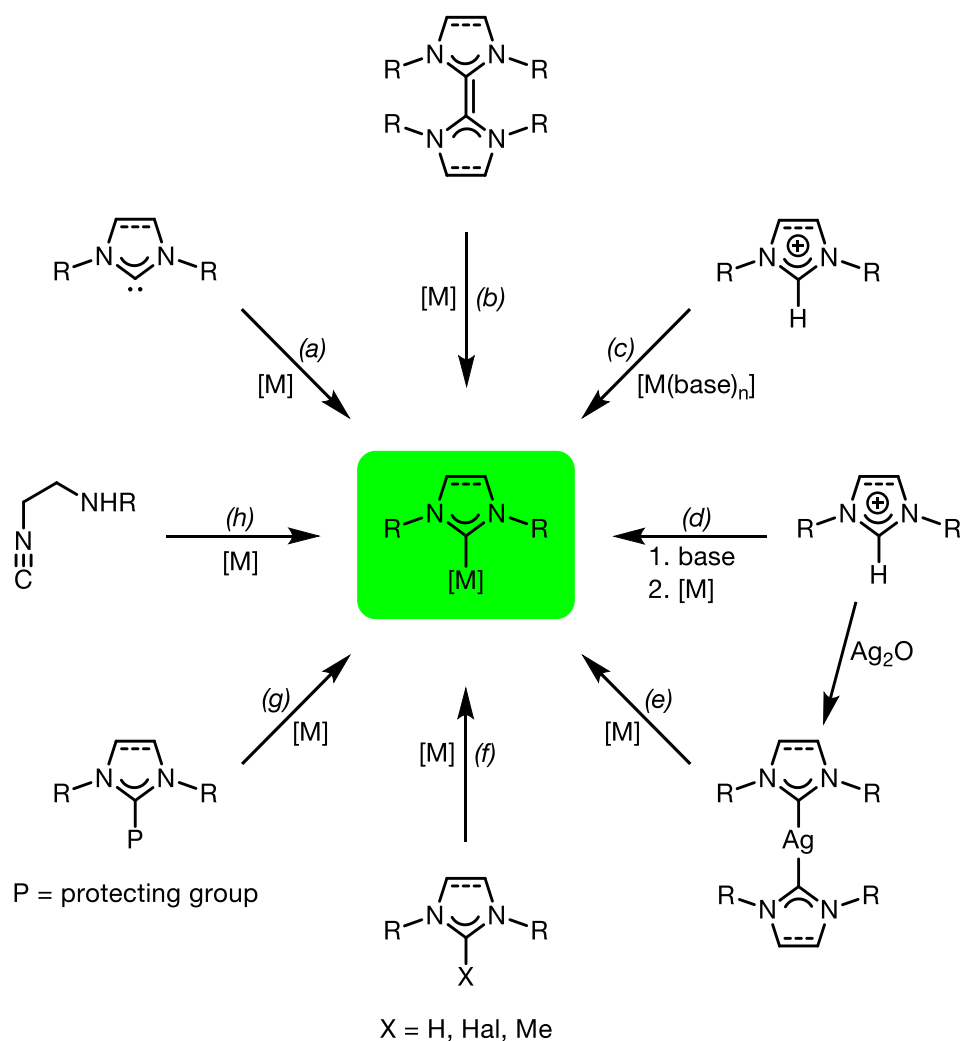


Figure 5. Schematic fan shaped NHC and cone shaped phosphine metal complexes.^{6,32}

1.2.2 Synthetic Access Routes to NHC Metal Complexes

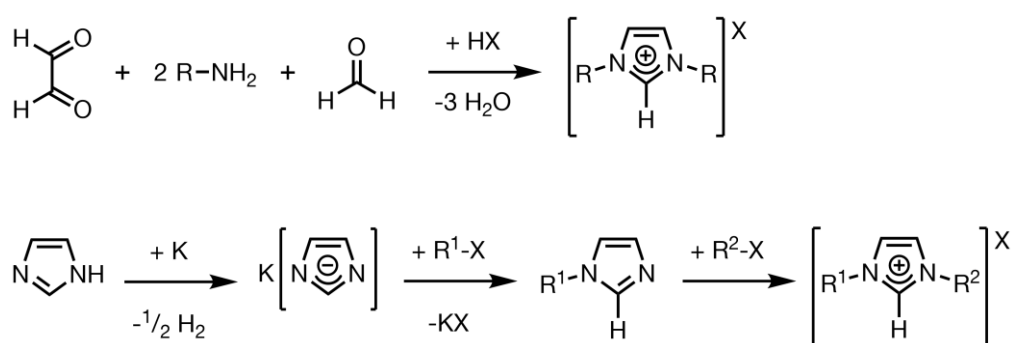
Nowadays several pathways leading to the formation of *N*-heterocyclic carbene (transition) metal complexes exist. The great variation in not only the metal precursors, but also in the employed NHC ligands with a plethora of electronic and steric properties renders different approaches more useful than others for specific target structures. The most prominent synthetic routes are depicted in Scheme 1.



Scheme 1. Varying synthetic methods towards NHC complexes.³³⁻³⁴

- (a) Reaction of the free carbene with a suitable metal precursor^{21,35-38}
- (b) Insertion of a coordinately unsaturated electrophilic metal center in enetetramines¹⁶⁻²⁰
- (c) Deprotonation of azolium salts using metal precursors with basic ligands, acting as internal bases^{13,15,39-41}
- (d) *In situ* deprotonation of azolium salts and reaction with metal precursors in an one-pot reaction^{36,42-44}
- (e) Transmetalation of silver NHC complexes⁴⁵⁻⁴⁷
- (f) Oxidative additions of suitable metal-precursors into C-X bonds (X = H, Hal, Me)⁴⁸⁻⁵¹
- (g) Synthesis with protected NHCs for *in situ* carbene generation^{43,52-54}
- (h) Template-controlled synthesis of protic NHC ligands⁵⁵⁻⁵⁹

Deprotonation of the NHC precursor is one of the most common routes to NHC metal complexes. Therefore, methods (a), (c), (d) and (e) are related as they all depend on the use of bases. The main advantage of preformed free NHCs is that they are directly used to replace labile ligands on a suitable metal complex precursor. The main disadvantage is their air and moisture sensitivity, which increases the synthetic effort. In case of method (c), *in situ* deprotonation is achieved by basic ligands coordinated to the metal precursors, for example acetates, hydrides or alkoxides. The most famous synthesis protocols using basic metal complexes were reported by Öfele and Wanzlick *et al.*, who synthesized the first imidazolylidene metal complexes in 1968.^{13,15} Method (d) relies on *in situ* deprotonation by an external base added to a mixture of the NHC precursor and a metal precursor. Various bases with differing basicity have been successfully employed for the generation of NHC complexes. However, especially strong bases are known to facilitate side reactions in ligand or metal precursors with electrophilic or acidic functional groups. These observations triggered the search for a viable milder alternative, which was established by Wang and Lin in 1998.⁴⁶ In this case, the azolium salt is deprotonated by Ag₂O, which acts as both base and metal source (method (e)). The easily generated Ag-NHC complex is subsequently used as an effective transmetalation agent, due to a comparably labile silver-carbene bond. The huge number of easily accessible azolium salts in combination with a mild transmetalation reaction, which tolerates a wide range of functional groups, paved the way for highly functionalized NHC metal complexes.⁴⁵ This prominent approach to synthesize transition metal NHC complexes is also employed in the context of this thesis.



Scheme 2. Straightforward synthetic routes to functionalized imidazolium salts. **Top:** Multi-component reaction of glyoxal, primary amine and formaldehyde under acidic conditions. **Bottom:** Alkylation/arylation of the imidazolide anion using reactive alky-/aryl halides.

Although various successful methods for the generation of NHC complexes have been described over the years, the availability of the corresponding suitable NHC precursors is

obviously still one of the controlling forces, which has been addressed in detail in several review articles.^{9,60-64} The most frequently applied ligand precursor subgroup are imidazolium salts, which are generally obtained using one of two routes:^{9,11,62} Either nucleophilic alkylation/arylation of the nitrogen in imidazoles,⁶⁵ or multi-component reactions of primary amines, glyoxal and formaldehyde are used to obtain the azolium salts (Scheme 2).^{23,66-67} Multi-component reactions are favored for bulky or functionalized substituents as well as for special modifications at the backbone atoms.

1.2.3 Efficient Variation of Steric and Electronic Properties of NHC Precursors

Improvement of the catalytic activity and stability of transition metal NHC complexes as well as expansion to other applications has always been a driving force in chemical research.⁶⁴ The key to success lies in understanding and subsequent tuning of their distinct properties. One of the early reported imidazole based air-stable, free NHCs is depicted in Figure 6 and general properties are discussed exemplarily.^{61,68-69} It has to be taken into account, that changes in the heteroatom from nitrogen to other atoms like phosphor, sulfur or oxygen or changes of the number or place of heteroatoms in the cycle have drastic effects on the electron density and the degree of carbene stabilization. These special cases have to be considered separately.

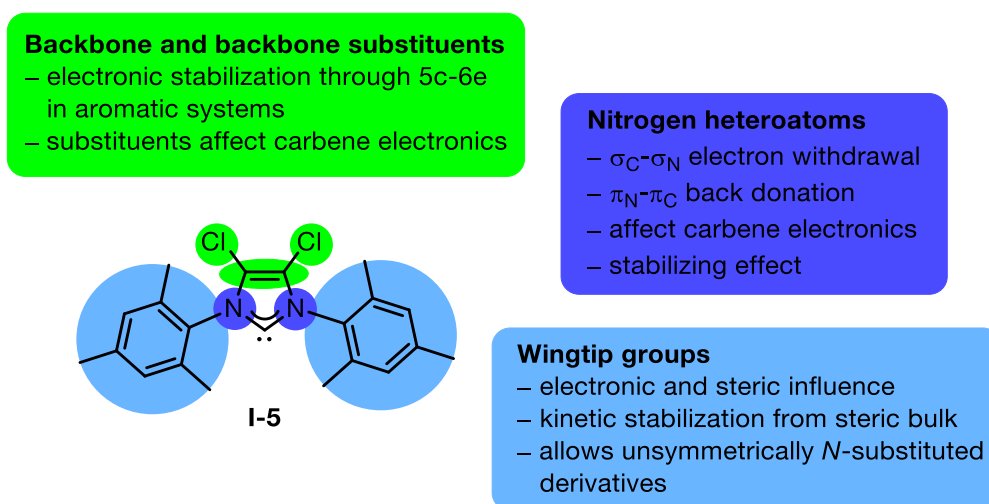


Figure 6. General structural features of imidazole based free NHCs, detailing the effects of substitution on the stability and reactivity.^{11,61,68} Five-center six-electron (5c-6e) π -delocalization is known to be a stabilizing factor in unsaturated imidazol-2-ylidenes (ca. 20 kcal mol⁻¹ compared to related imidazolin-2-ylidenes).²⁵

The steric demand of NHC ligands is strongly dependent on the N substituents. Therefore, no standard rule applies, and a quantification is additionally complicated by free rotation of the metal-carbene bond in monodentate complexes. In general, kinetic stabilization is achieved by bulky substituents, disfavoring dimerization reactions. In catalysis, however, steric bulk can be disadvantageous due to too crowded transition metal centers and subsequent decreased activity or even deactivation of the catalyst.

The cone angle model established by Tolman in 1977 for phosphine ligands has also been applied for early carbene ligands (see chapter 1.2.1, Figure 5).³¹ Especially development of more complex NHC ligands, e.g. polydentate NHCs, have rendered the TEP unprecise, if not useless.³² Hence, Nolan, Cavallo and coworkers developed the ‘percent buried volume’ method ($\%V_{bur}$), a model to quantify the steric bulk as a function of one parameter, the sphere radii (Figure 7).^{27,32,64,70-72}

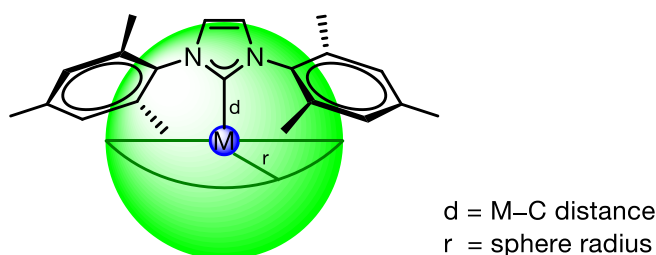


Figure 7. Schematic representation of the ‘percent buried volume’ model $\%V_{bur}$ developed by Nolan, Cavallo and coworkers.^{32,72}

A great advantage of the buried volume model is that information of different structure determination methods can be utilized. Typically, X-ray or quantum chemically calculated data are used for the determinations, which can be derived from transition metal complexes, free NHCs or azolium salts. For this reason, Cavallo and coworkers devised an easy to use web application, in order to calculate $\%V_{bur}$ values for different organometallic ligands, not limited to phosphines or NHCs.^{27,72} In an extensive study Nolan and coworkers compared the Tolman model with the newly established buried volume model, utilizing countless X-ray structures of phosphine complexes as well as NHC complexes.³² A correlation between the Tolman cone angle θ and the percent buried volume $\%V_{bur}$ was reported for phosphine complexes. Concerning the steric hindrance of the NHC ligands, an additional dependence on the environment of the metal center was established. Consequently, high structural flexibility of NHC ligands does not allow an easy general rule to predict steric hindrance. The metal center as well as the ligand field have to be taken into account.

Besides steric influence of the employed N-substituents, wingtip functionalization also allows for the introduction of chirality in the metal NHC complexes.⁷³⁻⁷⁹ One of the first strategies to induce chirality was based on N substitution with chiral groups. Other routes to chirality are stereogenic centers in the *N*-heterocycle, planar or axial chirality. Chiral metal NHC complexes are of particular interest for the growing field of asymmetric catalysis.^{75,77-78}

Steric protection and electronic influence of the wingtip groups, however, turned out to be not exclusively responsible for the stabilization of the free NHC as it was assumed after initial reports by Arduengo in 1991.²¹ Especially the electronic influence of the wingtip groups turned out to be relatively minor.⁸⁰⁻⁸¹ Reports on free NHCs with sterically less demanding wingtip groups,³⁶ triggered theoretical studies on the topic of electronic stabilization of free NHCs.⁸²⁻⁸⁴ Early-on *N*-heterocyclic carbenes were defined as a third class of carbenes, owing to their nucleophilic character and singlet state (Figure 8).¹¹ Hermann *et al.* and Heinemann *et al.* correlated the stability of free NHCs with their corresponding singlet-triplet gap, which was calculated to be of at least 65 kcal mol⁻¹ for stable NHCs.^{25,83} Accordingly, dimerization reactions of free NHCs were attributed to a small singlet-triplet gap, with an accessible excited triplet state at ambient conditions.

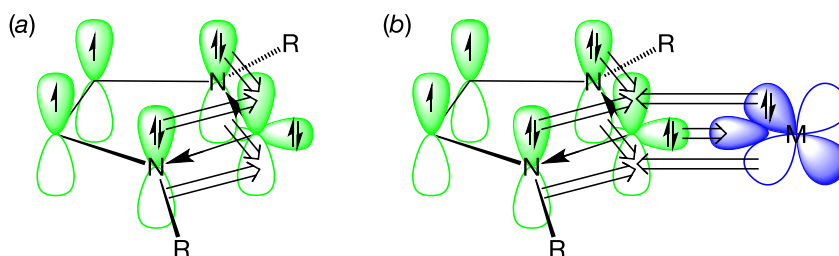


Figure 8. Electronic interactions in NHCs. (a) Graphical representation of an imidazole based NHC. $\sigma_C - \sigma_N$ electron withdrawal from the carbene carbon to nitrogen (thin arrows) and $\pi_N - \pi_C$ back donation of the N lone pairs to the carbene carbon (thick arrows). (b) Graphical representation of σ -bonding from the singlet carbene carbon lone pair to the metal orbital (thick arrow) and seldomly reported $\pi_M - \pi_C$ back-donation from the metal d-orbital to the carbene carbon (thick arrow).^{11,27,61,83}

Accordingly, the stability of NHCs is rather influenced by electronic than steric factors.^{11,27,83} Saturated carbenes have a smaller singlet-triplet gap of around 20 kcal mol⁻¹ compared to unsaturated carbenes, since 5c-6e π delocalization is no longer available.²⁵ Otherwise, the electronic stabilization is rather comparable, which also holds true for triazolium and tetrazolium based NHCs.¹¹

Another factor influencing the electronic properties is the choice of heteroatom. Thiazole⁸⁵⁻⁸⁶ and oxazole-derived carbenes⁸⁶ have been reported as well as five-membered *P*-heterocyclic

carbenes,⁸⁷⁻⁸⁹ with different orbital interactions and geometries (Figure 9).^{24-25,33,64} It has to be noted however, that oxazolylidene has not been isolated so far and has only been reported in quantum chemical calculations,⁸⁶ and as ligand coordinated to a metal center, employing template synthesis.⁹⁰⁻⁹²

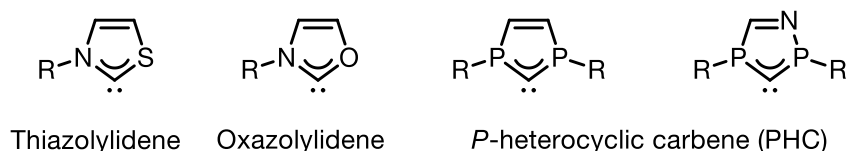


Figure 9. Generic representation of five-membered heterocycles with varied heteroatoms. Not all of these are stable as free carbenes, in some cases, the carbenes were only reported as ligands in metal carbene complexes.^{25,33,64}

Substitution on the backbone of the NHC additionally influences the electronic situation (Figure 6). The introduction of strong σ electron-withdrawing chlorine substituents allowed the isolation of the first air stable free imidazolium salt based carbene by Arduengo.⁶⁸ Substitution of the backbone with chloro-, cyano- or nitro-groups results in weaker σ -donor strength of the NHC due to the electron withdrawing effect, which in addition leads to a reduced ligands' basicity.⁹³⁻⁹⁴ A similar electron withdrawing effect is observed for benzimidazol-2-ylidene NHCs.⁹⁵

Backbone substitution was not only used to influence the electronic situation in the NHC ligand, but due to increasing environmental awareness among other things, considerable efforts have also been undertaken to enhance the metal NHC complex solubility in water.^{81,96-99} One of the most frequently reported routes is the introduction of alkyl chains functionalized with terminal polar substituents like sulfonate, carbonate or ammonium groups to the backbone of the NHC ligand.⁹⁸ Besides the enhanced water solubility, backbone modification also allows for immobilization on solid supports.¹⁰⁰⁻¹⁰⁴ Especially, recycling of known catalysts becomes accessible through immobilization on solid supports like polymers or silica, since the activity usually does not change upon immobilization.

1.2.4 Advances to Abnormal Coordination Modes

With increasing use of a large number of azolium salts as NHC precursors, various transition metals were investigated in their ability to coordinate highly functionalized NHC ligands. Imidazol-2-ylidene-based NHCs belong without doubt to one of the most prominent NHC

subgroups, as has been mentioned earlier. The constant search for new ways to tailor the electronic and steric properties of NHCs finally led to the discovery of abnormal *N*-heterocyclic carbenes (aNHC).^{34,105-110} Abnormal carbenes, also called mesoionic carbenes (MICs), since there is no resonance form with all-neutral formal charges, were first reported by Crabtree *et al.*¹¹¹ The terminus remote *N*-heterocyclic carbenes (rNHC) was introduced implying attachment of the metal nonadjacent to any heteroatom.^{34,112} The most common abnormal carbenes are shown in Figure 10, with imidazole-4-ylidene and triazole-4-ylidene being classified as MICs and pyrazol-4-ylidene as rNHC.

