Department Chemie,
Lehrstuhl für Anorganische Chemie der Technische Universität München

Catalyst Design and Optimization within a Framework of Green Chemistry

Evangeline Tosh

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

Doktors der Naturwissenschaften

gegehmigten Dissertation.

Vorsitzender: Univ.-Prof. Dr. F. E. Kühn

Prüfer der Dissertation:
1. Univ.-Prof. Dr. Dr. h. c. mult. W. A. Herrmann
2. Univ.-Prof. Dr. W. Beck, em.
   Ludwig-Maximilians-Universität München
3. Univ.-Prof. Dr. Dr. h. c. B. Rieger

Die Dissertation wurde am 06.07.09 bei der Technischen Universität München eingereicht und durch die Fakultät für Chemie am 09.09.09 angenommen.

to my research family

Die vorliegende Arbeit entstand in der Zeit von Juli 2006 bis Juli 2009 am Department Chemie, Lehrstuhl für Anorganische Chemie der Technischen Universität München.

Mein Dank gilt meinem verehrten Lehrer

Herrn Professor Dr. Dr. h.c. mult. Wolfgang A. Herrmann

für die Aufnahme in seinen Arbeitskreis, für das uneingeschränkte Vertrauen, und für die Forschungs Freiheit.

Diese Arbeit wurde durch ein Promotionsstipendium von Nanocat und der ElitenetzwerkBayern unterstützt.

My heartfelt thanks goes out to:

Dr. K. Öfele, not only guidance throughout my graduate career and the work within this thesis, but for also providing me with an example of the type of scientist I someday hope to become. I am very grateful for the encouragement, patience, support and guidance I have received from him during my work at the TUM.

My laboratory coworkers, Agnes Bitterman and Dr. Denys Baskakov, for creating a wonderful lab atmosphere.

Members of the carbene work group, Daniel Canella, Peter Gigler, Oliver Hiltner, Claudia Linninger, Stephanie Riederer, Lars-Arne Schlaper, Alexandrina Tenase, and Sandra Zinner for useful discussions.

Christian Taubmann for useful discussions, synthetic tips and collaborations on the carbocyclic carbene topic.

Dr. Christoph Rentzch and Dr. Alexandra Rost for useful discussions and collaborations within the area of green chemistry.

Dr. O. Schuster and Prof. Dr. L. Goossen for collaborations within the area of remote N-Heterocyclic carbenes and biaryl synthesis, respectively.

Ulrike Ammari, Rodica Dumitrescu, Anna Fuss, Georgeta Krutsch, Thomas Schröferi are thanked for assistance with and elemental analysis, mass spectrometry, procurement, NMR, GC/MS measurements, respectively.

Irmgard Grötsch, Roswitha Kaufmann, Renate Schuhbauer-Gerl, are thanked for assistance with administrative matters.

Dr. B. Bechlars and Prof. Dr. F. Kühn for encouragment and assistance in the editing of this thesis.

Markus Drees is thanked for his work in the coordination of the NanoCat program.

Prof. Härter, Dr. Eppinger, and Dr. Frey for initial supervision of my work within the group.

Carla Sanson, Daniel Betz, Tahir Farid, Draganco Vljanovski, Vladi Vljanovski, Stefan Faul, Alexander Marziale, Alice Schlichtiger, Andreas Brück, Magnus Buchner, Andreas Obenhuber, Klaus Ruhland, Anja Fredrich, Andy Grossman, Jenni Meiners, Akef Al Hmaideen, Philip Altmann, Hugh Chaffey-Millar, Bernd Diebl, Nadezda Domanovic, Christian Fischer, Serena Goh, Alev Günyar, Manuel Högerl, Valentina Korinth, Yang Li, Alejandro Capape Miralles, Silvana Rach, Alexander Raith, and Mingdong Zhou for their friendship and acting as guides in my ever continuing journey of discovery in all things German.

Mr. and Ms. Hiltner for providing hospitality on numerous visits to the Allgäu.

The Stantons, Kris, Michel, Rowan and Elijah for support and encouragement in all endeavors.

Dr. Markus Thaler for being a welcome distraction every now and again.

and last but not least,

My parents for providing support, endless encouragement and much needed perspective.

Those who have handled sciences have been either men of experiment or men of dogmas.The men of experiment are like the ant, they only collect and use; the reasoners resemble spiders, who make cobwebs out of their own substance. But the bee takes a middle course: it gathers its material from the flowers of the garden and of the field, but transforms and digests it by a power of its own. Not unlike this is the true business of philosophy; for it neither relies solely or chiefly on the powers of the mind, nor does it take the matter which it gathers from natural history and mechanical experiments and lay it up in the memory whole, as it finds it, but lays it up in the understanding altered and digested. Therefore from a closer and purer league between these two faculties, the experimental and the rational, much may be hoped.

- Francis Bacon (1561 –1626)

Table of Contents

compounds……………………………………………

Abbreviations

n-Bu:	*n*-butyl
t-Bu:	*tert*-butyl
C_3:	cyclopropenylidene
CHT:	cycloheptatrienylidene
CHTE:	cycloheptatetraene
COD:	cyclooctadiene
COE:	cyclooctene
Cp:	cyclopentadienyl
Cy:	cyclohexyl
dec:	decomposition
DFT:	density functional theory
DMF:	dimethylformamide
DMSO:	dimethylsulfoxide
EA:	elemental analysis
Et:	ethyl
GC:	gas chromatography
HOMO:	highest occupied molecular orbital
IMes:	di-N-mesitylimidazolinylidene
IPr:	di-N-propylimidazolinylidene
IR:	infrared spectroscopy
LUMO:	lowest unoccupied molecular orbital
Me:	methyl
Mes:	mesityl
MO:	molecular orbital

MS: mass spectroscopy

MTO: methyltrioxorhenium

Nap: naphthyl

NHC: N-heterocyclic carbene

NMP: *N*-methyl-2-pyrrolidone

OAc: acetoxy

HOTf: trifluoromethanesulfonic acid

Ph: phenyl

i-Pr: isopropyl

TCNQ: 7,7,8,8-tetracyano-1,4-quinodimethane

THF: tetrahydrofuran

TMEDA: N,N,N´,N´-tetramethylethylendiamine

TOF: turnover frequency

TON: turnover number

UV: ultraviolet spectroscopy

1 Introduction

1.1 What is Green Chemistry?

Green chemistry is development of products and processes that reduce or eliminate the use and generation of harmful substances and reduce the production of waste in the form of energy and feedstocks.[1]

The foundation of green chemistry are the "The twelve principles of green chemistry" shown below. This set of goals is used to aid in the development of cleaner chemical processes. Though ideally a new process would incorporate all 12 principles, in reality it may only be possible to optimize a few.

The twelve principles of green chemistry[1]

1. Prevent waste
2. Design safer chemicals and products
3. Design less hazardous chemical syntheses
4. Use renewable feedstocks
5. Use catalysts, not stoichiometric reagents
6. Avoid chemical derivatives
7. Maximize atom economy
8. Use safer solvents and reaction conditions
9. Increase energy efficiency
10. Design chemicals and products to degrade after use
11. Analyze in real time to prevent pollution
12. Minimize the potential for accidents

Moving beyond yield and selectivity as a judge for the success of a given reaction or process the twelve principles of green chemistry act as a framework for the development of sustainable processes. A sustainable process is one which meets the needs of the present without compromising the ability of future generations to meet their own needs.[2] For a given process to be sustainable, environmental, societal and economic factors must be considered. Much of the success of green chemistry is due to not only the reduced environmental damage made by innovations in the area, but also improvements in profit margins and brand recognition for companies which embrace these technologies. The development of classical process development to include the concept of design within a framework of green chemistry is shown in figure 1.1.

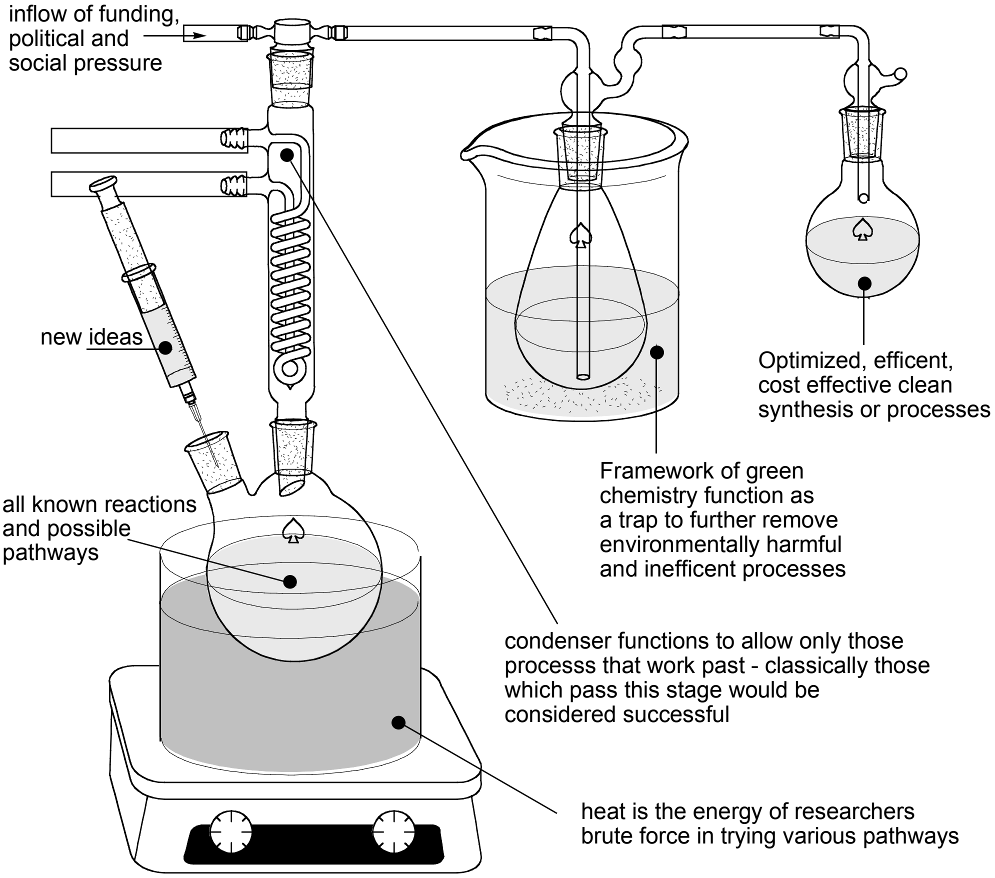


Figure 1.1 Chemical Process Design: A Conceptual Apparatus

Design principles can be grouped into the three main areas of sustainability:

1) **Conservation of physical resources** can be thought of as enhancing the economics of a given process. Physical resources can be chemical feedstocks, energy or transportation. Designing processes to reduce waste (1), to use catalysts (5), avoid chemical derivatives (6), maximize atom economy (7) and increase energy efficiency (9) not only benefit the environment but also the financial bottom line of companies. Many industrial processes have been developed with these ideas in mind before the emergence of green chemistry.

2) **Development** of safer chemicals, solvents, reaction conditions and products (2+8), and design for degradation after use (10) as well as the use of renewable feedstocks (4) and minimizing the potential for accidents (12) benefit the social component of the sustainability equation. Safer products less mean risk to the public, while the use of renewable feedstocks develops emerging economies and can facilitate economic growth in rural areas.

3) **Environmental protection** concerns are taken into consideration in all principles however principles dedicated solely to these include the analysis in real time to prevent pollution (11). Of the principles this can be the hardest to implement in emerging markets without government regulations.

Without directives and enforcements from governments, treating chemicals to render them less hazardous or disposing of chemicals properly can often be difficult to implement especially in emerging economies where the environmental impact of a given process is of secondary concern due to the incredible economic and social benefits to be gained. The use of green chemistry in the design phase of a given process is essential for ensuring clean technologies that can be successfully introduced in these markets. The principles, though through, are not all encompassing. Other considerations must be taken into account and are further discussed in sections 1.2.2 and 1.2.3.

1.2 Green Chemistry Metrics

Green chemistry metrics are how the relative "green-ness" of a process is determined. It is important to stress the use of the word relative in this sentence. Green processes do not eliminate all waste, but strive to minimize it. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

1.2.1 Mass Based Green Chemistry Metrics

The state of the art is currently choosing among options, with green chemistry metrics being a tool used to aid in this decision. Among the first green chemistry metrics the E factor developed by Roger Sheldon remains one of the most commonly applied in industrial calculations due to ease of use and flexibility in application to multi-step reactions. The E-factor gives a direct ratio of total waste relative to product based on mass (equation 1.1). The smaller the E-factor the greener a chemical process is said to be.[3] Other metrics based on mass include the effective mass yield, the reaction mass efficiency and the carbon efficiency, are calculated using in equations 1.2-1.4.[4]

Equ.1.1

E-Factor = Total Waste (kg) / Product (kg)

Equ. 1.2

Reaction Mass Efficiency = Mass of product x 100 / Mass of Reagents

Equ.1.3

Effective Mass Yield (%) = Mass of Products x 100 / Mass of Non-Benign Reagents

Equ. 1.4

Carbon Efficiency (%) = Amount of Carbon in Product x 100 / Total Carbon Present in Reactants.

Equ. 1.5

Atom economy = molecular weight of product/ sum of the molecular weights of all substances produced in the stoichiometric equation for the reaction involved

Atom economy (equation 1.5) can be particularly useful for evaluation of chemical processes at a molecular level. The goal of atom economy is to incorporate as many of the atoms of the reactants as possible into the desired products.[5b]

1.2.2 Life Cycle Analysis

Although mass based green chemistry metrics are a good place to begin when evaluating a given system, they are far from providing a definitive guide for the selection of green processes. Many of the metrics fail to incorporate the solvents or catalysts used and perhaps most importantly the energy consumption. It is at the discretion of the researcher to decide how benign a given reactant is in the case of effective mass yield percentage and as with all statistics and lampposts there is the temptation to use them for support rather than illumination, depending on the situation. To address these concerns the concept of Life Cycle Analysis is used. Though problems of the definition of hazards resulting from given reactants remain, especially in the case of novel multi-step reactions the life cycle analysis serves to assess the environmental impact of a given product or process throughout its lifespan. It is a tool used to compare the environmental performance of products and processes enabling developers to choose the least damaging option.[6]

As life cycle analysis involves complex and multi-component evaluations, entire teams of scientists and engineers with a variety of skill sets and backgrounds are required for accurate assessments. They are highly dependent on the basis set used, which are often greatly influenced by funding agencies.[7]

1.3 Concluding remarks

Section 2.1 and 2.2 discuss collaboration with Alexandra Rost of the Kühn Group. The excellent infrastructure and availability of a microwave reactor facilitated evaluation of the use of microwave technology as a method for rapid screening of NHC irridium catalysts for hydroborylation reactions done in cooperation with Christoph Rentzch outlined in section 2.3. The core of the synthetic work undertaken, on the synthesis of carbocyclic carbene complexes is outlined in section 3. Catalytic evaluations, in cooperation with Christian Taubman, Dr. O. Schuster, and the group of Prof. L. Goossen at the University of Kaiserslautern can be found in section 4.

In part due to the nature of research in the area of green chemistry, but also due to the exceptionally varied research interests and stimulating collaborative environment found within the Herrmann research group work undertaken in the course of this thesis spans a large variety of research topics. In the global economy, innovation not regulation will be the key to the successful implementation of more sustainable processes. The objective of this thesis was to explore preliminary steps which provide a foundation for sustainable systems using the key principles of chemistry.

2 Evaluation of Chemical Processes within a Framework of Green Chemistry

2.1 Overview

Previously reported synthetic pathways used in the synthesis of MTO require the use of highly toxic tin containing methylating agents. A more environmentally sound tin free synthetic route to the versatile catalyst MTO has been developed, using the principles of green chemistry (section 2.2).

An improved, environmentally sound three-component system, MTO/H_2O_2/LiBr, used to prepare biodegradable oxidized starch super absorbers is reported in section 2.3. In contrast to previous strategies, a highly acidic reaction media is avoided, thus limiting product depolymerisation to a low level. This section presents an optimized catalytic approach to make carboxy starch, which reduces overall reaction costs, and produces less harmful waste. An environmentally benign, catalytic oxidation process applying the three-component system MTO/H_2O_2/LiBr to prepare biodegradable oxidized starch super absorbers with high water absorption capacity has been developed.

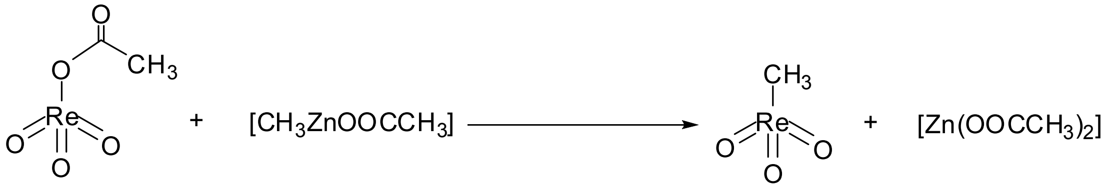
In section 2.4 a different catalyst is described, bridged and unbridged *N*-heterocyclic carbene (NHC) ligands were metalated with $[Ir(COD)Cl]_2$ to yield the iridium(I) mono- and biscarbene complexes [Ir(COD)NHC(Cl)] and $[Ir(COD)(NHC)_2][X]$ (X: I, PF_6, BF_4, CF_3COO, OTf). These were tested in the C-H borylation reaction of aromatic carbons with bis(pinacolato)diboron (B_2pin_2) and pinacolborane (HBpin). The use of microwave technology in this study not only facilitates a time efficient screening of a wide range of influences such as σ-donor strength of the ligand and structural motif as well as the effects of the counter ion, but also provides an energy efficient heating source. Catalyst **6^{TFA}**, which features a chelating NHC ligand, proved to be the most effective catalyst and further investigations with this complex in the borylation of mono- and disubstituted benzene derivatives exploring chemo- and regioselectivity were undertaken.

2.2 Methyltrioxorhenium revisited: evaluation of an improved synthesis for a versatile catalyst [33b]

Replacement of stoichiometric reagents with catalytic reagents is one of the founding principles of green chemistry.[1] Though catalysts lower the energy of activation, providing a more efficient energetic pathway to a given chemical target without being consumed in the reaction, they are often transition metal complexes, which are made using toxic and carcinogenic reagents and can require rigorous energy intensive procedures to prepare.

Methyltrioxorhenium (MTO) has been studied extensively in industry and academia due to the numerous reactions it is capable of catalyzing.[8] Previously reported synthetic routes to MTO require the use of tetramethyltin or related derivatives, which are highly toxic.[9-13] Industrial application of MTO is limited by the expensive and complex safety precautions required for synthesis and purification using tetramethyltin as a reagent. Recently an improved synthesis of MTO has been described.[14] In the following section the advantages of this synthetic route to MTO are elucidated in more detail using the principles of green chemistry as a guide, and its potential impact on the applications of MTO are discussed.

The preparation of alkylrhenium(VII) oxides *via* bis(alkyl) zinc precursors has been reported,[15] however in the presence of dimethylzinc, Re_2O_7 and related Re(VII) precursor compounds are easily reduced.[11,15] By substitution of bis(alkyl) zinc precursors with methyl zinc acetate,[16] we have observed a clean methylation, without any reduction of Re(VII) (scheme 2.1).



Scheme 2.1 Synthesis of MTO starting from perrhenylacetate and methylzinc acetate

The common synthesis of $[CH_3ZnOC({=}O)CH_3]$ is described in scheme 2.2. Methylzinc acetate can also be synthesized from inexpensive shelf chemicals and zinc acetate, the side product of the MTO synthesis.[14]

$$[Zn(CH_3)_2] + CH_3COOH \longrightarrow [CH_3ZnOOCCH_3] + CH_4$$

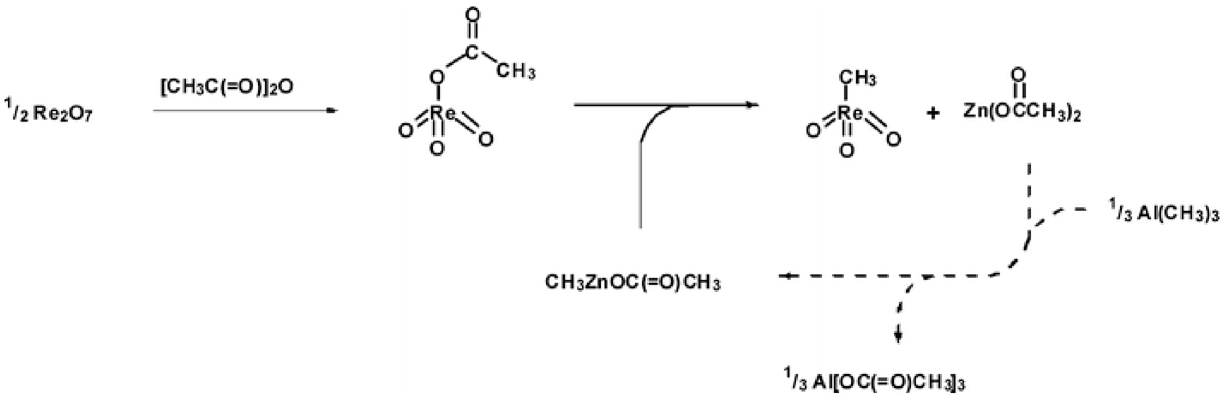
Equ. 2.2

$$[Zn(OOCCH_3)_2] + 1/3\,[Al(CH_3)_3] \longrightarrow [CH_3ZnOOCH_2CH_3] + 1/3\,[Al(OOCCH_3)_3]$$

Equ. 2.3

Scheme 2.2 Synthesis of methylzinc acetate

Re_2O_7 is dissolved in acetonitrile to form perrhenylacetate upon treatment with acetic anhydride. The methylating reagent, [Zn(MeOAc)], is then added slowly at –10 °C. For purification, the resulting solution is separated from the precipitated zinc acetate and the solvent is removed. The crude product is extracted with *n*-pentane and sublimated to yield pure MTO. The use of $[Zn(OOCCH_3)_2]$ not only reduces the cost of $[CH_3ZnOOCCH_3]$ production, but also eliminates the need to employ pyrophoric dimethzlyinc and uses one of the waste products from CH_3ReO_3 as a feed stock, as shown in scheme 2.3.



Scheme 2.3

Table 2.1 lists the development of production costs for MTO from the original synthesis published in 1979,[9d] to the new synthesis.[11-12] Since the first report, the total cost of production on a laboratory scale has reduced from ~. 834 g^{-1} to ~. 42 € /g^{-1}.

Table 2.1 Costs for common laboratory scale production of MTO (10 g Re_2O_7 scale)

Route for MTO synthesis	Price of MTO/ g^{-1}
$Me_6Re_2O_3$ or Me_3ReO_2 with air[9d]	833.92
Re_2O_7 with Me_4Sn[11]	73.07
$(CF_3CO)_2O$ with Bu_3SnMe[12]	49.69
$Ca(ReO_4)_2$ with Me_4Sn[13]	49.99
$Ag(ReO_4)$ with Me_4Sn[13]	66.90
Using MeZnOAc synthesised from Me_2Zn	46.00
Using MeZnOAc synthesised from $Al(CH_3)_3$	41.75
Using MeZnOAc synthesised from $Al(CH_3)_3$ + recycling of waste $Zn(OAc)_2$	41.71

This method also offers an improved atom economy (*ca.* 46%) compared to the currently most widespread lab scale synthesis for the production of MTO (Table 2.2).

Table 2.2 Atom economy by the production of MTO [*M* (MTO)/*M* (waste products) × 100, where *M* is the molecular weight]

Route for MTO synthesis	A.E. (%)
$Me_6Re_2O_3$ or Me_3ReO_2 with air[9d]	49.73
Re_2O_7 with Me_4Sn[11]	37.57
$(CF_3CO)_2O$ with Bu_3SnMe[12]	38.21
$Ca(ReO_4)_2$ with Me_4Sn[13]	43.11
$Ag(ReO_4)$ with Me_4Sn[13]	38.58
Using MeZnOAc synthesised from Me_2Zn	46.09

This synthetic method provides a convenient route to the homologues CH_3ReO_3 and $C_2H_5ReO_3$ to give 85% and 60% yields, respectively.

As previously mentioned, the precipitated zinc acetate can be recycled. However direct (*via* $Al(CH_3)_3$) or catalytic (by *in situ* generation of $[CH_3ZnOOCCH_3]$ alkylation would be ideal since derivatization would be eliminated or reduced, this is not possible due the decomposition of rhenium oxides in the presence of $Al(CH_3)_3$.

Reaction conditions described are optimized for minimum use of solvent and are as close to ambient conditions as possible to reduce the amount of waste generated and energy consumed, respectively. The use of auxillary substances were eliminated entirely in the purification and recovery of CH_3ReO_3, as this complex is isolated by sublimation.

Over the last 20 years significant improvements with respect to efficiency, cost, and environmental friendliness have been made with respect to the synthesis of the extremely versatile catalyst MTO. In particular, the most recent improvements of the synthesis represent a milestone in the context of the principles of green chemistry. Not only was it possible to eliminate the use of the hazardous tetramethyltin and related compounds, but the atom economy of the overall synthesis was also further improved. Nevertheless, many areas for optimization still remain. Further efforts to make the synthesis even more environmentally benign are currently being undertake, including the substitution of acetonitrile as a reaction solvent and catalyst immobilization to reduce the use of solvents and auxiliary substances in catalyst recovery.

2.3 Super absorbers from renewable feedstock by catalytic oxidation[235]

For the last century the primary feedstocks for chemical industry have been crude oil and natural gas. Due to the constant increase in costs for oil, and the current economic and environmental impact of the utilization of this resource, there exists a social and environmental pressure to develop renewable, economic and environmentally sound products which optimize the use of this feedstock, or if possible replace it. A switch from non-renewable, fossil resources to renewable raw materials, such as carbohydrates derived from biomass, is a necessary step to the development of a sustainable chemical industry. Materials produced from renewable feedstocks which are biocompatible, biodegradable, CO_2-neutral and less toxic, leave a smaller “environmental footprint” than many crude oil derived products.[8]

One renewable feedstock material which can be exploited is starch, one of the most abundant and versatile biopolymers. Super absorbers produced from starch[19] are quickly replacing synthetic polyacrylate-based super absorbents[20] which have poor biodegradability.[21] Examples for applications are self-tightening plastic fabrics used in concrete construction works, which make use of the pressure resulting from swelling upon contact with water, or these found in sanitary bags for infants.[19] For technical applications, the use of durable polymers may be necessary, however there is an ever increasing demand for super absorbing commodity products for medical or sanitary applications with short product lifetime requiring a quick and safe product decomposition after use.[19c] There is, accordingly, a clear need for a biodegradable and economical super absorber generated from starch.

Several industrial methods for the manufacture of oxidized starch are known. A common process used to oxidize starch applies TEMPO mediated oxidation with sodium hypochlorite, which generates stoichiometric amounts of sodium chloride as waste product.[22] An alternative method is the application of *in situ*-generated nitrogen oxides which, however, produces nitric oxides and nitrogen containing salts.[23] Finally an oxidizing system based on the catalyst methyltrioxorhenium (MTO)[24] was reported.[17] The three-component system MTO/H_2O_2/HBr in acetic acid catalyzes the selective oxidation of the C6 hydroxy methyl group yielding the corresponding carboxylic acid.

In this section an optimized catalytic approach using MTO to produce carboxy starch is discussed, which reduces overall reaction cost and produces less harmful waste.

There are a few limitations for the three-component system MTO/H_2O_2/HBr in acetic acid including the use of HBr as co-catalyst and acetic acid as solvent.[17] Many areas for improvement of this system still remain. Due to its multifunctionality, starch requires mild reaction conditions in polar aqueous solvents.[25] The replacement of highly corrosive HBr by another source of bromide, e.g. an alkaline metal salt, which would not be as problematic and harmful as HBr is desirable.[26] Lower operating costs are expected as the reaction mixture is less corrosive, and reactors, pipes and waste streams should be less damaging to the reactor which will require less up keep. The use of HBr is also undesirable as starch is not stable in the presence of strong acids. Glycosidic bonds undergo hydrolysis, and therefore the ability of the resultant products to absorb water decreases.[27] However, the addition of bromide is necessary as it accelerates the catalytic oxidation by the factor of 1000.[28] A less acidic medium is preferred to prevent the depolymerisation of starch in an acidic medium and the subsequent loss of water absorption capacity.[27,23c,d]

The success of a given oxidation reaction is quantified by the degree of oxidation determined by a German industrial standard DIN EN ISO 11214, which uses titration.[29] The water absorption is distinguished by TA- (total absorbency) and CRET-values (absorbency after centrifugation) determined by a previously reported literature method.[30]

2.3.1 Alternative Bromide Sources

Several alternative sources of bromide listed in table 2.3 were tested.

Table 2.3 Oxidation of potato starch in the presence of alternative bromide sources with the three-component system $MTO/H_2O_2/Br^-$.

Bromide	**TA**	**CRET**	**Degree of Oxidation [%]**
HBr	3.0	2.4	18.9
LiBr	6.2	4.5	12.1
NaBr	6.0	4.4	11.8
KBr	6.3	4.3	12.4

As expected, when HBr is used as co-catalyst the degree of oxidation is significantly higher than for the cases of the bromide salts. However, water absorption of the resultant product is lower because of the hydrolysis of the glycosidic bonds. All alkaline metal salts show comparable results. They achieve lower degrees of oxidation than HBr but the water absorption of resultant polymers is double. As a result, it is reasonable to propose alkaline bromides to be used as a replacement for the highly corrosive HBr in the described catalytic system. The solubility in polar aqueous solvents of the alkaline bromides declines with molar mass. Therefore the use of LiBr, with the best solubility (177 g per 100 mL H_2O), is most favourable for an optimized system. However, Li ions, which are not removed at water treatment stations, have physiological effects (e.g. as antidepressants), thus this bromide source can be replace by the economical more advantageous NaBr with a slightly lower oxidation performance.

2.3.2 Acidity

As described above, the application of 100 % acetic acid is detrimental to water absorption of the oxidation product. A neutral medium is optimal to minimize depolymerisation. However, the stability of the catalyst decreases with increasing hydroxide concentration. In the presence of $[OH]^-$, MTO and the catalytic active species (the mono- and bisperoxo complex derived from MTO), are deactivated to yield methanol and catalytic inactive perrhenate (see Equ (2.4-2.6)).[31]

$$CH_3ReO_3 + [HO_2]^- \longrightarrow CH_3OH + [ReO_4]^-$$
Equ 2.4

$$CH_3Re(O_2)_2O \xrightarrow{[OH^-]} CH_3ReO_3 + OOH^-$$
Equ 2.5

$$CH_3Re(O_2)O_2 + [OH]^- \longrightarrow CH_3OH + [ReO_4]^-$$
Equ 2.6

In the presence of hydrogen peroxide, the deactivation occurs more readily due to the formation of the hydroperoxide anion from hydrogen peroxide present in aqueous solutions as hydroperoxide is a better nucleophile.

$$H_2O_2 + H_2O \rightleftharpoons [HO_2]^- + [H_3O]^+$$
Equ 2.7

In this equilibrium (Equ. 2.7), the concentration of hydroperoxide can be lowered by an increase of the pH of the solution which would lead to significantly slowed deactivation. Various mixtures of water and acetic acid were tested to establish optimum solvent acidity for the oxidation of starch. The results are shown in Table 2.4.

Table 2.4 Oxidation of potato starch with the three-component system MTO/H_2O_2/Br^- using different mixtures of water and acetic acid as solvent.

Solvent	**TA**	**CRET**	**Degree of Oxidation [%]**
0 % HAc/100 % H_2O	2.9	2.1	1.3
25 % HAc/75 % H_2O	3.3	2.7	3.4
50 % HAc/50 % H_2O	7.1	5.9	10.3
75 % HAc/25 % H_2O	6.4	5.2	11.6
100 % HAc/0 % H_2O	6.2	4.5	12.1

By using pure acetic acid as solvent, the highest degree of oxidation is achieved (12.1 %). However, the water absorption of the product measured by TA- and CRET-values is not optimal due to the depolymerisation of the product in acidic conditions. The water absorption is highest when a 50/50 % acetic acid/water mixture is used. When the ratio of acid vs water decreases, catalyst deactivation is of greater impact than product depolymerisation, and both the degree of oxidation and the water absorption are very low. The 50/50 % acetic acid/water mixture appears to be a good balance between catalyst stability and substrate hydrolysis.

2.3.3 Addition rate of hydrogen peroxide

Another way to influence the equilibrium of the formation of hydroperoxide (Eq. 2.7) is by varying the rate of hydrogen peroxide addition. When the oxidant is added slowly, its concentration is low and therefore the concentration of hydroperoxide decreases based on the shown equilibrium. The speed of addition was controlled by a pump with variable solution additon velocity (1-0.05 eq./min). The results are shown in Table 2.5.