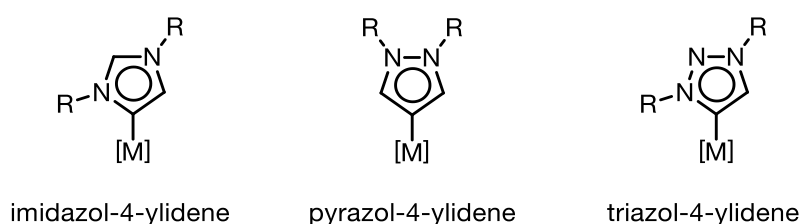


Figure 10. Generic representation of *N*-heterocyclic metal complexes featuring abnormal/mesoionic and remote NHC ligands.

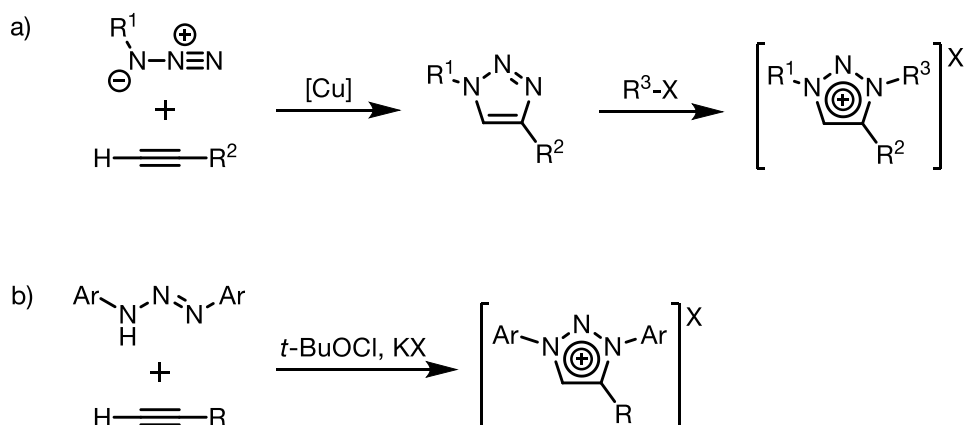
The most prominent advantage of abnormal carbenes is their enhanced σ -donor character compared to their normal or Arduengo-type *N*-heterocyclic carbene counterparts.^{105-107,110} This feature is attributed to a decreased heteroatom stabilization with the nitrogen in a more remote position and the lowered inductive electron withdrawing effect.¹⁰⁷⁻¹⁰⁸ The resulting zwitterionic resonance structure corresponds to a formally anionic ligand bonding and is assumed to be one of the factors responsible for the strong σ -donor character. Especially catalytic applications, which require high electron density at the metal center, benefit the most from these distinctly different properties. Oxidative addition sequences are easier accessible using highly basic metal centers.^{105,107} Therefore first applications in cross-coupling¹¹³ (Suzuki-Miyaura, Heck–Mizoroki) or (transfer) hydrogenation reactions¹¹⁴⁻¹¹⁵ were investigated in more detail utilizing metal aNHC complexes based on imidazolylidene.

In order to ensure an abnormal binding mode, two main strategies have been reported for imidazolylidene ligands. On the one hand, the backbone C(4) position has to be activated and on the other hand, the generally more active/acidic C(2) position has to be deactivated in the imidazolium salt based precursor.¹⁰⁷ For example, the activation of the C(4) position is achieved *via* halogenation of C(4) and subsequent oxidative addition of the resulting imidazolium salts to metal centers. Blocking of the acidic C(2) position by substitution with

alkyl or aryl groups has been reported by Crabtree¹¹⁶ and Lassaletta¹¹⁷ for example and resulted in abnormal coordination of the imidazolylidene to the metal precursor.

Pyrazol-4-ylidene palladium complexes have originally been described by Huynh *et al.*, using oxidative addition protocols.¹¹⁸⁻¹²⁰ Compared to imidazol-2-ylidene and even abnormal imidazol-4-ylidene ligands, pyrazol-4-ylidene show an increased σ -donor ability, which renders them especially interesting for catalytic applications like cross-coupling reactions.^{105,120-122} Bertrand *et al.* have also prepared free pyrazol-4-ylidene carbenes.¹²²⁻¹²³

Triazolylidenes have rapidly gained attention as a versatile subclass of abnormal *N*-heterocyclic carbene ligands after their first report by Albrecht *et al.* in 2008.¹²⁴ The most widely used synthetic strategy to prepare the triazole precursors is through a regioselective dipolar [2+3] copper(I) catalyzed ‘click’ cycloaddition of alkynes and azides (CuACC, Huisgen cycloaddition, Scheme 3a).¹²⁵⁻¹²⁸ The established ‘click’ protocols have been shown to be highly regio- and chemoselective and tolerant to various functional groups, in addition to proceeding in good to excellent yields.^{109,129-135}



Scheme 3. a) Schematic copper(I) catalyzed dipolar [2+3] ‘click’ cycloaddition of a functionalized azide and alkyne (CuACC) to initially form the triazole. Subsequent *N*-alkylation of the triazole yields the 1,3,4-substituted triazolium salts (R³ = alkyl). b) Schematic synthesis route of aryl-substituted triazolium salts by cycloaddition of 1,3-diaryl-2-azoniaallene salts and alkynes.

In case of unstable aryl or alkyl azides, protocols to generate the azides *in situ* have been reported and the reactions are carried out in one-pot synthesis without prior isolation of the azides. The corresponding triazolium salts, which are suitable precursors for triazolylidenes, are formed *via* selective *N*-functionalization (Scheme 3a). It has to be noted however, that arylation at the N3 position does not proceed *via* the same route as alkylation. It has rather been accomplished by cycloaddition of 1,3-diaryl-2-azoniaallene salts and alkynes (Scheme

3b).¹³⁶ Besides the special case of arylation of the N3 position, Kühn, Herrmann and coworkers recently reported the synthesis of ‘normal’ 1,2,3-triazolylidene transition metal complexes.¹³⁷⁻¹³⁹ However, the vast majority of triazolylidene ligands reported to date are based on the CuACC reaction, due to the large scope and easy accessibility of highly functionalized alkynes and azides.

Several synthetic methods towards metal triazolylidene complexes have been established mostly derived from previously reported procedures for metal imidazolylidene complexes (see chapter 1.2.2, Scheme 1).^{34,105,107,109} One of the most commonly employed protocols is the transmetalation from silver triazolylidene complexes.¹⁴⁰ It is noteworthy, that the silver carbene complexes are generally prepared *in situ* and subsequently treated with a suitable metal precursor. Only a few examples of stable silver triazolylidene complexes are known.¹⁴¹⁻¹⁴³ *In situ* formation of the silver carbene is usually proven by NMR spectroscopy and the characteristic disappearance of the triazolium proton. As mentioned before, the transmetalation protocol is based on Ag₂O acting as metal source as well as base. Therefore, base-mediated proton abstraction has been successfully investigated as metalation method as well.¹⁴⁴⁻¹⁴⁵ A distinction between proton abstraction (free triazolylidene as transient intermediate) and C–H activation (*in situ* generated [M(base)] intermediate) was attempted, but could not be resolved completely so far. Other well-known methods to obtain metal triazolylidene complexes include direct metalation (C–H bond activation)^{124,146} and coordination of the free carbene.¹⁴⁷⁻¹⁴⁸

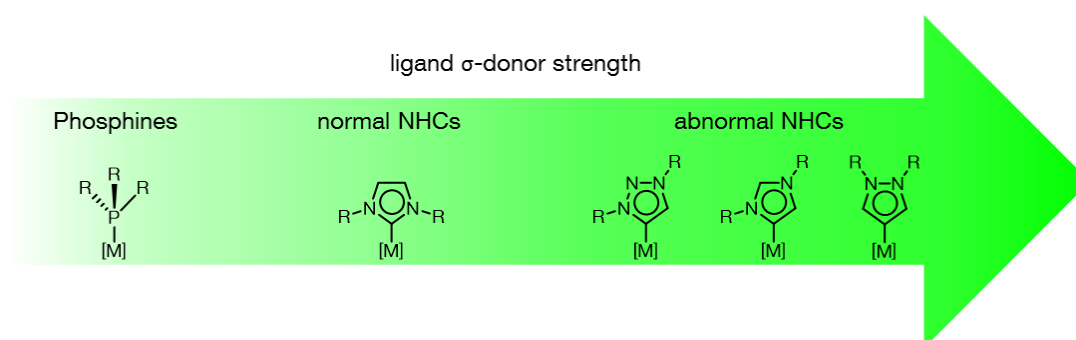


Figure 11. Generic representation of increasing σ -donor strength of phosphine and *N*-heterocyclic carbene ligands coordinated to transition metal centers.^{110,132,149-151}

The donor properties of triazolylidene ligands have been investigated and compared to the different subclasses of NHCs (Figure 11).^{105,109-110,132} Various strategies have been employed to evaluate donor strength of NHCs, for example, computational studies on pK_a values and energy decomposition analyses among others.^{86,149,152-153} The most widely used method, however, is the investigation of CO stretching frequencies of carbonyl transition metal

complexes using IR spectroscopy.^{105,109-110} According to various reports, including correlations between CO stretching frequencies and TEP analyses, the imidazol-2-ylidenes are weaker donors compared to 1,2,3-triazolylidenes, whereas imidazol-4-ylidenes show higher donor strength (Figure 11).^{105,109,116,144,148,154} It has to be noted, however, that CO stretching can be influenced by other factors, like stereoelectronic properties.¹⁵⁵ Therefore, care has to be taken during data interpretation. Other methods to determine and compare the donor strengths are X-ray photoelectron spectroscopy (XPS),^{114,156} which is based on the evaluation of enhanced electron density on the metal center, and NMR spectroscopy of palladium complexes, investigating the *trans* influence of isostructural dicarbene complexes.^{146,150,157}

No dimerization reactions of abnormal carbenes have been reported so far, which might be due to electrostatic repulsion caused by the anionic character of the carbenic centers.^{105,132,147-148,158} This feature allows for sterically less strained carbenes, which is also interesting with regard to catalytic applications and more accessible metal-carbon bonds.

1,2,3-Triazoles derived from CuACC, which are usually prepared as precursors for triazolylidenes in NHC chemistry, have also been used as ligands in coordination chemistry.^{132,159-160} Especially N3-coordination was investigated in detail. In order to evaluate the interaction of the triazole ligand with a metal center, electrostatic interactions as well σ - and π -donation have to be considered. Triazoles as neutral nitrogen donors show strong σ - and π -interactions with transition metal ions with partially filled d-orbitals.^{132,161} Therefore, the coordinative bond has a significant covalent character.^{132,152,161-162} Accordingly, pyridine was identified to be a stronger π -acceptor than triazole, whereas imidazole shows the strongest π -donor abilities of the three systems, which is also in accordance with the corresponding σ -lone pair energies (imidazole > pyridine > 1H-1,2,3-triazole).¹³²

1.2.5 Polydentate N-heterocyclic Carbenes

Following the increasing success of monodentate NHCs in catalysis, the concept of chelation, which has been applied to organometallic chemistry for decades, moved into the focus of NHC based research.^{29,56,163-169} One of the main advantages of chelating ligands is among others enhanced stability of transition metal complexes even under harsh conditions.^{56,163-164,167} In addition, stabilization of free coordination sites, introduction of hemilability or stabilization against reductive eliminations have been reported.¹¹ Consequently, a myriad of functionalized multidentate NHC ligands has emerged, taking advantage of the well-established wingtip substitution protocols.^{11,165,168-169} Chelating moieties include C-donors like

phenyl anions, *N*-donors like amines or pyridines, *O*-donors like carboxylates or alkoxides or *P*-donors like phosphines and many others.

Therefore, also a wide set of complexes with bis-, tris-, and tetra-NHCs, acting as bischelating, pincer, tripodal, or bridging ligands, have been reported.^{29-30,47,167,170-182} Some of them have even been mentioned in combination with chiral motifs to allow the synthesis of asymmetric catalysts. In addition, a few mixed normal/abnormal bis-NHCs have been prepared.¹⁸³⁻¹⁸⁵ This approach seems especially interesting regarding the electronic and steric tailoring of transition metal complexes for applications in catalysis. The focus in this thesis will be mainly on tri- and tetradentate NHC ligands and their impact in transfer hydrogenation reactions. In Figure 12 a generic overview over possible ligand motifs is given.

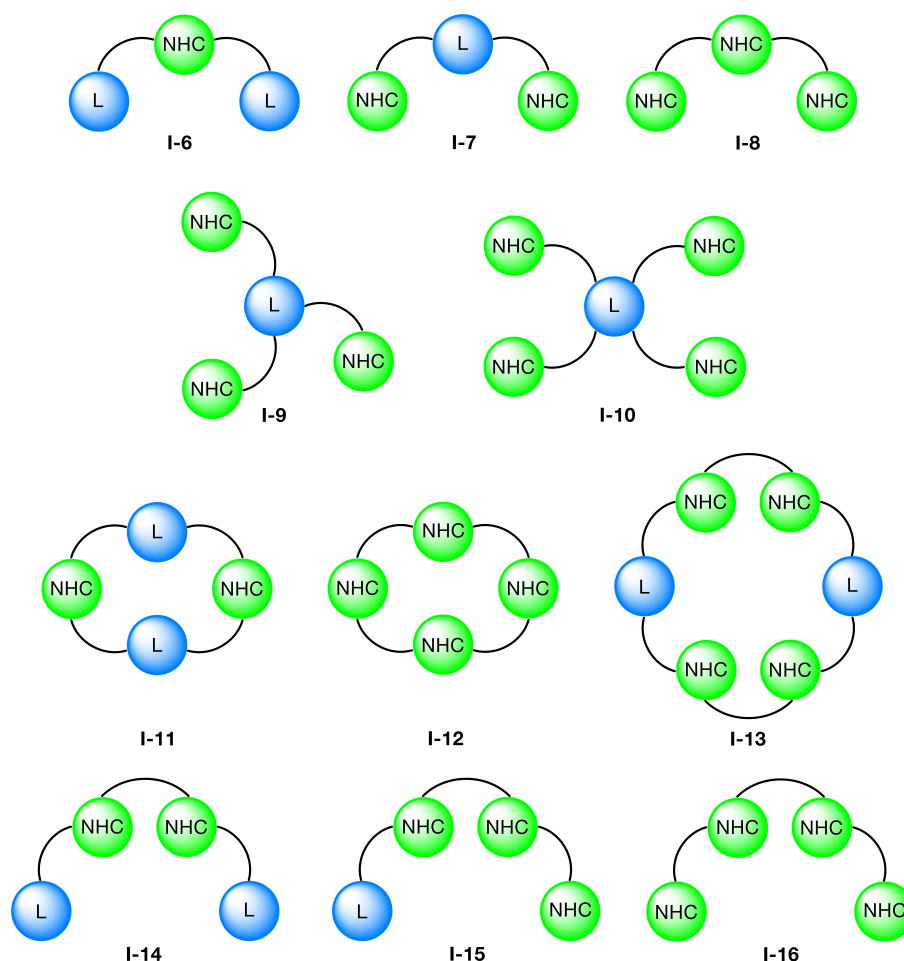


Figure 12. Generic overview of possible alkyl bridged acyclic and macrocyclic polydentate NHC ligands. NHC = (abnormal) *N*-heterocyclic carbene, L = linker (sometimes acting as donor functionality).

Chelating ligands with multiple carbene moieties, linked by alkyl bridges, rarely display fluxional or hemilabile behavior, due to the strong metal carbene interactions.^{164,166-167}

However, there have been a few studies on the fluxionality/ hemilability of polydentate NHC transition metal complexes with labile donor substituents.¹⁸⁶⁻¹⁸⁸

It has to be noted, that tris- and tetra-NHCs are less abundant than bis-NHCs, due to generally more complicated synthesis routes and purification issues.¹⁶⁷ During the last years, reports on poly-NHC ligands have increased significantly originating from new synthetic strategies like template based synthesis or formation of polyimidazolium salt precursors.^{58,189-192} The unique coordination modes of new tetra-NHC ligand systems and their applicability as spectator ligands in catalysis has been investigated in detail.¹⁹³⁻¹⁹⁹ As illustrated in Figure 12 various macrocyclic and acyclic ligand motifs are known and each motif has different advantages and limitations. Depending on the employed linker between the NHC moieties, mononuclear macrocyclic systems have been reported to bind metal ions with coordination numbers of four or higher, however, polynuclear metal NHC complexes have been described to also show lower coordination numbers (ligand motifs derived from **I-11**, **I-12** and **I-13**, Figure 12).^{57,189,195,198-214} Owing to a rather rigid macrocyclic structure, the resulting transition metal NHC complexes generally show an equatorial coordination of the ligand. However, two exceptions are known. In these cases, the steric demand of the macrocyclic ligand system allows for a tetrahedral coordination to cobalt or a trigonal prismatic geometry for iron.^{195,215} Another interesting macrocyclic NHC motif was established using classical pyrazole-bridged di-NHC ligands and dimerizing them to macrocyclic tetra-NHC analogs to afford dinuclear nickel(II) complexes.²¹⁶

The first acyclic tetra-NHC transition metal complexes were generated from rigid arene based tetra-NHC ligand moieties and therefore limited to metallosupramolecular architectures (ligand motifs derived from **I-10**, Figure 12).²¹⁷⁻²²¹ Hahn *et al.* also reported a similar macrocyclic structure using an arene based tri-NHC ligand.²²² In order to overcome these coordinative restrictions, acyclic silver tetra-NHC complexes with alkyl linkers of variable lengths were presented as highly useful transmetalation agents by Kühn *et al.* (ligand motifs derived from **I-16**, Figure 12).²²³ Subsequently, octahedral mononuclear iron(II) complexes displaying both equatorial or sawhorse-type geometries were isolated and hinted at the great potential of this new ligand motif (Figure 13; ligand motifs derived from **I-16**, Figure 12).²²⁴⁻²²⁵

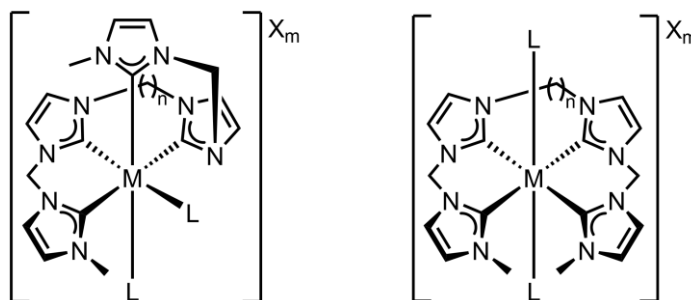
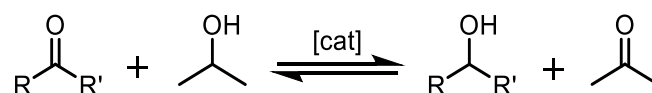


Figure 13. Schematic representation of acyclic alkyl-bridged tetra-NHC ligands with variable coordination modes (left: sawhorse-type coordination, right: equatorial coordination). M = transition metal; L = neutral coordinating ligand, e.g. solvent molecule; X = counter ion; n = number of bridging $-CH_2-$; m = charge of the complex.

Variation in the lengths of the alkyl bridges and the choice of the remaining ligands coordinating to the transition metal potentially influences the coordination mode of acyclic multi-NHC ligands. Additional variation in number of chelating NHC moieties leads to differing electronic situations at the metal center. Consequently, multi-NHC ligands and the resulting transition metal complexes seem to be an interesting field for future research and catalytic applications.