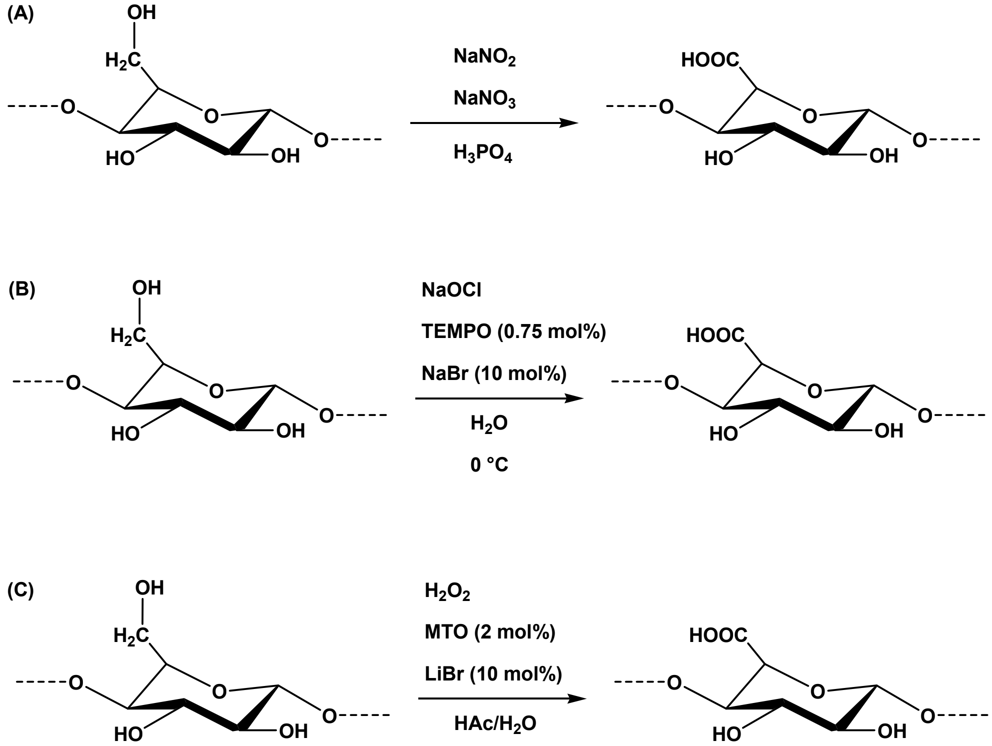
Table 2.5 Oxidation of potato starch applying various speeds of addition of hydrogen peroxide with the three-component system MTO/H_2O_2/Br^-.

Addition speed of H_2O_2 [eq./min]	**TA**	**CRET**	**Degree of Oxidation [%]**
0.05	8.5	6.8	23.3
0.1	7.4	5.4	17.9
0.5	5.3	3.9	6.6
1	3.4	2.7	2.3

Applying the slowest rate of H_2O_2 addition, 0.05 eq./min, the highest degree of oxidation and the best water absorption of the resultant product is observed. Increasing the rate leads to lower water absorption and oxidation. According to Eq. 2.7 the concentration of the hydroperoxide ion, which is responsible for the deactivation of MTO, can be minimized based on Le Chatelier’s principle. The only disadvantage is that the slowest rate of addition extends the total reaction time from one to two hours.

2.3.4 Comparison of the catalytic route with industrial methods

The oxidation of starch with the three-component system MTO/H_2O_3/Br^- under optimized conditions (see above) was compared with the two common industrial processes for the production of carboxy starch. The industrial processes, oxidation with *in situ*-generated nitrogen oxides[23] (A) and TEMPO mediated oxidation by sodium hypochlorite[22] (B) along with our optimized stratagy (C) are shown in (scheme 2.4).



Scheme 2.4 Processes yielding carboxy starch: (A) oxidation with *in situ*-generated nitrogen oxides[23]; (B) TEMPO mediated oxidation by sodium hypochlorite[22]; (C) oxidation applying the optimized three-component system MTO/H_2O_2/Br^-.

The evaluation of these different routes, by TA and CRET values, to oxidize starch are shown in table 2.6.

Table 2.6 Results of the oxidation of potato starch applying routes (A)-(C).

Oxidation method	**TA**	**CRET**	**Degree of Oxidation [%]**
Route A: *in situ*-generated nitrogen oxides	3.7	2.2	36.8
Route B: TEMPO/NaBr/NaOCl	8.2	7.1	27.7
Route C: catalytic three-component system MTO/H_2O_3/Br^-	8.5	6.8	23.3

The highest degree of oxidation, 36.8 %, is achieved using *in situ*-generated nitrogen oxides as an oxidant. However, the ability of water absorption of the resultant product is bad (reflected in low TA- and CRET-values) due to depolymerisation in the highly acidic reaction medium. The catalytic three-component system (C) and the oxidation process applying TEMPO and NaOCl (B) are comparable: (B) gives better yields, (C) results in a slightly better water absorption capacity.

The three-component system MTO/H_2O_2/Br^- is a significantly improved alternative method for the production of super absorber compared to those currently in use. The optimized system is composed of 2 mol% MTO, 10 mol% LiBr and 300 mol% H_2O_2 with 50 % acetic acid as solvent. Efforts significantly improve the ability of water absorption of resulting super absorbers, the degree of oxidation, however, differs only marginally. The TA-values are increased from 3.6 to 8.5 by a factor of 2.4, the CRET-value increases from 2.4 to 6.8 by a factor 2.8 and the degree of oxidation is improved from 18.9 % to 23.3 %. The highly corrosive bromide source HBr is successfully replaced by less problematic LiBr. The amount of the oxidant hydrogen peroxide required is reduced from 400 mol% to 300 mol% yielding better oxidation results. A 1:1 mixture of acetic acid and water was shown to be a good compromise between enhancing the stability of the catalyst MTO and limiting the hydrolysis of the substrate starch. In addition, the solvent is more environmentally benign as a result of using less acetic acid because less base is required for the neutralization of the waste water before it is purified in the sewage treatment plant. If hydrogen peroxide is added slowly the concentration of the hydroperoxide ion decreases significantly and therefore the deactivation of the catalyst is again minimized. The optimal rate for the addition of the oxidant was found to be 0.05 eq./min.

In comparison to the two industrial methods for the manufacture of carboxy starch described above, the three-component system MTO/H_2O_2/Br^- is more environmentally sound. The atom efficiency[32] (A.E. = M(product)/M(starting material)

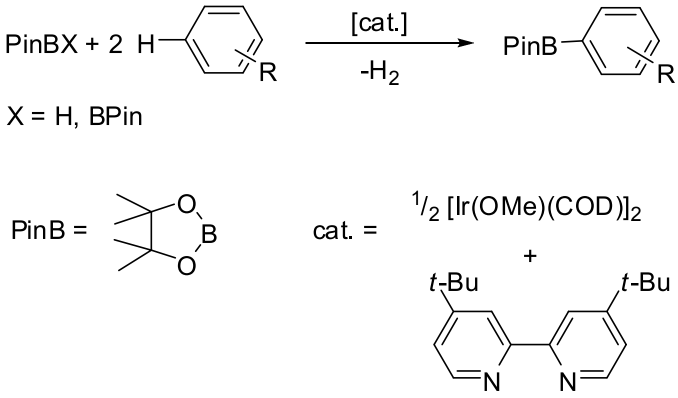
+ M(stoichiometric reagents)) of the oxidation with *in situ* generated nitrogen oxides is 56 %. In spite of a high degree of oxidation of the resultant carboxy starch, the water absorption is very low (TA = 3.7, CRET = 2.2) because depolymerisation of the starch occurs under acidic conditions. The stochiometic use of inorganic oxidants is not optimal as large amounts of nitric oxides (NO_x) and inorganic nitrogen salts are generated as waste products. The oxidation process applying TEMPO and sodium hypochlorite has a atom efficiency[32] of 57 %, a comparable water absorption and degree of oxidation as the three-component system. However, stochiometic amounts of sodium chloride are produced as a waste product and as a consequence of a side reaction, chlorinated starch derivatives[22] are generated as by-products decreasing the biodegradability of the resultant material. The atom efficiency[32] for the oxidation of starch applying the optimized three-component system $MTO/H_2O_2/Br^-$ is 77 %. This method is selective, environmentally benign and sustainable, because no by-products occur and the green oxidant hydrogen peroxide is used which only generate reducing the waste.

A selective oxidation process for the generation of a super absorber from biomass using the key principles of green chemistry, catalysis and the utilization of renewable resources, is described in section 2.3. By balancing the social, environmental and economic impact of a variety of possible alterations to the catalytic process a balance has been met that provides an economic and environmentally more advantageous process. The selective oxidation, applying the newly developed three-component system $MTO/H_2O_2/Br^-$, has been shown to be a convenient method for the manufacture of carboxy starch with mild reaction conditions that are not only environmentally sound but also cost-effective. With regard to the recently reported tin free synthesis of MTO[33] the above described method is superior to the hitherto industrial important processes applying TEMPO/NaOCl[22] or *in situ* generated nitrogen oxides.[23] Nevertheless, many areas for optimization still remain. The amount of the rhenium catalyst used in the reaction is high, because part of it is lost by deactivation of the active Re(VII) centres as perrhenate by hydroxide ions in the aqueous reaction medium. However, the inactive perrhenate can be easily recovered.[34] Thus, the valuable catalyst, which now is available by an improved, cost efficient and new synthetic route,[33] can be recycled with near quantitative yields. The resulting product is advantageous compared to conventional polyacrylate-based super absorbents, and although they display lower water absorption, super absorbents made with oxidized starch are completely biodegradable.

2.4 Iridium Complexes of *N*-Heterocyclic Carbenes in C-H-Borylation using Energy Efficient Microwave Technology: Influence of Structure, Ligand Donor Strength and Counter Ion on Catalytic Activity[236]

The selective transition metal catalyzed functionalization of “unreactive” C-H bonds remains a challenge in present day organometallic chemistry.[35] Since first reports by Chatt[36] in 1965 on the C-H activation of aliphatic and aromatic hydrocarbons mediated by ruthenium complexes, various transition metal complexes have been tested for activity in this reaction.[35,37] To date, only a few systems have been reported to catalytically facilitate C–H activation.[35-41]

Among catalytic transformations, the C–H borylation reaction proves to be a powerful tool for the direct synthesis of valuable alkyl or aryl boronic acid esters.[41] Boronic acid esters are employed as starting materials for the Suzuki-Miyaura reaction[42] and are readily transformed into functionalized amines or hydrocarbons such as alkenes and alcohols.[43] As a result, boronic acid ester derivatives are of high interest for the synthetic organic chemistry and recently several research groups have investigated rhenium, iridium, rhodium and ruthenium catalyzed C–H borylation of aliphatic and aromatic hydrocarbons.[44-56] The most active catalyst system reported for the C–H borylation of aromatic compounds with B_2pin_2 and HBpin is derived from $[Ir(COD)(OMe)]_2$ and 4,4'di-*tert.*-butyl-2,2'-bipyridine which can proceed in inert solvents (scheme 2.5)[48] and is tolerant to a wide range of functional groups.[42,49] In contrast, catalysts derived from iridium precursors $[Ir(COD)(X)]_2$ (X = Cl, OAc) displayed a significantly lower activity.[42a] Intramolecular C–H activation with Iridium-NHC-complexes has already been documented[57] and encouraged us to explore iridium biscarbene complexes as catalysts for the catalytic C–H borylation.

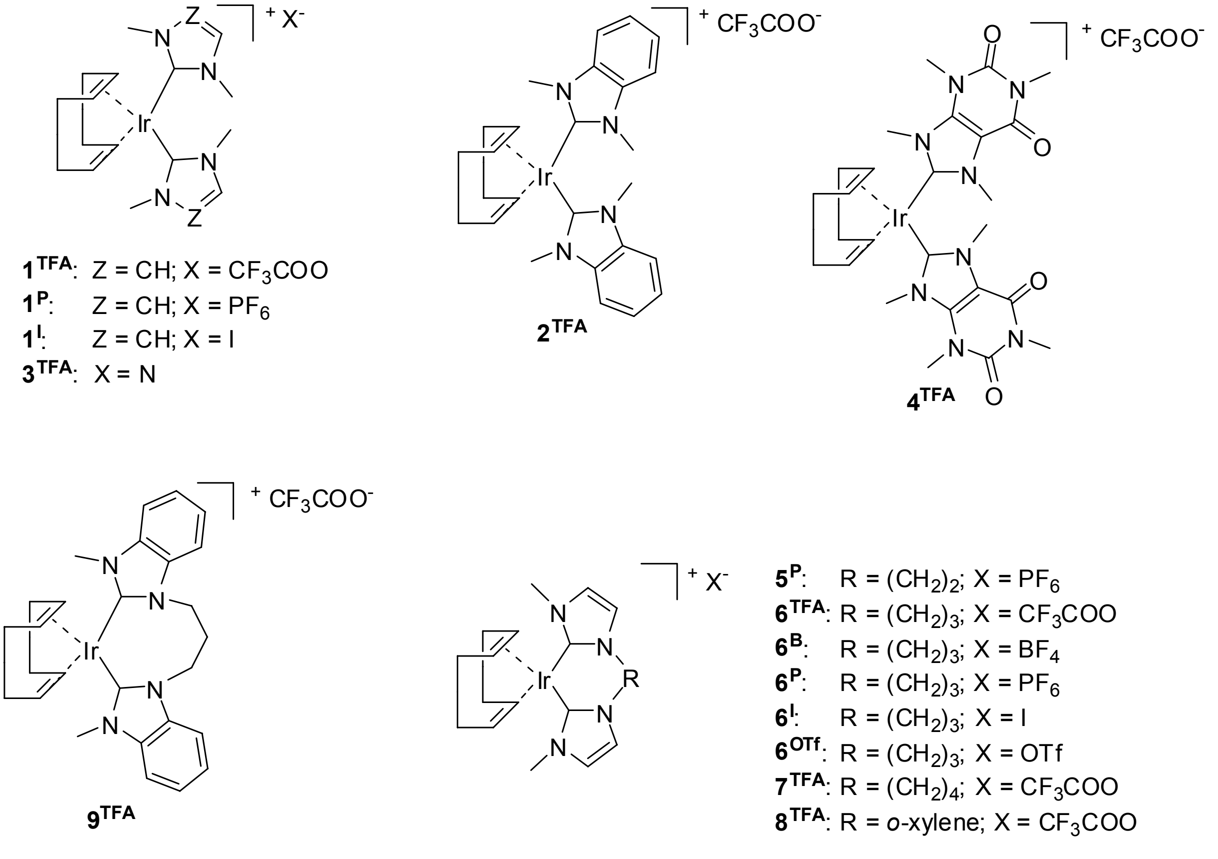


Scheme 2.5 C–H-Borylation of hydrocarbons

Over the past 18 years the use of *N*-heterocyclic carbenes as ligands for catalysts has brought about a renaissance in organometallic chemistry.[47b,c] These ligands have proven to be far more than simple well bound phosphine replacements, and substitution within and about the ring have resulted in a wide range of complexes that are not only highly stable but also catalytically active.[58] In recent years we[57,59,60] and others[61,62] have prepared a wide variety of iridium NHC complexes, and investigated the catalytic utility of these systems. In the following section a comparative study of various NHC iridium catalysts in the C–H borylation reaction is presented. By studying complexes which vary in the ligands steric and electronic properties as well as complex counter ion, the influence in catalysis of alterations on the basic motif were elucidated. Microwave conditions are known to accelerate the reaction progress through rapid heating. Moreover the reaction media is heated directly reducing decomposition via wall effects, and as such we decided to employ the microwave for our investigations.[63] To the best of our knowledge this is the first example of a catalytic C–H borylation under microwave conditions.

2.4.1 Preparation of bis-NHC complexes of iridium(I)

Synthesis of cationic iridium bis-NHC complexes (Scheme 2.6, **1** to **9**) was performed according the alkoxide route shown in Scheme 2.7.[57] The iridium precursor [Ir(COD)OEt]$_2$, was prepared *in situ* from [Ir(COD)Cl]$_2$ by reaction with NaOEt in ethanol at ambient temperature. Reaction with the azolium salt precursor (NHC*HX') in the presence of NaI resulted in the formation of the iridium biscarbene iodides, which were converted to the triflate, hexafluorophosphate, tetrafluoroborate and trifluoroacetate iridium complexes by salt metatheses reaction with the corresponding silver salts.



1^{TFA}: Z = CH; X = CF_3COO
1^{P}: Z = CH; X = PF_6
1^{I}: Z = CH; X = I
3^{TFA}: X = N

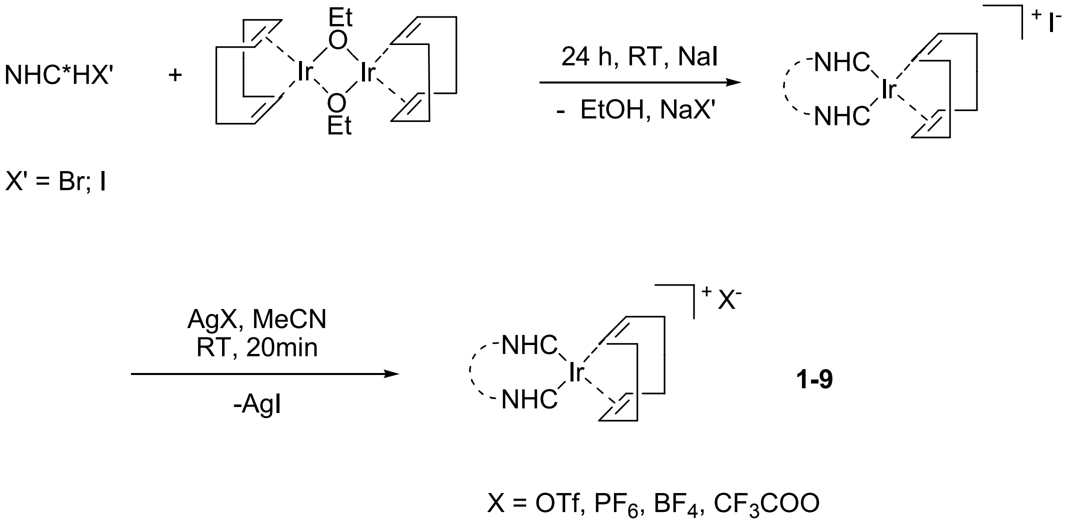
2^{TFA}

4^{TFA}

9^{TFA}

5^{P}: R = $(CH_2)_2$; X = PF_6
6^{TFA}: R = $(CH_2)_3$; X = CF_3COO
6^{B}: R = $(CH_2)_3$; X = BF_4
6^{P}: R = $(CH_2)_3$; X = PF_6
6^{I}: R = $(CH_2)_3$; X = I
6^{OTf}: R = $(CH_2)_3$; X = OTf
7^{TFA}: R = $(CH_2)_4$; X = CF_3COO
8^{TFA}: R = *o*-xylene; X = CF_3COO

Scheme 2.6 Bis-NHC catalysts of iridium(I) for the C-H borylation reaction



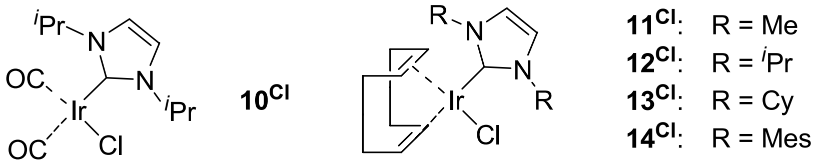
Scheme 2.7 Alkoxide route for the preparation of iridium NHC complexes

Isolation of $\mathbf{5}^{I}$ was not possible due to decomposition during purification. Crabtree *et al.* have previously reported that the presence of halides can result in complexes with limited stability, while the use of PF_6^- as a counter ion often leads to more stable products which can be isolated.[64] This proved to be the case with our system, where the *in situ* counter ion exchange of I^- for PF_6^- or **5^I** employing KPF_6 provides access to **5^P**, which could be isolated. With the exception of **6^{OTf}** (56 %) bis-NHC complexes with bidentate as well as monodentate ligands were prepared in good yields (67 - 81 %). Complexes **5^P** and **6^P** were prepared in considerably higher yields than with the previously reported silver route,[62] showing the alkoxide route to be an effective strategy for the preparation of iridium biscarbene complexes.

NHC complexes **1** - **9** were characterized by ^{1}H- and ^{13}C- NMR spectroscopy and FAB/MS, as well as ^{19}F-NMR spectroscopy for the fluorine containing compounds. The formation of the Ir–NHC bond is accompanied by loss of the C2 proton signal in the ^{1}H- NMR spectra at ~ 9.3 - 10.0 ppm and the ^{13}C-NMR spectra display signals at 175.9 to 178.2 ppm, in a region where the carbene signals for bis(imidazol-2-ylidenes) of Ir(I) would be expected, confirming the formation of Ir–C bonds.[57] The carbene signals appear low field for the coordinated azolinylidene ligands complexes $\mathbf{3^{TFA}}$, $\mathbf{4^{TFA}}$ (182 ppm, 180 ppm), and this effect is most pronounced for the benzimidazol-2-ylidene ligand in $\mathbf{2^{TFA}}$ and $\mathbf{9^{TFA}}$ (187.2 ppm, 189.1 ppm). The ^{19}F-NMR spectra display fluorine signals for complexes $\mathbf{1^{TFA}}$ - $\mathbf{9^{TFA}}$ (-72.7 to -75.1 ppm), $\mathbf{1^{P}}$, $\mathbf{6^{P}}$ (-69.5 to -70.1 ppm), $\mathbf{6^{B}}$ (-147.6 ppm) and $\mathbf{6^{OTf}}$ (-78.2 ppm), confirming that the exchange reaction with fluorine containing anions has occurred.

2.4.2 Screening of iridium NHC catalysts in the C-H borylation of benzene

Microwave conditions are known to accelerate the reaction progress through rapid heating simultaneously decreasing decomposition of the catalyst due to the absence of wall effects. In addition heat loss from the system is minimal with direct heating of the reaction media.[63] Preliminary experiments at 160 °C gave higher yields in a microwave reactor than under conventional heating due to very fast and selective heating of the reaction mixture. As a result catalyst screening employing microwave conditions were used. The C-H borylation was conducted in neat benzene or in organic solvents with B_2pin_2 or HBpin employing 0.5 - 3 mol % catalyst loading, thereby exploring the utility of a series of precatalysts (shown in scheme 2.6 and 2.8). The catalytic results are summarized in Table 2.7.



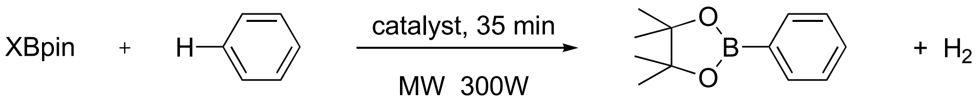
10$^{\mathbf{Cl}}$

11$^{\mathbf{Cl}}$: R = Me
12$^{\mathbf{Cl}}$: R = ^{i}Pr
13$^{\mathbf{Cl}}$: R = Cy
14$^{\mathbf{Cl}}$: R = Mes

Scheme 2.8 Monocarbene complex of iridium applied in the C-H borylation reaction

Catalysts **1**$^{\mathbf{TFA}}$ - **4**$^{\mathbf{TFA}}$ (Table 2.7; entries 1, 4 ,6 ,7) are listed in order of decreasing σ-donor strength,[60] and the superiority of stronger donating carbene ligands in C–H borylation is clearly observed. The superior product yields of chelating bis-NHC catalysts **6**$^{\mathbf{TFA}}$ and **9**$^{\mathbf{TFA}}$ (Table 2.7; entries 9, 20), suggest the enhancing influence of the bidentate ligand motif. In addition, a similar σ-donor trend is observed among these two complexes.

Table 2.7 Screening of iridium catalysts in the C–H borylation of benzene



Entry	Catalyst	Catalyst mol%	X	$n_{benzene}/n_{XBpin}$	% Yield [a]
1	$\mathbf{1}^{\mathbf{TFA}}$	1.5	H	30/1	48
2	$\mathbf{1}^{\mathbf{TFA}}$	1.5	Bpin	60/1	92
3	$\mathbf{1}^{\mathbf{TFA}}$	0.5	Bpin	60/1	64
4	$\mathbf{2}^{\mathbf{TFA}}$	1.5	H	30/1	32
5	$\mathbf{2}^{\mathbf{TFA}}$	0.5	Bpin	60/1	40
6	$\mathbf{3}^{\mathbf{TFA}}$	1.5	H	30/1	36
7	$\mathbf{4}^{\mathbf{TFA}}$	1.5	H	30/1	12
8	$\mathbf{5}^{\mathbf{P}}$	1.5	H	30/1	<1
9	$\mathbf{6}^{\mathbf{TFA}}$	1.5	H	30/1	89
10	$\mathbf{6}^{\mathbf{TFA}}$	0.5	H	30/1	85
11[b]	$\mathbf{6}^{\mathbf{TFA}}$	0.5	H	4/1	20
12[c]	$\mathbf{6}^{\mathbf{TFA}}$	0.5	H	4/1	0
13[d]	$\mathbf{6}^{\mathbf{TFA}}$	0.5	H	4/1	<1
14[e]	$\mathbf{6}^{\mathbf{TFA}}$	1.5	H	4/1	4
15[f]	$\mathbf{6}^{\mathbf{TFA}}$	1.5	Bpin	4/1	85
16[f]	$\mathbf{6}^{\mathbf{TFA}}$	0.5	H	4/1	27
17[f]	$\mathbf{6}^{\mathbf{TFA}}$	0.5	H	1/1	5
18	$\mathbf{7}^{\mathbf{TFA}}$	1.5	H	30/1	17
19	$\mathbf{8}^{\mathbf{TFA}}$	1.5	H	30/1	40
20	$\mathbf{9}^{\mathbf{TFA}}$	1.5	H	30/1	60
21[g]	$\mathbf{9}^{\mathbf{TFA}}$	1.5	H	30/1	87
22	$\mathbf{10}^{\mathbf{Cl}}$	1.5	H	30/1	<1
23	$\mathbf{11}^{\mathbf{Cl}}$	1.5	H	30/1	9
24	$\mathbf{12}^{\mathbf{Cl}}$	1.5	H	30/1	72
25	$\mathbf{12}^{\mathbf{Cl}}$	3	H	30/1	80
26	$\mathbf{12}^{\mathbf{Cl}}/PPh_3$	3	H	30/1	37
27	$\mathbf{12}^{\mathbf{Cl}}/PCy_3$	3	H	30/1	22

28	**12**$^{\mathrm{Cl}}$/PMe$_3$	3	H	30/1	<1
29	**13**$^{\mathrm{Cl}}$	1.5	H	30/1	68
30	**14**$^{\mathrm{Cl}}$	1.5	H	30/1	75

[a] 0.5 - 3.0 mol%; catalyst, yields determined *via* GC-FID applying dodecane as internal standard, 35 min, 300 W, MW; [b] in 1.6 mL dioxane; [c] in 1.6 mL ether, 1h, 125°C, MW; [d] in 1.6 mL cyclohexane; [e]; in 1.6 mL hexane; [f] in 1.6 mL THF; [g] reaction time 1h.

In addition to the effects of σ-donor strength, this work also reveals the influence of the design motif about the chelating NHC ligands on C–H borylation. Among bis-NHC catalysts bearing bidentate imidazol-2-ylidene ligands (**6**$^{\mathrm{TFA}}$, **9**$^{\mathrm{TFA}}$) the systems with a propylene bridged moiety produced the highest yields (Table 2.7; entries 9, 20). It may be concluded that the more sterically hindered *o*-xylene and *n*-butylene bridges (Table 2.7, entries 18,19) **7**$^{\mathrm{TFA}}$, **8**$^{\mathrm{TFA}}$ hamper the coordination of the incoming arene, which has already been found to be rate determining for bipyridine iridium catalysts,[53] and as a result the reaction rate is reduced.

Catalysts with bidentate propylene bridged azolylidene ligands result in higher yields than their monodentate homologues. This is observed for benzimidazolylidenes (**2**$^{\mathrm{TFA}}$, **9**$^{\mathrm{TFA}}$) as well as for imidazolylidenes (**1**$^{\mathrm{TFA}}$, **6**$^{\mathrm{TFA}}$). We propose that this is caused by the greater stability of complexes bearing propylene bridged NHC ligands. Decomposition of NHC-complexes may occur through reductive elimination of NHC hydride complex intermediates. The oxidative addition of NHC–H reforming the NHC carbene is more likely for chelating complexes because of favored intra vs slower inter molecular processes. Oxidative addition of the C2–H bond in imidazolium salts has already been demonstrated by Periana *et al.*[65] and C–H borylation with mono-NHC catalysts **10**$^{\mathrm{Cl}}$ – **14**$^{\mathrm{Cl}}$ resulted in lower yields than **6**$^{\mathbf{TFA}}$ due to decomposition, observed by the formation of a black suspension of metallic iridium (Table 2.7; entries 22 – 30).

Near quantitative conversion was observed using **9**$^{\mathbf{TFA}}$ after 60 minutes reaction time, suggesting that the difference in product yield is a result of catalyst activity and not decomposition of the catalyst (Table 2.7; entries 9, 20, 21). Catalyst **6**$^{\mathbf{TFA}}$ also facilitates the activation of benzene with catalyst loading as low as 0.5 mol % to near quantitative yields within 35 minutes (Table 2.7; entry 10).

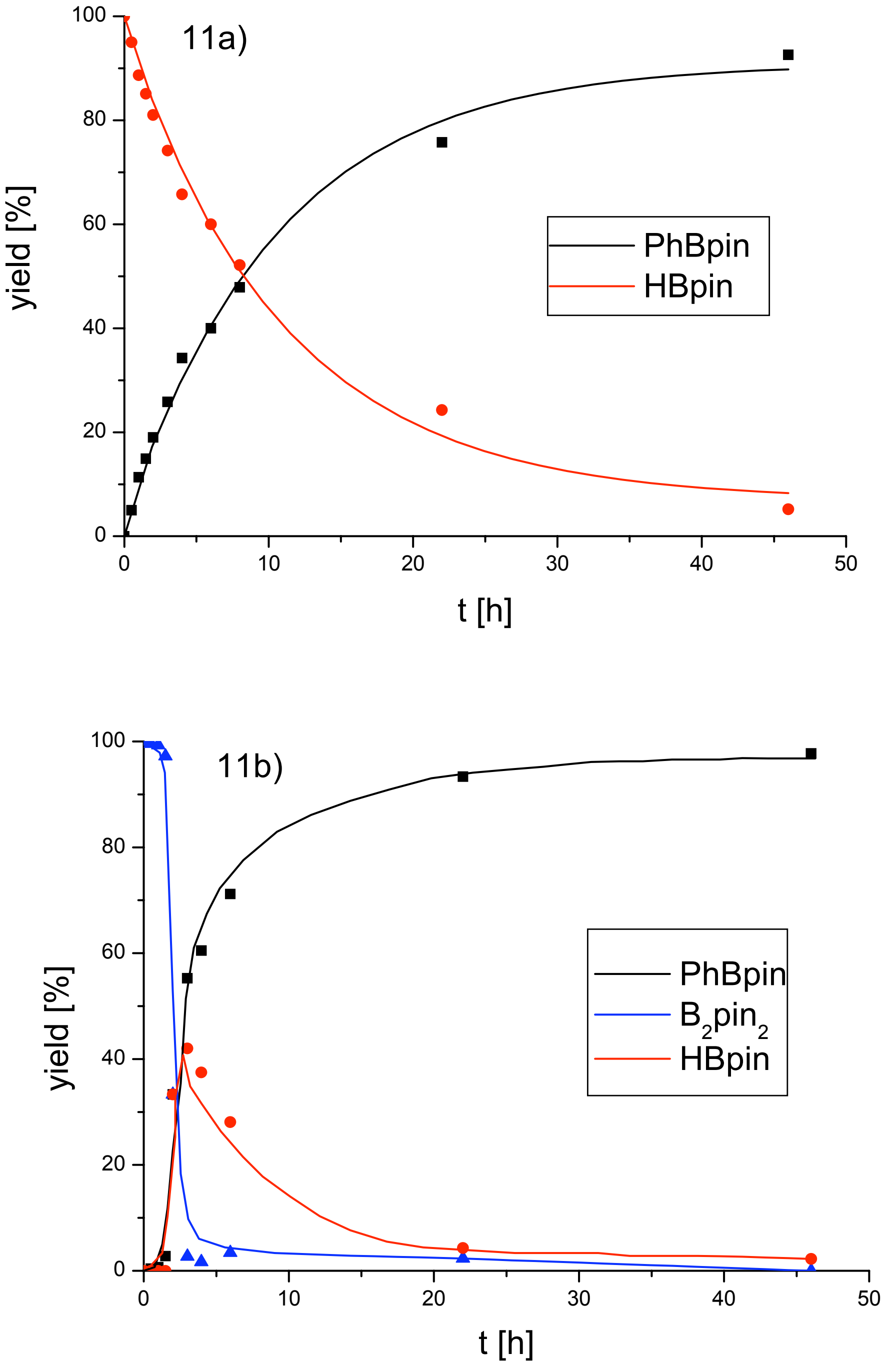


Figure 2.1 Reaction Progress a) reaction of 1 eq. HBpin b) reaction of 0.5 eq. B_2pin_2, conditions: 30 eq. benzene-d_6, 0.5 mol% **6**$^{\mathbf{TFA}}$, 125°C, NMR-tube; reaction progress is monitored by ^{1}H-NMR spectroscopy; δ = 1.10 (CH_3, PhBpin), 1.01 (CH_3, B_2pin_2), 0.98 (CH_3, HBpin).

Applying **6**$^{\mathbf{TFA}}$, the activity of bis-NHC catalysts in various solvents was investigated (Table 2.7; entries 11 - 17). The best results were obtained in THF (entry 15), however activation in neat benzene proceeds considerably faster (entry 10). In a 1:1 mixture of benzene and HBpin in THF, C–H borylation activity is greatly reduced. In addition, the reactant also influences catalytic activity as the use of B_2pin_2 resulted in a yield of 85%, in comparison to the slower, slightly less reactive HBpin (entries 15, 16). This trend was also observed using **1**$^{\mathbf{TFA}}$ and **2**$^{\mathbf{TFA}}$ (Table 2.7, entries 2, 3, 5) as catalysts. The difference in catalytic activity is attributed to the difference in bond energy of B–B (332 kJ/mol) and B–H (381 kJ/mol).

Intrigued by these results we investigated kinetics for the activation of C_6D_6 by means of HBpin and B_2pin_2 comparatively, monitoring the conversion and formation of the products by ^{1}H-NMR spectroscopy with conventional heating (Fig. 2.1). This investigation demonstrates that B_2pin_2 undergoes C–H borylation more readily, however, an initiation period of approximately one hour was observed. The initiation period of the C–H borylation is attributed to the formation of hydrogen while generating NHC boryl complexes of iridium.[50] In the case of B_2pin_2 the formation of H_2 is slowed down as activation of a stronger C–H bond (461 kJ/mol) is more difficult than activation of the B–H bond (381 KJ/mol). As a side reaction hydrogenation of the COD ligand was observed and formation of the reduction products cyclooctene (COE) and cyclooctane were detected via GC-MS analysis of the reaction mixture. In accordance with previous suggestions of Hartwig, the initial step of the catalytic cycle seems to be the partial dissociation of the olefin ligand.[50] The monodentate COE is more readily dissociated than the bidentate COD as a result of the chelate effect. Hence, a slower formation of H_2 when using B_2pin_2 results in slower dissociation of the olefin ligand which in turn leads to slower hydrogenation of the COD-ligand. Thus dissociation of the olefin ligand is retarded explaining the appearance of an induction period.

Table 2.8 Influence of the counter ions on C–H borylation with cationic iridium(I) complexes

Entry	Catalyst	Catalyst mol%	% Yield [a]	pK_a- Value[b]
1	**1^{TFA}**	1.5	48	0
2	**1^{I}**	1.5	<1	-11
3	**1^{P}**	1.5	<1	-20
4	**5^{P}**	1.5	<1	-20
5	**6^{TFA}**	1.5	89	0
6	**6^{TFA}**	0.5	85	0
7	**6^{B}**	0.5	68	-4.9
8	**6^{P}**	1.5	<1	-20
9	**6^{I}**	1.5	<1	-11
11	**6^{OTf}**	1.5	<1	-14

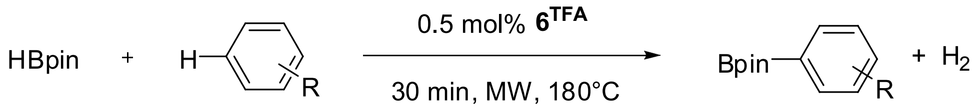
[a] 1eq. HBpin, 30 eq. benzene, 0.5 - 1.5 mol% catalyst, 35 min, 300W, MW, yields determined via GC-FID with dodecane as an internal standard; [b] pK_a-value of the corresponding acid.[66]

As mentioned previously, the catalytic potential of mono-NHC complexes was also investigated. C-H borylation was unsuccessful applying carbonyl complex **10^{Cl}** (Table 2.7; entry 22). Though within the family of all other studied monocarbene complexes (**11^{Cl}**, **12^{Cl}**, **13^{Cl}**, and **14^{Cl}**), comparable yields were observed with exception of less sterically hindered **11^{Cl}** (Table 2.7; entries 22 vs. 23, 24, 29, 30). The addition of one equivalent phosphine results in a lower product yield, and the addition of $P(Me)_3$ quenches catalytic activity (Table 2.7; entries 25 – 28).

For the first time, the use of mono-NHC complexes of Iridium as catalysts in the C–H borlyation reaction is examined. During subsequent studies of iridium catalysts **1**, **5**, and **6** (Table 2.8), we found that the basicity of employed counter ions[66] is crucial for the catalytic activity. Reactions conducted with catalysts containing PF_6^-, OTF^- and I^- as counter ions resulted in yields of less than 1 % (Table 2.8, entries 2 - 4, 8 - 11), however, catalysts containing BF_4^- and CF_3COO^- gave good to excellent yields (Table 2.8, entries 1, 5 - 7). As such it was possible to demonstrate that catalytic activity in the C–H borylation increases with growing basicities of the applied counter ions.

With the most active catalyst $\mathbf{6^{TFA}}$ the selectivity of mono substituted aromatic compounds was investigated. In addition, the relative rates k_{rel}, k_o, k_m and k_p were determined in a competitive reaction of benzene and a corresponding aromatic in THF. Results are shown in table 2.9.

Table 2.9 C–H Borylation of substituted benzene derivatives

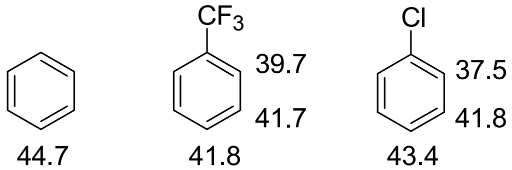


Entry	R	Yield (*o*/*m*/*p*) [%][a]	k_{rel} ($k_o/k_m/k_p$)[b]
1	Me_2N	<1 (0/64/35)	0.25 (0/0.15/0.10)
2	Me	35 (4/64/32)	0.47 (0.02/0.30/0.15)
3	OMe	47 (5/67/28)	0.52 (0.05/0.33/0.14)
4	Cl	85 (0/76/24)	3.38 (0/2.54/0.84)
5	CF_3	86 (0/69/31)	3.61 (0/2.42/1.19)
6	F	90 (17/55/28)	2.89 (0.46/1.59/0.84)
8[c]	I	11 (4)	---
9[c]	Br	25 (1)	---

[a] 0.64 mmol HBpin, 19.2 mmol benzene, 0.5 mol% **6**^{TFA}, 30 min, 180°C, MW, yields and selectivities determined via GC-FID (using dodecane as an internal standard) GC-MS and ^{13}B-NMR; [b] $k_{rel} = Y_{aromatic} / Y_{benzene}$, 0.64 mmol HBpin, 2.56 mmol benzene, 2.56 mmol benzene derivative, 0.5 mol% **6**^{TFA}, 1.6 mL THF, 35 min, 300W, yields and selectivities determined by GC-FID (using dodecane as internal standard) GC-MS and ^{13}B-NMR; [c] 0.64 mmol HBpin, 2.56 mmol aromatic, 1.6 mL THF, 35 min, 300 W, MW; yields of byproduct PhBpin in parenthesis; regioselectivity not determined;

Experiments performed in neat aromatic compounds result in observed values for k_{rel} conclusively showing that electron withdrawing groups favour the formation of the C–H borylation product (Table 2.10; entries 1 - 6). This observation is supported by the relative reaction rate k_{rel}, which emphasizes that the electron withdrawing groups accelerate the reaction progress. The activation of iodobenzene and bromobenzene in neat educts failed. However, borylation performed in THF employing 4 equivelents HBpin yielded halophenyl boronic acid pinacole ester in small quantities, while activation of the C-X bond (X = Br, I) and formation of phenyl boronic acid pinacole ester was also observed (Table 2.9; entries 8,9). The reactivity of these substrates is attributed to the comparatively low stability of the C–Br (81 kcal/mol) and C–I (65 kcal/mol) bond (C–Cl, 96 kcal/mol; C–F 126 kcal/mol).[67]

The regioselectivity is influenced by the steric hindrance of reactant substituents. Thus, functionalization is preferred in *meta*- and *para*-position, while the small fluoro substituent also enables activation of the *ortho*-postion. In addition there is a weak electronic effect that regulates the *meta* vs. *para* distribution. The C–H acidities are employed to quantify the electronic properties of aromatic compounds. In trifluorobenzene, *meta* and *para* product are formed in a nearly statistic ratio (*meta*:*para* is 2:1) due to the nearly equal acidity of the *meta*- and *para*-position. In contrast activation of chlorobenzene preferentially leads to the *para*-product due to a difference of 1.6 pK_a units (Scheme 2.9). Those results were confirmed by comparison of the relative rates k_m and k_p (Table 2.9, entries 4, 5).



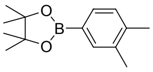
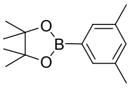
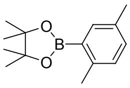
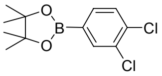
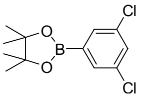
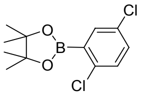
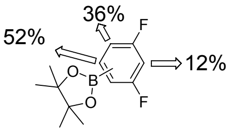
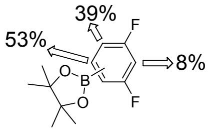
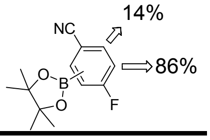
Scheme 2.9 C–H acidities of aromatic compounds[34]

The C–H borylation of disubstituted aromatic compounds was conducted in neat reactants or inert solvents under microwave conditions confirming results found for mono substituted compounds (Table 2.10). In comparison with xylene derivatives (Table 2.10; entries 1 - 3) electron withdrawing groups

(F, Cl) were found to undergo C–H borylation more readily and increased yields were observed (Table 2.10; entries 4 - 9), with the exception of the 1,4-derivatives. Reaction of the 1,4-isomers proceeded relatively slowly due to the steric hindrance of the substituents in ortho-position (Table 2.10; entries 3 ,6). Borylation of 1,3- and 1,2-isomers occurred only in *meta* or *para*-position, but not in *ortho*-position (Table 2.4; entries 1, 2, 4, 5). The 1,3-difluorobenzene was activated in the normally hampered *ortho*-position due to the low steric impact and high electronegativity of fluoro substituents (Table 2.10, entry 7). Comparing the reactivity 1,3- and 1,2-isomers of xylene and dichlorobenzene derivatives activation of 1,2-isomers resulted in higher yields due to the twofold availability of active positions. In addition, the otherwise unreactive catalyst **6^I^** promoted the formation of difluorophenyl boronic acid pinacoleester in small quantities (Table 2.10; entry 8). Activation of 4-fluorobenzonitrile produced high yields due to substitution with strongly electron-withdrawing groups. Regioselectivity is determined by the steric impact of the substituents, with ortho subsitution (with respect to the fluorine group) occurring preferentially.

Analogous to Hartwigs[53] studies the *π*-coordination of the aromatic compound on an iridium(III) centre is proposed to be the limiting step in the catalytic cycle. This is confirmed by high yields observed in the presence of strong *σ*-donor ligands and electron-withdrawing substituents located on the aromatic ring, as both effects favour the formation of arene complexes.[69]

Table 2.10 C–H borylation of disubstituted benzene derivatives

Entry	Aromatic	Catalyst mol%	% Yield [a]	
1	1,2-xylene	1.5	51	
2	1,3-xylene	1.5	28	
3	1,4-xylene	1.5	21	
4	1,2-dichlorobenzene	1.5	81	
5	1,3-dichlorbenzene	1.5	59	
6	1,4-dichlorobenzene	1.5	21	
7[b]	1,3-difluorobenzene	0.5	84	
8[c]	1,3-difluorobenzene	0.5	7	
9[d]	4-fluorobenzonitrile	0.5	81	

[a] 0.64 mmol HBpin, 19.2 mmol aromatic, 0.5 - 1.5 mol% $\mathbf{6}^{\mathbf{TFA}}$, 30 min, 180°C, MW, yields and selectivities determined via GC-FID (using dodecane as internal standard), GC-MS and ^{13}B-NMR; [b] 0.64 mmol HBpin, 2.56 mmol aromatic, 1.6 mL THF, 2 % C-F activation; [c] $\mathbf{6}^{\mathbf{I}}$; [d] 0.32 mmol HBpin, 1.28 mmol 4-fluorobenzonitrile, 0.4 mL hexane, 4 % double borylation; regioselectivity determined via F-NMR

Recently Periana and coworkers described C–H activation of benzene at Ir(III) or Pt(II) to proceed via an η^1-aryl intermediate, where the deprotonation step is mediated by a basic ligand.[70] We therefore postulate that the reaction proceeds via an η^1-aryl intermediate in which deprotonation of the benzene derivative is mediated by an anionic CF_3COO^- ligand. The primary kinetic isotope effect of 3.0 ± 0.1 determined in a mixture of benzene and deuterated benzene is attributed to the increased energy level of the η^1-aryl intermediate formed with deuterated aromatics resulting in a slower reaction rate. This isotope effect could also be indicative of an oxidative addition mechanism. However, recently Milstein has demonstrated that the stereo selectivity for C–H activation of benzene derivatives mediated by iridium(I) pincer complexes, which occurs by an oxidative addition pathway, is directed by electronic effects to give *ortho*- substituted products.[71] In contrast, the NHC complexes of iridium were shown to activate selectively in sterically unhindered *meta*- or *para*- positions, thereby confirming that acidity is the determining factor for selectivity in the system described.

Catalytic examinations using the energy efficient microwave as a heating source to screen a large family of in part highly active iridium catalysts bearing NHC moieties have been performed, in the atom efficient neat systems. The iridium(I) bis-NHC catalyst $\mathbf{6}^{\mathbf{TFA}}$ is shown to be particularly active. By varying different ligands and counter ions, the basicity of the counter ion proved to be the most important feature of the complex design motif. For the first time, the use of iridium mono-NHC catalysts in the C–H borylation is reported, however, the lower stability of these complexes, when compared to bis-NHC complexes, leads to decreased product yields. The influence of the counter ion, the ligand, the observed regioselectivity and chemoselectivity as well as the kinetic studies indicate a mechanism proceeding via an η^1-aryl intermediate with the formation of η^2-arene intermediate as rate determining side reaction. Further work should focus on the immobilization of systems based on the iridium complexes studied to take full advantage of the microwave heating method and facilitate catalyst product separation in solventless systems.

3 Carbocyclic Carbenes: Explorations in Synthesis and Complex Design for Catalysis

3.1 Overview

The goal of my work in this area was to explore synthetic strategies for the production of novel complexes bearing carbocyclic carbenes and evaluate their catalytic activity. A systematic overview of carbocyclic carbene complexes including synthetic methods employed for preparation (section 3.3), unique structure and bonding features (section 3.4) as well as reactivity (section 3.5) from initial discovery in the late 1960s to present provides a basis to discuss novel synthetic attempts. The most common synthetic strategies (subsections 3.3.1-3.3.5) were evaluated in attempts at substituted seven-membered carbocyclic carbene systems which are outlined at the end of each subsection. The information given in this section is essential for the evaluation of catalysts described in section 4.

3.2 Introduction

In 1968 the first metal complexes with N-heterocyclic carbene ligands were reported.[73,74] From this time many complexes of transition metals both in low and high oxidation states as well as main group metals bearing such ligands were synthesized and characterized.[75,76] These singlet carbenes gain stability from electron donation by adjacent heteroatoms into the vacant p orbital of the carbene carbon atom. This electron donation causes the nucleophilic character of N-heterocyclic carbenes, which act as typical σ-donor ligands comparable to phosphines or amines in metal coordination chemistry.[77]

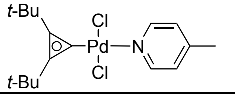
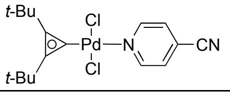
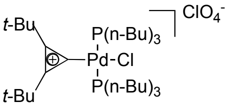
The exploration of carbocyclic carbenes began with the early work of W. M. Jones and coworkers, who, in 1967, showed for the first time that carbocyclic carbenes (cyclopropenylidene and cycloheptatrienylidene) can be stabilized by integration of the vacant p-orbital of the carbene into the p-electron system of an aromatic carbocycle and exist in a singlet configuration with nucleophilic behavior of the carbene.[78] This fundamental work inspired our efforts to use such carbenes without stabilizing heteroatoms as ligands in metal complexes comparable to N-heterocyclic carbene ligands. The first transition metal complexes with a carbocyclic 2-p electron carbene was synthesized in 1968 and 1970.[79,80] Since then, numerous articles have been published reporting the coordination of this ligand system to different metal centers, with variation of substituents at the cyclopropene ring, and alternative preparation methods for cyclopropenylidene complexes. Though relatively unexplored as a ligand class, work by G. Bertrand and coworkers, in which they succeeded in synthesizing a stable free cyclopropenylidene and the corresponding lithium adduct has stimulated research in this area.[81,82]

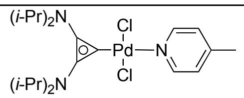
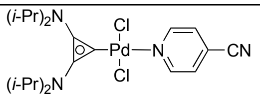
In 1978 the first transition metal complexes with the homologous carbocyclic 6-p electron carbene cycloheptatrienylidene (CHT) were described by W. M. Jones.[83] During the following 20 years the exploration was pushed forward exclusively by the group of W. M. Jones including the discovery, that the ligand C_7H_6 may exist in two different bonding modes, a carbene (cycloheptatrienylidene) or an allene (cycloheptatetraene) structure, depending on the electron configuration of the transition metal. Later on, other groups got involved in this work, primarily focusing on heterobimetallic complexes, in which the cycloheptatrienylidene simultaneously serves as an η-ligand comparable to Cp.

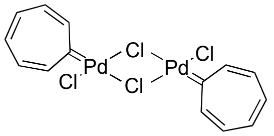
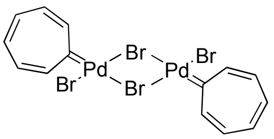
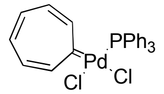
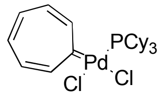
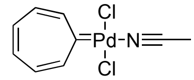
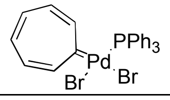
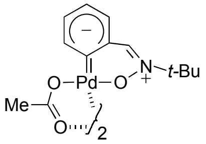
During the last three years carbocyclic carbenes have gained importance as ancillary ligands in palladium precatalysts for coupling reactions. Apart from these cyclopropenylidene and cycloheptatrienylidene complexes several reports concerning metal complexes bearing four or five-membered carbocyclic carbene ligands have been published. These ligands obviously lack an aromatic ring system and are therefore not as nucleophilic as carbenes based on an aromatic ring system, however, some of their metal complexes, especially ruthenium indenylidene complexes have been applied to metathesis reactions as active carbenes in the last ten years.

Selected known aromatic carbocyclic carbene palladium and platinum complexes, along with selected data are listed in table 3.1.

Table 3.1 Known aromatic carbocyclic carbene palladium and platinum complexes with selected data

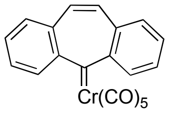
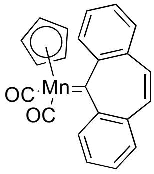
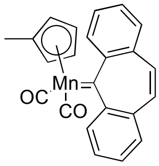
Compound	Method of Preparation (% yield)	Selected data	Ref.
[(*i*-PrC)$_2$C)PdCl$_2$]$_2$	3.3.4 (45)	orange; mp (°C) 164; ^{13}C$_{carbene}$ 181.2 ppm; EA (CHN).	146
[(*i*-PrC)$_2$C)PdBr$_2$]$_2$	3.3.4 (95)	orange; mp (°C) 172; EA (CH).	146
[(*t*-BuC)$_2$C)PdCl$_2$]$_2$	3.3.4 (60)	orange; mp (°C) 233 (dec.); ^{13}C$_{carbene}$ 183.1 ppm; EA (CH).	146, 147
[(PhC)$_2$C)PdCl$_2$]$_2$	3.3.4 (51)	yellow powder; ^{13}C$_{carbene}$ 174 ppm; EA (CHPd).	84, 149
[(MesC)$_2$C)PdCl$_2$]$_2$	3.3.4 (68)	yellow-orange powder; ^{13}C$_{carbene}$ 182.9 ppm; EA (CHPd). **M-C*carbene*** [Å]= monoclinic (a)1.919(4) (b) 1.908(4) 1.921(4) triclinic 1.907 (7) 1.910(7)	149
[(NapC)$_2$C)PdCl$_2$]$_2$	3.3.4 (34)	yellow powder; ^{13}C$_{carbene}$ not observed; EA (CHPd).	149
[(Me$_2$NC)$_2$C)PdCl$_2$]$_2$	3.3.4 (44)	red/orange crystals; mp (°C) 210 (dec.); IR; UV/Vis; EA (CHN).	148
[(*i*-Pr$_2$NC)$_2$C)PdCl$_2$]$_2$	3.3.4 (44)	reddish brown; mp (°C) 240 (dec.); IR (KBr) 1856, 1500 cm^{-1}.	85, 147
[(*i*-Pr$_2$NC)$_2$C)PdI$_2$]$_2$	3.3.4 (55)	reddish brown; mp (°C) 264 (dec.); IR (KBr) 1853, 1496 cm^{-1}; EA (CHN).	85
[((*i*-PrC)$_2$C)PdCl$_2$(P*n*-Bu$_3$)]	3.3.4 (69)	colorless; mp (°C) 153; ^{13}C$_{carbene}$ 205.7 ppm; EA (CH).	86, 146
[*trans*-(*i*-Pr$_2$C)$_2$C)PdCl(P*n*-Bu$_3$)$_2$]ClO$_4$	3.3.4in HClO$_4$ $_{(aq)}$	colorless; mp (°C) 151; ^{13}C$_{carbene}$ 205.4 ppm.	86, 146
[((*t*-BuC)$_2$C)PdCl$_2$(P*n*-Bu$_3$)]	3.3.4 (75)	colorless; mp (°C) 153 (dec.); ^{13}C$_{carbene}$ 205.2 ppm; EA (CH).	86, 146
[((*t*-BuC)$_2$C)PdCl$_2$(NCCH$_3$)]	3.3.4 (75)	orange; mp (°C) 183 (dec.); EA (CHN).	146
[((*t*-BuC)$_2$C)PdCl$_2$(Py)]	3.3.4 (82)	yellow; mp (°C) 82/150; IR (nujol) n 1604, 1345, 346, 328 cm^{-1}; ^{1}H; EA(CHN)	146, 147
	3.3.4	mp (°C) 147-148; IR (nujol) n 1618, 1350 cm^{-1}; ^{1}H; EA (CHClN).	147
	3.3.4	mp (°C) 128-129; IR(nujol) n 2230, 1612, 1344, 348, 330 cm^{-1}; ^{1}H; EA (CHClN).	147
[((*t*-BuC)$_2$C)PdCl$_2$(OS(CH$_3$)$_2$)]	3.3.4 (67)	yellow; mp (°C) 202 (dec.); EA (CH).	146
	3.3.4 in HClO$_4$ $_{(aq)}$ (68)	colorless; mp (°C) 164; ^{13}C$_{carbene}$ 205.8 ppm; EA (CH).	86,
[((PhC)$_2$C)PdCl$_2$(P*n*-Bu$_3$)]	3.3.4	^{13}C$_{carbene}$ 195.3 ppm.	86
cis-[((PhC)$_2$C)PdCl$_2$(PCy$_3$)]	3.3.4 (93)	yellow powder; mp (°C) 205 (dec.); ^{13}C$_{carbene}$ 197.7 ppm; ^{31}P; MS-FAB; EA (CHPd). **M-C*carbene*** [Å]= 1.931(4)	79, 149
cis-[((PhC)$_2$C)PdCl$_2$(PPh$_3$)]	3.3.4 (91)	yellow powder; mp (°C) 185 (dec.);	79, 149,

		$^{13}C_{carbene}$ 196.1 ppm, ^{31}P; MS-FAB; EA (CHPd). **M-C$_{carbene}$** [Å]= 1.945(2)	188, 189
$[((PhC)_2C)PdCl_2(OEt)]$	3.3.4	no details	79
$[((PhC)_2C)PdCl_2(OS(CH_3)_2)]$	3.3.4	no details	79
$[((PhC)_2C)PdCl_2(CNCH_3)]$	3.3.4	no details	79
$[((PhC)_2C)PdCl_2(Py)]$	3.3.4	no details	79
[*trans*-$(Ph_2C)_2C)PdCl(P$*n*-$Bu_3)_2]ClO_4$	3.3.4 in $HClO_{4(aq)}$	$^{13}C_{carbene}$ 195.2 ppm; EA (CH).	86, 146
cis and *trans*– $[((MesC)_2C)PdCl_2(Pcy_3)]$	3.3.4 (93)	yellowish powder, 2 isomers; mp (°C) 200 (dec.); $^{13}C_{carbene}$ 209.2 ppm (trans), $^{13}C_{carbene}$ 202.4 ppm (cis), ^{31}P; MS-FAB	86, 146
cis-$[((NapC)_2C)PdCl_2(PCy_3)]$	3.3.4 (81)	yellow green microcrystaline powder; mp (°C) 205 (dec.); $^{13}C_{carbene}$ 200.3 ppm, ^{31}P; MS-FAB	149
cis-$[((Me_2NC)_2C)PdCl_2(P$*n*-$Bu_3)]$	3.3.4 (85)	white crystals; mp (°C) 172; IR (KBr)n 2960, 2935, 2875, 1903, 1557, 1419, 1409, 1378, 1211 cm^{-1}; $^{13}C_{carbene}$ 125 ppm; UV/Vis; EA (CHN). **M-C$_{carbene}$** [Å]= 1.961(3)	86, 148
[*trans*-$(Me_2NC)_2C)PdCl(P$*n*-$Bu_3)_2]ClO_4$	3.3.4 in $HClO_4$ (aq)	$^{13}C_{carbene}$ 122.0 ppm; EA (CHN).	86, 146
[*trans*-$(Et_2NC)_2C)PdCl(P$*n*-$Bu_3)_2]ClO_4$	3.3.4 in $HClO_4$ (aq)	white; mp (°C) 78; $^{13}C_{carbene}$ 122.0 ppm; EA (CHN).	86, 146
cis-[(i-$Pr_2NC)_2C)PdCl_2(P$*n*-$Bu_3)]$	3.3.4 (78)	orange/white; mp (°C) 208; IR (KBr)n 1858, 1487 cm^{-1}; $^{13}C_{carbene}$ 128.4 ppm; EA (CHN).	85, 86
[Cis-(*i*-$Pr_2NC)_2C)PdI_2(P$*n*-$Bu_3)]$	3.3.4 (60)	orange; mp (°C) 145; IR (KBr)n 1848, 1486 cm^{-1}; EA (CHN).	85
[*trans*-(*i*-$Pr_2NC)_2C)PdCl(P$*n*-$Bu_3)_2]ClO_4$	Cycloaddition of alkynes to vinylidene complexes (67)	colorless/white; mp (°C) 120; IR (KBr) ν_{CO} 1855, 1492 cm^{-1}; $^{13}C_{carbene}$ 125.6 ppm; EA (CHN).	85, 86
[*trans*-(*i*-$Pr_2NC)_2C)PdBr(P$*n*-$Bu_3)_2]ClO_4$	3.3.1 (53)	colorless; mp (°C) 220 (dec.); IR (KBr) ν_{CO} 1855, 1495 cm^{-1}; EA (CHN).	85
[*trans*-(*i*-$Pr_2NC)_2C)PdI(P$*n*-$Bu_3)_2]ClO_4$	3.3.1 (49)	colorless; mp (°C) 210 (dec.); IR (KBr)n 1850, 1492 cm^{-1}; EA (CHN).	85
trans-[(i-$Pr_2NC)_2C)PdCl_2Py]$	3.3.4	mp (°C) 276 (dec.); IR (KBr), FIR (nujol)n 1851, 1500,1332, 337, cm^{-1};^{1}H; EA (CHClN).	147
	3.3.4	mp (°C) 276 (dec.); IR (KBr), FIR (nujol)n 1853, 1498, 1328 cm^{-1}; ^{1}H; EA (CHClN).	147
	3.3.4	mp (°C) 274 (dec.); IR (KBr), FIR (nujol)n 2225, 1848, 1498, 1322, 330, cm^{-1}, ^{1}H; EA (CHClN).	147
cis-[(*i*-$Pr_2NC)_2C)_2PdMe_2]$	3.3.2 (89)	mp(°C): 107 (dec), X-ray, colorless blocky crystals, $^{13}C_{carbene}$:165.5 ppm, TOF HRMS	97
[(*i*-$Pr_2NC)_2C)PtI_2]_2$	3.3.4 (18)	reddish brown; mp (°C) 226 (dec); IR (KBr) ν_{CO} 1846, 1484 cm^{-1}; EA (CHN).	85
cis-[(*t*-$BuC)_2C)PtCl_2]$	Reaction of ethoxylithioethylene followed by alkylation (33)	white crystals; mp (°C) 263 (dec.); IR (KBr) ν_{CO} 2950, 1474, 1370, 1330, 1230, 1176 cm^{-1}; $^{13}C_{carbene}$ 178.8 ppm; EA (CHCl).	193
cis-[(*t*-$BuC)_2C)PtCl_4]$	3.3.4 (19)	yellow crystals; mp (°C) 218 (dec.); IR(KBr)ν_{CO}:2950,1480, 1328,1226,	193

		1220 cm^{-1}; $^{13}C_{carbene}$ 166.6 ppm; EA (CHCl).	
[(*t*-BuC)$_2$C)PtCl$_2$(PBu$_3$)]	3.3.4 (22)	white crystals; mp (°C) 147; IR (KBr) ν_{CO}1960, 2925, 2875, 1485, 1466 cm^{-1}; $^{13}C_{carbene}$ 192.5 ppm; EA (CHPCl).	193
trans-[(*i*-Pr$_2$NC)$_2$C)$_2$PtCl$_2$]	Reaction of ethoxylithioethylene followed by alkylation (4)	white crystals; mp (°C) >300 (dec.); IR(KBr)ν_{CO}:2975, 2935, 2880, 1854, 1490, 1467, 1378,1337 cm^{-1}; $^{13}C_{carbene}$ 136.0; EA (CHNCl).	193
cis-[(*i*-Pr$_2$NC)$_2$C)$_2$PtI$_2$]	Reaction of ethoxylithioethylene followed by alkylation (>20)	yellow crystals; mp (°C) >300 (dec.); IR (KBr) ν_{CO} 2950, 1840, 1328,1160 cm^{-1}; EA (CHNI).	193
trans-[(*i*-Pr$_2$NC)$_2$C)$_2$PtI$_2$]	3.3.4 (>20)	yellow crystals; mp (°C) >300 (dec.); IR (KBr) ν_{CO} 2950, 1840, 1328,1160 cm^{-1}; $^{13}C_{carbene}$ 131.8 ppm; EA (CHNI).	193
[*trans*-(*t*-BuC)$_2$C)PtCl(PBu$_3$)$_2$]ClO$_4$	3.3.4+ KClO$_4$ (66)	IR (KBr) ν_{CO} 2960, 2925, 2875, 1480, 1467 cm^{-1}; $^{13}C_{carbene}$ 194.98 ppm; EA (CHNP).	193
[*trans*-(*i*-Pr$_2$NC)$_2$C)PtCl(P*n*-Bu$_3$)$_2$]ClO$_4$	3.3.1 (55)	colorless/ white; mp (°C) 225; IR (KBr) ν_{CO} 1862, 1494 cm^{-1}; EA (CHN).	85, 86
[*trans*-(*i*-Pr$_2$NC)$_2$C)PtBr(P*n*-Bu$_3$)$_2$]ClO$_4$	3.3.1 (48)	colorless/ pale yellow; mp (°C) 247/154; IR (KBr) ν_{CO} 1856, 1490 cm^{-1}; EA (CHN).	85, 86
[*trans*-(*i*-Pr$_2$NC)$_2$C)PtI(P*n*-Bu$_3$)$_2$]ClO$_4$	3.3.1 (46)	colorless; mp (°C) 255; IR (KBr) ν_{CO} 1855, 1490 cm^{-1}; EA (CHN).	85
	3.3.1 (64)	orange crystal, air stable; mp (°C) 150-160 (dec.); IR (nujol) $\nu_{Pd\text{-}Cl}$ 346, 313, 383 cm^{-1}; EA (CHPd).	115
	3.3.1 (97)	bright orange crystals, air stable; mp (°C) 179-184 (dec.); IR (nujol) $\nu_{Pd\text{-}Br}$ 250, 178, 161 cm^{-1}; ^{1}H, $^{13}C_{carbene}$ 217.5 ppm; EA (CHPd).	87, 115, 117
	3.3.1 (93)	yellow crystals, air stable; ^{1}H, ^{31}P; MS-FAB; EA (CHPd). **M-C*carbene*** [Å]= 1.968(2)	87, 117
	3.3.1	^{1}H, ^{31}P, MS-FAB; EA (CHPd).	87
	3.3.1 (51)	yellow crystals; ^{1}H, ^{13}C, $^{13}C_{carbene}$ not detected; EA (CHNPd).	117
	3.3.1	^{1}H, ^{31}P; MS-FAB; EA (CHPd). **M-C*carbene*** [Å] =1.983(3)	87
	Synthesis from aromatic nitrone precursors (82)	pale yellow solid, air stable, mixture of two diastereomers (trainsoid/cisoid 10:1); mp (°C) 213 (dec.); ^{1}H, ^{13}C (carbene not assigned); EA (CHN).	121

The successful routes reported for the synthesis of platinum and palladium complexes are given in 3.3.1 and 3.3.4. Using this work as a basis for elucidating successful clean synthetic pathways to carbocyclic carbene complexes, different possible pathways were tested. To date, several carbocyclic carbene complexes have been prepared, yet, only three dibenzosubstituted complexes have been reported shown in table 3.2. All of these were prepared via the diazo route further discussed in section 3.5.