1.2.6 Transfer Hydrogenation Catalysis

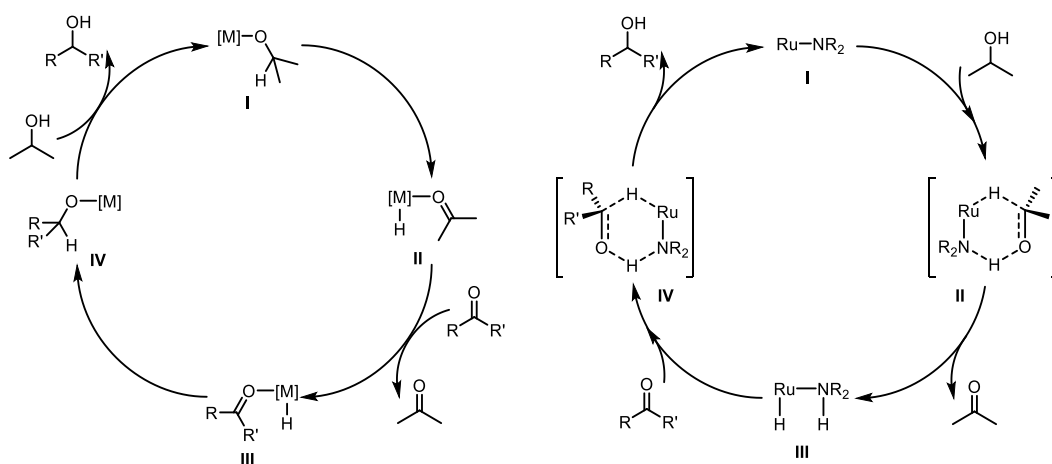
Catalytic hydrogenation reactions are among the most important chemical transformations and are employed in food technology during the solidification of fatty acids as well as in the petrochemical industry for hydrocracking of heavy residues into diesel.^{5,226} However, asymmetric hydrogenation is also a key step in drug synthesis used for treatment of Parkinson's disease.²²⁷ In general, these transformations are achieved either by direct hydrogenation using gaseous H_2 under pressure or by transfer hydrogenation (TH), where the hydrogen is provided by an alternative hydrogen source, like 2-propanol or formic acid (Scheme 4).



Scheme 4. Transition metal catalyzed transfer hydrogenation reaction using 2-propanol as hydrogen donor.

The first transfer hydrogenation reaction using palladium black was reported by Knoevenagel in 1903.²²⁸ Following this initial discovery, over the years different types of TH reactions were developed. Subsequently these reactions were divided into different types: Meerwein–Ponndorf–Verley (MPV) reductions, late transition metal-catalyzed reactions, thermal, base-catalyzed, enzyme-catalyzed, organocatalytic and uncatalyzed processes. The increased interest in TH can mainly be attributed to the following distinct advantages. No elaborate experimental setups are necessary and the use of pressurized H₂ gas is avoided. Another advantage are the readily accessible and inexpensive hydrogen donors. In addition, the resulting side products are recyclable and the employed catalysts are comparably easy to come by and rather robust.^{75,226,229-236}

Especially transition metal catalysts have received significant attention as an essential branch of TH starting as early as the 1960s.²³⁷⁻²³⁹ To date a plethora of homogeneous transition metal catalysts for TH have been developed and the most effective systems turned out to be ruthenium-, iridium or rhodium-based.^{226,230,232,235-236} Two mechanistic pathways for the homogeneous transition metal catalyzed transfer hydrogenation have been proposed and are widely accepted, the hydridic route also called “inner-sphere” mechanism and the dihydride mechanism (“outer-sphere” mechanism) (Scheme 5).^{229,235,240-241}



Scheme 5. Proposed mechanisms for transition metal catalyzed transfer hydrogenation reactions. Left: “inner-sphere” mechanism; right: “outer-sphere” mechanism.^{229,235,240-241}

The “inner-sphere” mechanism is most commonly observed for transition metal catalyzed TH reactions.^{229,240} In this case, the catalytically active species is a metal hydride and the hydrogen donor and the hydrogen acceptor interact separately with the metal in different steps of the catalytic cycle. After initial deprotonation of the hydrogen donor (e.g. 2-propanol)

by a base the reaction proceeds *via* an alkoxy complex (**I**).²⁴⁰ β -H-elimination leads to the metal hydride species (**II**). Subsequently, acetone is released, while the substrate is coordinated to the catalytic species (**III**). In the fourth step, a metal alkoxide is formed, *via* ketone insertion into the M–H bond (**IV**). The reduced substrate is cleaved off and 2-propanol is coordinated to form the active species (**I**). The “outer-sphere” mechanism was proposed by Noyori *et al.* and is observed for ruthenium complexes featuring a chelating ligand with an amino group (Ru-NR₂ fragment).²³⁵

Ruthenium-based NHC complexes feature a wide range of oxidation states and coordination geometries,^{23,33,60,73,77,98,226,234,242} and have therefore been the subject of numerous catalytic studies for metathesis,^{61,103,243-245} isomerization,²⁴⁶⁻²⁵¹ and polymerization reactions²⁵²⁻²⁵⁷ besides the already discussed hydrogenation reactions.^{29,61,226,258-262} However, ruthenium-based catalysts are by far the most widely used ones to mediate TH. One of the most active TH catalysts to date was described by Baratta and Kühn *et al.* in 2011, a Ru-based complex featuring abnormally coordinated NHC ligands.²⁶⁰ In order to take advantage of the chelating properties of tri- and tetra-NHC ligands without the coordinative limitations of macrocyclic systems, acyclic tri- and tetra-azolium salts are an interesting starting point for the synthesis of highly active ruthenium TH catalysts. The ability of Ru(II) to octahedral ligand coordination allows interesting structural motifs for acyclic chelating ligands like tri- and tetra-NHCs, which will be addressed in this thesis.

1.3 Transition Metal Mediated Transformation of Carbon Dioxide

In this section, a short introduction to the transformation of carbon dioxide will be given, focusing on the advantages and challenges.

A growing world population leads to an ever increasing energy demand.²⁶³⁻²⁶⁷ The efficient utilization of carbon dioxide as an alternative C₁ feedstock is a permanent subject in science and industry, in order to meet the challenges and requirements of the future. Great efforts are put into the development of new storage and recycling possibilities.²⁶⁸⁻²⁷⁰ Already established synthetic protocols for the industrial production of bulk chemicals like cyclic carbonates, urea, salicylic acid, polypropylene carbonate are relying on the advantages of carbon dioxide as non-toxic, abundant and cheap resource.²⁶⁵ However, the synthesis of alternative high value products is as much a goal of catalysis as the elucidation of new energy efficient pathways for already established basis chemicals.

Consequently, the activation and transformation of carbon dioxide in solution have been studied extensively during the last decades and several approaches through the assistance of homogeneous catalysis and transition metal complexes have been investigated.^{263-264,271-277} In general there are three steps for the transformation of carbon dioxide using transition metal complexes, first the coordination to the metal center, second the reaction with a neighboring ligand and third the release of the product with regeneration of the employed catalyst. Several different approaches have been reported over the years.

- (a) insertion of CO₂ into M–C σ -bonds leading to the formation of carboxylate species
- (b) insertion of CO₂ into M–H bonds leading to formic acid
- (c) insertion of CO₂ into M–O bonds leading to the synthesis of carbonate species
- (d) coupling of CO₂ with olefins at transition metal centers leading to acrylic acid and derivatives thereof
- (e) photocatalytic activation of CO₂ using transition metal complexes

The focus in this work will be on the conceptual discussion of the coupling of CO₂ with ethene (d) and synthetic approaches to the photocatalytic activation of CO₂ (e) using rhenium(I) phosphinine complexes.

1.4 From Homogeneous Catalysis to Novel Applications in Supramolecular Chemistry

Metal-based three dimensional capsules with nanocavities have attracted significant interest over the last decades. Especially metal-organic frameworks (MOFs) and supramolecular coordination complexes (SCCs) have been reported in this context, due to their applicability in catalysis.²⁷⁸⁻²⁸⁴ More important than catalytic applications, however, are molecular recognition and drug delivery, enabled through encapsulation of guest molecules into the cavities. In particular, SCCs show discrete two and three dimensional molecular entities with defined shapes and sizes.^{278-283,285} Encapsulation of guest molecules can be stabilized by Coulomb or van der Waals interactions. Hydrogen bonding, ion-pairing, metal-metal interactions and steric interdependencies additionally influence the encapsulation of guest molecules.

Cage-like structures are of particular interest and can be obtained *via* coordination-driven self-assembly resulting in complexes of the type M_xL_y (M = transition metal, L = ligand, x = number of transition metals, y = number of ligands). For example, M_2L_4 cage compounds feature a highly symmetric structure and a wide range of transition metals has successfully been applied for the self-assembly reactions resulting in distinct properties and applications. Additional functionalization of the ligand framework leads to highly efficient tuning of their chemical properties. In Figure 14, a generic representation of M_2L_4 cage compounds with *exo*- and *endo*-functionalization is depicted. *Exo*-functionalization allows for tuning of solubility and photophysical properties of the cage, whereas *endo*-functionalization aims at influencing the host-guest interaction.²⁸⁶⁻²⁸⁹

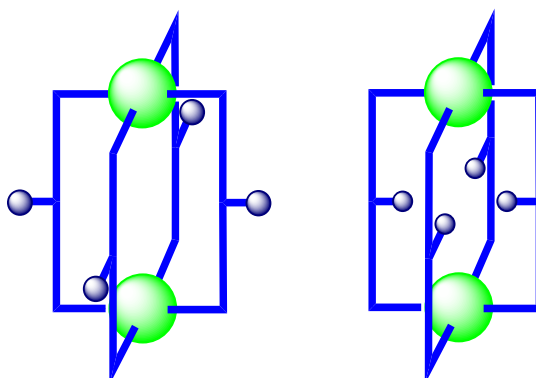


Figure 14. Generic representation of M_2L_4 cage compounds with *exo*- (left) and *endo*-functionalization (right).²⁷⁹

Highly luminescent cage compounds are of great interest for chemosensing,²⁹⁰⁻²⁹¹ material science²⁹²⁻²⁹³ or biological imaging.^{285,294} Despite some reports on fluorescent coordination complexes,^{292,295-298} the majority of these SCCs show hardly any emissive behavior.²⁹⁹⁻³⁰¹ In particular palladium-based M_2L_4 cage compounds, which are known to adopt a convenient square-planar coordination with defined cavities, rarely show luminescence due to the quenching effect of the heavy metal ions.^{288,302-304}

Biological imaging of supramolecular metallocages is gaining increased attention regarding the investigation of the cages as selective drug delivery vehicles. Crowley *et al.* reported the encapsulation of the highly effective anticancer drug cisplatin into a Pd_2L_4 cage (Figure 15).^{289,305} The cisplatin molecules are stabilized by hydrogen bonding and Pt-Pt interactions. Hence, several biological studies have been conducted using various SCCs as drug delivery vehicles,³⁰⁶⁻³¹² but also as anticancer drugs themselves.^{305,313-317}

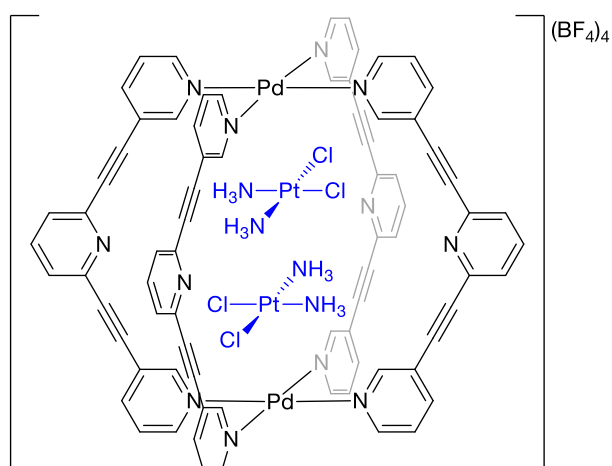


Figure 15. Supramolecular metallocage Pd_2L_4 encapsulating two cisplatin molecules reported by Crowley *et al.*²⁸⁹

2 OBJECTIVE

Functionalized *N*-heterocyclic carbene ligands have proven to be an exceptionally useful ligand class in transition metal mediated homogeneous catalysis. Especially, ruthenium based polydentate NHC complexes are the subject of this thesis.

Recent reports on macrocyclic tetra-NHC complexes with limited coordination modes, led to increased interest in the development of poly-NHC ligands with higher coordinative flexibility. Consequently, in the first section acyclic tetraimidazolium salts are chosen as precursors for the synthesis of ruthenium(II) tetra-NHC complexes (Figure 16). Particularly interesting is the influence of the alkyl chain length on the coordination geometry of the tetra-NHC ligand. In addition, ligand exchange experiments are conducted to examine the coordinative behavior of the open-chain tetra-NHC. The resulting ruthenium(II) complexes are especially interesting for applications like transfer hydrogenation reactions and their activity is tested using the model substrate acetophenone.

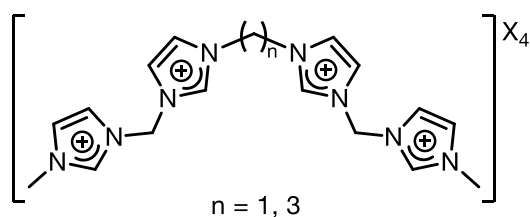


Figure 16. Tetraimidazolium salts as suitable precursors for ruthenium(II) tetra-NHC complexes.

In order to utilize the increased σ -donor strength of abnormal carbenes compared to normal carbenes, an innovative ligand motif based on 2-imidazolylidene and 1,2,3-triazolylidene moieties is developed. A mixed imidazolium/triazolium salt is applied as precursor in the synthesis of a ruthenium(II) tri-NHC complex (Figure 17). In order to evaluate potential beneficial catalyst properties, the tri-NHC complex is applied in transfer hydrogenation catalysis using the model substrate acetophenone.

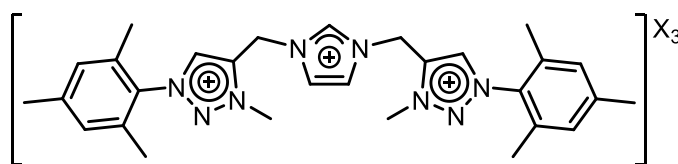


Figure 17. Mixed imidazolium/triazolium salt as precursor for a ruthenium(II) tri-NHC complex.

The transformation of carbon dioxide to useful basis or fine chemicals using homogeneous transition metal complexes will be of commercial relevance in the future. Herein, recent advances in the transformation of CO₂ to acrylic acid and acrylates are examined in detail. In addition, precursors for potentially active rhenium(I) biphosphinine photocatalysts are developed. Structural and theoretical investigations on their chemical properties are conducted.

Finally, supramolecular coordination cages are investigated, regarding their potential applicability as selective drug carriers for anticancer medication. Special attention is on the synthesis and characterization of these compounds and the possibility to encapsulate anticancer drugs like cisplatin. In order to evaluate the metallocage compounds with regard to cell interaction, biological imaging is also topic of this thesis. Therefore, rational approaches to luminescent metallocages are evaluated and discussed.

3 RESULTS – PUBLICATION SUMMARIES

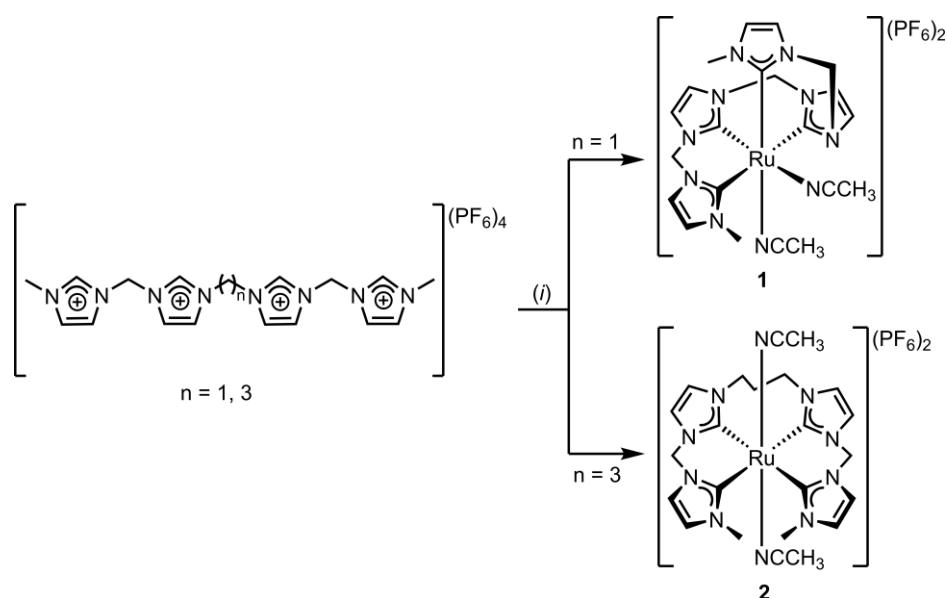
The individual contributions of M. Hollering to each of the following publications have been collected in Table A1 (Appendix).

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

MANUELA HOLLERING, DANIEL T. WEISS, MARIO J. BITZER, CHRISTIAN JANDL, AND FRITZ E. KÜHN

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

Open-chain multidentate NHC ligands allow various coordination modes to transition metals, especially when compared to rigid macrocyclic systems. Herein, the first Ru(II) tetra-NHC complexes derived from flexible acyclic tetraimidazolium salts are described, displaying either sawhorse-type (**1**) or equatorial (**2**) coordination of the ligand (Scheme 6).



Scheme 6. Microwave-assisted synthesis of ruthenium(II) tetra-NHC complexes **1** and **2**. (i) Microwave, Ag_2O , $[RuCl_2(p\text{-cymene})]_2$, $100\text{ }^\circ C$, 1 h, 100 W in acetonitrile.

The coordination geometry turned out to be strongly dependent on the length of the alkyl linker as well as the steric and electronic properties of the two other ligands. The longer propylene bridge in complex **2** enabled equatorial coordination with weakly coordinating acetonitrile ligands in *trans*-position (Figure 18).

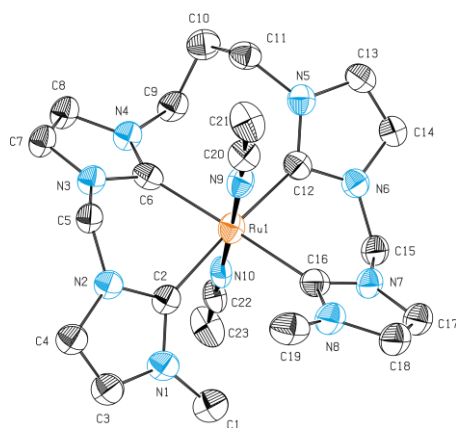


Figure 18. ORTEP style representation of the equatorial coordinated cationic complex fragment **2** with ellipsoids shown at a 50% probability level. Hydrogen atoms and PF_6^- counter ions are omitted for clarity. The complete tetra-NHC ligand is disordered (indicated by thin bonds) and therefore no bond lengths or angles are discussed in detail.

Upon addition of trimethylphosphine in excess, the sawhorse-type complex **1** is converted to its equatorially coordinated derivative **3**, replacing the acetonitrile ligands (Figure 19, left). Remarkably, the sawhorse-type coordination can be preserved, when the acetonitrile ligands in **1** are substituted by *tert*-BuNC to yield **4** (Figure 19, right).

Complexes **1** and **2** were applied as catalyst precursors in the catalytic transfer hydrogenation of acetophenone at a catalyst loading of 0.1 mol% and in particular the sawhorse-type coordinated system **1** exhibits remarkable activity with turnover frequencies of more than $100\,000\text{ h}^{-1}$ (98% conversion after 1 min).