Table 3.2

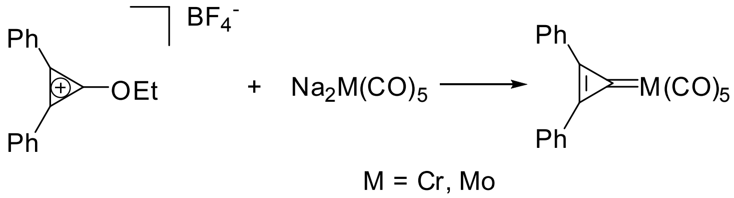
Compound	Method of Preparation (% yield)	Selected data	Ref.
	3.3.5 (67)	black solid; dec. > -20 °C; IR (hexane) v_{CO} 2068, 1987, 1958 cm^{-1}; ^{1}H, $^{13}C_{carbene}$ 404.24 ppm, $^{13}C_{COcis}$ 214.53 ppm, $^{13}C_{COtrans}$ 237.37 ppm; HR-MS.	113, 114
	3.3.5 (82)	brown needles, air stable ; mp (°C) 134-135; IR (C_6H_{14}) v_{CO} 1994, 1934 cm^{-1}; ^{1}H, $^{13}C_{carbene}$ 351.15 ppm; MS-EI; EA (CHMn).	112
	3.3.5 (84)	dark green oil, air sensitive; IR (C_6H_{14}) v_{CO} 1991, 1932 cm^{-1}; ^{1}H; MS-EI; EA (CHMn).	112

The following section, 3.3 - 3.5, includes a literature survey of synthetically sucessfull stratagies used in the synthesis of various carbocyclic carbene complexes along with how these were applied in the attempted synthesis of a substituted carbocyclic carbene complex. In addition, section 3.4, describing structure and bonding of previously reported carbocyclic carbene complexes has been included to provide a basis for discussion of structural influences of substitution of the carbocyclic carbene moiety. Reported reactivity is also summarized in section 3.5 to provide insight with regards to the catalytic activity of these complexes in catalysis, further explored in section 4.

3. 3 Synthetic Strategies

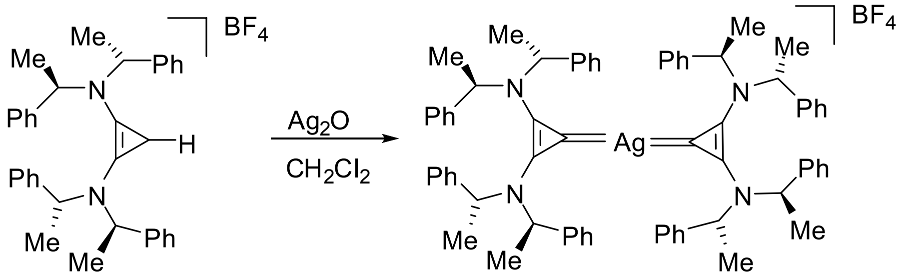
3.3.1 Synthesis via reaction of salts

Rees and coworkers were able to prepare molybdenum and chromium diphenylcyclopropenylidenpentacarbonyl complexes by reaction of 3-ethoxy-1,2-diphenylcyclopropenylium tetrafluoroborate (Scheme 3.1).[93]



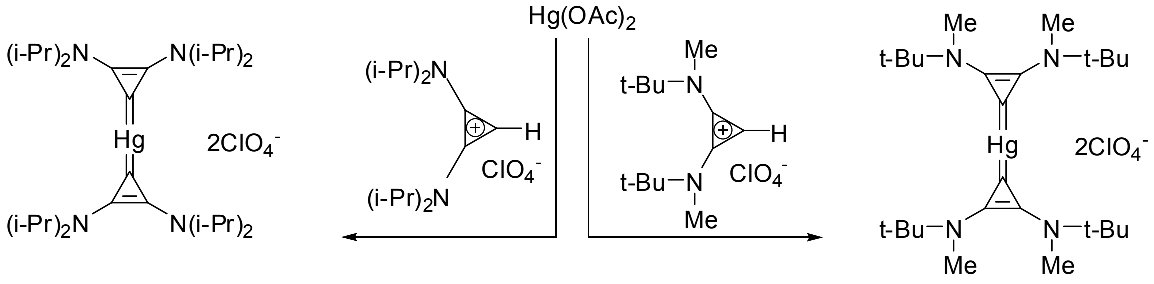
Scheme 3.1

Deprotonation of bis[di(*R*-1-phenylethyl)amino]cyclopropenylium tetrafluoroborate in the presence of a strong base with Ag_2O yields the corresponding chiral dicarbene silver(I) tetrafluoroborate complex in moderate yields (67%) (Scheme 3.2).[94] Silver carbene complexes have been shown to be very useful carbene transfer agents, and this strategy may be of use in preparation of complexes bearing highly reactive carbocyclic carbenes which are inaccessible by other synthetic routes.



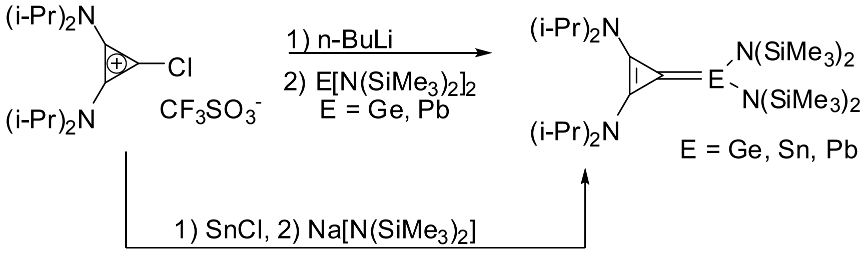
Scheme 3.2

Yoshida and coworkers have described the reaction of diaminocyclopropenium perchlorates with mercury acetate yielding the corresponding diaminocyclopropenylidene mercury complexes shown in Scheme 3.3.[95]



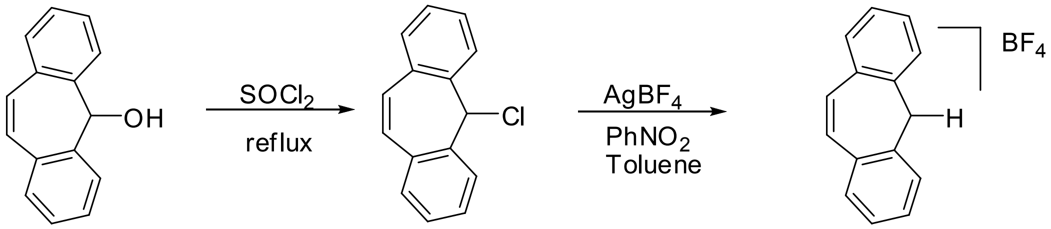
Scheme 3.3

Cyclopropenylidene complexes of germanium, tin and lead could be prepared by reaction of a cyclopropenium salt with *n*-BuLi, leading to cyclopropene lithium adducts, and subsequent reaction with group 14 bisamides (Scheme 3.4).[96]



Scheme 3.4

Based on these reports synthesis of the cycloheptatriene and dibenzocycloheptatrienylidene silver and mercury complexes from the corresponding tetrafluoroborate salts were attempted in hopes that the resultant complexes could be used as carbene transfer agents. The dibenzocycloheptatrienylidene salt was prepared by the reaction shown in scheme 3.5, and the unsubstituted tetrafluoroborate salt was purchased and used as received.



Scheme 3.5

Attempts to synthesize the corresponding silver carbene complex were based on previous reports.[95] The previously reported reaction of the tetrafluoroborate of both salts with Ag_2O did not afford the desired products.

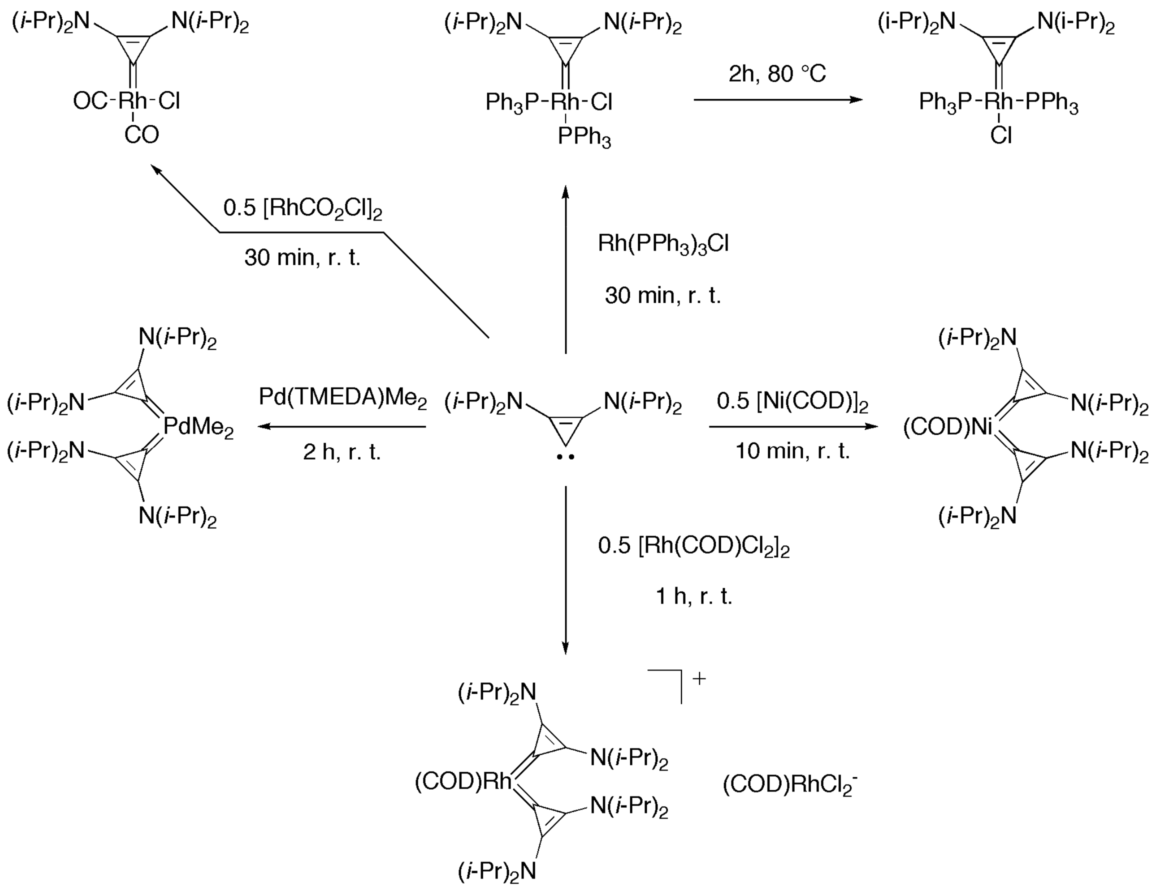
Further following Yoshida's strategy the carbenim tetrafloroborate salts were reacted with [Hg(OAc)$_2$]. Preliminary tests replicating original reaction conditions in DMSO only afforded the ketone precursor which is why acetonitrile was used as a solvent. In acetonitrile, a colorchange from colorless to yellow was observed when stirring the salt and mercury precursor. However, upon taking the mixture to dryness decomposition occurred and the formation of elemental mercury was observed. A small scale ^{13}C-NMR reaction was preformed in deuterated acetonitrile and did not show any evidence for the formation of a carbocyclic carbene. This does not rule out the generation of a carbocyclic carbene complex, only that such a species was not detected by ^{13}C NMR spectroscopy which is possible for such complexes.

It is known that NHC metal complexes can be synthesized via the in situ generation of silver carbene complexes which then participate in a transmetallation reaction upon exposure to metal complexes such as $[Rh(COD)Cl_2]$. In order to transfer this reaction stratagy to the synthesis of carbocyclic carbene complexes a dichloromethane solution of tetrafluoroborate salt of unsubstituted CHT and Ag_2O, that was stirred in the presence of molecular sieves, and then added to $[Rh(COD)Cl_2\ ]$ or $[Ir(COD)Cl_2]$. Both experiments did not yield the target Rh or Ir carbene complexes.

3.3.2 Synthesis via reaction of metal complexes with a stable free carbocyclic carbene

After their breakthrough isolation of free bis(diisopropylamino)cyclopropenylidene,[82] Bertrand and coworkers expanded their investigations into the reactivity of the free carbene for synthetic strategies based on ligand association/displacement reactions with metal complexes bearing labile ligands to yield novel cyclopropenylidene complexes (Scheme 3.6).

They have shown that the isolated carbene is able to displace bridging halogeno complexes as well as displace phosphine ligands, yielding mononuclear carbocyclic carbene complexes. Reaction of the free carbene with $[Pd(TMEDA)Me_2]$, $[Ni(COD)_2]$ or $[Rh(COD)Cl_2]_2$ results in the formation of mononuclear biscarbene complexes due to the restricted steric bulk of the cyclopropenylidene carbene moiety.[97] Although this synthetic strategy is limited to relatively stable diaminocarbenes, it is a diverse route which should spark renewed interest in these ligand systems.

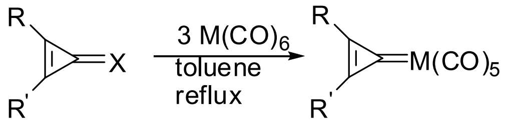


Scheme 3.6

It is supposed that the formation of the free carbenes and in situ trapping with a transmetallation agent may not be possible for the carbocyclic carbenes investigated herein in contrast to the relatively stable nitrogen substituted carbocyclic carbenes studied by Bertrand.[97]

3.3.3 Synthesis via deoxygenation, desulfurization and deselenization

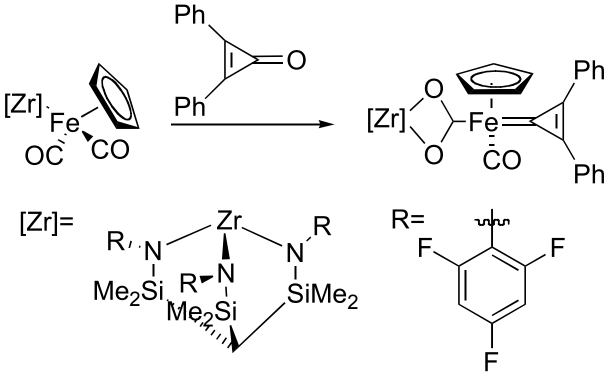
Cyclopropenethiones and cyclopropeneselones have been shown to provide access to cyclopropenylidene complexes via desulphurization and deselenization by reflux in toluene in the presence of group 6 metal hexacarbonyl complexes (Scheme 3.7). Through this method Yoshida and coworkers were able to prepare metal complexes with a range of carbocyclic carbenes bearing nitrogen, sulphur and aromatic substituents.[86]



X = S, Se
M = Cr, Mo, W
R, R' = Me_2N, *i*-Pr_2N, *t*-BuS, Ph

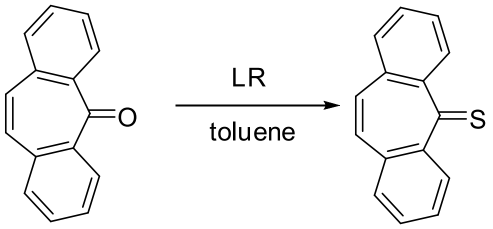
Scheme 3.7

Deoxygenation via oxygen transfer from cyclopropenone into an iron-zirconium bond to yield a bimetallic oxygen-bridged cyclopropenylidene complex (Scheme 3.8) was reported by Gade and coworkers. The reaction was shown to be a cooperative reaction of two complementary metal complexes as attempts to deoxygenate cyclopropenones by monometallic iron half-sandwich complexes did not yield carbene complexes but metallacyclopenta-2,5-diones instead.[101] Therefore this exceptionally attractive synthetic route based on readily available precursors, is limited to bimetallic systems of this type.



Scheme 3.8

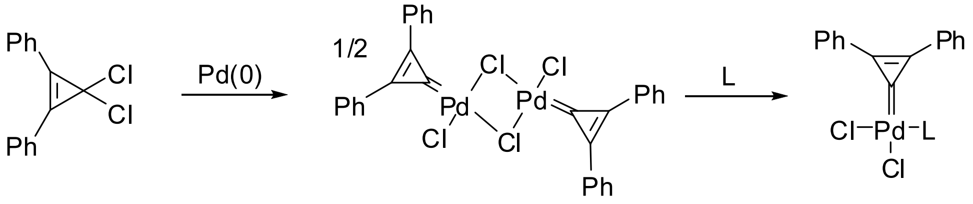
Based on the promising report of Yosihida et al. about the accesibility via thiones, dibenzosubsituted cycoloheptathione was prepared using Lawsons reagent (LR) (scheme 3.9). The utility of this route was tested for our systems using the knowledge that the chromium pentacarbonyl dibenzocyclohepatriene complex is one of the few previously reported dibenzo carbenes and decomposition and detection parameters of our target were already known.[113, 114] The ^{13}C NMR spectra for a J-Young scale reaction of chromium pentacarbonyl and dibenzocycloheptathione at < -65 ºC were recorded after 1,4 and 6 hours of reaction time. Although gas evolution was observed by a change in pressure over the course of the reaction, a signal for the expected carbene was not observed.



Scheme 3.9

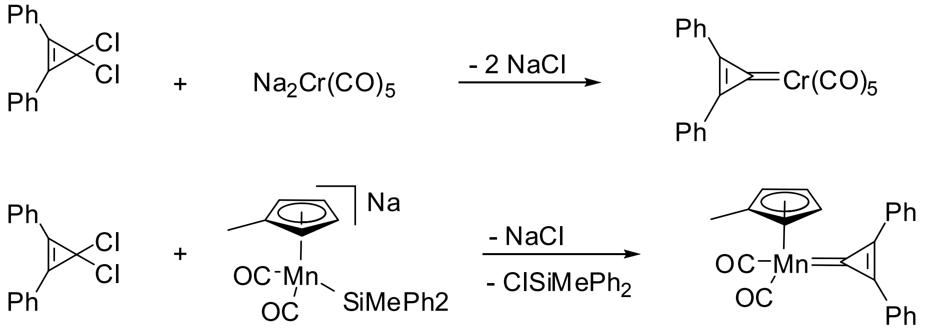
3.3.4 Synthesis via oxidative addition

Dimeric cyclopropenylidene complexes of several transition metals are readily accessible through the oxidative addition of geminal dihalocyclopropenes to metals such as palladium (Scheme 3.10).[84-86] The halogen bridge of the dinuclear complex can easily be cleaved through displacement by neutral donor ligands (L) such as pyridine, DMSO or phosphines affording the mononuclear complex.[79] The *in situ* formation of such complexes with labile ligands turned out to be useful in the preparation of catalysts bearing the cyclopropenylidene (C3) moiety and was employed in screening of catalytic precursors which may be difficult to isolate.[87]



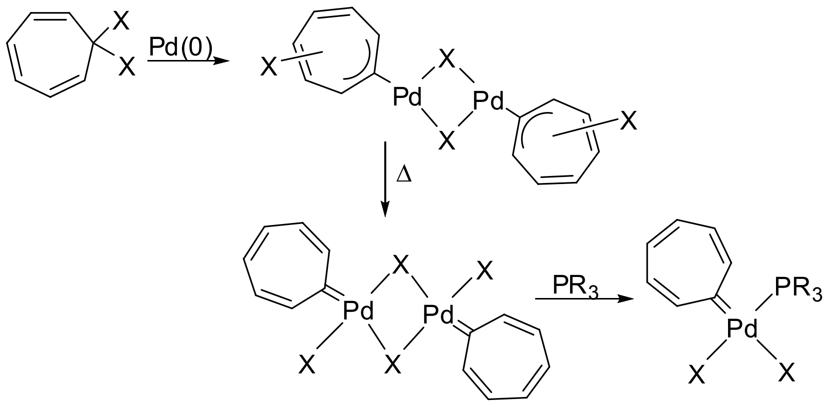
Scheme 3.10

In addition, transition metal complexes in low oxidation states such as carbonylmetallates of Cr, Mo, W and Mn have been shown to readily react with geminal dichlorocyclopropenes to form carbene complexes according to Scheme 3.11.[80,86,88-91] Anionic iron(0) silyl complexes also react in this manner.[91]



Scheme 3.11

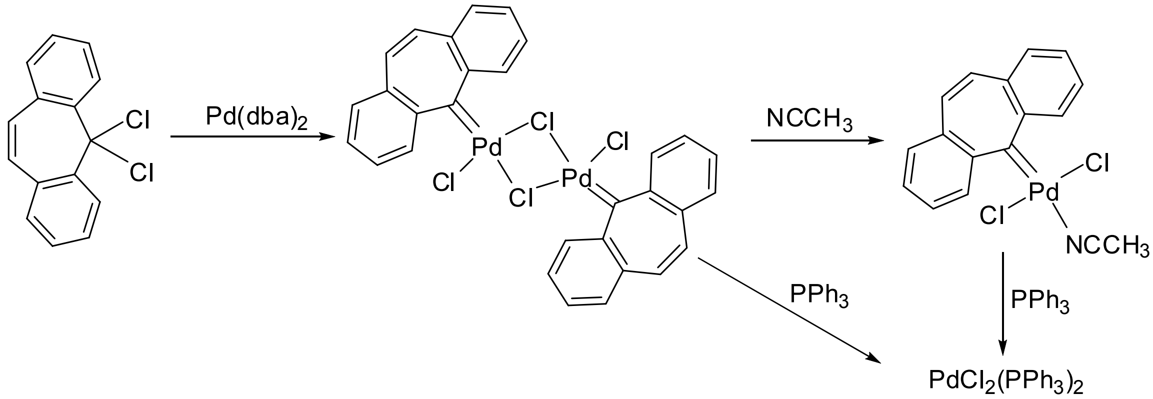
As reported by W. M. Jones, reductive decomposition occurs when dihalogenocycloheptatrienes react with carbonyl metallates or other low valent metal precursors.[53] In contrast to this behavior, the straightforward oxidative addition of 7,7'-dichloro or dibromocycloheptatriene to highly dispersed palladium metal leads to the formation of dimeric dihalogeno-CHT-palladium(II) complexes in very good yields. In the first reaction step an η^3-allyl palladium complex forms which was isolated and characterized.[128] After heating this complex rearragens to yield the carbene complex (Scheme 3.12).[128] As dihalogenocycloheptatrienes dissociate in polar solvents, the initial absorption of halogenide anions on the surface of the metal particles is assumed.[129-131]



Scheme 3.12

The reaction sequence is in agreement with W. M. Jones' suggestion that the cycloheptatriene must be fixed to the metal before its conversion into a carbene ligand. In addition to soluble Pd black, Pd(0) sources such as $Pd(dba)_2$ have also been used successfully as metal precursors in the preparation of CHT-Pd complexes by oxidative addition of 7,7'-dihalogenocycloheptatrienes.[87]

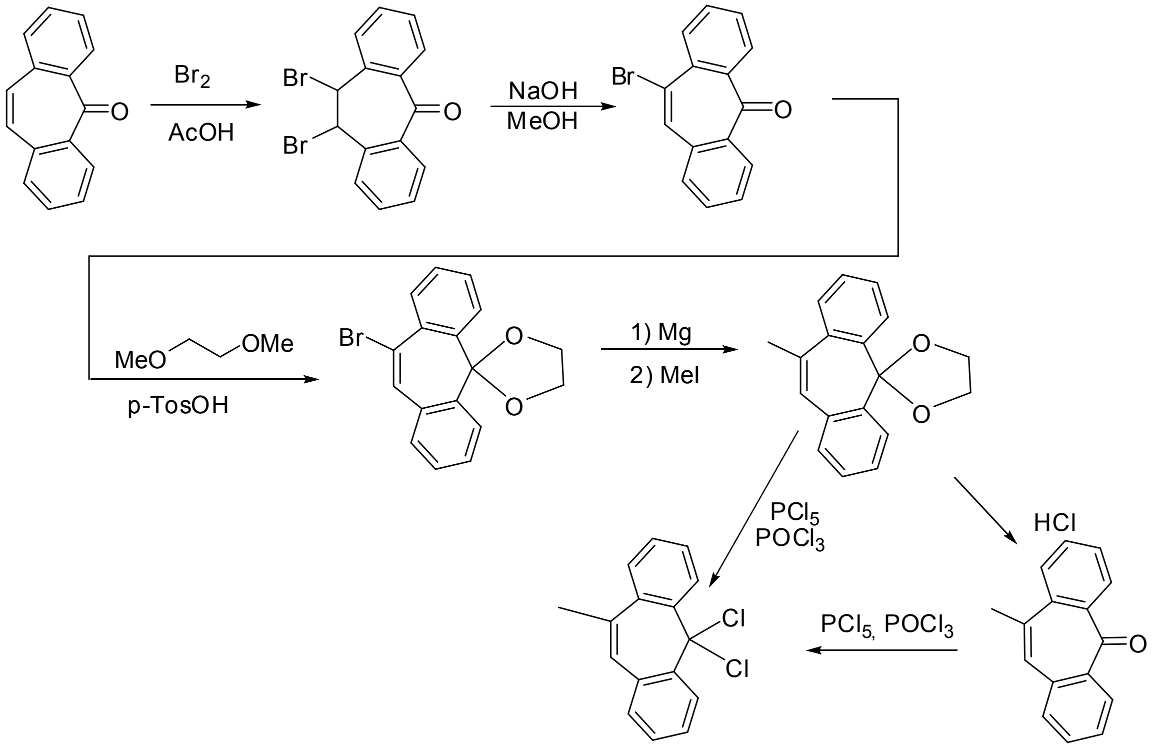
Synthesis via oxidative addition proved to be successful for the preparation of the bimetallic dibenzocycloheptatriene carbene palladium complex shown in scheme 3.13. Upon mixing the palladium precursor in THF with dichlorodibenzocycloheptatriene at -40 ºC, a dark red precipitate forms. After stirring the reaction mixture for several hours and allowing it to slowly warm to room temperature, the solution was decanted and the precipitate washed with THF and dried to afford a dark red powder. Whereas this powder was insoluble in THF, toluene, benzene, hexane, chloroform and dichloromethane it decomposed in DMSO showing the characteristic carbonyl carbon signal for the retrosynthetic ketone precursor. Upon addition of acetonitrile the resulting mononuclear complex (scheme 3.13) was formed as a bright red precipitate. The compound was characterized by elemental analysis only as it was not soluble enough to obtain an adequate ^{13}C-NMR spectra.



Scheme 3.13

The synthesis of a metallic dimer or a mononuclear precursor containing a labile ligand such as acetonitrile which can be easily displaced is particularly attractive as in situ catalyst formation is possible upon the addition of a phosphine. However, due to very limited solubility, addition of phosphine (always in great excess), resulted in the formation of [$PCl_2(PPh_3)_2$] as the only product in solution.

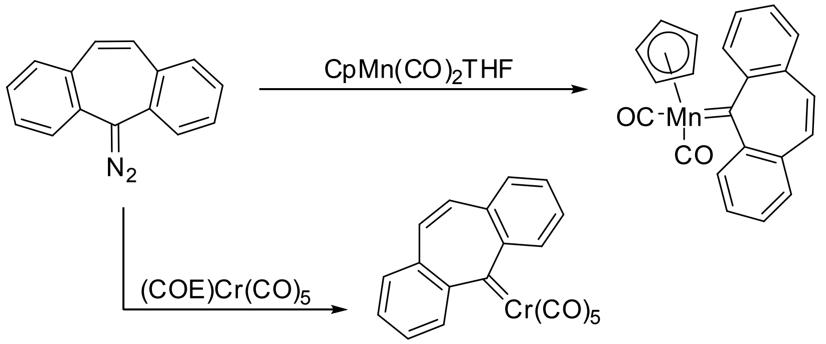
As insolubility was seen to severly hinder synthetic efforts and would also be a problem for catalytic evaluations, attempts to interrupt possible aromatic stacking which could occur in the solid state and prevent the compound from disolving were undertaken. Methylsubstituted deriatives shown in scheme 3.14 were synthesized. It is interesting to note that the deprotection (step 5), can be avoided and the desired product can be prepared directly from the protected compound. The reaction of the dichlorocompound with the [$Pd(dba)_2$] yielded the dimeric complex however this resultant product was even less soluble in acetonitrile. Elemental analysis yielded carbon and hydrogen contents lower than expected which is probably due to the presence of Pd(0).



Scheme 3.14

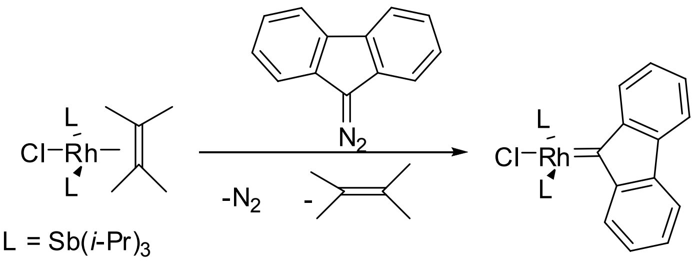
3.3.5 Synthesis via diazo precursors

Early investigations by W. M. Jones into the utility of diazo precursors only showed decomposition of troponetosylhydrazone in the presence of suitable transition metal precursors, but no evidence of the formation of carbene complexes. Later, W. A. Herrmann and K. M. Dötz succeeded in preparing dibenzannelated cycloheptatrienylidene complexes by the reaction of 5-diazo-5*H*-dibenzo[a,d]cycloheptene with manganese[125] and chromium precursors[126-127] bearing weakly bound ligands (Scheme 3.15).



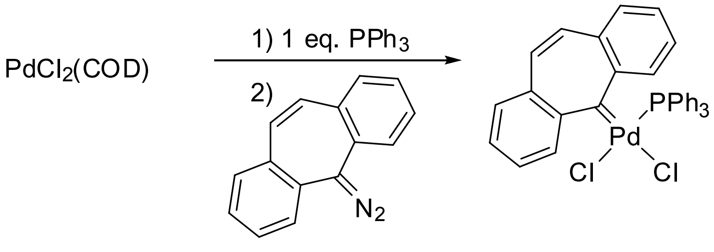
Scheme 3.15

It was shown that a carbene ligand can be transferred to coordinatively unsaturated metal centers by diazo compounds. The reaction of diazoalkanes with appropriate metal precursors such as [$Cr(CO)_5(COE)$], [$(Cp)Mn(CO)_2(THF)$], [$RuCl_2(PPh_3)_3$], [$RhCl_2(C_2H_4)(Sb$*i*-$Pr_3)_2$], and [$Pd(PPh_3)_2(C_2H_4)$] according to Scheme 3.16 proved to be a versatile method for the preparation of metal complexes with cyclopentadienylidene,[139] fluorenylidene,[126,127,140,142] and dibenzocycloheptenylidene.[125-127, 143]



Scheme 3.16

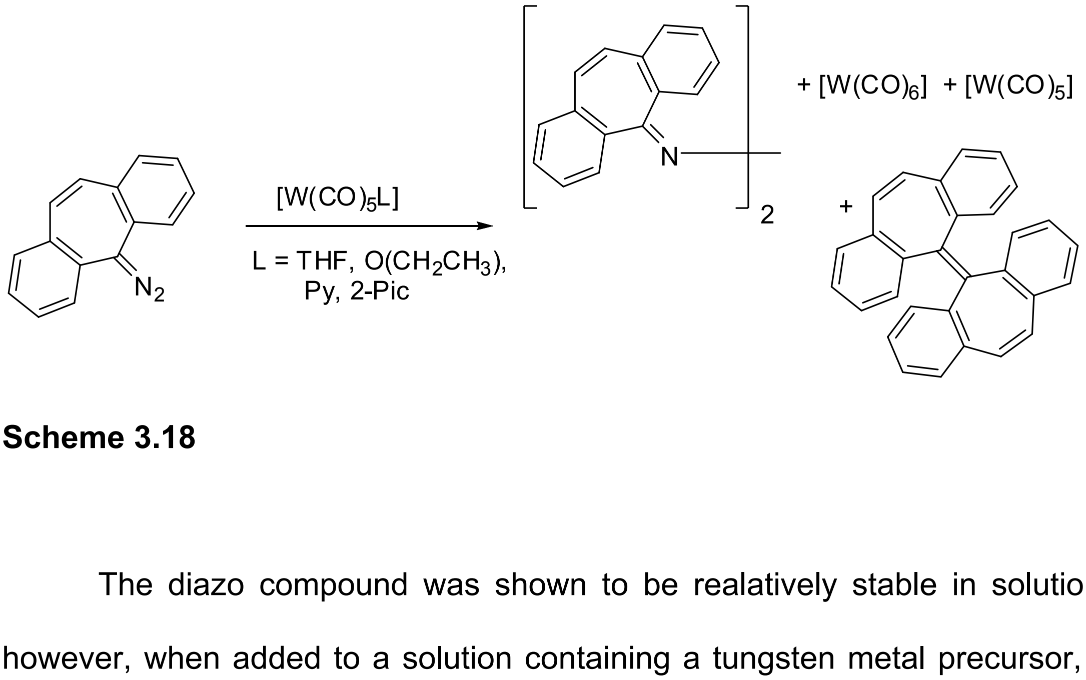
Christian Taubmann, was able to prepare the mononuclear complex [$PdCl_2(PPh_3)(L)$] (L= dibenzocycloheptatriene) by the synthesis shown in scheme 3.17. Selection of the appropriate solvent and the order of reactant addition was crutial to successful synthesis. The addition of triphenyl phosphine before the addition of the diazocompound inhibited the formation of the diphenyldichloropalladium complex discussed in the previous section. The diazocompound was added to a solution of metal precursor and triphenyl phosphine in THF at -78 ºC, which was allowed to warm to 25 ºC. The resulting red powder was shown to decompose in DMSO as well as DMF, it was insoluble in aromatic and hydrocarbon solvents and chloroform and only slightly soluble in dichloromethane. The product was identified via X-ray crystallography and FAB/MS.



Scheme 3.17

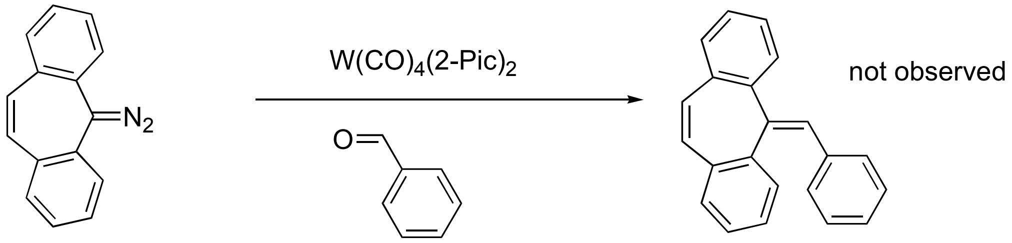
To learn more about the bonding properties of mononuclear complexes bearing the dibenzoCHT ligand attempts were made to synthesize group six carbonyl complexes, and study the resulting carbonyl streching frequecies.

Preliminary efforts were loosely based on the work of Dötz, previously discussed within this section. The diazo compound was reacted with $[W(CO)_5L]$ where L = THF, $O(CH_2CH_3)_2$, Py or 2-Pic at reaction temperature from -80, -60, -40, 0, 25 °C.(scheme 3.18) However all synthetic attempts led to the production of the azine in addition to the carbene dimer and decomposition of the tungsten complexes to afford tungsten hexa- and penta-carbonyl. IR carbonyl streatching frequencies and ^{13}C-NMR signals were used to identify metal carbonyl complexes and organic decomposition products, respectively.



Scheme 3.18

The diazo compound was shown to be realatively stable in solution, however, when added to a solution containing a tungsten metal precursor, it decomposed within 10 minutes. To find out if a carbene intermediate forms a witting type reaction was preformed with $[W(CO)_4(2\text{-Pic})_2]$ and benzaldehyde, but no carbene trapping was observed (scheme 3.19). It can be concluded that the decomposition of the diazo precursor is caused by end-on coordination or that the carbene species is too short lived to be trapped by this method.



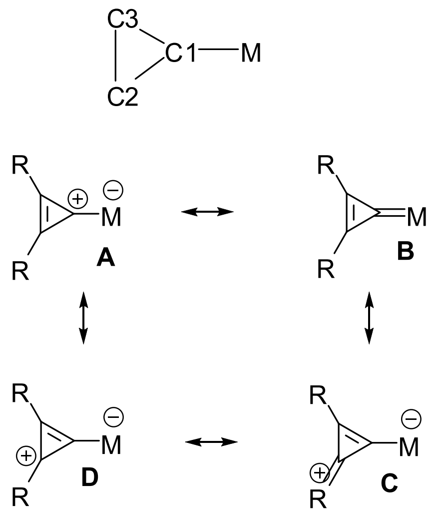
Scheme 3.19

3.4 Structure and bonding

In the following section to give an overview of general trends of metal complexes bearing carbocyclic carbenes, including the effects of metal substitution and substitution patterns of these ligands. Moreover, complexes with particularly interesting properties will be included and discussed though deeper insights are often restricted due to limited data. For structural information on complexes not mentioned in this section please refer to summary tables 3.1 and 3.2, which include selected structural details and relevant references for carbocyclic carbene complexes.

3.4.1 Cyclopropenylidene complexes

With transition metal complexes from group 6 to group 12, the cyclopropenylidene carbene is the most versatile of this ligand class. There are several binding modes of this ligand to transition metal atoms, shown in scheme 3.20. Donation from an electron rich substituent R can result in the shortening of the R–C_3 bond as shown in resonance structure **D** and contributes to the kinetic stability.[86, 133]



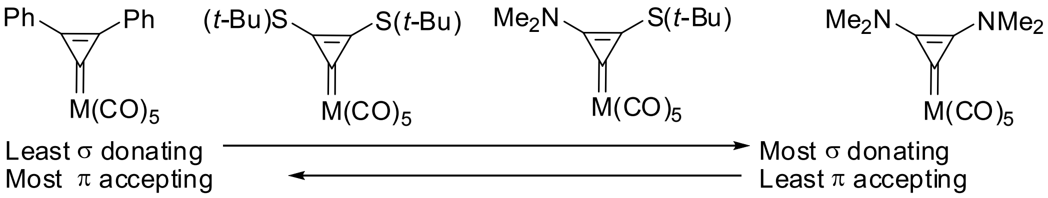
Scheme 3.20

Though general trends are observed upon metal substitution when moving down a period, or across a row, the complex's properties are most effected by varying the substituents on the carbocyclic carbene.

3.4.1.1 Cyclopropenylidene complexes of group 6 transition metals

The first major evaluation of this class of complexes was undertaken by Yoshida, who reported several metal complexes bearing the cyclopropenylidene moiety and provided a thorough discussion outlining the role and effects of substituents attached to the three-membered ring. In these studies, Yoshida used *in situ* IR techniques to examine group 6 carbonyl complexes. Complexes bearing cyclopropenylidene ligands with two amino substituents show the most δ-donor/least π-acceptor ability and those containing two phenyl groups show the least δ-donor/most π-acceptor ability for chromium and molybdenum pentacarbonyl complexes. Relative strengths are shown in Scheme 3.21 based on the frequencies of the CO stretching A_{1a}

bands. They state that the extended Hückel HOMO-LUMO gap for the free carbene is largest for ring systems substituted with electron donating substituents which act to shift the structure from a **B** to **A, C** or **D** depending on the extent of electron donation (scheme 3.20).[86] Confirming this work Scherer and coworkers recently evaluated cyclopropenylidene ligands using an experimental charge density approach including analysis of the topology of the Laplacian of the electron density distribution and the out of plane atomic quadrupole moments. They classify the alkyl and amino substituents as σ-donors with the latter showing greater stabilization of the cyclopropenium system through electron donation from the amino substituents.[142]



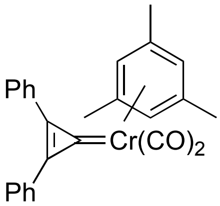
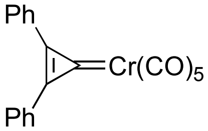
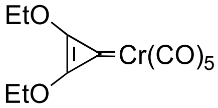
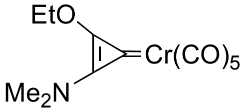
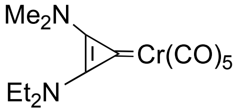
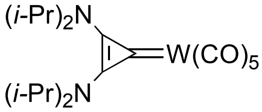
Scheme 3.21

The first mononuclear cyclopropenylidene metal complex which could be structurally characterized by X-ray crystallography, was $[(CO)_5Cr(C(CPh)_2)]$. This complex exhibits a typical octahedral geometry of a substituted group 6 pentacarbonyl complex with the plane of the C_3 ring at a 45° degree angle to the equatorial complex plane and the C2 and C3 carbons of the ring staggered between the carbonyl ligands in the equatorial position. One of the phenyl ring substituents is in plane with the three-membered ring and the other is twisted out of plane by 7.5°. The authors suggest twisting is due to repulsions between the phenyl *ortho*-hydrogens and the C1–Cr bond (distance of 2.0437 ± 0.0004 Å). The C2–C3 bond (1.3577(5) Å) is shorter than the C1–C2 (1.4076(5) Å) and the C1–C3 (1.4085(5) Å) bond.[142, 143]

Substitution of phenyl for an electron rich substituent results in stabilization of the group 6 pentacarbonyl carbene complexes. The bis-ethoxy substituted Cr compound has been prepared and structurally characterized. The C2–O and C3–O bond lengths are shorter compared to the C(Et)–O bond lengths (1.300(5) Å vs. 1.472(5) Å), suggesting electron donation from the oxygen atoms which act to stabilize the ring system. The C1–C2 and C1–C3 bond lengths are longer than the C2–C3 bond length (1.4010(8) Å vs. 1.337(7) Å).[92]

This trend of stabilization is also observed for amino substituents. In the tungsten pentacarbonyl bis(diisopropylamino)cyclopropenylidene complex, the nucleophilic carbene is a strong δ-donor and the W-C1 distance of 2.238(5) Å is comparable to that of the analogous unsaturated NHC complex. The C1–C2 and C1–C3 bond lengths are 1.376(7) Å and 1.373(7) Å, whereas the C2–C3 bond length is shorter (1.360(7) Å) .[144] Reported M–C bond lengths for group 6 metal carbonyl complexes are listed in Table 3.3.

Table 3.3

Structure	M-C1 bond length / Å	C1-C2/C1-C3 bond length / Å	C2-C3 bond length / Å
	1.956(4)	1.414(5)/1.416(5)	1.326(5)
	2.05(1)	1.39(1)/1.40(1)	1.35(1)
	2.010(7)	1.410(8)/1.410(8)	1.337(7)
	2.068(2)	1.360(3)/1.342(2)	1.350(3)
	2.086(1)	1.393(2)/1.393(2)	1.367(2)
	2.238(5)	1.376(7)/1.373(7)	1.360(7)

In addition to IR and crystallographic studies, ^{17}O-NMR spectroscopy performed by Kawada and coworkers has been shown to also be an effective probe to study M-C_{CO} bonds in pentacarbonyl carbene complexes including the cyclopropenylidene moiety. However, the amount of sample required (200-300 mg) is prohibitive for routine analysis.[145]

3.4.1.2 Cyclopropenylidene complexes of group 7 and 9 transition metals

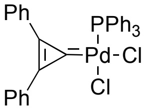
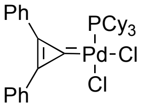
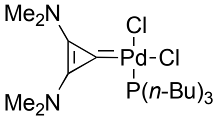
The manganese complex [(MeCp)Mn$(CO)_2$(C$(CPh)_2$)] has been structurally characterized by X-ray crystallography. While one phenyl substituent is coplanar with the C_3 ring, the other is twisted by 11°. The Mn-C1 bond length is 1.896(4) Å and the C1–C2, C1–C3 and C2–C3 distances are 1.424(6) Å, 1.424(6) Å, and 1.349(6) Å, respectively.[91]

Both mono and biscarbene complexes of rhodium have been prepared by Bertrand and coworkers. The mononuclear complex, *trans*-[RhCl$(PPh_3)_2$(C(CN(*i*-Pr$)_2)_2$)] is of distorted square planar geometry with the plane of the C_3 ring perpendicular to the coordination plane of the complex. The observed Rh–C1 bond length is 2.411(3) Å and C1–C2, C1–C3, and C2–C3 bond lengths are 1.352(16) Å, 1.390(16) Å and 1.378(17) Å, respectively. This represents a deviation from expected bond lengths since the C2–C3 distance is expected to be shorter than the C1,C2/C3 distances and is most likely due to steric conditions enforced by the phosphine ligands. Within the Rh(0) biscarbene complex, [(C(CN(*i*Pr$)_2)_2)_2$Rh(COD)] the Rh–C_1 bond lengths of 2.028(6) Å, and the C1–C2, C1–C3, C2–C3 bond lengths of 1.380(9) Å, 1.389(9) Å and 1.368(9) Å are found within the expected range.[97]

3.4.1.3 Cyclopropenylidene complexes of group 10 transition metals

Mononuclear carbene complexes of palladium of the type [(Carbene)MX_2PR_3] adopt square planar geometry with the plane of the carbene ligand ring perpendicular to the coordination plane of the complex. This was established by early work in the research group of Yoshida who used IR and ^{13}C- NMR spectroscopy as previously discussed in this section.[85, 86, 146, 147] The structure has been confirmed by X-ray crystallography.[148, 149] Listed in Table 3.4 are the lengths of C–C bonds in the diphenylcyclopropenylidene ligands of palladium complexes, which suggest a high degree of π delocalization about the ring though the C2–C3 bond is typically shorter. A similar geometry is observed for the diaminocyclopropenylidene complex, [$PdCl_2P(n\text{-}Bu)_3(C(C(NMe_2)_2)_2)$], reported by Ibers et al.[148] For this complex, sp^2 hybridization of the nitrogen atoms is observed resulting in a coplanar position to the C_3 ring. In addition, a relatively short C–N bond length of 1.320(4) Å is observed, giving further evidence of electron donation to maximize the complex's stability through charge separation for complexes bearing amino substituted cyclopropenylidene ligands.[148] It is noteworthy that for the $C(C(NR_2)_2)_2$ complex, the C–C bond lengths about the C_3 ring are almost equivalent and the $Pd\text{–}Cl_{trans}$ bond length longer suggesting that the carbene in this system is not as strong of a π-acceptor as $C(CPh_2)_2$, which is in agreement with observations in the chromium carbonyl systems discussed earlier.[87, 148]

Table 3.4

Structure	Pd-C_1	C_1-C_2	C_1-C_3	C_2-C_3	Pd-Cl_{trans}	Pd-Cl_{cis}
	1.945(2)	1.377(4)	1.381(3)	1.363(3)	2.3444(8)	2.3620(8)
	1.931(4)	1.380(5)	1.366(5)	1.333(6)	2.3439(10)	2.3615(10)
	1.961(3)	1.385(5)	1.380(4)	1.384(5)	2.361(1)	2.385(1)

The only example of a crystallographically characterized dimeric chloro-bridged cyclopropenylidene palladium complex is $[PdCl_2(C(CMes)_2)]_2$ which has been reported by W. A. Herrmann and coworkers. Mesitylene substituents bound to the carbocyclic carbene ring are not coplanar to it. This disruption in conjugation results in the remarkable solubility of this complex, in contrast to $[PdCl_2(C(CPh)_2)]_2$ and $[PdCl_2(C(CNap)_2)]_2$. The Pd-C1 bond lengths are slightly shorter than those found in the corresponding mononuclear phosphine substituted carbene complexes (0.01 to 0.05 Å shorter).[149]

Bertrand and coworkers were able to synthesize the biscarbene palladium complex $[Pd(C(C(NMe_2)_2)_2Me_2]$, via the free carbene route introduced in chapter 3.3.2 . The carbene complex geometry is distorted square-planar with the C_3 rings twisted, but not perpendicular to the coordination plane of the molecule, presumably due to steric hindrance of the amino substituents. The Pd-C1 bond lengths are 2.0242(13) Å and 2.0306(12)

Å. As expected the bond lengths for bond lengths for C1–C2 and C1–C3 (1.3903(19) Å, 1.3923(18) Å) are longer than for the C2–C3 bond (1.3708(19) Å).[97]

3.4.1.4 Cyclopropenylidene complexes of group 11 and group 14 elements

A chiral bis(diamino)cyclopropenylidene complex of silver has been reported by Tamm et al.[94] It crystallizes with two crystallographically independent bis-carbene-silver cations of almost linear shape (C-Ag-C angles: 172.1(2)° and 175.3(2)°). The planes of the two cyclopropenylidene moieties in each cation are twisted from coplanarity (torsion angles: 62.6° and 37.3°). In comparison to the free carbene, which was isolated and characterized by the same group, the coordinated carbene exhibits shorter N–C_{ring} bonds and longer C–C bonds. Whether or not the stereochemistry of the cyclopropenylidene moiety is conserved upon further transmetallation, for which this complex would be well-suited, remains to be seen.[94]

Not limited to transition metal complexes, the cyclopropenylidene moiety has also been observed and characterized as a ligand in a series of group 14 complexes of the type $[((i\text{-}Pr_2NC)_2C)M(N(SiMe_3)_2)_2]$, where M = Ge, Sn, Pb. A lengthening of the M-C bond from 2.085(3) Å to 2.303(9) Å to 2.423(8) Å is observed for M = Ge, Sn and Pb, respectively.[96]

3.4.2 CHT and CHTE complexes

The monocyclic C_7H_6 intermediate can exist in two valence isomeric structures: a carbene form **A** (cycloheptatrienylidene, CHT) and a twisted allene form **B** (cycloheptatetraene, CHTE) shown in Figure 3.1. The latter appears to be the ground state.[150, 151]

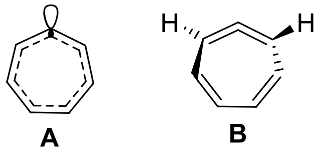


Figure 3.1

3.4.2.1 Allene complexes

The CHTE ligand structure so far has been observed in some Pt(0) complexes. Due to a d^{10} -configuration the Pd(0) lack a low energy LUMO with a_1 symmetry that could be used to form a δ-bond to a carbene carbon.[123] An X-ray crystal structure analysis of $[(\eta^{2-}\text{CHT})\text{Pt}(\text{PPh}_3)_2]$ has been reported: the Pt atom is asymmetrically bound to carbon and phosphorous atoms.[152] The Pt–C1 is shorter than the Pt–C2 bond length, with C1 exerting a slightly stronger *trans*-influence than C2 due to higher electron density π bond around it. The Pt atom is situated in the plane of coordination which forms an angle of 131.5° with the planes of the allene moiety C1–C2–C3–C7.[153] The molecule shows no fluxionality at room temperature. As determined by spin saturation transfer experiments an activation enthalpy of 26.8 kcal/mol is required for the platinum to move between the double bonds (C1–C2 / C2–C3) following an intermolecular mechanism superimposed on a lower energy intramolecular process. The same minimum enthalpy is neccessary for the conversion into its valence isomeric carbene form.[165] An acceleration of the fluxional process was observed after addition of a η^6-bound $Mo(CO)_3$ moiety to the heptatriene array as in $[\eta^{6-}(\eta^{2-}CHT)Pt(PPh_3)_2]Mo(CO)_3$ with simultaneous movement of Pt and $Mo(CO)_3$ along the allene double bonds and the heptatriene system respectively at 20 °C.[154] Mono- and dibenzanellated cycloheptatetraenes do not differ from the parent ring in forming the allene complexes with Pt(0); their structure has not been resolved by X-ray structure analysis, but has been sufficiently elucidated by spectroscopic methods.[122] According to MO calculations, benzannelation at the C_7H_6 ring increases the energy separation between the allene and the carbene form.[104] Correspondingly, by rearrangement of a metastable dibenzonorcaradiene complex of tungsten the tungsten-dibenzocycloheptatetraene complex is formed and not the alternative cycloheptatrienylidene complex.[124] The structure of this allene complex was confirmed by single-crystal X-ray analysis. The molecule adopts a pseudo tetragonal pyramidal configuration and its metal-allene array is quite similar to that of the platinum cycloheptatetraene complex $[(\eta^{2-}CHT)Pt(PPh_3)_2]$ and to that of an cycloheptatrienylidene iron complex.[106]

3.4.2.2 Carbene complexes

Among all other complexes of W, Fe, Ru, Pd, Pt and Ir with C_7H_6 ligands and their benzannelated analogues hitherto described the carbene structure (CHT) of the carbocyclic ligand is the preferred coordination mode. This has been confirmed single-crystal X-ray structural analysis for several examples of this type of complexes. In no case has the conversion from an allene-type C_7H_6 complex to the isomeric carbene complex and reverse been observed. Aromaticity of the tropylium resonance form in the seven-membered ring and low-lying vacant σ-orbitals on the metal atoms are important features which enable the formation of a σ-bond between the carbene carbon and the metal atom in these complexes.[105] In this aspect CHT complexes may also be described as substituted tropylium salts which is elucidated in the following passages.

3.4.2.2.1 CHT complexes of group 6 and group 7 transition metals

The tungsten complex $[(C_7H_6)W(CO)_5]$ is one of the first described CHT complexes, but was not yet structurally characterized by X-ray diffraction. The high dipole moment of 7.7± 0.2 D, however, is conclusive evidence for a dipolar character due to substantial contribution from a resonance form with positive charge at the carbene ring shown in Figure 3.2.

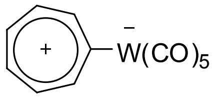


Figure 3.2

Less M-$C_{carbene}$ π-backbonding than in other pentacarbonyl tungsten carbene complexes is deduced by comparison of the CO-stretching force constants.[83, 88]

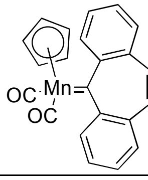
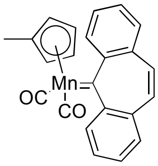
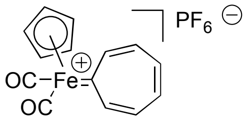
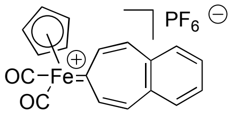
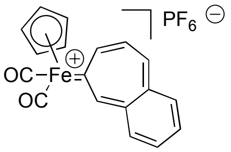
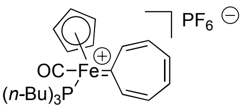
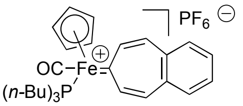
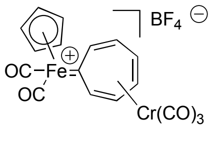
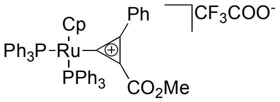
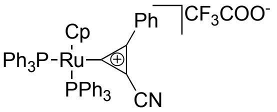
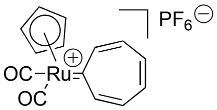
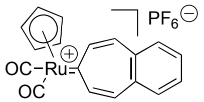
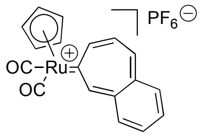
In the pentacarbonyl-chromium complex[113, 114] and the cyclopentadienyl-dicarbonyl-manganese complexes[112] bearing the dibenzannelated carbene, the coordinated carbene may be formally considered as a CHT complex. The free dibenzannelated carbene shows a triplet ground state [103] and reacts as an electrophilic carbenes, in contrast to CHT. Correspondingly, this carbene which adopts a nonplanar seven-membered central carbocycle[155, 157] behaves as a diphenylcarbene ligand. The M-$C_{carbene}$ in complexes exhibit an unprecedented downfield shift in ^{13}C NMR, which together with very high CO-stretching frequencies suggests strong M-$C_{carbene}$ π-back-bonding as observed for analogous diphenylcarbene complexes. The analogous metal complexes with a -CH_2-CH_2- backbone in the seven-membered ring of the tricyclic ligand show very similar spectroscopic data (^{13}C-NMR and IR).

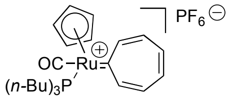
3.4.2.2.2 CHT complexes of group 8 transition metals.

The molecular structures of the cationic CHT-iron complexes (entry 3 and 5 of table 3.5)[106,158] have been resolved by single crystal X-ray analysis. In both pseudotetrahedral molecules the CHT rings as well as the annelated benzene ring in entry 5 are planar. The C–C distances in the C_7 rings do not differ significantly with mean values of 1.49 ± 0.03 Å (entry 3) and 1.39 ± 0.02 Å (entry 5), and are in agreement with the average C–C distances in the phenyltropylium ion (1.39 ± 0.08 Å). Moreover, the mean values for the internal angles of the seven-membered rings in entry 3 and 5 (129 ± 3° and 129 ± 4°, respectively) are consistent with the idealized value (128.6°) for a regular heptagon. These structural features indicate that aromaticity of the CHT rings in the discribed complexes has been maintained and the carbene ligands principally act as σ-donors.

The $C_{carbene}$-resonance signal in the ^{13}C-NMR spectrum is shifted significantly to high field compared to most transition metal carbene complexes which also confirms the above described structure since incorporation of the carbene carbon into a tropylium ring should increase the separation of the HOMO (σ-bond) and the LUMO and delocalize the latter into the ring which reduces the paramagnetic contribution to the chemical shift.[104] Hence, there is sufficient evidence from crystallographic (p-π acceptor orbitals of CHT suitably oriented to backbond with filled 1a´d-π orbitals of Fe) and spectroscopic data that d π–p π backbonding is not completely absent.[158] It is suggested to be significant in the parent CHT complex (entry 3) and less in the benzannelated analogue (entry 5).

Table 3.5

Compound	Entry	$^{13}C_{carbene}$	$^{13}C_{CO}$ /IR v_{co}	Additional notes	Ref.
	1	351.15 ppm	-/ 1994, 1934 cm^{-1} (hexane)	Brown needles, air stable, mp 134-135	112
	2	-	-/ 1991, 1932 cm^{-1} (hexane)	Dark green oil, air sensitive	112
	3	242.3 ppm	-/ 2045, 1996 cm^{-1} (CH2Cl2)	Yellow orange solid, airstable mp 180-181(dec)	83, 103, 106, 157
	4	265.9 ppm	2045, 2000 cm^{-1} (CH2Cl2) /-	Red brown solid, air stable, mp 177-178(dec)	103, 106, 157
	5	201.0 ppm	-/ 2037, 1992 cm^{-1} (CH2Cl2)	Violet solid stable, mp 176-177 (dec)	106, 157
	6	278.8 ppm	217.5 ppm/1920 cm^{-1} (neat)	Purple plates, air stable in crystal from, slowly decompose in solution,	103
	7	-	-	Blue purple solid, air sensitive, decomposes at room temperature	103
	8	159.1ppm	235.1ppm(Cr-CO), 217.5, 216.7ppm(Fe-CO)/ 2025, 1972, 1958, 1893, 1860 cm-1 (CH2Cl2)	-	107, 108
	**9**	213.6 ppm	-	Orange	100
	**10**	213.0 ppm;	-	orange, sensitive to ether	100
	11	223.56 ppm	198.66 ppm/ 2020, 1980cm^{-1} (CDCl3)	Brown solid, air stable, mp(C) 180-181	104
	12	244.75 ppm	-/-	Yellow brown solid, (impure)	104
	13	186.63 ppm	200.27ppm/-	Yellow brown solid (impure)	104

	14	256.2ppm	179.0 ppm/ 2020,1980 cm-1	Red solid mp 110-111	104
cis-$((i\text{-Pr}_2\text{NC})_2\text{C})\text{RhCl(CO)}_2$	**15**	141.2 ppm.	-/(CH_2Cl_2) 2070, 1992 cm^{-1}	mp (°C) 95	97
cis-$((i\text{-Pr}_2\text{NC})_2\text{C})\text{RhCl(PPh}_3)_2$	**16**	138.2 ppm.	-	observed as an intermediate in the formation of the analogous trans complex	97
trans-$((i\text{-Pr}_2\text{NC})_2\text{C})\text{RhCl(PPh}_3)_2$	**17**	139.8 ppm	-	orange; mp (°C) 218 (dec.)	97

The ruthenium complexes 11, 12, and 13 (table 3.5) of the type [(η-CHT)(η^5-C_5H_5)Ru$(CO)_2$]$^+$ have not been characterized by X-ray analysis,[104] but ^{1}H-and ^{13}C-NMR data unequivocally confirm their nature as carbene σ-ligands, analogous to the above mentioned iron complexes 3, 4, and 5. The barrier of rotation about the metal-CHT bond of the phosphine-substituted ruthenium complex 14 was found to be lower than that of the corresponding iron complex entry 6. This indicates that going from iron to ruthenium reduced steric constraint must be more important than increased backbonding.[104]

3.4.2.2.3 CHT complexes of group 9 transition metals

A bis(phosphinomethyl) substituted CHT-pincer ligand is coordinated to iridium complex and the solid state structure has been deduced by X-ray crystal structure analysis.[110] The coordination sphere of the iridium center is best described as a distorted octahedron with the phosphine ligands bent away from the chloro ligand. As in all other hitherto known CHT complexes the seven-membered ring is almost planar due to an aromatic 6π electron arrangement delocalized over all seven ring carbon atoms. This delocalization is reflected by the C–C bond lengths in the carbocycle (mean value: 1.40 ± 0.02 Å), whose distribution is in accordance with values obtained by DFT calculations of a CHT fragment in the closed-shell singlet state.[150] The crystal structure data match well with those obtained by DFT quantum chemical calculations (B3LYP). Differences in the coordination geometry around the iridium center are attributed to packing effects in the crystalline state.[150]

3.2.2.4 CHT complexes of group 10 transition metals

Structural data in the solid state are available for palladium-CHT complexes [(CHT)PdCl$_2$(PPh$_3$)] and [(CHT)PdCl$_2$(PCy$_3$)].[87,115] Both compounds exhibit a square planar geometry in *cis*-configuration with nearly identical C–C bond lengths in the seven-membered ring (mean values 1.39 ± 0.01 Å), suggesting extensive 6π delocalization as observed for all CHT complexes mentioned in this article. The Pd–C$_{carbene}$ distances are within the same range observed for analogous Pd-NHC complexes. A substantially lower π-acceptor character of the CHT ligand compared to cyclopropenylidene ligands, even to the strong donating 2,3-diaminocyclopropenylidene, can be concluded from a considerably shorter Pd–Cl$_{trans}$ bond in [(CHT)PdCl$_2$(PPh$_3$)] relative to the corresponding palladium-cyclopropenylidene complexes. Accordingly, as compared to the latter, [(CHT)PdCl$_2$(PPh$_3$)] exhibits a slightly longer Pd–C$_{carbene}$ distance (1.986 vs. 1.945 Å).[149]

Arguments for the preferred carbene structure of the cationic platinum-CHT complex [(CHT)PtBr(PPh$_3$)$_2$]BF$_4$ in solution are based on the absence of evidence of fluxionality at room temperature and the similarity of the ^{1}H- and ^{13}C- NMR spectra to those of the iron and ruthenium complexes entry 3 and 11 in table 3.5. Also notable is that the C$_{carbene}$ resonance (δ = 210.5 ppm) is significantly shifted to lower field compared to that of the central carbon of an allene complex (e.g. δ = 150.1 ppm for a 1,2-cycloheptadiene-iron complex). An orbital interaction diagram shows good overlap between the 2a$_1$ LUMO of Pt(II) and the a$_1$ HOMO of the carbene. The coupling constant, $^1J_{Pt\text{-}C}$ of C$_{carbene}$ (969 Hz) is comparable with those of other Pt(II) carbene complexes.[105] In the solid state the molecule adopts a square planar geometry with phosphines *trans* to each other and a planar CHT ligand, which is oriented almost perpendicular to the coordination plane. Dependent on the solvent, it crystallizes either in the monoclinic or in the orthorhombic crystal system. While Pt-$C_{carbene}$ distances in both crystal systems are in good agreement with each other, there are significant differences between the Br–Pt–$C_{carbene}$ angles and the position of the CHT plane relative to the coordination plane.[105]

The palladium complexes containing a six-membered congener ligand of CHT exist as a mixture of two diastereoisomers of the dinuclear molecule, with the C_2-symmetric *transoid* form as the major isomer (shown in Figure 3.3).