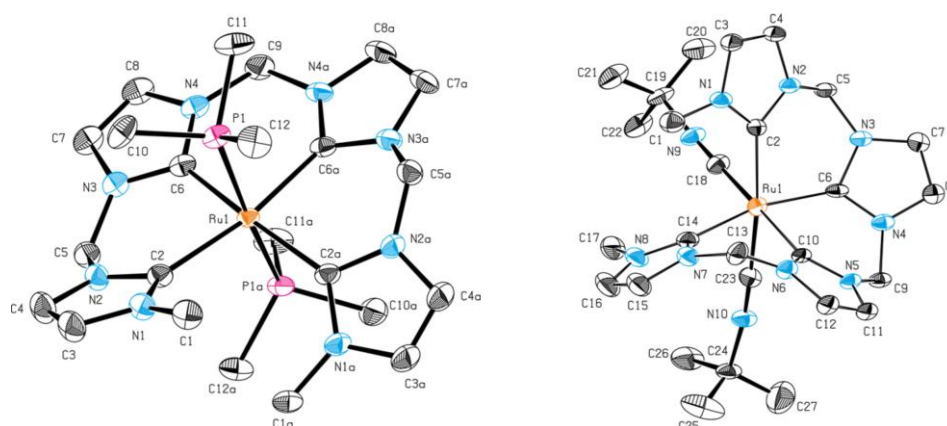


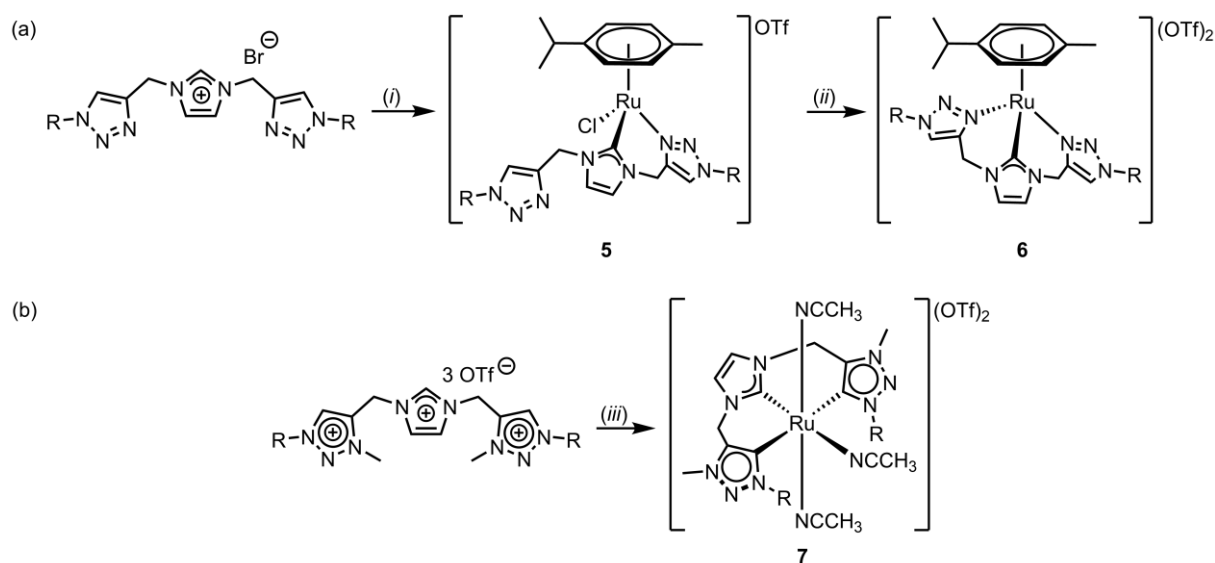
Figure 19. ORTEP style representation of the cationic complex fragments **3** (left) and **4** (right) with ellipsoids shown at a 50% probability level. Hydrogen atoms and PF_6^- counter ions are omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$] for complex fragment **3**: Ru1–C2, 2.113(3); Ru1–C6, 2.034(3); Ru1–P1, 2.3612(5); C2–Ru1–C6, 87.95(12); C2–Ru1–C6a, 170.0(1); C2–Ru1–P1, 85.09(8); C6–Ru1–P1, 88.16(6); P1–Ru1–P1a, 172.45(3). In complex fragment **4** the tetra-NHC ligand is disordered (indicated by thin bonds). Therefore, no bond lengths and angles are discussed.

3.2 Bonding and Catalytic Application of Ruthenium *N*-Heterocyclic Carbene Complexes Featuring Triazole, Triazolylidene and Imidazolylidene Ligands

MANUELA HOLLERING, MARTIN ALBRECHT, AND FRITZ E. KÜHN

ORGANOMETALLICS 2016, 35, 2980-2986.

Abnormal carbene systems have gained significant importance over the last years due to their distinctly different donor properties. Therefore, the combination of imidazolylidene and triazolylidene carbenes is an interesting addition to known NHC pincer ligands with regard to structural and catalytic versatility. Herein, the first examples of Ru(II) NHC complexes bearing chelating mixed normal/abnormal NHC ligands are presented (Scheme 7).



Scheme 7. (a) Synthesis of two Ru(II) monocarbene complexes **5** and **6** with an 2-imidazolylidene skeleton and 1,2,3-triazoles acting as neutral nitrogen donors. (i) One-pot synthesis using Ag_2O , $[\text{RuCl}_2(p\text{-cymene})]_2$, r.t., 72 h, KOTf in dichloromethane; (ii) AgOTf, 50 °C, overnight in acetonitrile. (b) Microwave-assisted synthesis of Ru(II) tri-NHC complex **7**. (iii) Microwave, Ag_2O , $[\text{RuCl}_2(p\text{-cymene})]_2$, 100 °C, 1 h, 100 W in acetonitrile.

Two monocarbene complexes were isolated and characterized with either one (**5**) or two (**6**) triazole moieties acting as neutral nitrogen donors (Figure 20). Both complexes exhibit a classical three-legged piano stool geometry. VT-NMR studies at elevated temperatures reveal no decoordination of the triazole moieties, however, *p*-cymene displacement is observed for both complexes at 130 °C.

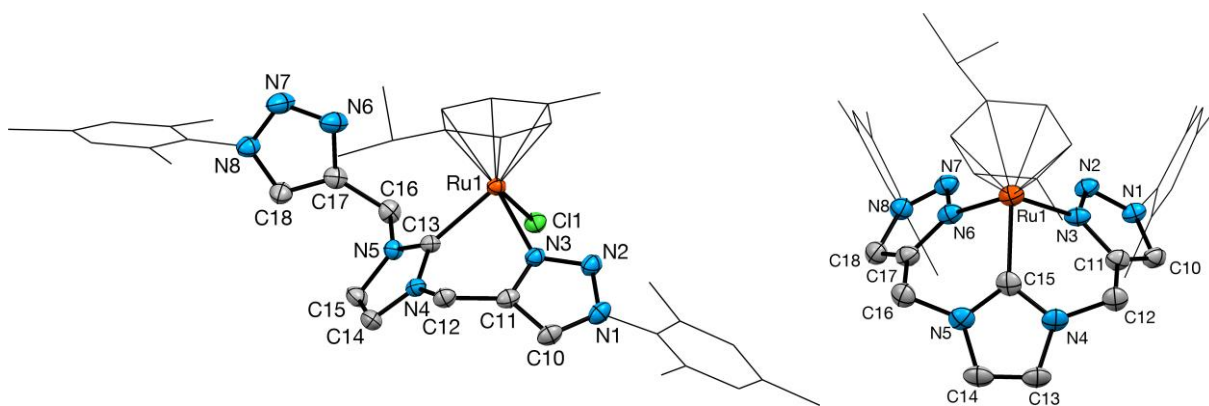


Figure 20. ORTEP style representations of the cationic complex fragments of **5** (left) and **6** (right) with thermal ellipsoids shown at a 50% probability level. Hydrogen atoms and counter ions (PF_6^- for **5** and 2xOTf^- for **6**) are omitted for clarity. The coordinated *p*-cymene and the mesityl wingtip groups are displayed as wireframe for transparency.

The tridentate Ru(II) NHC complex featuring a normal 2-imidazolylidene and two abnormal 1,2,3-triazolylidene moieties is obtained *via* a microwave-assisted one-pot reaction and the ligand is coordinated in a meridional fashion (Figure 21).

Complexes **5**, **6** and **7** were applied as catalyst precursors in the catalytic transfer hydrogenation of the model substrate acetophenone at a catalyst loading of 0.5 mol%. Complex **6** with both triazole moieties coordinated to the ruthenium center exhibits the highest (initial) turnover frequency of $1\ 100\ \text{h}^{-1}$, but slows down after a conversion of 60%. Of the three complexes only complex **7** ($\text{TOF}_{2\text{min}} = 580\ \text{h}^{-1}$) reaches full conversion (98% after 80 min) and is accordingly a more robust TH catalyst precursor than **5** and **6**.

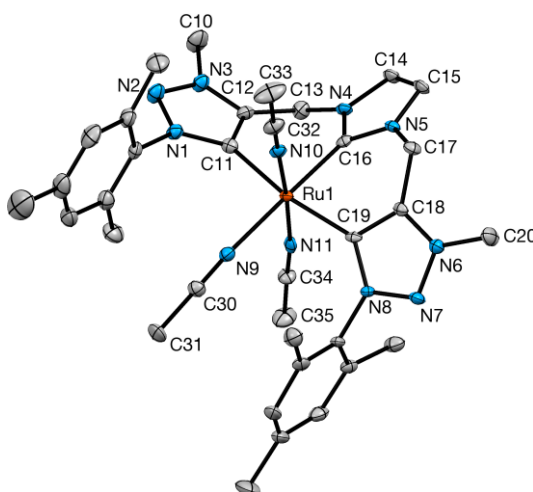


Figure 21. ORTEP style representation of the cationic complex fragment of **7** with thermal ellipsoids shown at a 50% probability level. Hydrogen atoms and OTf counter ions are omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: Ru1–C11, 2.096(4); Ru1–C16, 2.015(5); Ru1–C19, 2.091(4); C11–Ru1–C16, 85.3(2); C11–Ru1–C19, 170.1(2); C11–Ru1–N9, 95.5(2); C11–Ru1–N10, 92.5(2).

3.3 Transition metal mediated coupling of carbon dioxide and ethene to acrylic acid/acrylates

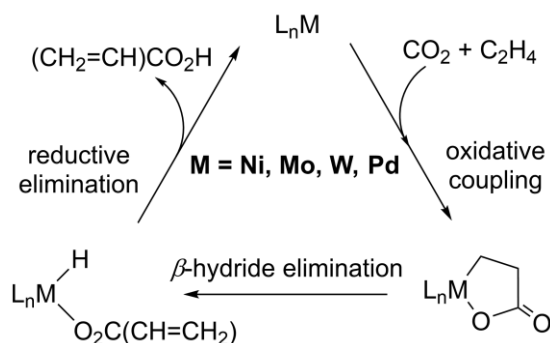
MANUELA HOLLERING,[#] BARNALI DUTTA,[#] AND FRITZ E. KÜHN

[#] M. Hollering and B. Dutta contributed equally to this work.

COORDINATION CHEMISTRY REVIEWS **2016**, 309, 51-67.

This review article is directed at experts in the field of transition metal mediated transformation of carbon dioxide to acrylic acid and derivatives thereof. Depleting fossil fuels and other fossil carbon sources, an increasing human population and a growing interest in environmental issues, has affected the search for regenerative alternative energy sources during the last years. In this comprehensive review article the recent developments regarding the formation of acrylates and acrylic acid, starting from carbon dioxide are surveyed. The focus lies on synthetic insights on the one hand and on current findings in theoretical studies on the other hand.

Especially homogeneous catalysis in solution is known to be an attractive alternative to heterogeneous procedures and utilizes carbon dioxide as cheap and abundant starting material. Consequently, the synthesis of acrylates has been studied employing various transition metal complexes. The three main steps of this hypothetical catalytic cycle are depicted in Scheme 8 and are oxidative coupling of the substrates (CO₂ and ethene) to form a metallalactone, followed by β -hydride elimination forming a hydridoacrylate, and afterwards reductive elimination of the acrylate to regenerate the M(0) species.



Scheme 8. Outline of the hypothetical catalytic cycle of the formation of acrylic acid, starting from carbon dioxide and ethene.

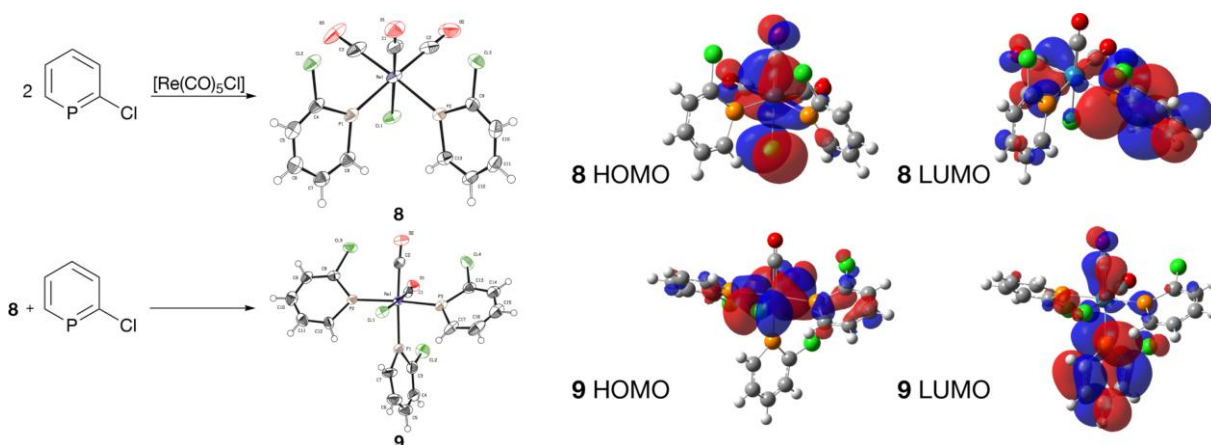
Ni-, Mo/W- and Pd-mediated pathways face different obstacles, due to their distinct chemical properties. For group VI transition metal centers, oxidative coupling as well as β -hydride elimination takes place at ambient conditions, easily forming Mo/W-acrylate complexes. However, reductive removal of the acrylate is hindered due to the strong oxophilicity of the metal centers. For Ni systems, high gas pressures and temperatures are reported to be necessary with the rate limiting step being the β -hydride elimination step and transformation to the acrylate. However, lower oxophilicity is proposed to easier facilitate acrylate removal compared to group VI metals. The first reported closed catalytic applications using nickel and palladium complexes described the advantages of different bases for deprotonation of the metallalactone to avoid side reactions with carbon dioxide. This review provides an overview on concepts and current methodologies for the employment of various transition metal complexes, giving a perspective view on mechanistic studies.

3.4 [Re(CO)₃Cl(C₅H₄CIP)₂] and [Re(CO)₂Cl(C₅H₄CIP)₃]: synthesis and characterization of two novel rhenium(I) phosphinine complexes

MANUELA HOLLERING, RICHARD O. REITHMEIER, SIMON MEISTER, EBERHARDT HERDTWECK, FRITZ E. KÜHN,* AND BERNHARD RIEGER*

RSC ADVANCES 2016, 6, 14134-14139.

Various coordination modes of phosphinines and their derivatives to numerous transition metals as well as their application in homogeneous catalysis have been reported. Herein, the synthesis of two novel rhenium(I) phosphinine complexes [Re(CO)₃Cl(η¹-C₅H₄CIP)₂] (**8**) and [Re(CO)₂Cl(η¹-C₅H₄CIP)₃] (**9**) was described and the molecular structures were determined by single crystal X-ray diffraction (Scheme 9, left).



Scheme 9. Left: Synthesis of rhenium(I) complexes **8** and **9** (represented in an ORTEP style plot with ellipsoids shown at 50% probability). **Right:** Graphical representation of frontier molecular orbitals of **8** and **9** as determined by a computational study on the B3LYP/6-31+G** level of theory.

In compound **8** the two coordinated phosphinine ligands are arranged in *cis* position. Consequently, only one set of resonances is observed for the phosphinine ligand motif at room temperature in ¹H, ¹³C and ³¹P spectra of **8** in solution. A VT-³¹P-NMR study revealed significant broadening of the singlet at elevated temperatures, while a sharp singlet is obtained at lower temperatures. The three η¹-coordinated phosphinines in compound **9** are arranged in a *meridional* structural motif, resulting in two phosphinines in *trans* position. In solution, two sets of signals are observed in ¹H, ¹³C and ³¹P spectra of **9**. A combined analysis of NMR and IR spectroscopic data and single crystal X-ray data reveals both σ-donor and π-

acceptor properties of the phosphinine ligand. In Scheme 9 (right) calculated frontier orbitals of complex **8** and **9** are depicted. The corresponding HOMO–LUMO gap of complex **8** ($\Delta E = 3.98$ eV) is slightly bigger than for complex **9** ($\Delta E = 3.82$ eV). According to NBO analysis, the general trend of increased metal-to-ligand back-bonding is due to step-wise removal of carbonyl ligands and addition of phosphinine ligands.

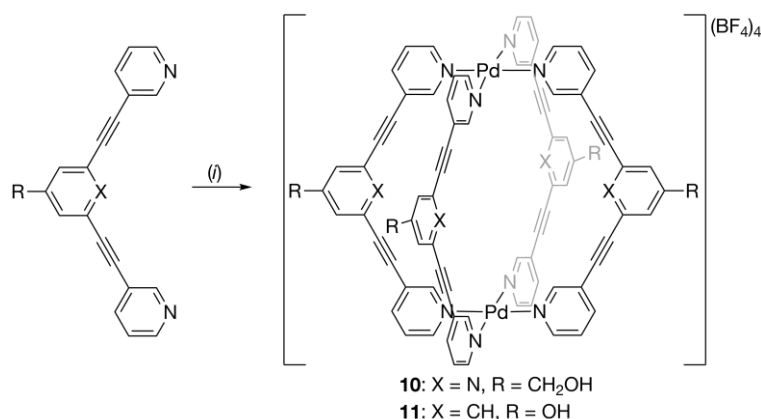
Accordingly, complexes **8** and **9** are interesting precursors for the synthesis of rhenium(I) biphosphinine systems, which might be a promising alternative to established rhenium(I) bipyridine systems for the photocatalytic activation of carbon dioxide.

3.5 Evaluation of New Palladium Cages as Potential Delivery Systems for the Anticancer Drug Cisplatin

ANDREA SCHMIDT, VIVIANA MOLANO, **MANUELA HOLLERING**, ALEXANDER PÖTHIG, ANGELA CASINI, AND FRITZ E. KÜHN

CHEMISTRY – A EUROPEAN JOURNAL **2016**, *22*, 2253–2256.

Metal-mediated self-assembled supramolecular coordination complexes (SCCs) have been shown to possess a wealth of remarkable physical-chemical properties. Especially host-guest interactions make them suitable for the growing field of molecular recognition and encapsulation of a wide range of guest molecules. This report endeavors to exploit the unique characteristics of a new series of cage compounds of the type Pd₂L₄ (L = ligand) and subsequent encapsulation of the anticancer drug cisplatin (Scheme 10).



Scheme 10. Exemplary synthesis of Pd(II) cages **10** and **11** using bidentate ligands and a Pd(II) precursor *via* self-assembly. (i) [Pd(NCCH₃)₄](BF₄)₂, r.t., 1 h, in DMSO.

Consequently, the antiproliferative effects of the described cages and their combination with cisplatin were examined *in vitro* in cancer cell lines. Fluorescence microscopy was used to monitor the uptake of the cages into the cells. However, only very low fluorescence quantum yields are obtained for the cage compounds due to the quenching effect of palladium. Interestingly, the hydroxymethyl-functionalized Pd(II) cage **10** with encapsulated cisplatin exhibited an improved cytotoxic effect against human ovarian cancer cells compared to free cisplatin (Figure 22).