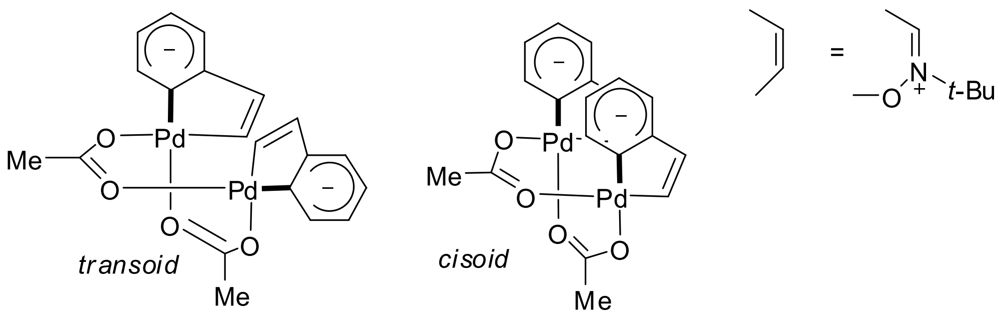


Figure 3.3

In contrast to solution the complex crystallizes as a single diastereoisomer in the *transoid* form. The nitrogen atom adopts a nearly planar geometry. Bond lengths at the benzylic carbon (C–C: 1.44 Å, C=N: 1.29 Å) and bond distances in the benzene ring are highly indicative of a zwitterionic iminium resonance form with a major contribution of the structure shown in Figure 3.4.[121]

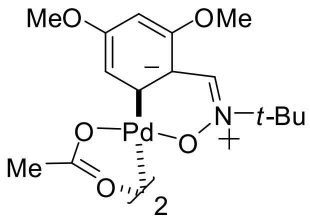


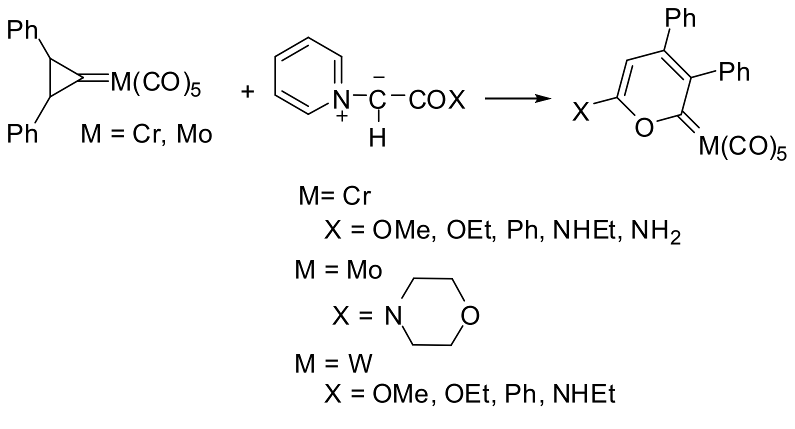
Figure 3.4

3.5 Properties and reactions

3.5.1 Cyclopropenylidene complexes

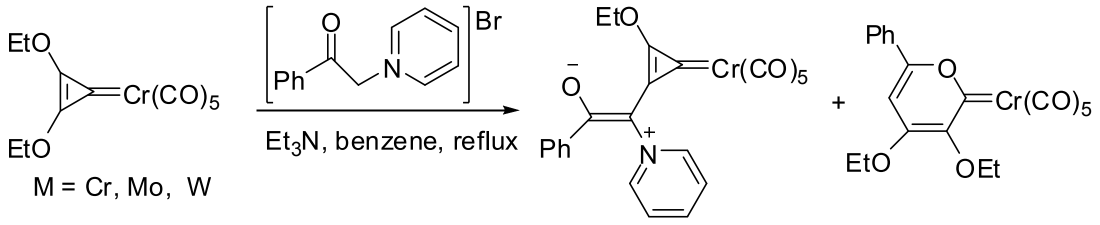
3.5.1.1 Ring insertion to the cyclopropenylidene carbene moiety

Rees and coworkers were the first to report ring insertion reactions for cyclopropenylidene complexes.[93] By addition of equimolar amounts of pyridinium ylides to diphenylcyclopropenylidene pentacarbonyl complexes they were able to synthesize a series of chromium and molybdenum pyran-2-ylidene complexes (Scheme 3.22).[180]



Scheme 3.22

A similar ring insertion was observed by Hegedus and coworkers with $[((EtOC)_2C)Cr(CO)_5]$, which undergoes reaction with a pyridinium ylide yielding a mixture of the corresponding pyran-2-ylidene complex as a minor product (23%) and a product resulting from displacement of an ethoxy group by the ylide moiety (Scheme 3.23).[92]

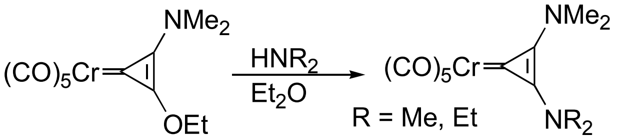


Scheme 3.23

The different behavior of phenyl and ethoxy-substituted cyclopropenylidene ligands in the reaction with pyridinium ylides is ascribed to the poor lability of a phenyl group in comparison to an ethoxy group.

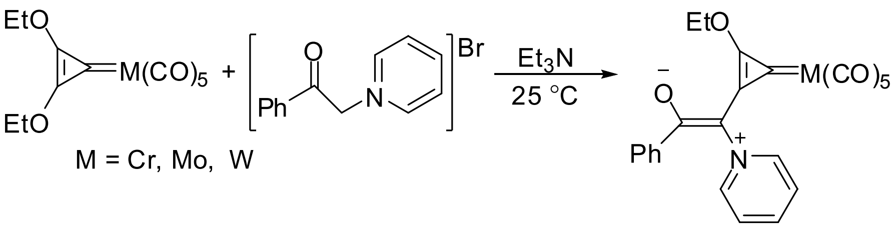
3.5.1.2 Substitution of ethoxy groups present in the cyclopropenylidene ligand

The substitution of functional groups bound to the cyclopropenylidene ring was explored by de Meijere and coworkers who showed that the reaction of aminoalkoxycyclopropenylidene chromium complexes with dialkylamines yields dialkylamino-substituted cyclopropenylidene pentacarbonyl chromium complexes in excellent yields (Scheme 3.24).[181]



Scheme 3.24

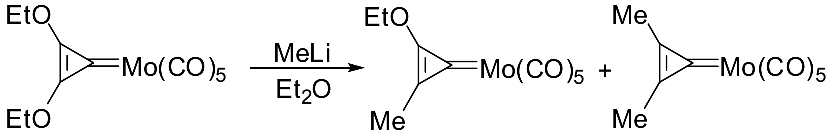
Divergent from the reaction described in scheme 3.23 [M((EtOC)$_2$C)(CO)$_5$] and pyridiniumylid react at moderate conditions to yield the ylide substituted derivative, but not an additional pyran-2-ylidene complex (Scheme 3.25).[92]



Scheme 3.25

Substitution of one or both ethoxy groups for methyl groups in [(diethoxycyclopropenylidene)Mo(CO)$_5$] by reaction with methyllithium

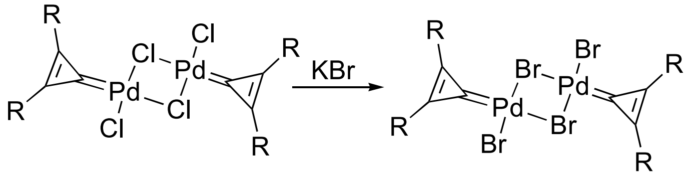
(Scheme 3.26) was reportet by Hegedus and coworkers. The products were characterized by NMR and IR spectroscopy.[92]



Scheme 3.26

3.5.1.3 Reactions at the metal center

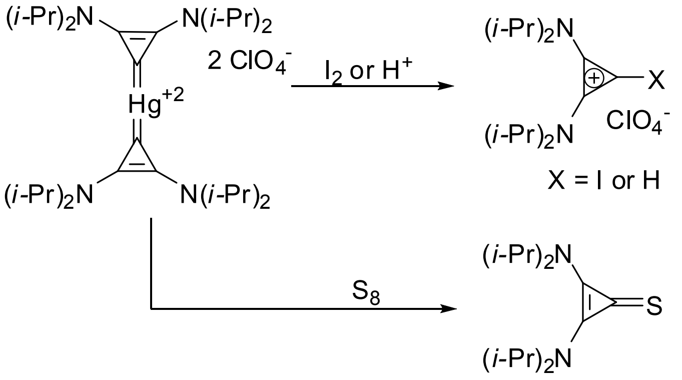
The substitution of the halogeno ligands in a dinuclear carbene complex has also been shown to be possible. Chlorine was replaced with bromine by the reaction of binuclear chloro complexes with KBr in acetone (Scheme 3.27).[196]



Scheme 3.27

3.5.1.4 Generation of retrosynthetic products in the presence of an electrophile

In the presence of an electrophile such as I_2, S_8, or H^+ cationic cyclopropenylidene mercury complexes, studied by Yoshida et al., were found to decompose yielding the retrosynthetic cyclopropenium salts or cyclopropenethiones (Scheme 3.24).[95]



Scheme 3.28

3.5.2 C_7H_6 complexes

3.5.2.1 Allene complexes

The platinum-allene complex **A**, shown in figure 3.5, can be prepared by the reaction of $[Pt(PPh_3)_3]$ and an excess of *in situ* generated biscycloheptatriene. The same reaction was observed with the analogous benzannelated ligand, which yielded the corresponding complex **B**.[123]

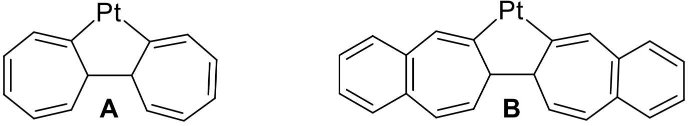


Figure 3.5

Addition of [(η^6-*p*-xylene)Mo(CO)$_3$] dissolved in THF to the allene complex **A** or **B** yields the heterobimetallic complex illustrated in figure 3.6, which, in contrast to the thermally stable parent mononuclear platinum complex **A** or **B** decomposes slowly at room temperature.[123]

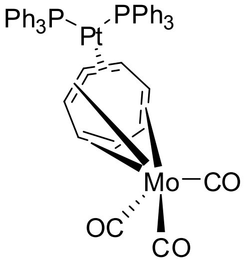


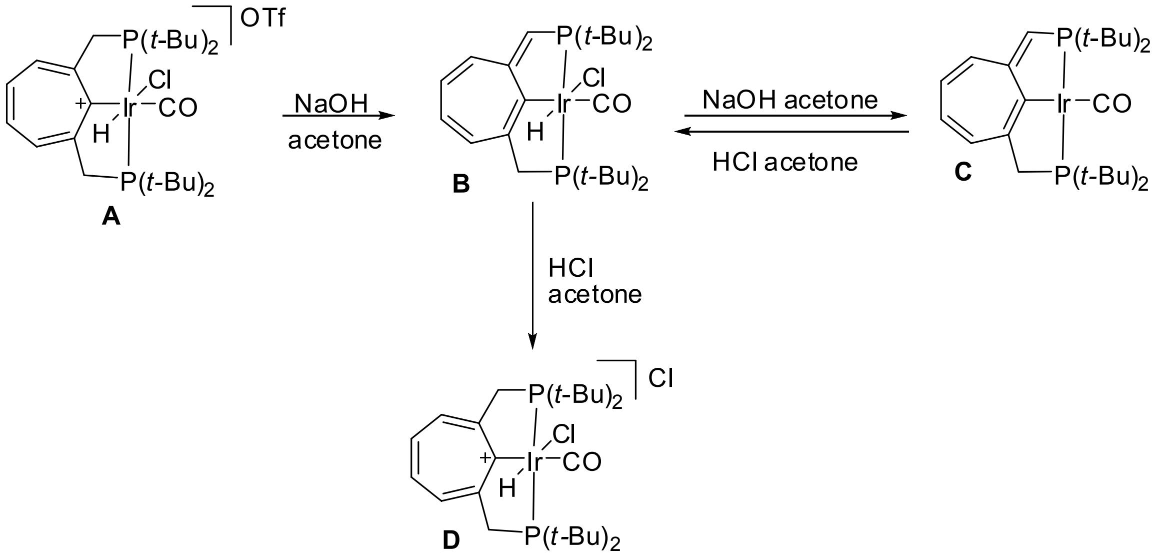
Figure 3.6

3.5.2.2 Carbene complexes

The pentacarbonyltungsten-CHT complex is much more reactive than the analogous cyclopropenylidene complex. In contrast to the latter it rapidly undergoes decomposition when it is refluxed in heptane (under formation of heptafulvalene), and reacts with dry HCl in CH_2Cl_2. The solutions are also sensitive to air and light, and reacts with DMSO to form tropone.[88] This greater reactivity of the CHT complex has been ascribed to easier loss of CO from the W(CO)$_5$ moiety due to stronger W→carbene dπ–pπ-backbonding in the CHT complex than in the corresponding cyclopropenylidene complex.[88] However, this suggestion is not supported by later studies on palladium complexes, according to which the π-acceptor character of the CHT ligand is substantially lower compared to that of cyclopropenylidene ligands .[149]

Differences in reactivity appear less pronounced between CHT and cyclopropenylidene complexes of palladium and platinum. The dinuclear halogeno-bridged CHT-Pd(II) complexes as well as their cyclopropenylidene analogues readily react with donor ligands such as phosphines or acetonitrile to give the mononuclear donorsubstituted CHT complexes. All these compounds are thermally stable and inert against air at room temperature.[87,115,118] However, their reaction with DMSO leads to substitution of the CHT ligand and its conversion to tropone.[149]

Reactions at the CHT ligand without breaking the metal–carbene bond have been reported for the CHT pincer complex of iridium shown in scheme 3.29. As a consequence of the positively charged seven-membered ring the hydrogen atoms on the methylene bridges to the phosphine groups become acidic and can be deprotonated yielding a neutral cycloheptatrienyl pincer complex of Ir(III) **(A)** with an extension of the π-system into one of the phosphine bridges (Scheme 3.29).



Scheme 3.29

Treatment of the deprotonated product **B** with a second equivalent of base removes HCl from the iridium center forming the Ir(I) complex **C** in a reversible reaction. Addition of excess HCl to **B** restores the CHT complex **D**, differing from the initial complex only by the counterion.[110]

A further reaction at the CHT ligand of the iridium complex occurs upon addition of [(η^6-*p*-xylene)Mo(CO)$_3$], yielding the heterobimetallic complex shown in figure 3.7 with a Mo(CO)$_3$ moiety which is η^6- coordinated to by the tropylium ring.[110]

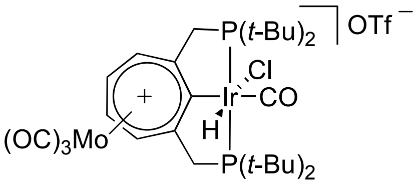


Figure 3.7

With the exception of the above mentioned iridium-pincer complex none of the hitherto reported CHT complexes contain a substituted cycloheptatrienylidene ligand. However, several examples of metal complexes with the benzannelated CHT ligands **E**, **F** and **G** (Figure 3.8) have been described.

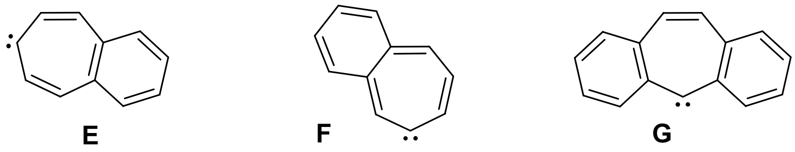
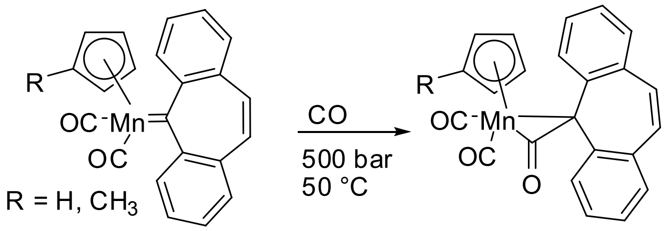


Figure 3.8

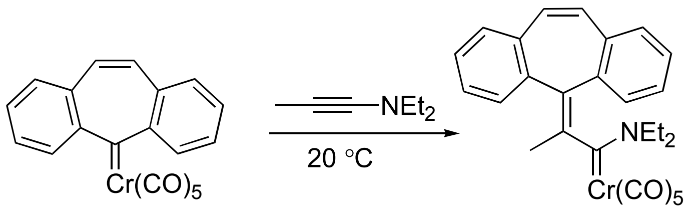
Comparing the iron complexes – entries 4, 5 and 7, and the ruthenium complexes, 12 and 13 of table 3.5 containing the benzannelated ligands **E** and **F** with their analogous nonannelated CHT complexes 3, 6 and 11, no significant difference in the chemical and spectroscopical properties is observed. Chemical shifts for the metal-bound carbene carbon observed in the ^{13}C-NMR spectrum and barriers of rotation about the M C bond in these complexes indicate slightly stronger M-C dπ-pπ-backbonding to the benzannelated ligand **E** than to the monocyclic cycloheptatrienylidene. The benzannelated carbene **F** on the other hand is an even better π-acceptor than **E**.[103, 104]

The reactivity of all hitherto described metal complexes containing the dibenzannelated cycloheptatrienylidene **G** reflect the electrophilic character of this carbene ligand (different from the nonannelated and benzannelated congeners **E** and **F**). They undergo insertion reactions into the metal-carbene bond similar to complexes with diphenylcarbene and other "Schrock-type" carbenes. The dicarbonyl (η^5-cyclopentadienyl)manganese complexes are reacted to yield η^2-ketene complexes by high pressure carbonylation (Scheme 3.30).[155]



Scheme 3.30

The pentacarbonylchromium complex reacts with nucleophilic alkynes such as ynamines under formation of unsaturated aminocarbene complexes (Scheme 3.31).[113,114]



Scheme 3.31

Unfortunately no analogous metal complexes of the same type, both with the tricyclic carbene **G** and with the monobenzannelated CHTs **E** and **F**, are known for detailed comparative studies of their ligand properties.

3.6 Concluding remarks

This section highlights the wide range of carbocyclic complexesthat have been prepared and studied regarding their structure and reactivity. Due to their strong σ-donor property they are expected to replace simple phosphine ligands similar to the work that has been done for N-heterocyclic carbene ligands. In the case of cyclopropenylidenes a large variety of substituents at the carbocycle is available to influence the metal ligand bond and consequently reactivity of the complexes. However, their ability to alter the steric environment around the metal center is limited due to the position of the substituents at the back of the cyclopropene ring pointing away from the metal center. The cycloheptatrienylidene motif would be better suited for tailored ligands since the steric environment around the metal atom as well as the electronic properties can be controlled by introducing substituents into the 2- and 7- positions. These alterations should expand the utility of such complexes for special applications e.g. in homogeneous catalysis. The range of substituted CHT ligands is currently rather limited. Therefore the focus in this field should be on the synthesis of CHT derivatives. In addition, new generally more facile methods to prepare CHT metal complexes are necessary, though the free carbene route could be challenging to apply to CHT systems due to the high dimerization tendency of free cycloheptatriene. Furthermore, modern computational studies investigating the influence of substituents and benzannelation at the cycloheptatriene moiety on the M-C bond and the properties of resulting CHT metal complexes would be helpful. Recent computational studies[190] on the feasibility of silicon and germanium analogues of cyclopropenylidene suggest that these species could be viable targets to expand the class of isoelectronic complexes.

4 Catalysis: an Inherently Green Chemical Process

4.1 Overview

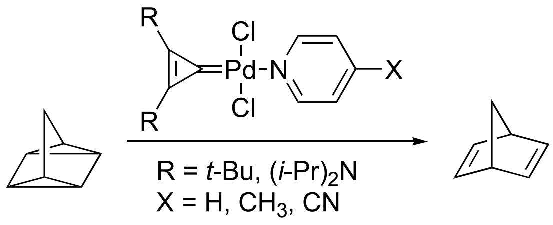
Extending the catalytic applications of carbocyclic carbenes was a focus of this section. Palladium complexes bearing cycloheptatrienylidene carbene ligands were tested and shown to be effective catalysts for CN coupling. Catalytic performance, was directly compared to the analogous 2,3-diphenyl cyclopropenylidene complexes. Though the three- and seven-membered carbocyclic carbene catalysts are less active or stable than analogous NHC complexes for C–N coupling, these investigations not only provide comparative data but also useful insight into this relatively unexplored ligand class. Investigations of catalytic C–N coupling reactions were extended to include non-classical NHC complexes. Furthermore, the catalytic applicability of carbocyclic carbene complexes was expanded to include Cu/Pd-catalyzed decarboxylative coupling. Preliminary tests show that the ligand has an influence on catalysis, however extreme reaction conditions lead to rapid catalyst deactivation.

4.2 Carbocyclic carbenes in catalysis

Early research of carbocyclic carbene complexes focused primarily on synthesis, structure and reactivity. The application of these compounds in homogeneous catalysis was of minor interest and limited to a few highly sophisticated reactions and catalyst systems. However, in part due to a recent focus on catalysis and in part due to environmental and economic pressures catalysis has taken center stage in the past 10 years. Of particular note are Grubbs type ruthenium catalysts bearing the novel structural motif of a carbocyclic indenylidene ligand, which have spawned an entire family of metathesis catalysts. Also of interest are palladium catalysts supported by carbocyclic carbene ligands used in the extensively active field of C–C and C–N coupling reactions.

4.2.1 Isomerization of quadricyclane to norbornadiene

The first application of a carbocyclic carbene ligand in catalysis was reported by Yoshida et al. in 1988.[147] Interested in molecular energy storage processes, they found that cyclopropenylidene palladium complexes were able to catalyze the exothermic valence isomerization of quadricyclane to norbornadiene (Scheme 4.1). Complexes were shown not only to exhibit comparably high activities with respect to di-m-chloro-bis(norbornadiene)dirhodium(I), but also to be stable in air.



Scheme 4.1

A detailed mechanistic study revealed that the catalytically active species is formed by dissociation of the weakly coordinated pyridine derivative.[107] The polymerization reaction was monitored by ^{1}H- and ^{29}Si-NMR spectroscopy and the formation of a regioregular cyclic polymer was concluded. By MALDI-TOF mass spectrometry of the isolated polymeric material molecular peaks for oligomers between $n = 5$ and $n = 23$ were detected. A similar reactivity is suggested for the vanadium analogue.[107] For catalysts shown in scheme 4.1, the electronic nature of the carbene ligand (governed by the tertiary butyl or the diisopropylamino substituents) as well as the σ-donor strength of the leaving ligand were shown to affect the rate of reaction. A very similar concept was recently introduced with the PEPPSI (PEPPSI = pyridine-enhanced precatalyst preparation, stabilization and initiation) by M. G. Organ and co-workers for NHC palladium catalysts, this appears to be an early and overlooked application of this concept.[183-185]

4.2.2 Olefin metathesis

A derivative of the Grubbs family of catalysts, the stable ruthenium-indenylidene complex **A**, originally regarded as allenylidene species, has been used to spawn a novel class of metathesis precatalysts shown in figure 4.1. Offering several benefits like the ease of access, improved activity and stability as well as functional group tolerance the congeners **B** to **F** can be regarded as valuable extension of established alkylidene-based catalyst systems.

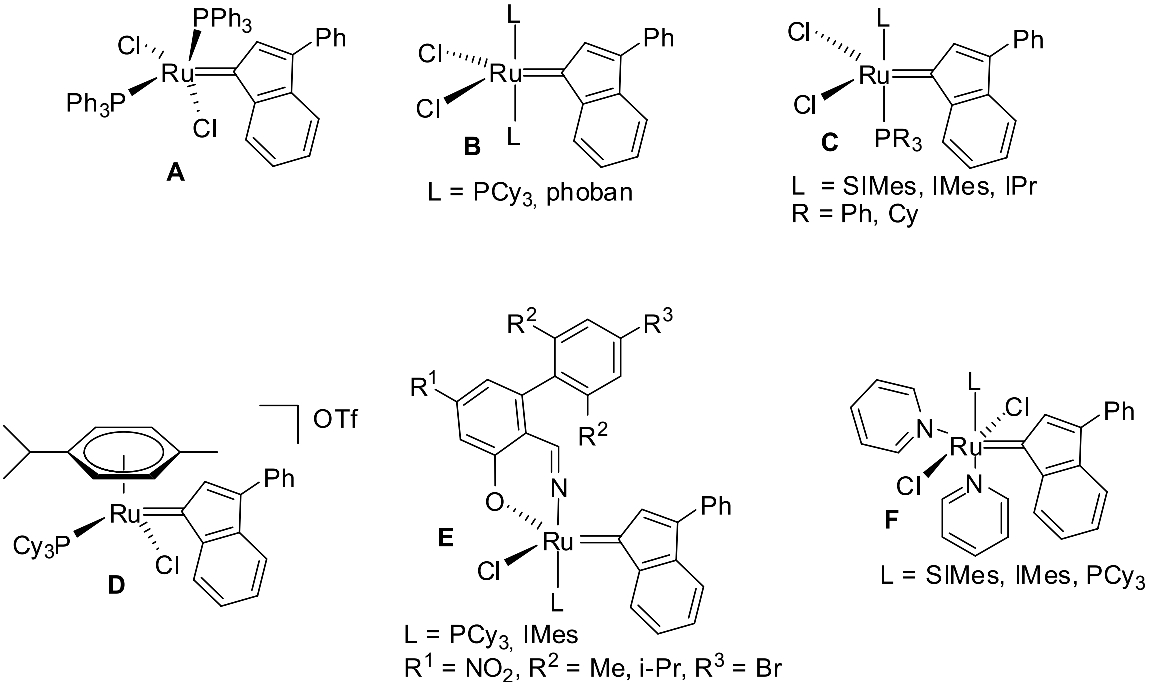


Figure 4.1

These catalysts are useful for a wide range of polymerization reactions including ring-opening metathesis polymerization, ROMP; atom-transfer radical polymerization, ATRP), ring closing reactions (RCM) and olefin cross metathesis reactions. They have also been shown to exhibit catalytic activity in non-metathesis reactions, specifically, in nucleophilic additions and hydrosilylations of alkynes.[176,186,187]

4.2.3 Cross coupling reactions

First applications investigated by our group were the unsubstituted, carbocyclic carbene cycloheptatrienylidene (CHT) as a supporting ligand in palladium catalyzed C–C coupling reactions in 2006 highlighted the utility of this ligand concept.[115] The activities found were comparable with or even superior to well-established NHC systems. The complex [*cis*-(CHT)(PPh_3)$PdCl_2$] produced good results in numerous variants of Heck and Suzuki coupling reactions. With only 10^{-4} mol% of this molecularly defined precatalyst *p*-bromoacetophenone and *n*-butyl acrylate were reported to undergo C–C coupling at 145 °C, with turn over numbers (TON) of the order of 10^6 with turn over frequencies (TOF) of »10^3 h^{-1}.[115] Biphenyl was obtained quantitatively from bromobenzene and phenylboronic acid at 130°C (10^{-3} mol % Pd) with TON in the order of 10^4 to 10^6. With higher catalyst loadings chloroarenes could also be coupled efficiently.[115] In addition the CHT-supported system did not suffer from an induction period. D. F. Wass et al. found high activities in Heck and Suzuki reactions for the 2,3-

diphenylcyclopropenylidene ligand.[188] However, only conversions, that is the loss of reactants were reported.

A more detailed study of Suzuki coupling reactions including a direct comparison of catalysts containing the CHT ligand or 2,3-diarylcyclopropenylidene ligand in our group revealed the superior role of the CHT complexes. Faster initiation in line with generally higher yields was observed. A variation of the aryl substituents of the cyclopropenylidene ligand had only little influence on the catalytic activity.[149] The hitherto highest efficiencies involving a carbocyclic carbene complex were reported by Yao et al. for Heck reactions of aryl bromides who used palladium precatalysts bearing the bidentate six-membered anionic carbene ligand shown figure 4.2. For example, using a very low catalyst loading of 8×10^{-5} mol% based on palladium the deactivated substrate *p*-bromoanisole with styrene could be coupled with a TON greater than 900 000. However, high temperatures (140 to 160 °C) and long reaction times (20 to 169 h) are required. For chloro arenes a significant loss in activity was observed.[121]

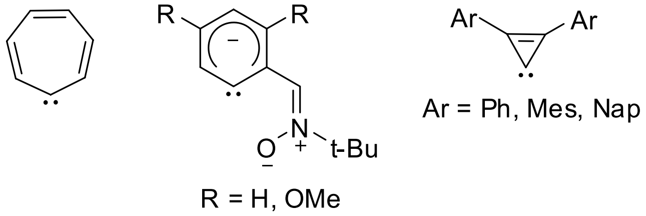


Figure 4.2

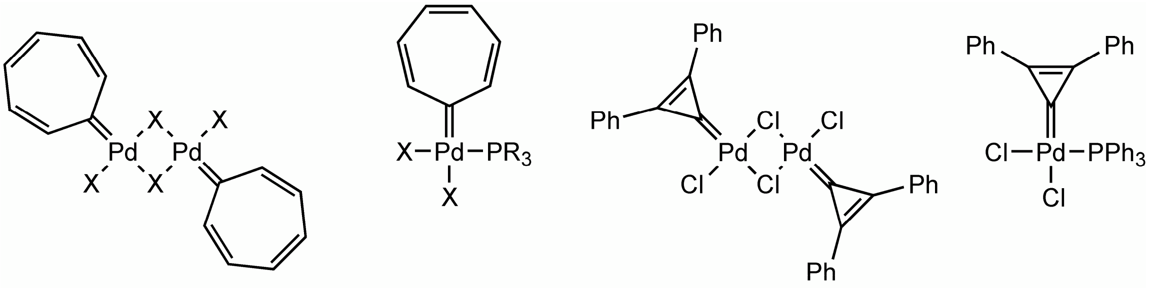
4.2.3.1 Carbocyclic Carbene Ligands in Palladium catalyzed C,N-coupling reaction

Since the pioneering work of Hartwig and Buchwald palladium catalyzed aromatic amination reactions have become a powerful tool for the synthesis of a great variety of products ranging from laboratory to industrial scale.[219,220] In general the palladium metal centers are supported and controlled by strong donor ligands during these reactions. It is noteworthy and probably intrinsic for these systems that ligand free catalysis is intensely discussed for C-C coupling, but not yet for C-N coupling reactions.[221] The most common ligand systems comprise a wide range of phosphines, including phosphapalladacycles, and *N*-heterocyclic carbenes (NHC).[223]

Through the research with and beyond NHCs in organometallic chemistry and catalysis our group has established that the simple carbocyclic carbene, cycloheptatrienylidene (CHT), is comparable and in some cases even superior as a supporting ligand in catalysis in comparison to well-established NHC systems.[115,117] This observation was unforeseen and seems even more astonishing when one takes into account that transition metal complexes of both NHCs and carbocyclic carbenes have the same origins,[74,79,80] though the latter were treated as laboratory curiosities for decades.[85,86,104,105,148,193,223] C. Taubmann has described the first application of this ligand class first with the example of the corresponding palladium complexes in Heck and Suzuki coupling reactions.

Expanding efforts to explore and optimize this new class of catalysts also included the analogous palladium complexes bearing the smallest possible carbocyclic carbene ligand cyclopropenylidene.[149,188] The three-membered ring systems resulted in inferior observed catalytic activity in C-C coupling, especially for deactivated chloro arenes. Hence work was focused on the seven-membered ring system and in this communication reported a further utility of the CHT ligand as well as the direct comparison to the 2,3-diphenylcyclopropenylidene ligand,[189] here, in C-N coupling catalysis.

A series of dinuclear halo-bridged carbocyclic carbene palladium (II) complexes **1**, **2**, and **5** and the deduced mononuclear compounds **3a**, **3b**, **4**, and **6** bearing a carbocyclic carbene and a phosphine ligand (Figure 4.5) were used for the evaluation of the catalytic activity for Hartwig-Buchwald amination reactions.



1 (X = Cl)
2 (X = Br)

3a (X = Cl; R = PPh_3)
3b (X = Cl; R = PCy_3)
4 (X = Br; R = PPh_3)

5

6

Figure 4.5. Palladium precatalysts supported by carbocyclic carbene ligands.

The synthesis of the cyclopropenylidene Pd(II) complex **5** was possible through straightforward addition to the molecularly defined soluble palladium source, [$Pd(dba)_2$] as reported by Wass et al.[189] instead of palladium black. This variation proved useful in the synthesis of the seven-membered ring complexes and provided near quantitative yields for the complex bis[dibromo(cycloheptatrienylidene)palladium(II)] **2.** Though this reaction is attractive from a yield perspective, the poor atom economy ($M(Pd(dba)_2)$ = 575.0 g/mol vs. M(Pd) = 106.4 g/mol), high price as well as air sensitivity of this molecularly defined precursor must be seen as major drawbacks to the use of this method. Areas for optimization exist in recycling of the dba ligand as well as exploration of other molecularly defined systems for synthesis.

Catalytic studies were extended to include the bromo derivatives **2** and **4**, with particular attention to the effects of structural differences on catalytic functionalities. Similar metal carbene bond lengths were observed by x-ray diffraction, which were within the expected range typical for NHC-Pd complexes (Table 4.1). The considerable *trans*-influence of the CHT ligand indicated by a longer Pd-Br2 bond length compared to Pd-Br1 bond (Δ = 0.017 Å) in **4** is a further hint for the strong δ-donor and poor π-acceptor character of this carbene ligand. Nearly identical C-C bond lengths (1.39 ± 0.02 Å) in the seven-membered ring suggest extensive 6p π-delocalization including the carbene p orbital in the bromo derivative.

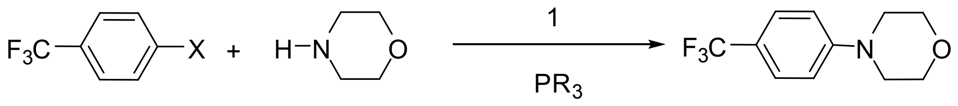
Table 4.1 Selected bond lengths [Å] and angles [°] of the CHT palladium complexes [*cis*-Pd(CHT)X_2(PPh_3)] (X = Br, Cl) [87]

X	**Cl**	**Br**
Pd-C1	1.968(2)	1.983(3)
Pd-X1	2.3697(6)	2.4895(5)
Pd-X2	2.3884(7)	2.5064(4)
Pd-P	2.2483(6)	2.2575(9)
X1-Pd-X2	91.83(2)	92.38(2)
X1-Pd-P	175.89(2)	175.15(3)
X1-Pd-C1	85.14(7)	84.78(11)
X2-Pd-P	92.27(2)	92.42(3)
X2-Pd-C1	174.55(6)	174.63(9)
P-Pd-C1	90.76(7)	90.38(11)

A similar stabilization for the three-membered ring system (2p-e^--aromaticity) proposed by Wass et al.[189] was recently discounted by an experimental charge-density approach for free as well as coordinated cyclopropenylidene carbenes by Scherer et al..[142] A higher π-acceptor capability relative to *N*-heterocyclic carbenes was shown.

For the catalytic evaluation established standard protocols[188,189] were followed to facilitate the comparison of the results obtained. An extended phosphine screening was undertaken with compound **1** (Table 4.2) as this in-situ method provides an efficient and valuable probe for identifying catalytic systems which warrant further study. The halo-bridged complexes **1**, **2**, and **5** are known to be easily cleaved by phosphines yielding the catalytically relevant precatalysts. It was found that for the coupling of the activated bromo substrate *p*-bromo benzotrifluoride with morpholine at elevated temperatures the CHT complex is active with a variety of phosphines tested (Table 4.2, entries 2-7). For the corresponding chloro substrate distinct differences were observed. Appreciable yields could only be obtained with the more basic alkyl phosphines such as PCy_3 and P^tBu_3 (Table 4.2, entries 13 and 14). It is notworthy that the phophine with the largest cone angle, $PMes_3$, seemed not to be compatible with the CHT ligand and yielded the same poor results as the phosphine-free runs (Table 2, entries 1, 5, 8 and 12) showing the crucial role of a second suitable donor ligand attached to the palladium metal center and ruling out the influence of the cone angle on catalytic activity. Comparing GC-based conversions and yields in terms of catalyst selectivity for several runs more than 30 % higher conversion than yield was observed due to side reactions (Table 4.2, e.g. entries 6 and 13). This shows that employing only conversion as a measure for catalyst activity is in a way misleading and reporting the yield is of great importance.[188] Subsequent screening experiments, delivered superior results using the CHT complexes compared to preliminary data published by Wass et al. for the 2,3-diphenylcyclopropenylidene system (with the exception of entry 1 table 4.2).[188]

Table 4.2 Phosphine Screening

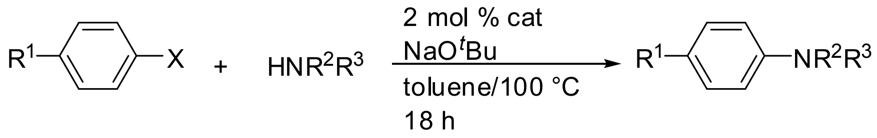


run [a]	phosphine	X	conversion[b] /%	yield[c]/%
1	none	Br	35	19
2	P(*p*-F-Ph)$_3$	Br	100	69
3	PPh$_3$	Br	100	70
4	P(*o*-Tol)$_3$	Br	100	90
5	PMes$_3$	Br	37	20
6	PCy$_3$	Br	100	68
7	P^{t}Bu$_3$	Br	100	100
8	none	Cl	5	1
9	P(*p*-F-Ph)$_3$	Cl	1	1
10	PPh$_3$	Cl	1	1
11	P(*o*-Tol)$_3$	Cl	10	5
12	PMes$_3$	Cl	8	3
13	PCy$_3$	Cl	100	64
14	P^{t}Bu$_3$	Cl	100	98

[a] conditions: 1.0 mmol of aryl halide, 1.2 mmol of morpholine, 1.4 mmol of NaO^{t}Bu, 2.0 mol % of **1**, 1.0 equiv of phosphine, 8 ml toluene, 100 °C, 18 h.[b] GC conversion based on aryl halide with *n*-eicosane as the internal standard. [c] GC yield with *n*-eicosane as the internal standard.

Various substrates were screened to find an optimized system as a comparable standard. Results are summarized in table 4.3 together with results obtained by Wass who performed a similar screening reactions for the three membered ring system.[188]

Table 4.3



Entry	Catalyst	R^1	X	R^2, R^3	yield/%	yield using 5 ^{1}% [88]
1	**3a**	CF_3	Br	$-CH_2CH_2OCH_2CH_2-$	70	63
2	**3a**	H	Br	$-CH_2CH_2OCH_2CH_2-$	75	64
3	**3a**	Me	Br	$-CH_2CH_2OCH_2CH_2-$	60	50
4	**3a**	MeO	Br	$-CH_2CH_2OCH_2CH_2-$	31	23
5	**6**	MeO	Br	$-CH_2CH_2OCH_2CH_2-$	30	
6	**3a**	CF_3	Br	H, 2-C_6H_4(Me)		20
7	**3a**	CF_3	Br	H, 2,4,6-$C_6H_2(Me)_3$		51
8	**3a**	CF_3	Br	C_6H_5, C_6H_5		100
9	**3a**	CF_3	Br	C_6H_5, Me		45
10	**1** + P^tBu_3	MeO	Cl	$-CH_2CH_2OCH_2CH_2-$	1	
11	**5** + P^tBu_3	MeO	Cl	$-CH_2CH_2OCH_2CH_2-$	100	
12	$(PhCN)_2PdCl_2$ + 2 eq P^tBu_3	MeO	Cl	$-CH_2CH_2OCH_2CH_2-$	31	
13	$(PhCN)_2PdCl_2$ + 1 eq P^tBu_3	MeO	Cl	$-CH_2CH_2OCH_2CH_2-$	50	

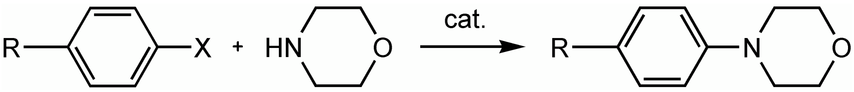
Bearing in mind the strong influence of the participating phosphine, further investigations as to the effects of aryl halide deactivation, catalyst loading, temperature, base, etc. were undertaken (Table 4.4). Similar yields were observed for application of an in-situ mixture in comparison to the isolated precatalyst suggesting the same active species is present in both (Table 4.2, entry 3 vs. Table 4.4, entry 1). The amination of chloro arenes is possible with precatalyst **3b**. However, the efficiency is dominated by the degree of substrate activation (Table 4.4, entries 5-7). This clearly demonstrates the limitations of catalyst **3b**, whilst emphasizing the importance of the $P^{t}Bu_3$ in this catalytic system. A significant loss of activity was also observed by decreasing the catalyst concentration from 2 to 0.5 % (Table 4.4, entries 9, 11 and 12).

An excess of phosphine is rather detrimental to the system as reported before (Table 4.4, entry 22).[224] The use of the stronger base $KO^{t}Bu$ instead of $NaO^{t}Bu$ only resulted in slightly higher yields (Table 4.4, entries 1 and 9). A carbene-free palladium source was employed to reassure the important role of the carbocyclic carbene ligand (Table 4.4, entry 22).

As previously mentioned the role of the halogen attached to the palladium was elucidated by parallel screening of the halo-bridged complexes **1** and **2** and the mononuclear complexes **3a** and **4**. Both, **1** and **2** in combination with $P^{t}Bu_3$ are able to aminate even deactivated chloro-arenes in excellent yields (Table 4.4, 18 and 19). In comparison to its chloro derivative compound **4** generated significantly higher yields in the coupling *p*-bromo anisole (Table 4.4, entries 2 and 8). Moreover, higher performance at moderate temperatures could be observed (Table 4.4, entries 14 and 15). Though for the room temperature coupling of deactivated chloro arenes, e.g. *p*-chloro anisole (Table 4.4, entry 21) catalyzed by our CHT-system further optimization is needed in order to be competitive with other highly active catalysts.[225]

As observed in the phosphine screening experiments (Table 4.2) the CHT system turned out to be superior to the 2,3-cyclopropenylidene system both employed as isolated mixed carbene phosphine complexes (Table 4.4, entries 1-4) and when prepared in-situ (Table 4. 4, entries 18 and 20).

Table 4.3 C-N Coupling screening reactions



Entry	cat.	mol % Pd	T/°C	base	R	X	yield[b]/%
1	**3a**	2.0	100	NaO^{t}Bu	F_3C	Br	70
2	**3a**	2.0	100	NaO^{t}Bu	MeO	Br	31
3	**5**	2	100	NaO^{t}Bu	F_3C	Br	63
4	**5**	2	100	NaO^{t}Bu	MeO	Br	23
5	**3b**	2.0	100	NaO^{t}Bu	F_3C	Cl	66
6	**3b**	2.0	100	NaO^{t}Bu	H	Cl	41
7	**3b**	2.0	100	NaO^{t}Bu	MeO	Cl	12
8	**4**	2.0	100	NaO^{t}Bu	MeO	Br	62
9	**3a**	2.0	100	KO^{t}Bu	F_3C	Br	77
10	**4**	2.0	100	KO^{t}Bu	F_3C	Br	81
11	**3a**	1.0	100	KO^{t}Bu	F_3C	Br	78
12	**3a**	0.5	100	KO^{t}Bu	F_3C	Br	37
13	**3a**	2.0	75	KO^{t}Bu	F_3C	Br	79
14	**3a**	2.0	50	KO^{t}Bu	F_3C	Br	50
15	**4**	2.0	50	KO^{t}Bu	F_3C	Br	81
16	**1** [c]	2.0	50	KO^{t}Bu	F_3C	Br	100
17	**5** [c]	2.0	50	KO^{t}Bu	F_3C	Br	100
18	**1** [c]	2.0	100	NaO^{t}Bu	MeO	Cl	100
19	**2** [c]	2.0	100	NaO^{t}Bu	MeO	Cl	94
20	**5** [c]	2.0	100	NaO^{t}Bu	MeO	Cl	86
21	**2** [c]	2.0	r.t.	KO^{t}Bu	MeO	Cl	11
22	$Pd(PhCN)_2Cl_2$ [c]	2.0	100	NaO^{t}Bu	MeO	Cl	50
23	$Pd(PhCN)_2Cl_2$ [d]	2.0	100	NaO^{t}Bu	MeO	Cl	31

[a] conditions: 1.0 mmol of aryl halide, 1.2 mmol of morpholine, 1.4 mmol of base, 8 ml toluene, 18 h. [b] GC yield with *n*-eicosane as the internal standard. [c] *in situ* with 1.0 equiv P^{t}Bu$_3$.[d] *in situ* with 2.0 equiv P^{t}Bu$_3$.

Carbocyclic carbene supported palladium precatalysts do not exhibit an induction period.[115,117,149,188,189] These findings were confirmed for C-N coupling catalysis – even at room temperature. It was surprising that even for the strongly activated substrate p-bromo benzotrifluoride a remarkable advantage of the CHT system in comparison to the 2,3-diphenylcyclopropenylidene system could be observed (Figure 4.6). Quantitative yield was reached after 10 minutes whereas with the diphenylcyclopropenylidene system a yield of not higher than 70 % could be obtained.

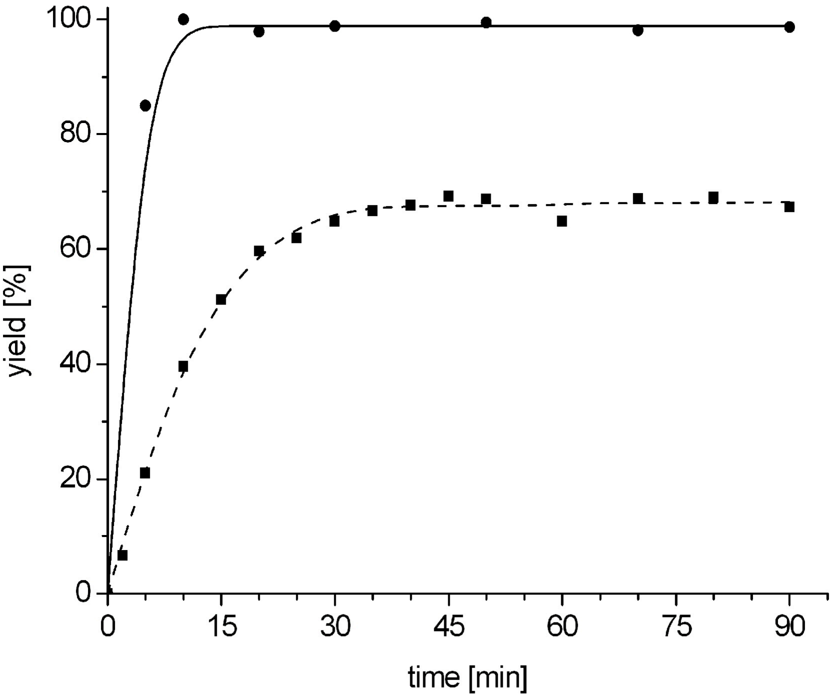
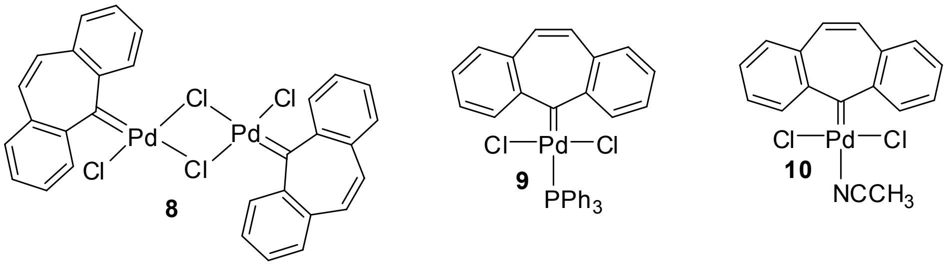


Figure 4.6. Yield vs. time plot at room temperature for the coupling of p-bromo benzotrifluoride (1.0 mmol) with morpholine (1.2 mmol) catalyzed by **1** (—●—) and **5** (--■--) *in situ* with 1.0 equiv P^{t}Bu$_3$ (other conditions: 2 mol % Pd, 1.4 mmol NaO^{t}Bu, 8 ml toluene; GC yield with *n*-eicosane as the internal standard).

Dibenzylsubstiuted catalysts (figure 4.7) were tested at optimized conditions for activity as catalysts in C–N coupling. The results, which are summarized in table 4.4, show that these compounds are ineffective coupling catalysts under the tested conditions. Their poor performance is attributed in part to the extremely poor solubility of the precatalysts. It was hoped, that the solubility would improve by the introduction of a methyl group to the carbene moiety which might help to disturb possible π- stacking interactions, however this complex was also insoluble and as such further catalytic experiments with this family of compounds were performed.

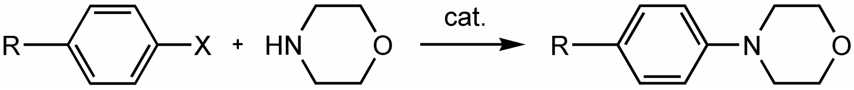
$Pd(NCCH_3)_2Cl_2$
7



8 **9** **10**

Figure 4.7

Table 4.4 Preliminary Testing of Subsituted Carbocyclic Carbene Complexes



Vial [a]	X	R	Phosphine	Catalyst	Yield % [b]
1	Br	F_3C	PPh_3	7	4
2	Br	F_3C	P^tBu_3	7	10
3	Cl	MeO	PPh_3	7	0
4	Br	F_3C	PPh_3	8	9
5	Br	F_3C	P^tBu_3	8	7
6	Cl	MeO	PPh_3	8	0
7	Br	F_3C	-	9	8
8	Cl	MeO	-	9	0
9	Br	F_3C	PPh_3	10	6
10	Br	F_3C	P^tBu_3	10	8
11	Cl	MeO	PPh_3	10	0

[a] conditions: 1.0 mmol of aryl halide, 1.2 mmol of morpholine, 1.4 mmol of NaO^{t}Bu, 2.0 mol % of Pd, 1.0 equiv of phosphine, 8 ml toluene, 100 °C, 18 h.[b] GC conversion based on aryl halide with *n*-eicosane as the internal standard. GC yield with *n*-eicosane as the internal standard.

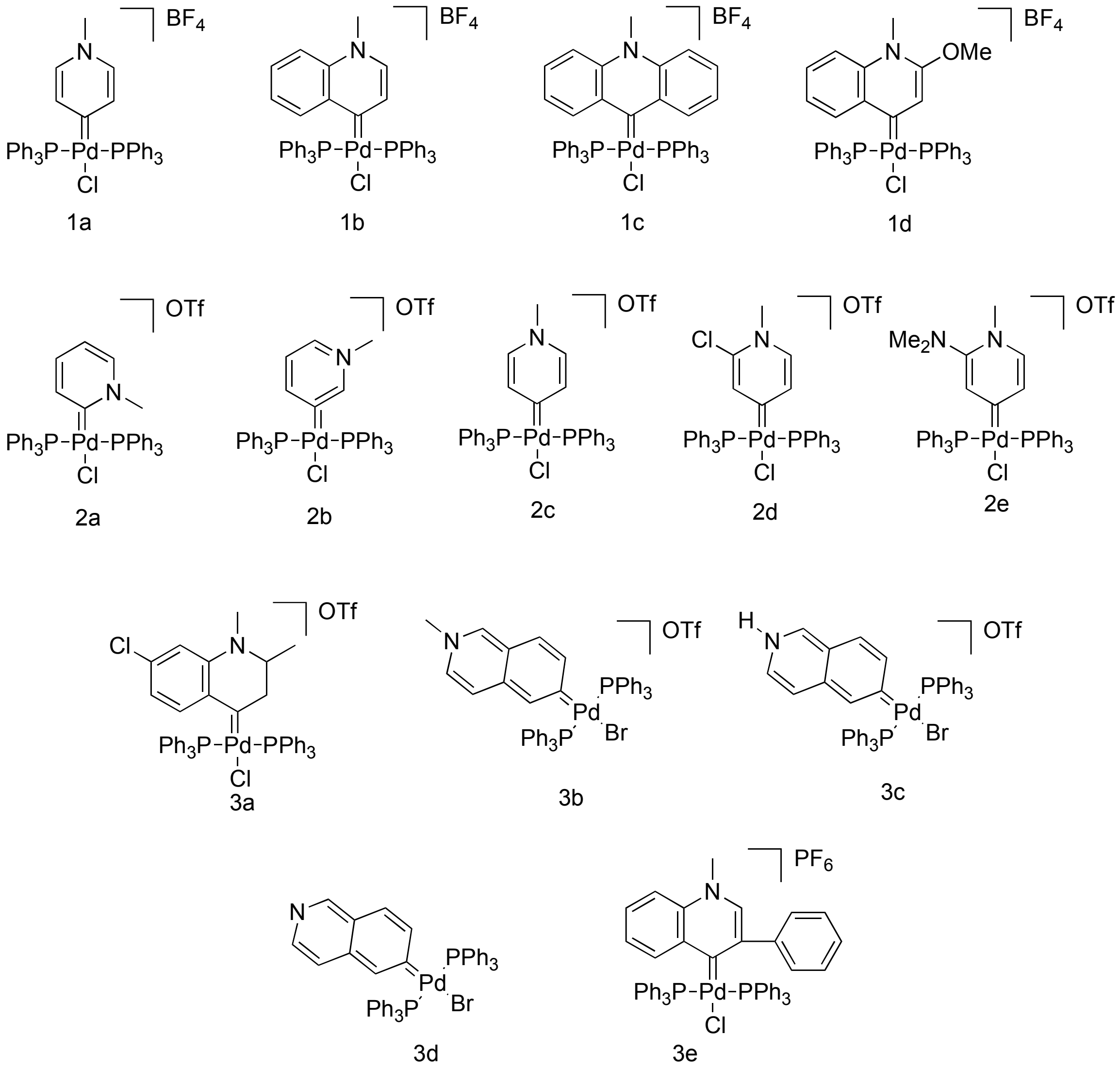
4.2.3.1.1 Conclusion and outlook

Carbocyclic carbene palladium complexes show high activity in Hartwig-Buchwald amination reactions. In each particular screening experiment the CHT supported palladium precatalysts formed in combination with a phosphine ligand proved to be more catalytically active than the related 2,3-diphenylcyclopropenylidene systems. Both isolated mononuclear complexes [*cis*-(CHT)(PPh3)PdX$_2$] (X = Cl, Br) exhibit very similar structural features in the solid state, however, the catalytic activity of the bromo derivative is significantly higher. Dibenzylsubstituted CHT ligand systems were shown to be ineffective catalysts for C–N coupling under the conditions tested. Work will continue to modify the CHT ligand electronically as well as sterically, and to elucidate the role of the carbocyclic carbene ligand in the catalytic cycle. Due to physical properties of carbocyclic carbenes, specifically insolubility, there is a tremendous opportunity for catalyst immobilization. Relative insolubility of the complex in benzene, toluene, and THF would mean minimal catalyst leaching. Another area for further exploration is the immobilization of carbocyclic carbene complexes for use in heterogeneous or capture release homogeneous catalysis. By virtue of the poor solubility of the precatalytic complex catalyst leaching would be expected to be minimal. Preliminary work on utilizing the clevage of the dinuclear complex with an immobilized phosphine source such as triphenyl phosphine polystyrene is underway. It is belived that the classical homogeneous phosphines, such as triphenyl phosphine or tricyclohexylphosphine, are directly replaced with a phosphine immobilized on a support. Future collaborations with solid state chemists are required for the characterization of the compound produced. It is expected that during the catalysis the complex should dissociate, and be free to take part in reactions in the homogeneous phase. After productive catalysis the electronically unsaturated catalyst should return to the starting heterogeneous resting state, in a mechanism that may be called “capture-release” system. Studies of these systems and the possibility of catalyst recovery are expected to further expand the utility of this ligand class.

4.2.4.3 C–N Coupling with Non-Classical N-Heterocyclic Carbene Complexes

In collaboration with Dr. O. Schuster, a highly variable family of pyridynlidenes were for activity in C-C cross coupling catalysis. The results of this study of highly variable remote N-heterocyclic carbene palladium family shown in figure 4.8 were subsequently presented in combination with Dr. Schusters work in the area of C-C coupling.[226]

Reaction screenings were carried out with catalyst **3e** at various temperatures with various time probes (10 minutes to 214 hours) to find conditions where yield and conversion were good but not optimal. The rational behind this was the influences of proximity of the π-electron donor and substitutions at the carbene moiety as well as of the counter ion could be monitored. The C–N screening reactions were preformed at 40 °C and 80 °C and results are summarized in tables 4.5.



1a 1b 1c 1d

2a 2b 2c 2d 2e

3a 3b 3c

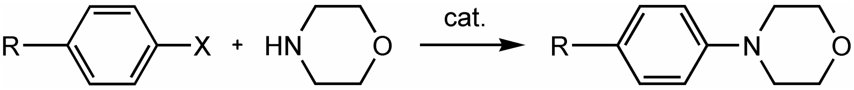
3d 3e

Figure 4.8

Effects of varying the position of the nitrogen group (entries 5-7, 17-19), changing of counter ion (entries 1,7,15,19), substituting of the carbene ring (entries 7-9,19-21), substitution of the carbene ring at the nitrogen (entries 11-13, 23-25) had no visible effect on observed yield or conversion. Addition of one phenyl ring (1b and 1d vs 1a) appears to reduce yield, presumably because of a less stable carbene bond as electron density would accumulate at to the substituent ring via aromatic stabilization. Substitution of two phenyl rings (1c) appears to result in slightly better yields than the monosubstituted complexes possibly through aromatic delocalization allowing for more electron density at the N-heterocyclic carbene moiety(entries 1-4). Higher reaction temperatures do not appear to increase yield greatly, but to increase side reactions, observed in a loss of substrate with no gain in yield (entrys 1-14 vs 15-26). Catalysis occurred in sealed airtight reaction vesels and therefore loss of substrate via evaporation can be excluded.

To gain further insight into the effects of reaction time on conversion of starting material and product yield a time vs reaction study (at 40 ºC using catalyst 3e, 1.0 mmol of aryl halide (X: Br, R: CF_3), 1.2 mmol of morpholine, 1.4 mmol of NaO*t*Bu, 2.0 mol % of Pd, toluene, GC conversion based on aryl halide with *n*-eicosane as the internal standard. GC yield with *n*-eicosane as the internal standard) shown in figure 4.9, was undertaken. The rate of conversion is fastest for the first 110 hours and slows down greatly thereafter suggesting catalyst deactivation. The generation of side products, observed by a decrease in product and reactant, also appears to reach a maximum at this point.

Table 4.5



Entry	temperature/ C	cat.	% aryl halide	% yield	% product and starting material
1	40	1a	14	69	83
2	40	1b	32	54	86
3	40	1c	28	58	86
4	40	1d	29	51	80
5	40	2a	28	60	88
6	40	2b	23	58	81
7	40	2c	16	62	78
8	40	2d	35	52	86
9	40	2e	19	60	79
10	40	3a	26	53	79
11	40	3b	26	60	85
12	40	3c	27	54	81
13	40	3d	23	58	81
14	40	3e	36	50	86
15	80	1a	8	64	72
16	80	1b	2	57	58
17	80	2a	3	59	62
18	80	2b	2	61	63
19	80	2c	2	61	63
20	80	2d	2	65	67
21	80	2e	2	64	65
22	80	3a	8	68	70
23	80	3b	2	63	65
24	80	3c	3	63	66
25	80	3d	2	60	62
26	80	3e	2	67	70

conditions: 1.0 mmol of aryl halide(X: Br, R: CF_3), 1.2 mmol of morpholine, 1.4 mmol of NaO^tBu, 2.0 mol % of Pd, toluene, 210 h. GC conversion based on aryl halide with *n*-eicosane as the internal standard. GC yield with *n*-eicosane as the internal standard.

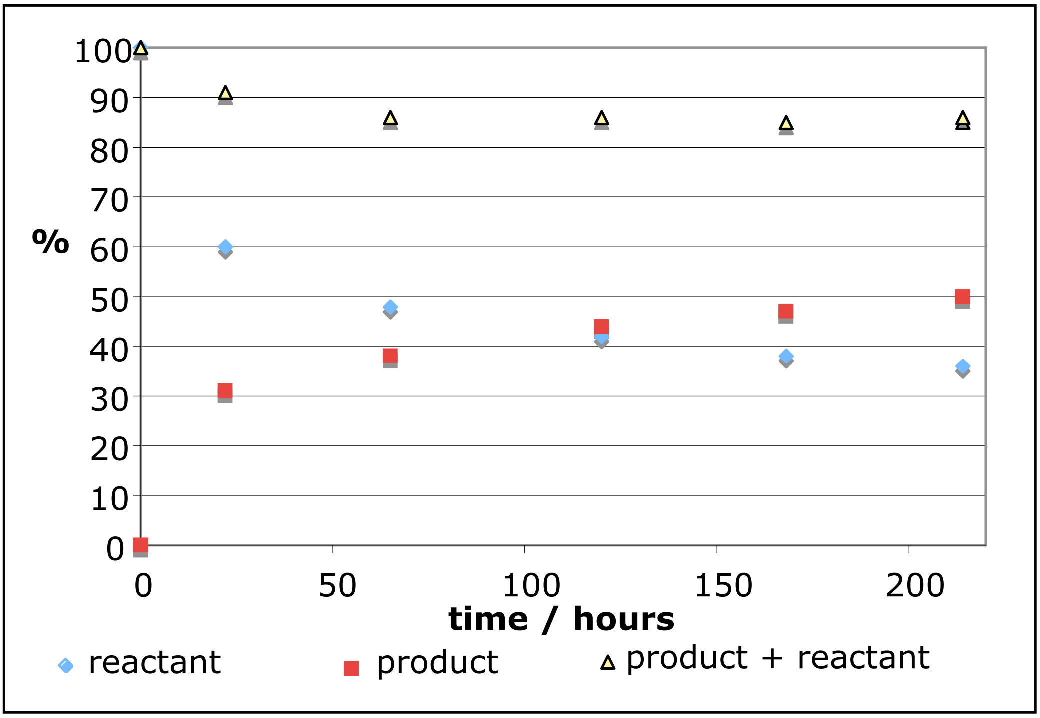

100
90
80
70
60
50
40
30
20
10
0
%
0
50
100
150
200
time / hours
reactant
product
product + reactant

Figure 4.9

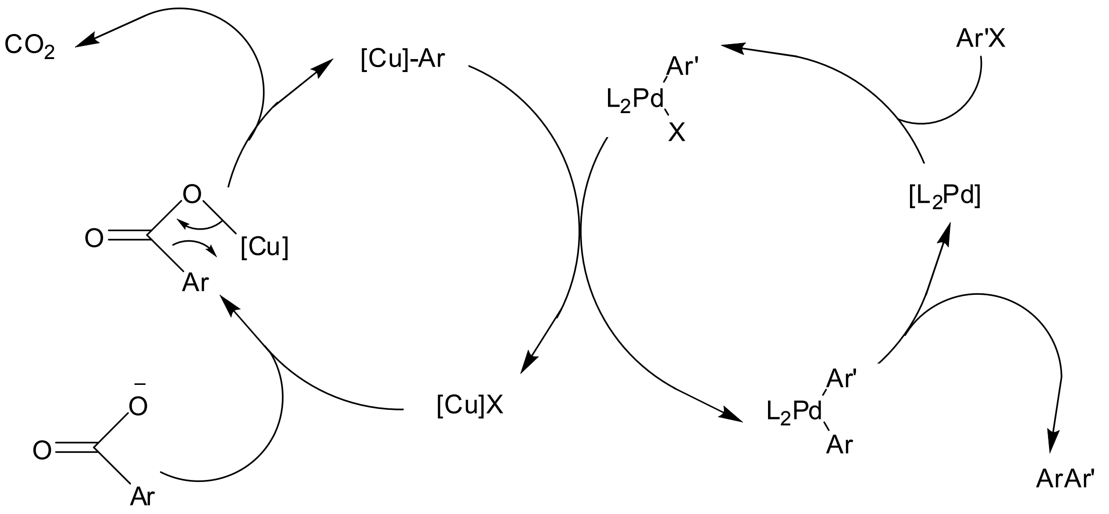
4.2.4 Decarboxylative biaryl synthesis

In the search to expand the catalytic utility of carbocyclic carbene complexes an approach similar to that of early researchers in the area of NHCs was used. Specifically, literature was surveyed for catalytic reactions in which phosphine or NHC complexes were used as catalysts. It is a simple, yet powerful approach. Two catalytic transformations were identified to be particularly attractive were alpha-keto arylation and decarboxilative biaryl synthesis.

As alpha-keto arylation testing was carried out by Ms. Kevsa Mantas. Work undertaken evaluating the decarboxylative biaryl synthesis was performed, following a very kind invitation of Prof. Dr. Lukas Goossen, at the University of Kaiserslautern.

The Goossen group has established decarboylative cross coupling as an alternative to classical C-C bond formation reactions which is advantageous as it avoids the use of expensive and sensitive organometallic reagents such as organoboron, tin, zinc, copper, silicon and magnesium.[226-231] This approach was first successful for the reaction of aromatic carboxylates and aryl halides.[232] The involved chemical transformation is attractive from a green chemistry point of view because of the lower cost and facile handling of the carboxylative substrates.[233]

The proposed mechanism is shown in scheme 4.2.[234] Goossen and coworkers were able to show by mechanistic studies, that catalysis is limited by thermodynamically unfavorable exchange of a halide for non ortho-substituted benzoate derivatives at the copper center.[234] To overcome this the use of aryl triflates were used in the place of arylhalides as carboxylates are more able to compete against the poorly corrdinating triflate ions for meta- and para- substituted benzoate derivatives. [233]



Scheme 4.2 [234]

Carbocyclic carbene and remote N-heterocyclic carbene complexes shown in figure 4.10, were tested in dicarboxylative synthesis using both arylbromides and aryl triflates as coupling partners.

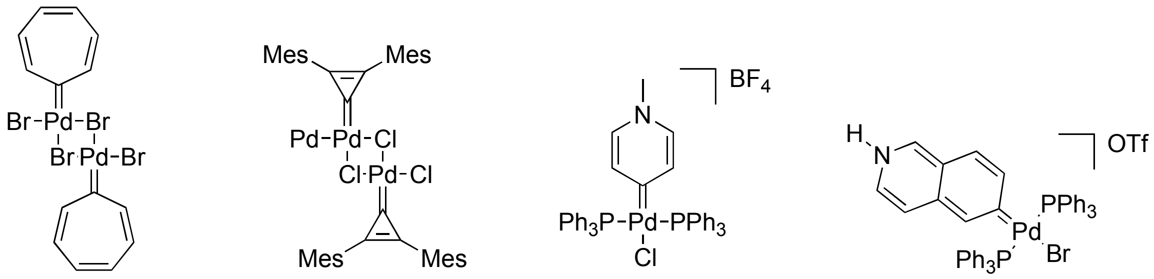
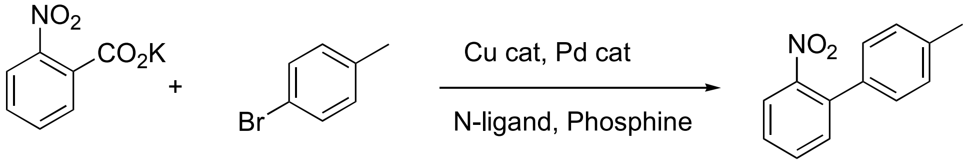

1 2 3 4

Figure 4.10

In order to first establish catalytic utility of the complexes depicted in figure 4.10, the cross-coupling between 4-bromotoluene and potassium 2-nitrobenzoate was tested as a model reaction. Based on this reaction a phosphine screening was preformed and various combinations of palladium salts and ligands were systematically tested. These preliminary tests revealed that the investigated Pd complexes are efficient precatalysts for the decarboxylative biaryl synthesis and the results are summarized in table 4.6.