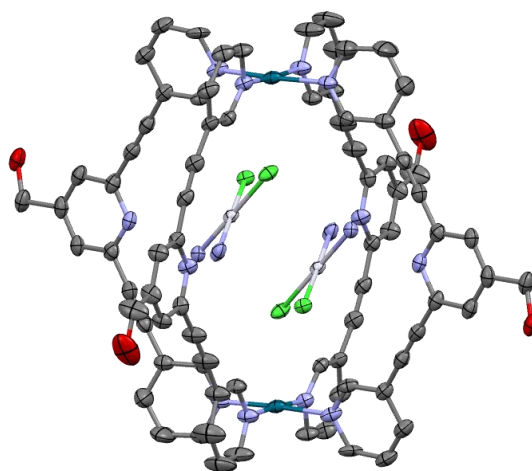


Figure 22. Molecular structure of the cationic cage **10** encapsulating two cisplatin molecules. Ellipsoids are shown at 50% probability. Hydrogen atoms, BF_4^- counterions, and solvent molecules are omitted for clarity. Selected hydrogen bond lengths [Å]: N–H \cdots N 2.057/2.9314(1), Cl \cdots H–C 2.550/3.3705(1), N–H \cdots Cl 2.666/3.3605(1). Due to an inversion center in the center of the cavity, only half of the cage and one cisplatin molecule are present in the asymmetric unit. Symmetry code: 1/2–x, 1/2–y, 1–z.

In addition, the toxicity of Pd_2L_4 cages was evaluated *ex vivo* in healthy rat-liver tissues using the precision cut-tissue slices technology, exhibiting scarce effects on liver viability. It is noteworthy, that some of the described cage compounds turned out to be cytotoxic in human cancer cell lines, which make them suitable anticancer agents by themselves. In view of these results, the potential of self-assembled Pd_2L_4 cages for biological applications is emphasized.

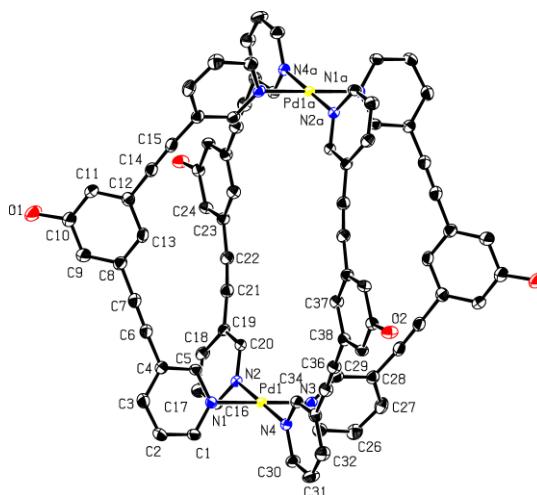


Figure 23. ORTEP style representation of the cationic cage **11** with ellipsoids shown at 50% probability. Hydrogen atoms, BF_4^- counterions and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–N1 2.0186(19), Pd1–N2 2.0259(19), Pd1 \cdots Pd1a 11.7429(7), C37 \cdots C37a 10.7536(6), O1 \cdots O1a 18.130(1), N1–Pd1–N2 90.22(7), N2–Pd1–N3 90.24.

3.6 Supramolecular *exo*-functionalized palladium cages: fluorescent properties and biological activity

ANDREA SCHMIDT, MANUELA HOLLERING, MARKUS DREES, ANGELA CASINI, AND FRITZ E. KÜHN

DALTON TRANSACTIONS **2016**, 45, 8556–8565.

In this article *exo*-functionalized self-assembled Pd₂L₄ cage compounds with attached fluorophore moieties were investigated, in order to enable the visualization of the uptake and distribution of the cages in cells by fluorescence microscopy. The structural motif of these type of Pd₂L₄ cages is depicted in Figure 24.

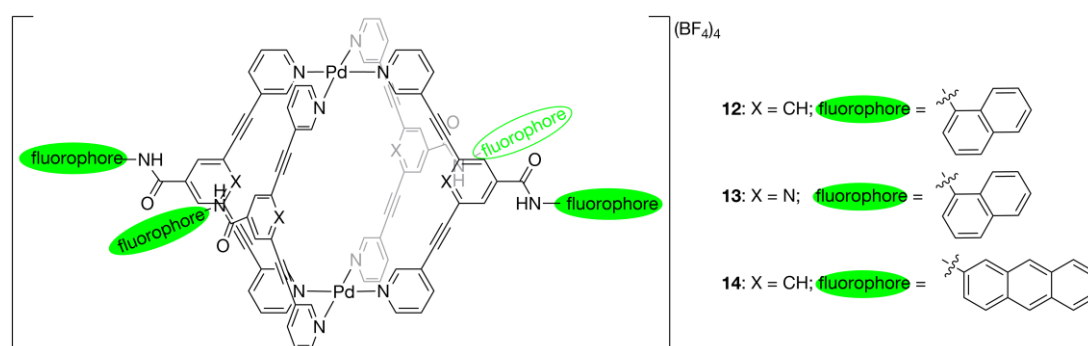


Figure 24. Schematic structure of Pd₂L₄ cage compounds **12**, **13** and **14** with attached fluorophore moieties.

In vitro tests in human lung and ovarian cancer cell lines revealed a higher cytotoxic effect for the reported cages than for cisplatin. However, fluorescence was significantly lower than expected especially when taking the introduction of fluorophore moieties into account. Contrary to previously observed quenching effects upon cage formation, even the fluorophore-based ligands display fluorescence quantum yields below 1%. In order to gain new insights into the quenching effect of palladium, time-dependent density functional theory (TD-DFT) calculations were executed.

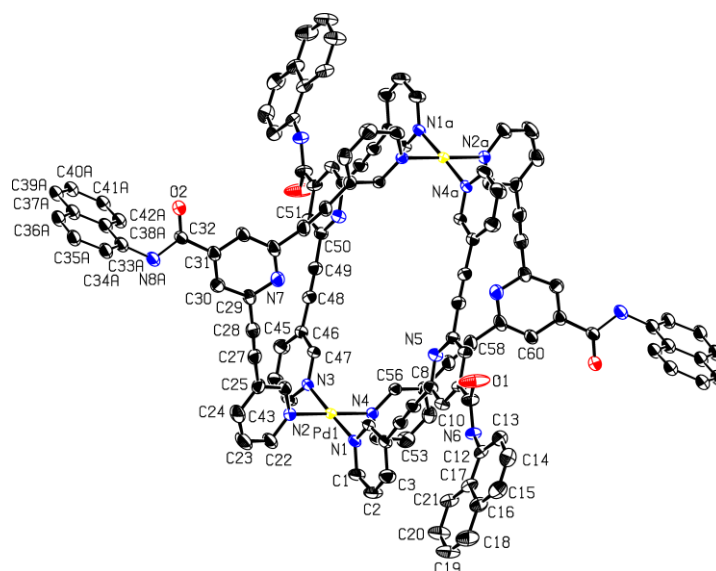


Figure 25. ORTEP style representation of the cationic cage **13** with ellipsoids shown at the 50% probability level. Hydrogen atoms, BF_4^- counterions and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–N1 2.013(3), Pd1–N2 2.031(3), Pd1...Pd1a 11.9308(6), N7...N7a 10.5029(6), N1–Pd1–N2 88.54(12), N2–Pd1–N3 92.45(12).

As a result, TD-single point calculations were performed on the ligands. It turned out, that the low fluorescence of the ligands with the fluorophore moieties is attributed to two main factors. On the one hand, the probability of the HOMO-LUMO excitation is extremely low for some of the ligands. On the other hand, energy differences between the highest excited state and the non-relaxed ground state reveal no emission in the visible region, but rather an emission in the IR region (2000 nm) (Figure 26). A change of the linker between the bipyridyl ligands and the fluorescent tags might be an interesting possibility to avoid the predicted torsion of the amide bond angle in the excited state.

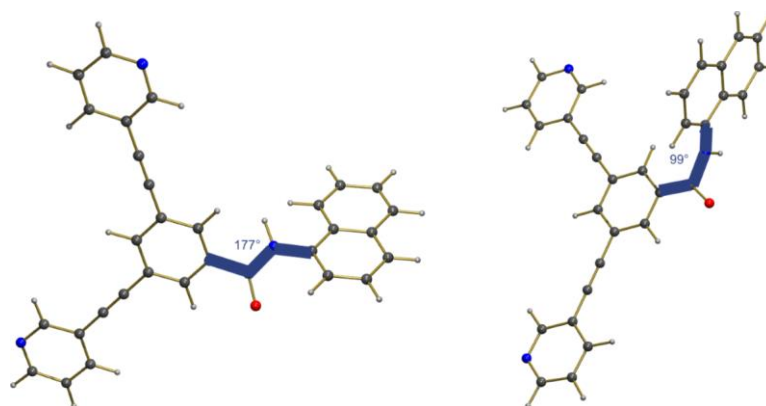


Figure 26. Calculated geometry of the ground state of the ligand of cage **12** (left) and the optimized first excited state after light absorption (right). Disruption of the chromophoric system leads to high energy differences and an emission wavelength outside the visible region.

3.7 Self-assembly of highly luminescent heteronuclear coordination cages

ANDREA SCHMIDT, **MANUELA HOLLERING**, JIAYING HAN, ANGELA CASINI, AND FRITZ E. KÜHN

DALTON TRANSACTIONS **2016**, *45*, 12297-12300.

In this communication *exo*-functionalized self-assembled Pd₂L₄ cage compounds with attached Ru(II) pyridine complexes are reported (Figure 27). Incorporation of luminescent functional groups like anthracene, naphthalene or ruthenium pyridine complexes into the ligand framework have been reported before, but did not enhance the emissive properties as desired. Based on previous findings regarding the quenching of luminescence in Pd₂L₄ cages, a rational approach to highly luminescent metallocsupramolecular coordination cages is presented.

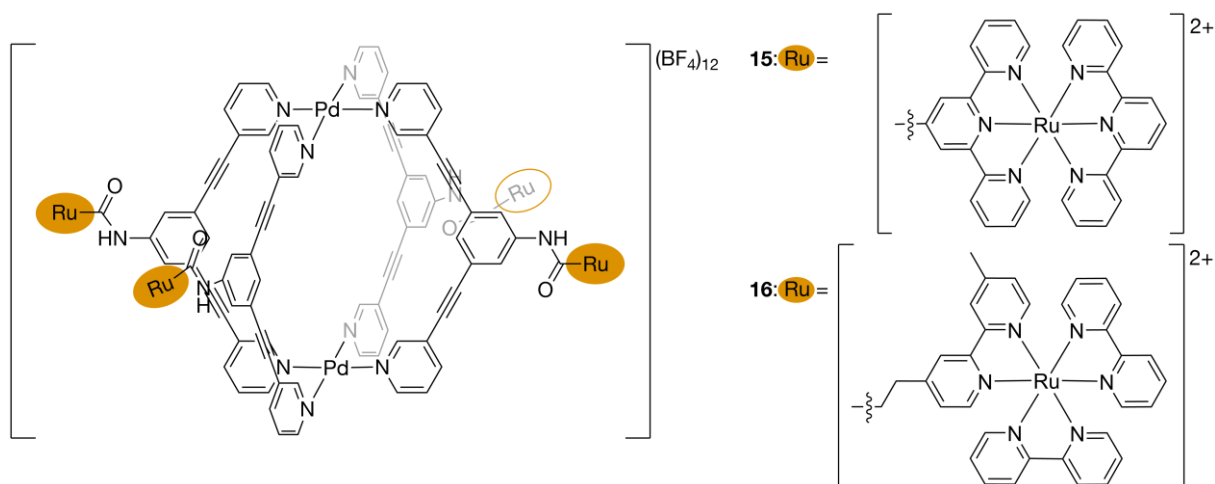


Figure 27. Schematic structure of *exo*-functionalized Pd₂L₄ cage compounds **15** and **16** with attached Ru(II) pyridine complexes.

In order to evaluate the influence of separation of the luminescent tag from the emissive ligand, two cage compounds are synthesized (Figure 27). Cage **15** with a ruthenium terpyridine ligand system and no spacer is compared to cage **16** with a ruthenium bipyridine ligand system and an ethyl bridge spacer. The molecular structure of the ligand of cage **15** was determined using single crystal X-ray diffraction and is depicted in Figure 28.

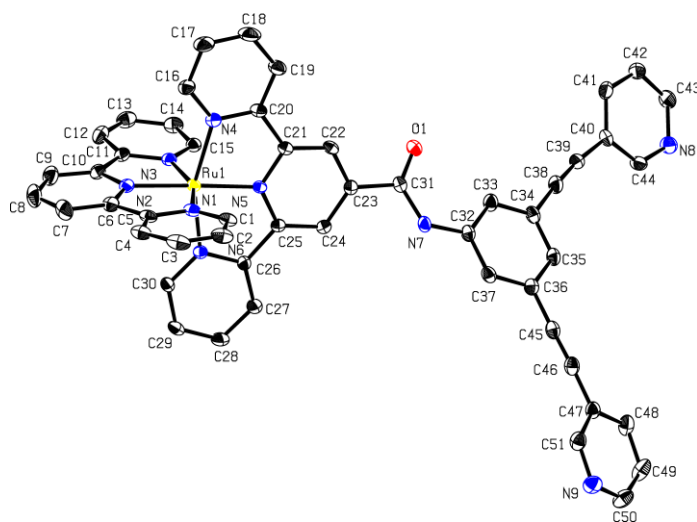


Figure 28. ORTEP style representation of the cationic ligand of cage **15** with ellipsoids shown at the 50% probability level. Hydrogen atoms, PF_6^- counterions and solvent molecules are omitted for clarity. Selected bond lengths [Å]: Ru1–N1 2.0729(2), Ru1–N2 1.9796(2), Ru1–N3 2.0683(1), Ru1–N4 2.0690(1), Ru1–N5 1.9694(2), Ru1–N6 2.0703(2), C31–N7 1.3631(1).

A calculated geometry optimized structure of cage **16** using a semi-empirical method (PM6) is shown in Figure 29. UV/Vis, excitation and emission spectroscopy was carried out on the ligands and the cage compounds. One of the highest reported quantum yields so far of 66% was achieved for the palladium cage **16** with a spacer in the ligand system, whereas the other one with no spacer did not exhibit any luminescence at all. The presented results support the assumption that the insertion of a spacer prevents quenching effects and leads to exceptionally high quantum yields and therefore highly emissive cage compounds, rendering it a promising strategy for future considerations.

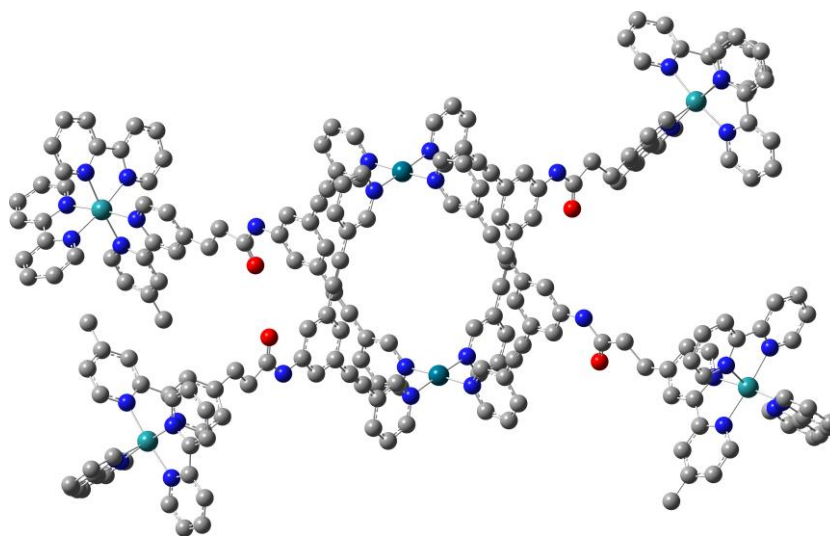


Figure 29. Molecular modeling of cage **16** using semi-empirical methods (PM6).

4 CONCLUSION AND OUTLOOK

The first part of this work addresses the synthesis and characterization as well as the application of polydentate NHC complexes of ruthenium.

Flexible acyclic tetraimidazolium salts were employed as precursors for ruthenium(II) tetra-NHC complexes. Depending on the length of the alkyl bridges, the sawhorse-type geometry or the equatorial coordination of the acyclic tetra-NHC was favored. Ligand exchange experiments with stronger donors than acetonitrile led to differing coordination geometries. DFT calculations also suggest, that sawhorse-orientation is only observed when the energetic difference between both geometries is rather small. Previously reported iron(II) complexes featuring the same ligands showed fluxional behavior, which was not observed for the heavier ruthenium homologs.²²⁴ Figure 30 shows the generic representation of a tetra-NHC based ruthenium(II) complex with sawhorse type geometry. Complex **1** (L = MeCN, R = methyl, n = 1, X = PF₆⁻) turned out to be among the most active transfer hydrogenation precatalysts reported so far, achieving TOFs up to 110 000 h⁻¹.

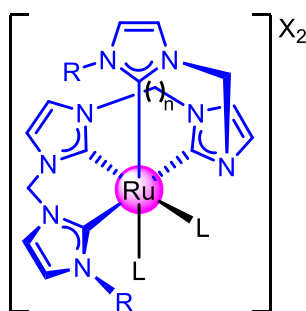


Figure 30. Ruthenium(II) tetra-NHC complex presented in this work (Complex **1**: L = MeCN, R = methyl, n = 1, X = PF₆⁻) and possibilities for modifications and subsequent catalyst improvement.

Future work in this field should focus on a wider substrate screening and even lower catalyst loadings, in order to better understand the limitations of the precatalyst **1**. However, modifications of this ligand motif might offer even greater potential for additional research on ruthenium(II) tetra-NHC based transfer hydrogenation precatalysts. Especially wingtip substitution might favor the sawhorse type geometry, which turned out to be beneficial for transfer hydrogenation reactions. Accordingly, sawhorse type geometry might be feasible even with elongated alkyl bridges. Variation of the labile ligand L might influence the initial turnover frequency additionally.

Following these promising results, the combination of imidazolylidene and triazolylidene carbenes was carried out, since abnormal NHCs are well known for their increased σ -donor properties. Ruthenium(II) tri-NHC complexes were chosen for their additional variability in

coordination modes and choice of non-carbene ligands compared to tetra-NHC complexes. A mixed methylene bridged azolium salt with one imidazolium and two attached triazolium moieties was prepared and used as precursor in a microwave-assisted one-pot reaction to yield the normal/abnormal Ru(II) tri-NHC in meridional coordination. Complex **7** achieved an initial TOF of 580 h⁻¹ when applied as transfer hydrogenation precatalyst of acetophenone in 2-propanol. Although the catalytic activity does not reach the highest reported reactivity for ruthenium based transfer hydrogenation precatalysts it still provides a platform for further investigation of this motif. In addition two chelating monocarbene Ru(II) complexes were obtained when the triazole moieties were not alkylated at the N3 position. In this case, the triazole acted as a neutral nitrogen donor and either one or both coordinated to the ruthenium center. The coordination turned out to be rather stable even at elevated temperatures and no hemilabile behavior was observed.

Screening of a wider substrate scope would be interesting in the future. Until now, only the model substrate acetophenone was tested, however, especially fluorinated substrates might benefit from the increased σ -donor strength of the abnormal carbene moieties in complex **7**. Additional wingtip group modification would allow for specific tailoring of the steric demand and accessibility of the precatalyst.

In the second part of this work the focus is on the transformation of carbon dioxide using transition metal complexes. Besides the conceptual approach and presentation of the first catalytic transformations of carbon dioxide and ethene to acrylates, the synthesis and characterization of promising precursors for rhenium(I) biphosphinine complexes was reported. As an alternative to established rhenium(I) bipyridine systems for the photocatalytic activation of carbon dioxide, rhenium(I) biphosphinine complexes might be obtained using the described rhenium(I)-phosphinine complexes. Future work in this field should examine coupling reactions in the coordination sphere of a disubstituted rhenium(I) phosphinine complex. Especially coupling *via* a halogen to lithium exchange, subsequently followed by C-C bond formation with a suitable coupling reagent could be a promising option.

Furthermore, a series of *exo*-functionalized Pd₂L₄ cage compounds was synthesized *via* self-assembly. Noteworthy, we were able to demonstrate the encapsulation of the anticancer drug cisplatin using NMR spectroscopy and single-crystal X-ray diffraction. In addition, biological studies were carried out, proving an increased cytotoxic effect for one of the host guest systems, compared to the cage and cisplatin on their own. *Ex vivo* experiments with healthy rat liver tissue, displayed very limited toxicity of the same cage. In order to improve biological imaging *via* fluorescence microscopy a rational approach to highly luminescent cage compounds was reported. Consequently, *exo*-functionalized Pd₂L₄ cage compounds with

attached fluorophore moieties were investigated. TD-DFT calculations revealed a torsion of the amide bond angle of the ligand in the excited state, which resulted in quenching of the fluorescence of the ligands. This was due to a low probability of the HOMO-LUMO excitation among other things. Additional *in vitro* tests showed a higher cytotoxic effect of the cage compounds than cisplatin. In order to overcome the predicted torsion of the amide bond, a spacer was inserted to separate the emissive ligand from the ruthenium pyridine based luminescent tag in a subsequent study. It was indeed possible to synthesize a highly emissive cage compound with an ethyl bridge as spacer, while the cage without spacer showed no luminescence.

These findings pave the way for rational modifications to yield highly luminescent *exo*-functionalized Pd₂L₄ cage compounds. Taking advantage of the luminescent properties of the resulting metallocages, their accumulation can be investigated in various cells using fluorescence microscopy. The ability to use biological imaging allows for the elucidation of drug uptake, distribution and release mechanisms in the cell lines in future studies.

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MANUELA HOLLERING, DANIEL T. WEISS, MARIO J. BITZER, CHRISTIAN JANDL, AND FRITZ E. KÜHN

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5.2 Bonding and Catalytic Application of Ruthenium *N*-Heterocyclic Carbene Complexes Featuring Triazole, Triazolylidene and Imidazolylidene Ligands

MANUELA HOLLERING, MARTIN ALBRECHT, AND FRITZ E. KÜHN

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5.3 Transition metal mediated coupling of carbon dioxide and ethene to acrylic acid/acrylates

MANUELA HOLLERING,[#] BARNALI DUTTA,[#] AND FRITZ E. KÜHN

[#] M. Hollering and B. Dutta contributed equally to this work.

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MANUELA HOLLERING, RICHARD O. REITHMEIER, SIMON MEISTER, EBERHARDT HERDTWECK, FRITZ E. KÜHN,* AND BERNHARD RIEGER*

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ANDREA SCHMIDT, VIVIANA MOLANO, **MANUELA HOLLERING**, ALEXANDER PÖTHIG, ANGELA CASINI, AND FRITZ E. KÜHN

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5.6 Supramolecular *exo*-functionalized palladium cages: fluorescent properties and biological activity

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5.7 Self-assembly of highly luminescent heteronuclear coordination cages

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**6 BIBLIOGRAPHIC DATA OF
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Controlling Coordination Geometries: Ru–Carbene Complexes with Tetra-NHC Ligands

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Bonding and Catalytic Application of Ruthenium *N*-Heterocyclic Carbene Complexes Featuring Triazole, Triazolylidene and Imidazolylidene Ligands

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Transition metal mediated coupling of carbon dioxide and ethene to acrylic acid/acrylates

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[Re(CO)₃Cl(C₅H₄CIP)₂] and [Re(CO)₂Cl(C₅H₄CIP)₃]: synthesis and characterization of two novel rhenium(I) phosphinine complexes

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Evaluation of New Palladium Cages as Potential Delivery Systems for the Anticancer Drug Cisplatin

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Supramolecular *exo*-functionalized palladium cages: fluorescent properties and biological activity

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Self-assembly of highly luminescent heteronuclear coordination cages

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7 REFERENCES

- (1) *The European Chemical Industry - Facts & Figures 2016*. Cefic, the European Chemical Industry Council: 2016.
- (2) Hagen, J., In *Industrial Catalysis*, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2015.
- (3) Kühn, F. E.; Herrmann, W. A., *Coord. Chem. Rev.* **2011**, *255*, 1439.
- (4) Crabtree, R. H., *The Organometallic Chemistry of the Transition Metals*. John Wiley & Sons, Inc.: Hoboken, New Jersey, 2014.
- (5) Behr, A.; Neubert, P., *Applied homogeneous catalysis*. Wiley-VCH Weinheim 2012
- (6) Glorius, F., *N-Heterocyclic Carbenes in Transition Metal Catalysis*. Springer-Verlag Berlin Heidelberg: Berlin Heidelberg, 2007.
- (7) Fischer, E. O.; Maasböl, A., *Angew. Chem. Int. Ed.* **1964**, *3*, 580-581.
- (8) Schrock, R. R., *J. Am. Chem. Soc.* **1974**, *96*, 6796-6797.
- (9) Jahnke, M. C.; Hahn, E. M., *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools*. The Royal Society of Chemistry: 2011.
- (10) Nolan, S. P., *N-Heterocyclic Carbenes in Synthesis*. Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2006.
- (11) Köhl, O., *Functionalised N-Heterocyclic Carbene Complexes*. John Wiley & Sons, Ltd: Chichester, 2010.
- (12) Fischer, E. O.; Maasböl, A., *Angew. Chem.* **1964**, *76*, 645-645.
- (13) Öfele, K., *J. Organomet. Chem.* **1968**, *12*, P42-P43.
- (14) Öfele, K., *Angew. Chem.* **1969**, *81*, 936-936.
- (15) Wanzlick, H. W.; Schönherr, H. J., *Angew. Chem. Int. Ed.* **1968**, *7*, 141-142.
- (16) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F., *Chem. Rev.* **1972**, *72*, 545-574.
- (17) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F.; Manojlovic-Muir, L.; Muir, K. W., *J. Chem. Soc. D* **1971**, 400-401.
- (18) Cetinkaya, B.; Dixneuf, P.; Lappert, M. F., *J. Chem. Soc., Chem. Commun.* **1973**, 206-206.
- (19) Cardin, D. J.; Cetinkaya, B.; Cetinkaya, E.; Lappert, M. F., *J. Chem. Soc., Dalton Trans.* **1973**, 514-522.
- (20) Cetinkaya, B.; Dixneuf, P.; Lappert, M. F., *J. Chem. Soc., Dalton Trans.* **1974**, 1827-1833.
- (21) Arduengo, A. J.; Harlow, R. L.; Kline, M., *J. Am. Chem. Soc.* **1991**, *113*, 361-363.
- (22) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J., *Angew. Chem. Int. Ed.* **1995**, *34*, 2371-2374.
- (23) Herrmann, W. A., *Angew. Chem. Int. Ed.* **2002**, *41*, 1290-1309.
- (24) Nelson, D. J.; Nolan, S. P., *N-Heterocyclic Carbenes*. Wiley-VCH Verlag GmbH & Co. KGaA: 2014.
- (25) Herrmann, W. A.; Köcher, C., *Angew. Chem. Int. Ed.* **1997**, *36*, 2162-2187.
- (26) Arduengo, A. J., *Acc. Chem. Res.* **1999**, *32*, 913-921.
- (27) Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L., *Coord. Chem. Rev.* **2009**, *253*, 687-703.
- (28) Crudden, C. M.; Allen, D. P., *Coord. Chem. Rev.* **2004**, *248*, 2247-2273.
- (29) Peris, E.; Crabtree, R. H., *Coord. Chem. Rev.* **2004**, *248*, 2239-2246.
- (30) Poyatos, M.; McNamara, W.; Incarvito, C.; Clot, E.; Peris, E.; Crabtree, R. H., *Organometallics* **2008**, *27*, 2128-2136.
- (31) Tolman, C. A., *Chem. Rev.* **1977**, *77*, 313-348.
- (32) Clavier, H.; Nolan, S. P., *Chem. Commun.* **2010**, *46*, 841-861.
- (33) Hahn, F. E.; Jahnke, M. C., *Angew. Chem. Int. Ed.* **2008**, *47*, 3122-3172.
- (34) Schuster, O.; Yang, L.; Raubenheimer, H. G.; Albrecht, M., *Chem. Rev.* **2009**, *109*, 3445-3478.
- (35) Arduengo, A. J.; Dias, H. V. R.; Harlow, R. L.; Kline, M., *J. Am. Chem. Soc.* **1992**, *114*, 5530-5534.
- (36) Öfele, K.; Herrmann, W. A.; Mihalios, D.; Elison, M.; Herdtweck, E.; Scherer, W.; Mink, J., *J. Organomet. Chem.* **1993**, *459*, 177-184.

- (37) Dorta, R.; Stevens, E. D.; Hoff, C. D.; Nolan, S. P., *J. Am. Chem. Soc.* **2003**, *125*, 10490-10491.
- (38) Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P., *J. Am. Chem. Soc.* **2005**, *127*, 2485-2495.
- (39) Gründemann, S.; Kovacevic, A.; Albrecht, M.; Faller, J. W.; Crabtree, R. H., *J. Am. Chem. Soc.* **2002**, *124*, 10473-10481.
- (40) Herrmann, W. A.; Mihalios, D.; Öfele, K.; Kiprof, P.; Belmedjahed, F., *Chem. Ber.* **1992**, *125*, 1795-1799.
- (41) Köcher, C.; Herrmann, W. A., *J. Organomet. Chem.* **1997**, *532*, 261-265.
- (42) Clyne, D. S.; Jin, J.; Genest, E.; Gallucci, J. C.; RajanBabu, T. V., *Org. Lett.* **2000**, *2*, 1125-1128.
- (43) Bittermann, A.; Baskakov, D.; Herrmann, W. A., *Organometallics* **2009**, *28*, 5107-5111.
- (44) Poyatos, M.; Sanaú, M.; Peris, E., *Inorg. Chem.* **2003**, *42*, 2572-2576.
- (45) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B., *Chem. Rev.* **2009**, *109*, 3561-3598.
- (46) Wang, H. M. J.; Lin, I. J. B., *Organometallics* **1998**, *17*, 972-975.
- (47) Jantke, D.; Cokoja, M.; Pöthig, A.; Herrmann, W. A.; Kühn, F. E., *Organometallics* **2013**, *32*, 741-744.
- (48) Mas-Marzá, E.; Sanaú, M.; Peris, E., *Inorg. Chem.* **2005**, *44*, 9961-9967.
- (49) Clement, N. D.; Cavell, K. J.; Jones, C.; Elsevier, C. J., *Angew. Chem. Int. Ed.* **2004**, *43*, 1277-1279.
- (50) Duin, M. A.; Clement, N. D.; Cavell, K. J.; Elsevier, C. J., *Chem. Commun.* **2003**, 400-401.
- (51) Gründemann, S.; Albrecht, M.; Kovacevic, A.; Faller, J. W.; Crabtree, R. H., *J. Chem. Soc., Dalton Trans.* **2002**, 2163-2167.
- (52) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H., *Org. Lett.* **1999**, *1*, 953-956.
- (53) Blum, A. P.; Ritter, T.; Grubbs, R. H., *Organometallics* **2007**, *26*, 2122-2124.
- (54) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H., *J. Am. Chem. Soc.* **2003**, *125*, 2546-2558.
- (55) Kunz, R.; Grel, P. L.; Fehlhammer, W. P., *J. Chem. Soc., Dalton Trans.* **1996**, 3231-3236.
- (56) Jahnke, M. C.; Hahn, F. E., *Coord. Chem. Rev.* **2015**, *293-294*, 95-115.
- (57) Hahn, F. E.; Langenhahn, V.; Lügger, T.; Pape, T.; Le Van, D., *Angew. Chem. Int. Ed.* **2005**, *44*, 3759-3763.
- (58) Hahn, F. E.; Langenhahn, V.; Pape, T., *Chem. Commun.* **2005**, 5390-5392.
- (59) Hahn, F. E.; Langenhahn, V.; Meier, N.; Lügger, T.; Fehlhammer, W. P., *Chem. Eur. J.* **2003**, *9*, 704-712.
- (60) Díez-González, S.; Marion, N.; Nolan, S. P., *Chem. Rev.* **2009**, *109*, 3612-3676.
- (61) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F., *Nature* **2014**, *510*, 485-496.
- (62) Benhamou, L.; Chardon, E.; Lavigne, G.; Bellemin-Laponnaz, S.; César, V., *Chem. Rev.* **2011**, *111*, 2705-2733.
- (63) de Frémont, P.; Marion, N.; Nolan, S. P., *Coord. Chem. Rev.* **2009**, *253*, 862-892.
- (64) Dröge, T.; Glorius, F., *Angew. Chem. Int. Ed.* **2010**, *49*, 6940-6952.
- (65) Chan, B.; Chang, N.; Grimmett, M., *Aust. J. Chem.* **1977**, *30*, 2005-2013.
- (66) Herrmann, W. A.; Köcher, C.; Gooßen, L. J.; Artus, G. R. J., *Chem. Eur. J.* **1996**, *2*, 1627-1636.
- (67) Böhm, V. P. W.; Weskamp, T.; Gstötmayr, C. W. K.; Herrmann, W. A., *Angew. Chem. Int. Ed.* **2000**, *39*, 1602-1604.
- (68) Arduengo, A. J.; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Khasnis, D.; Marshall, W. J.; Prakasha, T. K., *J. Am. Chem. Soc.* **1997**, *119*, 12742-12749.
- (69) Díez-González, S.; Nolan, S. P., *Coord. Chem. Rev.* **2007**, *251*, 874-883.
- (70) Hillier, A. C.; Sommer, W. J.; Yong, B. S.; Petersen, J. L.; Cavallo, L.; Nolan, S. P., *Organometallics* **2003**, *22*, 4322-4326.

- (71) Ragone, F.; Poater, A.; Cavallo, L., *J. Am. Chem. Soc.* **2010**, *132*, 4249-4258.
- (72) Poater, A.; Cosenza, B.; Correa, A.; Giudice, S.; Ragone, F.; Scarano, V.; Cavallo, L., *Eur. J. Inorg. Chem.* **2009**, *2009*, 1759-1766.
- (73) Cesar, V.; Bellemin-Laponnaz, S.; Gade, L. H., *Chem. Soc. Rev.* **2004**, *33*, 619-636.
- (74) Gade, L. H.; Bellemin-Laponnaz, S., *Coord. Chem. Rev.* **2007**, *251*, 718-725.
- (75) Gladiali, S.; Alberico, E., *Chem. Soc. Rev.* **2006**, *35*, 226-236.
- (76) Mauduit, M.; Clavier, H., Asymmetric Catalysis with Metal N-Heterocyclic Carbene Complexes. In *N-Heterocyclic Carbenes in Synthesis*, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2006.
- (77) Perry, M. C.; Burgess, K., *Tetrahedron: Asymmetry* **2003**, *14*, 951-961.
- (78) Tornatzky, J.; Kannenberg, A.; Blechert, S., *Dalton Trans.* **2012**, *41*, 8215-8225.
- (79) Douthwaite, R. E., *Coord. Chem. Rev.* **2007**, *251*, 702-717.
- (80) Cornils, B.; Herrmann, W. A., Development of Methods: Section 3.1.3-3.1.13.4. In *Applied Homogeneous Catalysis with Organometallic Compounds*, Wiley-VCH Verlag GmbH: 2008.
- (81) Velazquez, H. D.; Verpoort, F., *Chem. Soc. Rev.* **2012**, *41*, 7032-7060.
- (82) Dixon, D. A.; Arduengo, A. J., *J. Phys. Chem.* **1991**, *95*, 4180-4182.
- (83) Heinemann, C.; Müller, T.; Apeloig, Y.; Schwarz, H., *J. Am. Chem. Soc.* **1996**, *118*, 2023-2038.
- (84) Boehme, C.; Frenking, G., *J. Am. Chem. Soc.* **1996**, *118*, 2039-2046.
- (85) Arduengo, A. J.; Goerlich, J. R.; Marshall, W. J., *Liebigs Annalen* **1997**, *1997*, 365-374.
- (86) Gusev, D. G., *Organometallics* **2009**, *28*, 6458-6461.
- (87) Cantat, T.; Mezailles, N.; Maigrot, N.; Ricard, L.; Le Floch, P., *Chem. Commun.* **2004**, 1274-1275.
- (88) Martin, D.; Baceiredo, A.; Gornitzka, H.; Schoeller, W. W.; Bertrand, G., *Angew. Chem. Int. Ed.* **2005**, *44*, 1700-1703.
- (89) Masuda, J. D.; Martin, D.; Lyon-Saunier, C.; Baceiredo, A.; Gornitzka, H.; Donnadiou, B.; Bertrand, G., *Chem. Asian J.* **2007**, *2*, 178-187.
- (90) Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. J., *Inorg. Chem.* **1988**, *27*, 85-92.
- (91) Hahn, F. E.; Tamm, M., *J. Organomet. Chem.* **1993**, *456*, C11-C14.
- (92) Kembach, U.; Lügger, T.; Hahn, F. E.; Fehlhammer, W. P., *J. Organomet. Chem.* **1997**, *541*, 51-55.
- (93) Khramov, D. M.; Lynch, V. M.; Bielawski, C. W., *Organometallics* **2007**, *26*, 6042-6049.
- (94) Bittermann, A.; Härter, P.; Herdtweck, E.; Hoffmann, S. D.; Herrmann, W. A., *J. Organomet. Chem.* **2008**, *693*, 2079-2090.
- (95) Hahn, F. E.; Wittenbecher, L.; Le Van, D.; Fröhlich, R., *Angew. Chem. Int. Ed.* **2000**, *39*, 541-544.
- (96) Li, C.-J., *Chem. Rev.* **2005**, *105*, 3095-3166.
- (97) Shaughnessy, K. H., *Chem. Rev.* **2009**, *109*, 643-710.
- (98) Schaper, L.-A.; Hock, S. J.; Herrmann, W. A.; Kühn, F. E., *Angew. Chem. Int. Ed.* **2013**, *52*, 270-289.
- (99) Levin, E.; Ivry, E.; Diesendruck, C. E.; Lemcoff, N. G., *Chem. Rev.* **2015**, *115*, 4607-4692.
- (100) Sommer, W. J.; Weck, M., *Coord. Chem. Rev.* **2007**, *251*, 860-873.
- (101) Buchmeiser, M. R., *Chem. Rev.* **2009**, *109*, 303-321.
- (102) Wang, Z.; Chen, G.; Ding, K., *Chem. Rev.* **2009**, *109*, 322-359.
- (103) Samojłowicz, C.; Bieniek, M.; Grela, K., *Chem. Rev.* **2009**, *109*, 3708-3742.
- (104) Leadbeater, N. E.; Marco, M., *Chem. Rev.* **2002**, *102*, 3217-3274.
- (105) Crabtree, R. H., *Coord. Chem. Rev.* **2013**, *257*, 755-766.
- (106) Arnold, P. L.; Pearson, S., *Coord. Chem. Rev.* **2007**, *251*, 596-609.
- (107) Albrecht, M., *CHIMIA* **2009**, *63*, 105-110.
- (108) Albrecht, M., *Chem. Commun.* **2008**, 3601-3610.

- (109) Donnelly, K. F.; Petronilho, A.; Albrecht, M., *Chem. Commun.* **2013**, 49, 1145-1159.
- (110) Krüger, A.; Albrecht, M., *Aust. J. Chem.* **2011**, 64, 1113-1117.
- (111) Grundemann, S.; Kovacevic, A.; Albrecht, M.; Faller Robert, J. W.; Crabtree, H., *Chem. Commun.* **2001**, 2274-2275.
- (112) Schneider, S. K.; Roembke, P.; Julius, G. R.; Loschen, C.; Raubenheimer, H. G.; Frenking, G.; Herrmann, W. A., *Eur. J. Inorg. Chem.* **2005**, 2005, 2973-2977.
- (113) Lebel, H.; Janes, M. K.; Charette, A. B.; Nolan, S. P., *J. Am. Chem. Soc.* **2004**, 126, 5046-5047.
- (114) Heckenroth, M.; Kluser, E.; Neels, A.; Albrecht, M., *Angew. Chem. Int. Ed.* **2007**, 46, 6293-6296.
- (115) Yang, L.; Krüger, A.; Neels, A.; Albrecht, M., *Organometallics* **2008**, 27, 3161-3171.
- (116) Chianese, A. R.; Kovacevic, A.; Zeglis, B. M.; Faller, J. W.; Crabtree, R. H., *Organometallics* **2004**, 23, 2461-2468.
- (117) Alcarazo, M.; Roseblade, S. J.; Cowley, A. R.; Fernández, R.; Brown, J. M.; Lassaletta, J. M., *J. Am. Chem. Soc.* **2005**, 127, 3290-3291.
- (118) Han, Y.; Huynh, H. V., *Chem. Commun.* **2007**, 1089-1091.
- (119) Han, Y.; Huynh, H. V.; Tan, G. K., *Organometallics* **2007**, 26, 6581-6585.
- (120) Han, Y.; Huynh, H. V., *Dalton Trans.* **2011**, 40, 2141-2147.
- (121) Iglesias, M.; Albrecht, M., *Dalton Trans.* **2010**, 39, 5213-5215.
- (122) Lavallo, V.; Dyker, C. A.; Donnadiou, B.; Bertrand, G., *Angew. Chem. Int. Ed.* **2008**, 47, 5411-5414.
- (123) Fernández, I.; Dyker, C. A.; DeHope, A.; Donnadiou, B.; Frenking, G.; Bertrand, G., *J. Am. Chem. Soc.* **2009**, 131, 11875-11881.
- (124) Mathew, P.; Neels, A.; Albrecht, M., *J. Am. Chem. Soc.* **2008**, 130, 13534-13535.
- (125) Kolb, H. C.; Finn, M. G.; Sharpless, K. B., *Angew. Chem. Int. Ed.* **2001**, 40, 2004-2021.
- (126) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B., *Angew. Chem. Int. Ed.* **2002**, 41, 2596-2599.
- (127) Himoto, F.; Lovell, T.; Hilgraf, R.; Rostovtsev, V. V.; Noodleman, L.; Sharpless, K. B.; Fokin, V. V., *J. Am. Chem. Soc.* **2005**, 127, 210-216.
- (128) Tornøe, C. W.; Christensen, C.; Meldal, M., *J. Org. Chem.* **2002**, 67, 3057-3064.
- (129) Bock, V. D.; Hiemstra, H.; van Maarseveen, J. H., *Eur. J. Org. Chem.* **2006**, 2006, 51-68.
- (130) Moses, J. E.; Moorhouse, A. D., *Chem. Soc. Rev.* **2007**, 36, 1249-1262.
- (131) Hein, J. E.; Fokin, V. V., *Chem. Soc. Rev.* **2010**, 39, 1302-1315.
- (132) Schulze, B.; Schubert, U. S., *Chem. Soc. Rev.* **2014**, 43, 2522-2571.
- (133) Diez-Gonzalez, S., *Catal. Sci. Technol.* **2011**, 1, 166-178.
- (134) Meldal, M.; Tornøe, C. W., *Chem. Rev.* **2008**, 108, 2952-3015.
- (135) Haldon, E.; Nicasio, M. C.; Perez, P. J., *Org. Biomol. Chem.* **2015**, 13, 9528-9550.
- (136) Wirsching, W.; Jochims, J. C., *Synthesis* **1997**, 1997, 233-241.
- (137) Schaper, L.-A.; Ofele, K.; Kadyrov, R.; Bechlars, B.; Drees, M.; Cokoja, M.; Herrmann, W. A.; Kühn, F. E., *Chem. Commun.* **2012**, 48, 3857-3859.
- (138) Schaper, L.-A.; Graser, L.; Wei, X.; Zhong, R.; Öfele, K.; Pöthig, A.; Cokoja, M.; Bechlars, B.; Herrmann, W. A.; Kühn, F. E., *Inorg. Chem.* **2013**, 52, 6142-6152.
- (139) Schaper, L.-A.; Wei, X.; Hock, S. J.; Pöthig, A.; Öfele, K.; Cokoja, M.; Herrmann, W. A.; Kühn, F. E., *Organometallics* **2013**, 32, 3376-3384.
- (140) Delgado-Rebollo, M.; Canseco-Gonzalez, D.; Hollering, M.; Mueller-Bunz, H.; Albrecht, M., *Dalton Trans.* **2014**, 43, 4462-4473.
- (141) Cai, J.; Yang, X.; Arumugam, K.; Bielawski, C. W.; Sessler, J. L., *Organometallics* **2011**, 30, 5033-5037.
- (142) Keske, E. C.; Zenkina, O. V.; Wang, R.; Crudden, C. M., *Organometallics* **2012**, 31, 456-461.

- (143) Schulze, B.; Escudero, D.; Friebe, C.; Siebert, R.; Görls, H.; Köhn, U.; Altuntas, E.; Baumgaertel, A.; Hager, M. D.; Winter, A.; Dietzek, B.; Popp, J.; González, L.; Schubert, U. S., *Chem. Eur. J.* **2011**, *17*, 5494-5498.
- (144) Guisado-Barrios, G.; Bouffard, J.; Donnadiou, B.; Bertrand, G., *Organometallics* **2011**, *30*, 6017-6021.
- (145) Hohloch, S.; Su, C.-Y.; Sarkar, B., *Eur. J. Inorg. Chem.* **2011**, *2011*, 3067-3075.
- (146) Poulain, A.; Canseco-Gonzalez, D.; Hynes-Roche, R.; Müller-Bunz, H.; Schuster, O.; Stoeckli-Evans, H.; Neels, A.; Albrecht, M., *Organometallics* **2011**, *30*, 1021-1029.
- (147) Guisado-Barrios, G.; Bouffard, J.; Donnadiou, B.; Bertrand, G., *Angew. Chem. Int. Ed.* **2010**, *49*, 4759-4762.
- (148) Bouffard, J.; Keitz, B. K.; Tonner, R.; Guisado-Barrios, G.; Frenking, G.; Grubbs, R. H.; Bertrand, G., *Organometallics* **2011**, *30*, 2617-2627.
- (149) Bernhammer, J. C.; Frison, G.; Huynh, H. V., *Chem. Eur. J.* **2013**, *19*, 12892-12905.
- (150) Yuan, D.; Huynh, H. V., *Organometallics* **2012**, *31*, 405-412.
- (151) Lee, M.-T.; Hu, C.-H., *Organometallics* **2004**, *23*, 976-983.
- (152) Tonner, R.; Heydenrych, G.; Frenking, G., *Chem. Asian J.* **2007**, *2*, 1555-1567.
- (153) Magill, A. M.; Cavell, K. J.; Yates, B. F., *J. Am. Chem. Soc.* **2004**, *126*, 8717-8724.
- (154) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H., *Organometallics* **2003**, *22*, 1663-1667.
- (155) Song, G.; Zhang, Y.; Li, X., *Organometallics* **2008**, *27*, 1936-1943.
- (156) Terashima, T.; Inomata, S.; Ogata, K.; Fukuzawa, S.-i., *Eur. J. Inorg. Chem.* **2012**, *2012*, 1387-1393.
- (157) Heckenroth, M.; Neels, A.; Garnier, M. G.; Aebi, P.; Ehlers, A. W.; Albrecht, M., *Chem. Eur. J.* **2009**, *15*, 9375-9386.
- (158) Ung, G.; Mendoza-Espinosa, D.; Bouffard, J.; Bertrand, G., *Angew. Chem. Int. Ed.* **2011**, *50*, 4215-4218.
- (159) Crowley, J. D.; McMorran, D. A., "Click-Triazole" Coordination Chemistry: Exploiting 1,4-Disubstituted-1,2,3-Triazoles as Ligands. In *Click Triazoles*, Košmrlj, J., Ed. Springer Berlin Heidelberg: Berlin, Heidelberg, 2012.
- (160) Struthers, H.; Mindt, T. L.; Schibli, R., *Dalton Trans.* **2010**, *39*, 675-696.
- (161) Frenking, G.; Fröhlich, N., *Chem. Rev.* **2000**, *100*, 717-774.
- (162) Heydenrych, G.; von Hopffgarten, M.; Stander, E.; Schuster, O.; Raubenheimer, H. G.; Frenking, G., *Eur. J. Inorg. Chem.* **2009**, *2009*, 1892-1904.
- (163) Riener, K.; Haslinger, S.; Raba, A.; Högerl, M. P.; Cokoja, M.; Herrmann, W. A.; Kühn, F. E., *Chem. Rev.* **2014**, *114*, 5215-5272.
- (164) Nelson, D. J.; Nolan, S. P., *Chem. Soc. Rev.* **2013**, *42*, 6723-6753.
- (165) Bierenstiel, M.; Cross, E. D., *Coord. Chem. Rev.* **2011**, *255*, 574-590.
- (166) Mata, J. A.; Poyatos, M.; Peris, E., *Coord. Chem. Rev.* **2007**, *251*, 841-859.
- (167) Poyatos, M.; Mata, J. A.; Peris, E., *Chem. Rev.* **2009**, *109*, 3677-3707.
- (168) Pugh, D.; Danopoulos, A. A., *Coord. Chem. Rev.* **2007**, *251*, 610-641.
- (169) Köhl, O., *Chem. Soc. Rev.* **2007**, *36*, 592-607.
- (170) Tubaro, C.; Bertinazzo, D.; Monticelli, M.; Saoncella, O.; Volpe, A.; Basato, M.; Badocco, D.; Pastore, P.; Graiff, C.; Venzo, A., *Eur. J. Inorg. Chem.* **2014**, *2014*, 1524-1532.
- (171) Unger, Y.; Meyer, D.; Strassner, T., *Dalton Trans.* **2010**, *39*, 4295-4301.
- (172) Gandolfi, C.; Heckenroth, M.; Neels, A.; Laurenczy, G.; Albrecht, M., *Organometallics* **2009**, *28*, 5112-5121.
- (173) Unger, Y.; Zeller, A.; Taige, M. A.; Strassner, T., *Dalton Trans.* **2009**, 4786-4794.
- (174) Unger, Y.; Zeller, A.; Ahrens, S.; Strassner, T., *Chem. Commun.* **2008**, 3263-3265.
- (175) Heckenroth, M.; Neels, A.; Stoeckli-Evans, H.; Albrecht, M., *Inorg. Chim. Acta* **2006**, *359*, 1929-1938.
- (176) Herrmann, W. A.; Schwarz, J.; Gardiner, M. G.; Spiegler, M., *J. Organomet. Chem.* **1999**, *575*, 80-86.

- (177) Fehlhammer, W. P.; Bliss, T.; Kernbach, U.; Brüdgam, I., *J. Organomet. Chem.* **1995**, *490*, 149-153.
- (178) Mejuto, C.; Garcia-Eleno, M. A.; Guisado-Barrios, G.; Spasyuk, D.; Gusev, D.; Peris, E., *Org. Chem. Front.* **2015**, *2*, 936-941.
- (179) Naziruddin, A. R.; Zhuang, C.-S.; Lin, W.-J.; Hwang, W.-S., *Dalton Trans.* **2014**, *43*, 5335-5342.
- (180) Visbal, R.; Gimeno, M. C., *Chem. Soc. Rev.* **2014**, *43*, 3551-3574.
- (181) Das Adhikary, S.; Samanta, T.; Roymahapatra, G.; Loiseau, F.; Jouvenot, D.; Giri, S.; Chattaraj, P. K.; Dinda, J., *New J. Chem.* **2010**, *34*, 1974-1980.
- (182) Poyatos, M.; Mata, J. A.; Falomir, E.; Crabtree, R. H.; Peris, E., *Organometallics* **2003**, *22*, 1110-1114.
- (183) Viciano, M.; Feliz, M.; Corberán, R.; Mata, J. A.; Clot, E.; Peris, E., *Organometallics* **2007**, *26*, 5304-5314.
- (184) Zuo, W.; Braunstein, P., *Organometallics* **2012**, *31*, 2606-2615.
- (185) Danopoulos, A. A.; Tsoureas, N.; Wright, J. A.; Light, M. E., *Organometallics* **2004**, *23*, 166-168.
- (186) Riener, K.; Bitzer, M. J.; Pöthig, A.; Raba, A.; Cokoja, M.; Herrmann, W. A.; Kühn, F. E., *Inorg. Chem.* **2014**, *53*, 12767-12777.
- (187) Chen, J. C. C.; Lin, I. J. B., *Organometallics* **2000**, *19*, 5113-5121.
- (188) Zanardi, A.; Peris, E.; Mata, J. A., *New J. Chem.* **2008**, *32*, 120-126.
- (189) McKie, R.; Murphy, J. A.; Park, S. R.; Spicer, M. D.; Zhou, S.-z., *Angew. Chem. Int. Ed.* **2007**, *46*, 6525-6528.
- (190) Chellappan, K.; Singh, N. J.; Hwang, I.-C.; Lee, J. W.; Kim, K. S., *Angew. Chem. Int. Ed.* **2005**, *44*, 2899-2903.
- (191) Wong, W. W. H.; Vickers, M. S.; Cowley, A. R.; Paul, R. L.; Beer, P. D., *Org. Biomol. Chem.* **2005**, *3*, 4201-4208.
- (192) Yoon, J.; Kim, S. K.; Singh, N. J.; Kim, K. S., *Chem. Soc. Rev.* **2006**, *35*, 355-360.
- (193) Altmann, P. J.; Weiss, D. T.; Jandl, C.; Kühn, F. E., *Chem. Asian J.* **2016**, *11*, 1597-1605.
- (194) Haslinger, S.; Kück, J. W.; Hahn, E. M.; Cokoja, M.; Pöthig, A.; Basset, J.-M.; Kühn, F. E., *Inorg. Chem.* **2014**, *53*, 11573-11583.
- (195) Cramer, S. A.; Hernandez Sanchez, R.; Brakhage, D. F.; Jenkins, D. M., *Chem. Commun.* **2014**, *50*, 13967-13970.
- (196) Liu, X.; Chen, W., *Dalton Trans.* **2012**, *41*, 599-608.
- (197) Liu, X.; Chen, W., *Organometallics* **2012**, *31*, 6614-6622.
- (198) Cramer, S. A.; Jenkins, D. M., *J. Am. Chem. Soc.* **2011**, *133*, 19342-19345.
- (199) Findlay, N. J.; Park, S. R.; Schoenebeck, F.; Cahard, E.; Zhou, S.-z.; Berlouis, L. E. A.; Spicer, M. D.; Tuttle, T.; Murphy, J. A., *J. Am. Chem. Soc.* **2010**, *132*, 15462-15464.
- (200) Chandrachud, P. P.; Bass, H. M.; Jenkins, D. M., *Organometallics* **2016**, *35*, 1652-1657.
- (201) Anneser, M. R.; Haslinger, S.; Pöthig, A.; Cokoja, M.; Basset, J.-M.; Kühn, F. E., *Inorg. Chem.* **2015**, *54*, 3797-3804.
- (202) Schulte to Brinke, C.; Ekkehardt Hahn, F., *Dalton Trans.* **2015**, *44*, 14315-14322.
- (203) Meyer, S.; Krahe, O.; Kupper, C.; Klawitter, I.; Demeshko, S.; Bill, E.; Neese, F.; Meyer, F., *Inorg. Chem.* **2015**, *54*, 9770-9776.
- (204) Kück, J. W.; Anneser, M. R.; Hofmann, B.; Pöthig, A.; Cokoja, M.; Kühn, F. E., *ChemSusChem* **2015**, *8*, 4056-4063.
- (205) Cramer, S. A.; Sturgill, F. L.; Chandrachud, P. P.; Jenkins, D. M., *Dalton Trans.* **2014**, *43*, 7687-7690.
- (206) Bass, H. M.; Cramer, S. A.; McCullough, A. S.; Bernstein, K. J.; Murdock, C. R.; Jenkins, D. M., *Organometallics* **2013**, *32*, 2160-2167.
- (207) Meyer, S.; Klawitter, I.; Demeshko, S.; Bill, E.; Meyer, F., *Angew. Chem. Int. Ed.* **2013**, *52*, 901-905.
- (208) Schulte to Brinke, C.; Pape, T.; Hahn, F. E., *Dalton Trans.* **2013**, *42*, 7330-7337.

- (209) Lu, Z.; Cramer, S. A.; Jenkins, D. M., *Chem. Sci.* **2012**, *3*, 3081-3087.
- (210) Wu, Y.; Wu, S.-X.; Li, H.-B.; Geng, Y.; Su, Z.-M., *Dalton Trans.* **2011**, *40*, 4480-4488.
- (211) Radloff, C.; Gong, H.-Y.; Schulte to Brinke, C.; Pape, T.; Lynch, V. M.; Sessler, J. L.; Hahn, F. E., *Chem. Eur. J.* **2010**, *16*, 13077-13081.
- (212) Bass, H. M.; Cramer, S. A.; Price, J. L.; Jenkins, D. M., *Organometallics* **2010**, *29*, 3235-3238.
- (213) Hahn, F. E.; Radloff, C.; Pape, T.; Hepp, A., *Chem. Eur. J.* **2008**, *14*, 10900-10904.
- (214) Schulte to Brinke, C.; Hahn, F. E., *Eur. J. Inorg. Chem.* **2015**, *2015*, 3227-3231.
- (215) Park, S. R.; Findlay, N. J.; Garnier, J.; Zhou, S.; Spicer, M. D.; Murphy, J. A., *Tetrahedron* **2009**, *65*, 10756-10761.
- (216) Altmann, P. J.; Jandl, C.; Pothig, A., *Dalton Trans.* **2015**, *44*, 11278-11281.
- (217) Ahamed, B. N.; Dutta, R.; Ghosh, P., *Inorg. Chem.* **2013**, *52*, 4269-4276.
- (218) Bullough, E. K.; Little, M. A.; Willans, C. E., *Organometallics* **2013**, *32*, 570-577.
- (219) Rit, A.; Pape, T.; Hahn, F. E., *J. Am. Chem. Soc.* **2010**, *132*, 4572-4573.
- (220) Rit, A.; Pape, T.; Hepp, A.; Hahn, F. E., *Organometallics* **2011**, *30*, 334-347.
- (221) Liu, Q.-X.; Huo, R.; Liu, J.; Wei, Q.; Zhao, X.-J.; Zhao, Z.-X., *Organometallics* **2015**, *34*, 3167-3174.
- (222) Rit, A.; Pape, T.; Hahn, F. E., *Organometallics* **2011**, *30*, 6393-6401.
- (223) Weiss, D. T.; Haslinger, S.; Jandl, C.; Pöthig, A.; Cokoja, M.; Kühn, F. E., *Inorg. Chem.* **2015**, *54*, 415-417.
- (224) Weiss, D. T.; Altmann, P. J.; Haslinger, S.; Jandl, C.; Pöthig, A.; Cokoja, M.; Kühn, F. E., *Dalton Trans.* **2015**, *44*, 18329-18339.
- (225) Weiss, D. T.; Anneser, M. R.; Haslinger, S.; Pöthig, A.; Cokoja, M.; Basset, J.-M.; Kühn, F. E., *Organometallics* **2015**, *34*, 5155-5166.
- (226) Wang, D.; Astruc, D., *Chem. Rev.* **2015**, *115*, 6621-6686.
- (227) Rylander, P. N., Hydrogenation and Dehydrogenation. In *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2000.
- (228) Knoevenagel, E.; Bergdolt, B., *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 2857-2860.
- (229) Andersson, P. G.; Munslow, I. J., *Modern Reduction Methods*. Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2008.
- (230) Brieger, G.; Nestrick, T. J., *Chem. Rev.* **1974**, *74*, 567-580.
- (231) Johnstone, R. A. W.; Wilby, A. H.; Entwistle, I. D., *Chem. Rev.* **1985**, *85*, 129-170.
- (232) Zassinovich, G.; Mestroni, G.; Gladiali, S., *Chem. Rev.* **1992**, *92*, 1051-1069.
- (233) Wang, C.; Wu, X.; Xiao, J., *Chem. Asian J.* **2008**, *3*, 1750-1770.
- (234) Kitamura, M.; Noyori, R., Hydrogenation and Transfer Hydrogenation. In *Ruthenium in Organic Synthesis*, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2005.
- (235) Noyori, R.; Hashiguchi, S., *Acc. Chem. Res.* **1997**, *30*, 97-102.
- (236) Knowles, W. S.; Noyori, R., *Acc. Chem. Res.* **2007**, *40*, 1238-1239.
- (237) Trocha-Grimshaw, J.; Henbest, H. B., *Chem. Commun.* **1967**, 544-544.
- (238) Haddad, Y. M. Y.; Henbest, H. B.; Husbands, J.; Mitchell, T. R. B., *Proc. Chem. Soc., London* **1964**, 361-365.
- (239) McPartlin, M.; Mason, R., *Chem. Commun.* **1967**, 545-546.
- (240) Bäckvall, J.-E., *J. Organomet. Chem.* **2002**, *652*, 105-111.
- (241) Clapham, S. E.; Hadzovic, A.; Morris, R. H., *Coord. Chem. Rev.* **2004**, *248*, 2201-2237.
- (242) Dragutan, V.; Dragutan, I.; Delaude, L.; Demonceau, A., *Coord. Chem. Rev.* **2007**, *251*, 765-794.
- (243) Vougioukalakis, G. C.; Grubbs, R. H., *Chem. Rev.* **2010**, *110*, 1746-1787.
- (244) Grubbs, R. H., *Angew. Chem. Int. Ed.* **2006**, *45*, 3760-3765.
- (245) Grubbs, R. H.; O'Leary, D. J., *Handbook of Metathesis*. Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2003.
- (246) Schwartsburd, L.; Whittlesey, M. K., Ruthenium N-Heterocyclic Carbene Complexes for the Catalysis of Nonmetathesis Organic Transformations. In *N-Heterocyclic Carbenes*, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2014.

- (247) Arisawa, M.; Terada, Y.; Takahashi, K.; Nakagawa, M.; Nishida, A., *J. Org. Chem.* **2006**, *71*, 4255-4261.
- (248) Fekete, M.; Joó, F., *Catal. Commun.* **2006**, *7*, 783-786.
- (249) Hanessian, S.; Giroux, S.; Larsson, A., *Org. Lett.* **2006**, *8*, 5481-5484.
- (250) Terada, Y.; Arisawa, M.; Nishida, A., *Angew. Chem. Int. Ed.* **2004**, *43*, 4063-4067.
- (251) Arisawa, M.; Terada, Y.; Nakagawa, M.; Nishida, A., *Angew. Chem. Int. Ed.* **2002**, *41*, 4732-4734.
- (252) Miyashita, T.; Nomura, K., *Macromolecules* **2016**, *49*, 518-526.
- (253) Atallah, P.; Wagener, K. B.; Schulz, M. D., *Macromolecules* **2013**, *46*, 4735-4741.
- (254) Yamamoto, N.; Ito, R.; Geerts, Y.; Nomura, K., *Macromolecules* **2009**, *42*, 5104-5111.
- (255) Sauvage, X.; Borguet, Y.; Noels, A. F.; Delaude, L.; Demonceau, A., *Adv. Synth. Catal.* **2007**, *349*, 255-265.
- (256) Enders, D.; Niemeier, O.; Henseler, A., *Chem. Rev.* **2007**, *107*, 5606-5655.
- (257) Kamigaito, M.; Ando, T.; Sawamoto, M., *Chem. Rev.* **2001**, *101*, 3689-3746.
- (258) Bitzer, M. J.; Pothig, A.; Jandl, C.; Kuhn, F. E.; Baratta, W., *Dalton Trans.* **2015**, *44*, 11686-11689.
- (259) Baratta, W.; Baldino, S.; Calhorda, M. J.; Costa, P. J.; Esposito, G.; Herdtweck, E.; Magnolia, S.; Mealli, C.; Messaoudi, A.; Mason, S. A.; Veiros, L. F., *Chem. Eur. J.* **2014**, *20*, 13603-13617.
- (260) Witt, J.; Pöthig, A.; Kühn, F. E.; Baratta, W., *Organometallics* **2013**, *32*, 4042-4045.
- (261) Baratta, W.; Schütz, J.; Herdtweck, E.; Herrmann, W. A.; Rigo, P., *J. Organomet. Chem.* **2005**, *690*, 5570-5575.
- (262) Dharmasena, U. L.; Foucault, H. M.; dos Santos, E. N.; Fogg, D. E.; Nolan, S. P., *Organometallics* **2005**, *24*, 1056-1058.
- (263) Cokoja, M.; Bruckmeier, C.; Rieger, B.; Herrmann, W. A.; Kühn, F. E., *Angew. Chem. Int. Ed.* **2011**, *50*, 8510-8537.
- (264) Drees, M.; Cokoja, M.; Kühn, F. E., *ChemCatChem* **2012**, *4*, 1703-1712.
- (265) Song, C., *Catal. Today* **2006**, *115*, 2-32.
- (266) Aresta, M., *Carbon Dioxide as Chemical Feedstock*. Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2010.
- (267) Omae, I., *Catal. Today* **2006**, *115*, 33-52.
- (268) MacDowell, N.; Florin, N.; Buchard, A.; Hallett, J.; Galindo, A.; Jackson, G.; Adjiman, C. S.; Williams, C. K.; Shah, N.; Fennell, P., *Energy Environ. Sci.* **2010**, *3*, 1645-1669.
- (269) Mikkelsen, M.; Jorgensen, M.; Krebs, F. C., *Energy Environ. Sci.* **2010**, *3*, 43-81.
- (270) Quadrelli, E. A.; Centi, G.; Duplan, J.-L.; Perathoner, S., *ChemSusChem* **2011**, *4*, 1194-1215.
- (271) Limbach, M., Chapter Four - Acrylates from Alkenes and CO₂, the Stuff That Dreams Are Made of. In *Adv. Organomet. Chem.*, Pedro, J. P., Ed. Academic Press: 2015; Vol. Volume 63, pp 175-202.
- (272) Gibson, D. H., *Coord. Chem. Rev.* **1999**, *185-186*, 335-355.
- (273) Gibson, D. H., *Chem. Rev.* **1996**, *96*, 2063-2096.
- (274) Yin, X.; Moss, J. R., *Coord. Chem. Rev.* **1999**, *181*, 27-59.
- (275) Leitner, W., *Coord. Chem. Rev.* **1996**, *153*, 257-284.
- (276) Behr, A., *Angew. Chem. Int. Ed.* **1988**, *27*, 661-678.
- (277) Palmer, D. A.; Van Eldik, R., *Chem. Rev.* **1983**, *83*, 651-731.
- (278) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J., *Chem. Rev.* **2011**, *111*, 6810-6918.
- (279) Schmidt, A.; Casini, A.; Kühn, F. E., *Coord. Chem. Rev.* **2014**, *275*, 19-36.
- (280) Cook, T. R.; Stang, P. J., *Chem. Rev.* **2015**, *115*, 7001-7045.
- (281) Vardhan, H.; Yusubov, M.; Verpoort, F., *Coord. Chem. Rev.* **2016**, *306*, Part 1, 171-194.
- (282) Leenders, S. H. A. M.; Gramage-Doria, R.; de Bruin, B.; Reek, J. N. H., *Chem. Soc. Rev.* **2015**, *44*, 433-448.
- (283) Cook, T. R.; Zheng, Y.-R.; Stang, P. J., *Chem. Rev.* **2013**, *113*, 734-777.

- (284) Dalgarno, S. J.; Power, N. P.; Atwood, J. L., *Coord. Chem. Rev.* **2008**, *252*, 825-841.
- (285) Thanasekaran, P.; Lee, C.-H.; Lu, K.-L., *Coord. Chem. Rev.* **2014**, *280*, 96-175.
- (286) Lewis, J. E. M.; John McAdam, C.; Gardiner, M. G.; Crowley, J. D., *Chem. Commun.* **2013**, *49*, 3398-3400.
- (287) Johnson, A. M.; Hooley, R. J., *Inorg. Chem.* **2011**, *50*, 4671-4673.
- (288) Johnson, A. M.; Moshe, O.; Gamboa, A. S.; Langloss, B. W.; Limtiaco, J. F. K.; Larive, C. K.; Hooley, R. J., *Inorg. Chem.* **2011**, *50*, 9430-9442.
- (289) Lewis, J. E. M.; Gavey, E. L.; Cameron, S. A.; Crowley, J. D., *Chem. Sci.* **2012**, *3*, 778-784.
- (290) Kumar, A.; Sun, S.-S.; Lees, A. J., *Coord. Chem. Rev.* **2008**, *252*, 922-939.
- (291) Thomas, J. A., *Dalton Trans.* **2011**, *40*, 12005-12016.
- (292) Yan, X.; Cook, T. R.; Wang, P.; Huang, F.; Stang, P. J., *Nat. Chem.* **2015**, *7*, 342-348.
- (293) Yan, X.; Wang, M.; Cook, T. R.; Zhang, M.; Saha, M. L.; Zhou, Z.; Li, X.; Huang, F.; Stang, P. J., *J. Am. Chem. Soc.* **2016**, *138*, 4580-4588.
- (294) Wang, J.; He, C.; Wu, P.; Wang, J.; Duan, C., *J. Am. Chem. Soc.* **2011**, *133*, 12402-12405.
- (295) Frischmann, P. D.; Kunz, V.; Würthner, F., *Angew. Chem. Int. Ed.* **2015**, *54*, 7285-7289.
- (296) Li, Z.; Kishi, N.; Hasegawa, K.; Akita, M.; Yoshizawa, M., *Chem. Commun.* **2011**, *47*, 8605-8607.
- (297) Yamashina, M.; Sartin, M. M.; Sei, Y.; Akita, M.; Takeuchi, S.; Tahara, T.; Yoshizawa, M., *J. Am. Chem. Soc.* **2015**, *137*, 9266-9269.
- (298) Wang, M.; Vajpayee, V.; Shanmugaraju, S.; Zheng, Y.-R.; Zhao, Z.; Kim, H.; Mukherjee, P. S.; Chi, K.-W.; Stang, P. J., *Inorg. Chem.* **2011**, *50*, 1506-1512.
- (299) Klosterman, J. K.; Yamauchi, Y.; Fujita, M., *Chem. Soc. Rev.* **2009**, *38*, 1714-1725.
- (300) Holliday, B. J.; Mirkin, C. A., *Angew. Chem. Int. Ed.* **2001**, *40*, 2022-2043.
- (301) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B., *Acc. Chem. Res.* **2005**, *38*, 369-378.
- (302) Lewis, J. E. M.; Elliott, A. B. S.; McAdam, C. J.; Gordon, K. C.; Crowley, J. D., *Chem. Sci.* **2014**, *5*, 1833-1843.
- (303) Li, Z.; Kishi, N.; Yoza, K.; Akita, M.; Yoshizawa, M., *Chem. Eur. J.* **2012**, *18*, 8358-8365.
- (304) Elliott, A. B. S.; Lewis, J. E. M.; van der Salm, H.; McAdam, C. J.; Crowley, J. D.; Gordon, K. C., *Inorg. Chem.* **2016**, *55*, 3440-3447.
- (305) Cook, T. R.; Vajpayee, V.; Lee, M. H.; Stang, P. J.; Chi, K.-W., *Acc. Chem. Res.* **2013**, *46*, 2464-2474.
- (306) Zava, O.; Mattsson, J.; Therrien, B.; Dyson, P. J., *Chem. Eur. J.* **2010**, *16*, 1428-1431.
- (307) Therrien, B.; Süss-Fink, G.; Govindaswamy, P.; Renfrew, A. K.; Dyson, P. J., *Angew. Chem. Int. Ed.* **2008**, *47*, 3773-3776.
- (308) Barry, N. P. E.; Zava, O.; Dyson, P. J.; Therrien, B., *Chem. Eur. J.* **2011**, *17*, 9669-9677.
- (309) Mattsson, J.; Zava, O.; Renfrew, A. K.; Sei, Y.; Yamaguchi, K.; Dyson, P. J.; Therrien, B., *Dalton Trans.* **2010**, *39*, 8248-8255.
- (310) Pitto-Barry, A.; Barry, N. P. E.; Zava, O.; Deschenaux, R.; Dyson, P. J.; Therrien, B., *Chem. Eur. J.* **2011**, *17*, 1966-1971.
- (311) Schmitt, F.; Freudenreich, J.; Barry, N. P. E.; Juillerat-Jeanneret, L.; Süss-Fink, G.; Therrien, B., *J. Am. Chem. Soc.* **2012**, *134*, 754-757.
- (312) Zheng, Y.-R.; Suntharalingam, K.; Johnstone, T. C.; Lippard, S. J., *Chem. Sci.* **2015**, *6*, 1189-1193.
- (313) Vajpayee, V.; Yang, Y. J.; Kang, S. C.; Kim, H.; Kim, I. S.; Wang, M.; Stang, P. J.; Chi, K.-W., *Chem. Commun.* **2011**, *47*, 5184-5186.
- (314) Dubey, A.; Min, J. W.; Koo, H. J.; Kim, H.; Cook, T. R.; Kang, S. C.; Stang, P. J.; Chi, K.-W., *Chem. Eur. J.* **2013**, *19*, 11622-11628.
- (315) Mishra, A.; Jeong, Y. J.; Jo, J.-H.; Kang, S. C.; Lah, M. S.; Chi, K.-W., *ChemBioChem* **2014**, *15*, 695-700.

- (316) Garci, A.; Dobrov, A. A.; Riedel, T.; Orhan, E.; Dyson, P. J.; Arion, V. B.; Therrien, B., *Organometallics* **2014**, *33*, 3813-3822.
- (317) Grishagin, I. V.; Pollock, J. B.; Kushal, S.; Cook, T. R.; Stang, P. J.; Olenyuk, B. Z., *Proc. Natl. Acad. Sci.* **2014**, *111*, 18448-18453.

8 COMPLETE LIST OF PUBLICATIONS

- [1] **Manuela Hollering**, Daniel T. Weiss, Mario J. Bitzer, Christian Jandl and Fritz E. Kühn, "Controlling Coordination Geometries: Ru-Carbene Complexes with Tetra-NHC Ligands", *Inorg. Chem.* **2016**, *55*, 6010-6017.
- [2] **Manuela Hollering**, Martin Albrecht and Fritz E. Kühn, "Bonding and Catalytic Application of Ruthenium *N*-Heterocyclic Carbene Complexes Featuring Triazole, Triazolylidene and Imidazolylidene Ligands ", *Organometallics* **2016**, *35*, 2980-2986.
- [3] **Manuela Hollering**,# Barnali Dutta# and Fritz E. Kühn, "Transition Metal Mediated Coupling of Carbon Dioxide and Ethene to Acrylic Acid/Acrylates", *Coord. Chem. Rev.* **2016**, *309*, 51-67.
- [4] **Manuela Hollering**, Richard O. Reithmeier, Simon Meister, Eberhardt Herdtweck, Fritz E. Kühn, and Bernhard Rieger, "[Re(CO)₃Cl(C₅H₄CIP)₂] and [Re(CO)₂Cl(C₅H₄CIP)₃]: synthesis and characterization of two novel rhenium(I) phosphinine complexes", *RSC Adv.* **2016**, *6*, 14134-14139.
- [5] Andrea Schmidt, Viviana Molano, **Manuela Hollering**, Alexander Pöthig, Angela Casini and Fritz E. Kühn, "Evaluation of novel palladium cages as potential delivery systems for the anticancer drug cisplatin", *Chem. Eur. J.* **2016**, *22*, 2253-2256.
- [6] Andrea Schmidt, **Manuela Hollering**, Angela Casini and Fritz E. Kühn, "Supramolecular *exo*-functionalized palladium cages: fluorescent properties and biological activity", *Dalton Trans.* **2016**, *45*, 8556-8565.
- [7] Andrea Schmidt, **Manuela Hollering**, Jiaying Han, Angela Casini and Fritz E. Kühn, "Self-assembly of highly luminescent heteronuclear coordination cages", *Dalton Trans.* **2016**, *45*, 12297-12300.
- [8] **Manuela Hollering**, Christian Jandl, Alexander Pöthig, and Fritz E. Kühn, "Application of open chain tetraimidazolium ruthenium-NHC complexes in catalysis", *PacifiChem2015*, **2015**, poster presentation.
- [9] Andrea Schmidt, **Manuela Hollering**, Alexander Pöthig, Angela Casini and Fritz E. Kühn, "M₂L₄ coordination cages as potential drug delivery systems for anticancer agents", *PacifiChem2015*, **2015**, oral presentation.
- [10] Manuela Delgado-Rebollo, Daniel Canseco-Gonzalez, **Manuela Hollering**, Helge Mueller-Bunz and Martin Albrecht, "Synthesis and catalytic alcohol oxidation and ketone transfer hydrogenation activity of donor-functionalized mesoionic triazolylidene ruthenium(II) complexes", *Dalton Trans.* **2014**, *43*, 4462-4473.

Equally contributing co-authors.

9 APPENDIX

Table A1. Contribution of Ph. D. candidate M. Hollering to individual publications. * = equally contributed as first author (refers to publications in Chapter 3.3).

Bibliographic Data	Chapter	Author	Contribution
<i>Inorganic Chemistry</i> 2016 , 55, 6010-6017.	3.1	1 st	research, experimental work and related data interpretation, DFT study, conception and writing of manuscript
<i>Organometallics</i> 2016 , 35, 2980-2986.	3.2	1 st	research, experimental work and related data interpretation, conception and writing of manuscript
<i>Coordination Chemistry Reviews</i> 2016 , 309, 51-67.	3.3	1 ^{st*}	research, conception and writing of manuscript
<i>RSC Advances</i> 2016 , 6, 14134-14139.	3.4	1 st	research, experimental work and related data interpretation, DFT study, conception and writing of manuscript
<i>Chemistry – A European Journal</i> 2016 , 22, 2253-2256.	3.5	3 nd	experimental work and related data interpretation, support of 1 st author (A. Schmidt) in conception and wording of manuscript
<i>Dalton Transactions</i> 2016 , 45, 8556-8565.	3.6	2 nd	experimental work and related data interpretation, support of 1 st author (A. Schmidt) in conception and wording of manuscript
<i>Dalton Transactions</i> 2016 , 45, 12297-12300.	3.7	2 ^{nd*}	experimental work and related data interpretation, DFT study, support of 1 st author (A. Schmidt) in conception and wording of manuscript