Table 4.6



Entry	Pd-source	Phosphine	Yield/%
1	Pd(acac)$_2$	-	74
2	Pd(acac)$_2$	4 mol% P(*p*-tol)$_3$	57
3	PdBr$_2$	-	65
4	PdCl$_2$	-	0
5	1	6 mol% P(*p*-tol)$_3$	72
6	1	4 mol% P(*p*-tol)$_3$	71
7	1	2 mol% P(*p*-tol)$_3$	47
8	1	-	76
9	2	6 mol% P(*p*-tol)$_3$	78
10	2	4 mol% P(*p*-tol)$_3$	60
11	2	2 mol% P(*p*-tol)$_3$	51
12	2	-	41
13	3	-	75
14	3	2 mol% PPh$_3$	58
15	4	-	70
16	4	2 mol% PPh$_3$	69

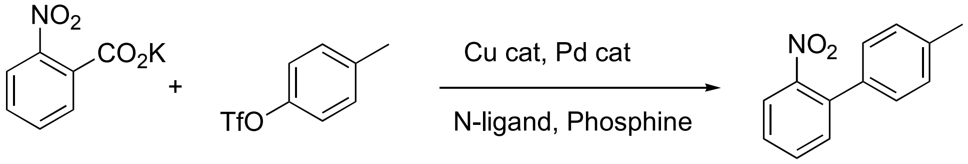
Reaction conditions: 1.00 mmol potassium 2-nitrobenzoate, 2.00 mmol 4-methylphenyl trifluoromethanesulfonate, 2.5 mol% CuI, 5 mol% 1,10-phenanthroline, 2 mol% Pd-source, 4 mL NMP, 170 °C, 1 h. Conversions were determined by GC analysis using *n*-tetradecane as internal standard.

In the absence of phosphine, the activity of [(CHT)PdBr$_2$]$_2$ (entry 8) was comparable to the conversion achieved with the corresponding PdBr$_2$ (entry 3), suggesting the retrosynthetic formation of the unsubstiuted precursor. Complex **2**, [(CPE)PdCl$_2$]$_2$ (entry 12), gave superior yields compared to the unsubsituted PdCl$_2$ (entry 4). Similarly promising results were observed for the non-classical N-heterocyclic carbene complexes **3** and **4** (entry 13 and 15).

Single turnovers were observed when the reaction was carried out with a non-activated carboxylic acid. This result was not surprising as copper-catalyzed protodecarboxylations of non-ortho-substituted benzoic acids are diminished by the addition of potassium halide formed in the decarboxylative cross-coupling as previously reported by Goossen and coworkers.[233] As such, studies were then extended to include the use of aryl triflates as halogen free coupling partners. The use of aryl triflates is not only advantageous from a green chemistry point of view because of the lower cost and facile handling of the carboxylative substrates as previously mentioned but also in that reactions occur without the addition of excess phosphine.[233] The presence of excess phosphine accelerates decomposition of complex **1** and results in the formation of the $[PdCl_2(PR_3)_2]$ and can retard the decarboxylation of non-activated carboxylates.

Selected results from screening experiments are summarized in Table 4.7. Preliminary experiments were focused on the coupling of 4-tolyltriflate with potassium 2-nitrobenzoate. When the carbocyclic carbene ligands are used, a 1:2 ratio (Pd:P) is required to achieve a similar activity to the standard bifunctional system (entries 1, 9 and 15) as would be expected for the in situ formation of the mononuclear catalytic precursor. This was not required for catalysts **3** and **4** as they are pre-formed and already bear a dissociating phosphine ligand (entries 17 and 19).

Table 4.7

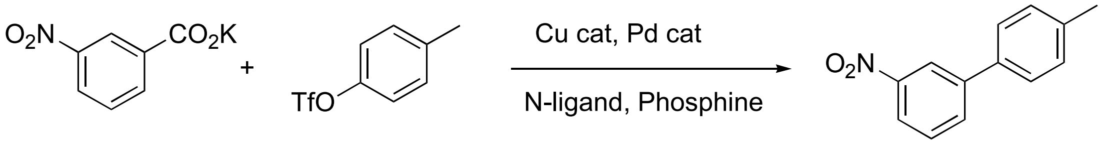


Entry	Pd-source	Phosphine	Yield/%
1	2 mol% PdI_2	3 mol% Tol-Binap	74
2	2 mol% PdI_2	6 mol% P(*p*-tol)$_3$	83
3	2 mol% PdI_2	4 mol% P(*p*-tol)$_3$	72
4	2 mol% PdI_2	2 mol% P(*p*-tol)$_3$	16
5	2 mol% $PdBr_2$	4 mol% P(*p*-tol)$_3$	59
6	2 mol% $PdBr_2$	2 mol% P(*p*-tol)$_3$	10
7	1 mol% 1	-	19
8	1 mol% 1	6 mol% P(*p*-tol)$_3$	81
9	1 mol% 1	4 mol% P(*p*-tol)$_3$	78
10	1 mol% 1	2 mol% P(*p*-tol)$_3$	48
11	2 mol% $PdCl_2$	4 mol% P(*p*-tol)$_3$	35
12	2 mol% $PdCl_2$	2 mol% P(*p*-tol)$_3$	19
13	1 mol% 2	-	9
14	1 mol% 2	6 mol% P(*p*-tol)$_3$	81
15	1 mol% 2	4 mol% P(*p*-tol)$_3$	78
16	1 mol% 2	2 mol% P(*p*-tol)$_3$	33
17	2 mol% **3**	-	77
18	1 mol% 3	2 mol% PPh_3	71
19	2 mol% **4**	-	76
20	2 mol% **4**	2 mol% PPh_3	66

Reaction conditions: 1.00 mmol potassium 2-nitrobenzoate, 2.00 mmol 4-methylphenyl trifluoromethanesulfonate, 2.5 mol% Cu_2O, 5 mol% 1,10-phenanthroline, 2 mol% Pd-source, 4 mL NMP, 170 °C, 1 h. Conversions were determined by GC analysis using *n*-tetradecane as internal standard.

Decarboxylative biaryl synthesis with meta- and para-substituted carboxylic acids are shown in tables 4.8 and 4.9, respectively.

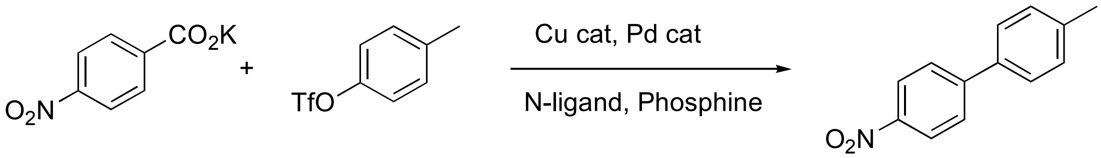
Table 4.8 Decarboxylative biaryl synthesis with non-ortho carboxylic acids.



Entry	Pd-source	Phosphine	Yield/ %
1	3 mol% PdI_2	4.5 mol% R-tol-BINAP	55
2	3 mol% PdI_2	6 mol% P(*p*-tol)$_3$	29
3	3 mol% PdI_2	3 mol% P(*p*-tol)$_3$	23
4	3 mol% $PdBr_2$	6 mol% P(*p*-tol)$_3$	24
5	3 mol% $PdBr_2$	3 mol% P(*p*-tol)$_3$	35
6	3 mol% $PdCl_2$	6 mol% P(*p*-tol)$_3$	42
6	1.5 mol% 1	6 mol% P(*p*-tol)$_3$	53
7	1.5 mol% 2	6 mol% P(*p*-tol)$_3$	47
8	3 mol% **3**	-	40
9	3 mol% **3**	6 mol% P(*p*-tol)$_3$	48
10	3 mol% **4**	-	47
11	3 mol% **4**	6 mol% P(*p*-tol)$_3$	50

Reaction conditions: 1.00 mmol potassium 3-nitrobenzoate, 2.00 mmol 4-methylphenyl trifluoromethanesulfonate, 7.5 mol% Cu_2O, 15 mol% 1,10-phenanthroline, 3 mol% Pd-source, 8 mL NMP, 170 ºC, 16 h. Conversions were determined by GC analysis using n-tetradecane as internal standard. Reactions run at 0.25 mmol-scale.

Table 4.9 Decarboxylative biaryl synthesis with non-ortho carboxylic acids.



Entry	Pd-source	Phosphine (eq)	Yield/%
1	3 mol% PdI_2	4.5 mol% R-tol-BINAP	55
2	1.5 mol% 1	6 mol% P(*p*-tol)$_3$	24
3	1.5 mol% 2	6 mol% P(*p*-tol)$_3$	41
4	3 mol% **3**	-	35
5	3 mol% **3**	6 mol% P(*p*-tol)$_3$	30
6	3 mol% **4**	-	37
7	3 mol% **4**	6 mol% P(*p*-tol)$_3$	37

Reaction conditions: 1.00 mmol potassium 4-nitrobenzoate, 2.00 mmol 4-methylphenyl trifluoromethanesulfonate, 7.5 mol% Cu_2O, 15 mol% 1,10-phenanthroline, 3 mol% Pd-source, 8 mL NMP, 170 °C, 16 h. Conversions were determined by GC analysis using *n*-tetradecane as internal standard.

4.2.4.1 Conclusions and outlook

In summary, the concept of using a carbocyclic carbene ligand for palladium as demonstrated here could open a new opportunity for the development of a novel Pd-catalyst for the Cu/Pd-catalyzed decarboxylative coupling. Though preliminary results are promising several challenges remain. Of particular concern is the rather excessive temperature required for catalysis. Trial reactions performed at lower temperatures were unsuccessful as the copper co-catalyst requires these extreme temperatures. Carbocyclic carbene complexes may be too fragile for these conditions, however, if a copper catalyst with a lower temperature of activation can be found, carboxylic carbene complexes may be ideal for this reaction. In this regard, work is currently under way with Yang Li and more weakly dissociating copper catalysts have been sent to Kaiserslautern for testing. Another area for optimization of this reaction would be in providing a vented reaction vessel. If the reaction temperature can be lowered, below the boiling point of the reactants, an open or vented vessel may provide enhanced yields in that the extrusion of CO_2 will be more facile, shifting reaction equilibrium to the products side of the reaction by Le Chatelier's principle.

5 Summary

This thesis is divided in to two main parts. Evaluation of existing catalytic reactions within a framework of green chemistry for the MTO and iridium NHC complexes is found section 2. The second part, covered in sections 3 and 4, focus on carbocyclic carbene synthesis and application of carbocyclic and non-classical N-heterocyclic carbene complexes in C-N cross coupling reactions and decarboylative byaryl synthesis, respectively.

In section 2.2, a tin free synthetic method to MTO, a valuable oxidation catalyst, was evaluated with green chemistry metrics and shown to be a more environmentally sound route (figure 5.1).[33b]

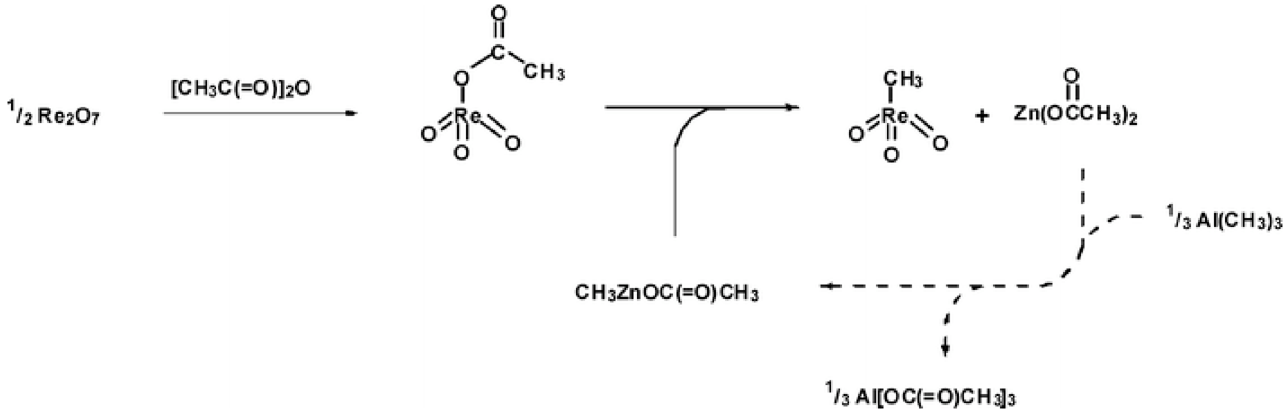


Figure 5.1

Chapter 2.3 describes the evaluation of the three-component system, MTO/H_2O_2/LiBr, used to prepare biodegradable oxidized starch super absorbers. In contrast to previous systems, a highly acidic reaction medium is avoided, thus limiting product depolymerisation to a low level. An optimized catalytic approach to make carboxy starch, which reduces overall reaction cost, and produces less harmful waste was elucidated and examined using the principles of green chemistry. An environmentally benign, catalytic oxidation process, applying the three-component system MTO/H_2O_2/LiBr to prepare biodegradable oxidized starch super absorbers with high water absorption capacity, was shown to be a more sustainable alternative to previously reported methods.[235]

The catalytic properties of the bridged and unbridged NHC complexes [Ir(COD)NHC(Cl)] and [Ir(COD)$(NHC)_2$][X] (X: I, PF_6, BF_4, CF_3COO, OTf) in C–H borylation reactions were evaluated in section 2.4. The C–H borylation of aromatic carbons with bis(pinacolato)diboron and pinacolborane were preformed with microwave technology which was shown to facilitate a time efficient screening of a wide range of influences such as ligand σ-donor strength and structural motif as well as the effects of the complex counter ion and furthermore provide an energy efficient heating source. A catalyst featuring a chelating NHC ligand, proved to be the most effective catalyst and further investigations with this complex in the borylation of mono- and disubstituted benzene derivatives exploring chemo- and regioselectivity were undertaken.[236]

In the second part of my thesis, a search for efficient synthetic strategies to generate novel carbocyclic carbene complexes for catalysis was undertaken (section 3.3). A systematic overview of carbocyclic carbene complexes from the synthetic methods employed for preparation, unique structure and bonding features to reactivity provides a basis to discuss synthetic attempts. Synthesis of the dinuclear palladium complex $[PdCl_2(L)]_2$ (L = dibenzocycloheptenylidene), shown in figure 5.2 was successful via oxidative addition to Pd(0). As a result of extremely poor solubility further synthetic attempts employing this complex as a precursor to prepare mononuclear palladium compounds with the addition of a phosphine proved unsuccessful and resulted in the production of $[PdCl_2(PPh_3)_2]$. Upon addition to acetonitile the mononuclear compound is formed, but adding phosphine again resulted in the formation of $[PdCl_2(PPh_3)_2]$. To enhance solubility, possibly limited by π-stacking of the aromatic system in the solid state, a methyl substituted benzosubstituted seven membered carbocyclic carbene complex, also shown in figure 5.3, was synthesized. Unfortunately, solubility and decomposition pathways for this system were shown to be analogous to that of the unsubstituted system and these novel complexes were only studied briefly in catalysis as the limited solubility resulted in next to no catalytic activity.

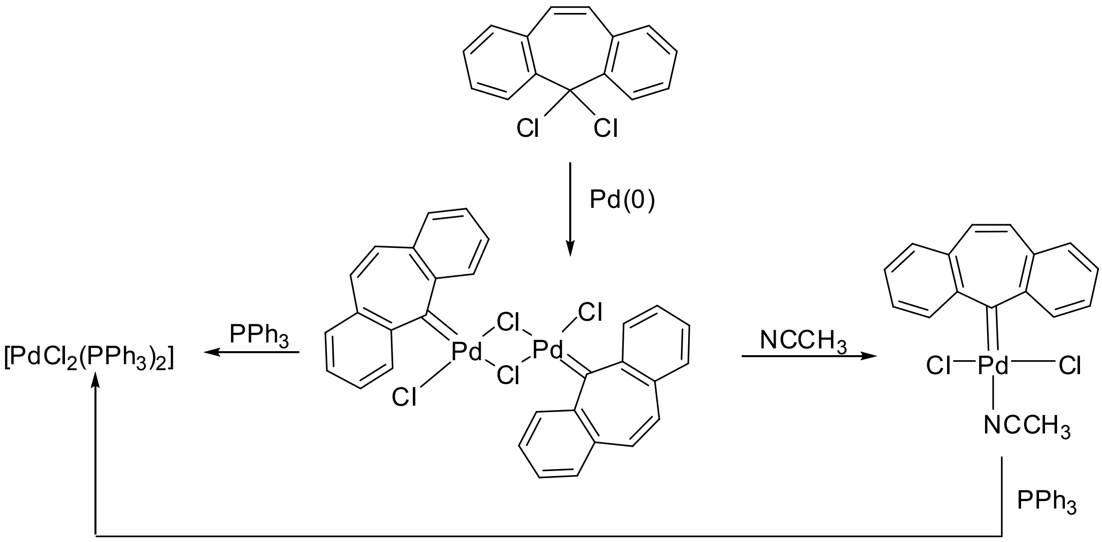


Figure 5.2

Extending the catalytic applications of carbocyclic carbenes, palladium complexes bearing cycloheptatrienylidene carbene ligands were shown to be effective catalysts for C–N coupling (section 4.2.3.1). Catalytic performance, was directly compared to the analogous 2,3-diphenyl cyclopropenylidene complexes. Though the three- and seven- membered carbocyclic carbene systems were shown to be less active or stable than analogous NHC complexes for C–N coupling, these investigations provide useful insight in and comparative data about this relatively unexplored ligand class (figure 5.3).[87] The seven-membered ring complexes were shown to be more catalytically active with the exception of the dibenzosubstituted cycloheptatriene carbene complexes.

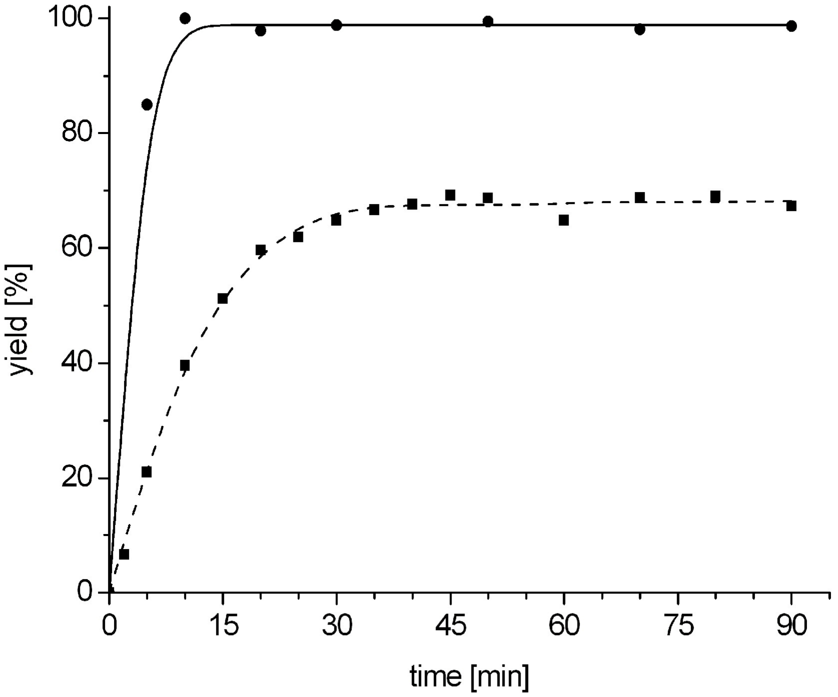


Figure 5.3. Yield vs. time plot at room temperature for the coupling of p-bromo benzotrifluoride (1.0 mmol) with morpholine (1.2 mmol) catalyzed by **1** (—●—) and **5** (--■--) *in situ* with 1.0 equiv P^{t}Bu$_3$ (other conditions: 2 mol % Pd, 1.4 mmol NaO^{t}Bu, 8 ml toluene; GC yield with *n*-eicosane as the internal standard).

Investigations of catalyzed C–N coupling reactions were also extended to include non-classical NHC systems.[237] Remote N-heterocyclic carbene palladium complexes were shown to be effective C–N coupling catalysts, however there were no observed effects upon varying the proximity of the π–electron donor, substitution at the carbene moiety or when changing the complex counter ion (section 4.2.4.3).

The catalytic applicability of carbocyclic carbene and remote N-heterocyclic carbene palladium complexes were further expanded to include Cu/Pd-catalyzed decarboxylative coupling (section 4.2.4, Figure 5.4). Although preliminary catalytic results are promising, the stability of the carbene must be enhanced, possibly through alternative substitution, or reaction conditions must be modified for this system to be worthwhile, more weekly dissociating copper catalysts have been sent to collaborators and testing is ongoing.

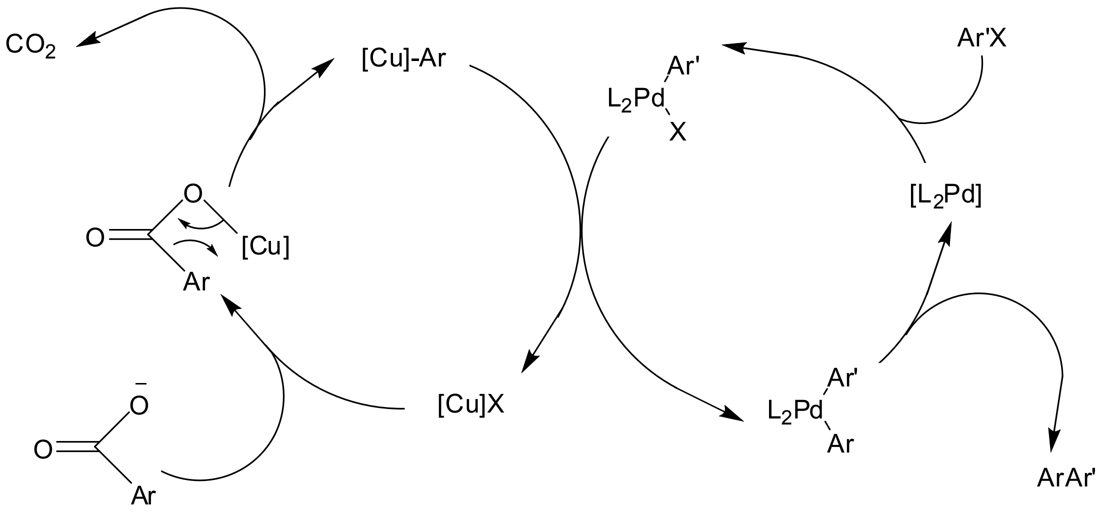


Figure 5.4

6 Experimental

6.1 Methods and Handling of Chemicals

Synthesis, storage and characterization of air and moisture sensitive compounds were preformed under an argon atmosphere using standard Schlenk techniques or a glove box. Distillation, sublimation, and removal of volatiles were preformed under vacuum generated by an oil pump (0.1 mbar).

Solvents were dried using an alumina/copper-based solvent purification system or standard procedures and stored over molecular sieves. Solvents used in reactions where carbocyclic or free carbene generation was expected were distilled just before use. Solvents used in catalytic testing were distilled 24 hours before use. Deuterated solvents used in NMR scale reactions were dried over NaK and distilled prior to use.

Preparative flash chromatography was preformed using 30 to 100 fold excess on silica gel 60 (Merck) or with basic alumina (Aldrich), with a 1.3 bar overpressure where noted. All other materials used were obtained from commercial sources and used as delivered unless otherwise noted.

6.2 Techniques Used for Characterization

6.2.1 Elemental analysis

Elemental analyses were carried out in the microanalytical laboratory of the Anorganisch-chemisches Institut at the Technischen Universitaet Muenchen.

6.2.2 Gas Chromatography Mass Spectrometry

A Varian CP-3800 gas chromatograph coupled with a mass spectrometer (electron impact source, 70 eV), GC/MS, was used for identification of organic products as well as inorganic decomposition products. A VF-5mf (length 30m, inner diameter 0.25 mm, film thickness 0.25 μm) column was used to facilitate separation, helium was employed as the carrier gas, and injection port temperature split injector flow, and temperature ramp were varied to optimize peak separation with a minimum run time. Resulting mass spectra were matched to the information contained in the instrument spectral library to elucidate molecules present in the reaction mixture. A GC/MS/MS was carried out under similar conditions on a Varian CP-3800 1200L quadrupole MS/MS in parent-daughter mode to further identify organic molecules.

6.2.3 Gas Chromatography Flame Ionization Detection

A Varian CP-3800 gas chromatograph coupled with a flame ionization detector was used for quantification of organic products and reactants in catalytic tests. A VF-5mf (length: 30m, inner diameter: 0.25 mm, film thickness: 0.25 μm) column was used to facilitate separation, helium was employed as a carrier gas, and injection port temperature split injector flow, and temperature ramp were varied to optimize peak separation with a minimum run time were kept consistent among comparative runs.

6.2.4 Infrared spectroscopy

Infrared spectra were recorded on a JASKO FT/IR4000 spectrometer, bands were reported in wavenumbers (cm^{-1}). Samples of isolated air and water stable compounds were measured as KBr pellets or made up in a solvent and a dilute solution was evaporated on a thin film of Teflon. IR spectra of these compounds as well as more sensitive compounds were also run in solution using a KBr plate solution cell in various solvents.

6.2.5 Mass spectrometry

Mass spectra preformed by the laboratory of the Anorganisch-chemische Institut at the Technischen Universitaet Muenchen were measured on either a Finnigan MAT-90 or MAT-331. Ionisation techniques used included electron impact (70 electron volts), chemical ionization (with isobutene reaction gas, in both positive and negative ion mode) as well as fast atom bombardment (with 4-nitrobenzylalcohol). Mass spectra are presented in the standard form, m/z (percent intensity relative to the base peak).

6.2.6 Melting point

A Reichter Thermovar (Type 300429) instrument was used for the determination of melting points.

6.2.7 Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) were recorded on a Jeol-JNM-GX-270, Jeol-JNM-GX-400 or a Bruker AMX-400 spectrometer operating on the frequencies shown in table 6.1. Residual solvent signals for acetonitrile (1.94/118.1), benzene (7.15/128), chloroform (7.25/77.2), dichloromethane (5.31/53.80) and dimethylsulfoxide (2.5/39.52) were used as internal standards for $^1H/^{13}C$-NMR. Aqueous H_3PO_4 (85%) was used as an external standard to reference the ^{31}P-spectra.

Table 6.1. Operating frequencies of NMR spectrometers used

NMR	^1H/MHz	^{13}C/ MHz	^{31}P/ MHz
Bruker AMX-400	400.13	100.61	161.98
Jeol-JNM-GX-270	270.16	67.93	109.37
Jeol-JNM-GX-400	399.80	100.51	161.83

Chemical shifts, σ, are given in ppm relative to the operating frequency of the spectrometer used. Hyperfine splitting is described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (p), septet (sept), multiplet (m), broad signal (br) and coupling constants are given in Hz.

6.2.8 Thermogravimetric mass spectrometry

Thermogravimetric mass spectrometry (TG-MS) were preformed on a Netzsch TG209 system using ~10 mg sample heated at a ramp of 10 K per minute under argon from 35 °C to a maximum of 1000 °C.

6.2.9 Thin layer chromatography

Thin layer chromatrography was used to track the progress of air and moisture stable organic targets. Aluminum plates Merck coated with silica 60 F254 were used and a UV lamp (254 nm) or iodine vapors were employed to identify spots.

6.2.10 X-ray analysis

X-ray analysis were carried out by Dr. E. Herdtweck in the Anorganisch-chemische Institut at the Technischen Universitaet Muenchen. The single-crystal X-ray diffraction experiment was performed using a Bruker APEX2 diffractometer equipped with a Mo-anode (Mo-K_α radiation: λ= 7.1073 Å).

6.3 Working Procedures

6.3.1 Calculation of Atom Economy

$$\text{Atom Economy} = \frac{\text{Molecular Weight of Products}}{\text{Molecular Weight of Reactants}} *100\%$$

For:

$$O(ReO_3)_2 \xrightarrow[2)\ 2\ Sn(CH_3)_4]{1)\ O(F_3CO)_2} 2\ ReO_3CH_3 + 2\ (CH_3)_3SnOCOCF_3$$

$$\text{Atom Economy} = \frac{mw(ReO_3CH_3)}{mw\ (1/2\ O(ReO_3)_2) + mw\ (1/2\ O(F_3CO)_2) + mw(Sn(CH_3)_4)} *100\%$$

$$= \frac{735.84}{(1/2*485.88) + (1/2*185.98) + (180.00)} *100\%$$

$$= 37.5\ \%$$

Care was taken to minimize unnecessary consumption of reagents, solvents, energy and consumables. Column purification was avoided in favor of other purification techniques such as sublimation when everpossible. In addition the deprotection of 10-methyl-5H-dibenzo[a,d]cyclohepten-5-acetal in the synthesis of 5,5-dichloro-10-methyl-5H-dibenzo[a,d]cycloheptene (further discussed in section 6.3.2) was avoided entirely.

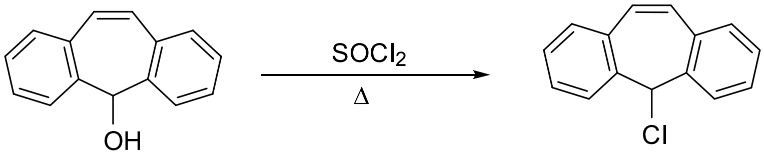
6.4 Synthesis of ligand precursors and organometallic compounds

Most compounds were synthesized via modified literature procedures as shown in table 6.2.

Table 6.2 Summary table of ligand precursors and organometallic compounds

Compound number	Name	Modified from reference
6.4.1	Dibenzo[a,d]cyclohepten-5-yl-chloride	238
6.4.2	5H-Dibenzo[a,d]tropylium tetrafluoroborate	238
6.4.3	10,11-Dibromo-10,11-dihydro-5H-dibenzo[a,d]cyclohepten-5-one	239
6.4.4	10-bromo-5H-dibenzo[a,d]cyclohepten-5-one	239
6.4.5	10,10,11-Dibromo-11-hydro-5H-dibenzo[a,d]cyclohepten-5-one	239
6.4.6	10,11-Dibromo-5H-dibenzo[a,d]cyclohepten-5-one	239
6.4.7	10-Bromo-5H-dibenzo[a,d]cyclohepten-5-acetal	240
6.4.8	10-Methyl-5H-dibenzo[a,d]cyclohepten-5-acetal	240
6.4.9	10-Methyl-5H-dibenzo[a,d]cyclohepten-5-one	240
6.4.10	7,7-Dichlorocycloheptatriene	242
6.4.11	5,5-Dichloro-5H-dibenzo[a,d]cycloheptene	243
6.4.13	5-Thioxo-10,11-dihydro-5H-dibenzo[a,d]cycloheptene	241
6.4.14	Pentacarbonyl(tetrahydrofuran)tungsten	244
6.4.15	Pentacarbonyl(cyclooctene)tungsten	245
6.4.16	Pentacarbonyl(diethylether)tungsten	246
6.4.17	Pentacarbonyl(pyridine)tungsten	247,248
6.4.18	Pentacarbonyl(2-picoline)tungsten	247,248
6.4.19	Tetracarbonyl di(pyridine)tungsten	247,248
6.4.20	Tetracarbonyl di(2-picoline)tungsten	247
6.4.21	Tetracarbonyl di(2-picoline)molybdenum	247
6.4.22	*bis*-Dichlorocycloheptatrienylidenepalladium	115
6.4.23	*bis*-(Dichloro(5H-dibenzo[a,d] cycloheptenylidene)palladium)	115
6.4.24	*bis*-(Dichloro(10-methyl-5H-dibenzo[a,d]cycloheptenylidene) palladium)	115

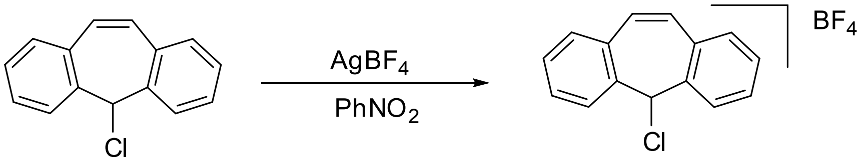
6.4.1 Dibenzo[a,d]cyclohepten-5-yl-chloride[238]



2.0 g (9.6 mmol) of dibenzo[a,d]cyclohepten-5-ol was dissolved in 10 mL of $SOCl_3$. This mixture was refluxed for 15 minutes at 75 ºC, and the solvent removed at reduced pressure. The resulting off white residue was triturated with 12 mL CCl_4 yielding the pure colorless product as a precipitate. A new peak in the ^{13}C-NMR at $\delta = 92.3$ ppm confirms the product synthesis.

Yield: 82% (1.62g, 7.8 mmol)

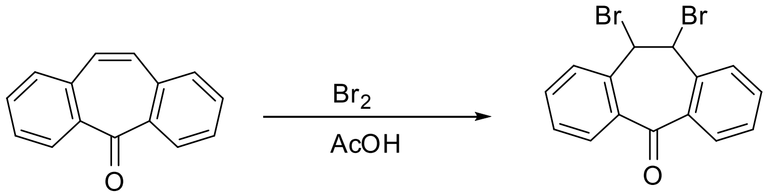
6.4.2 5H-Dibenzo[a,d]tropylium tetrafluoroborate[238]



0.86 g (4.4 mmol) of $AgBF_4$ was dissolved in 20 mL toluene. To this solution 1.0 g (4.4 mmol) of dibenzo[a,d]cyclohepten-5-yl-chloride in 10 mL of PNO_2 was added. The solution changed from colorless to red. After 3 hours of stirring, the red solution was filtered via canula, and recrystalised yielding fine red needles. Product synthesis was confirmed by ^{1}H- and ^{13}C-NMR spectroscopy which showed chemical shifts similar to the ClO_4 analogue.

Yield: 20% (0.39 g, 1.1 mmol)

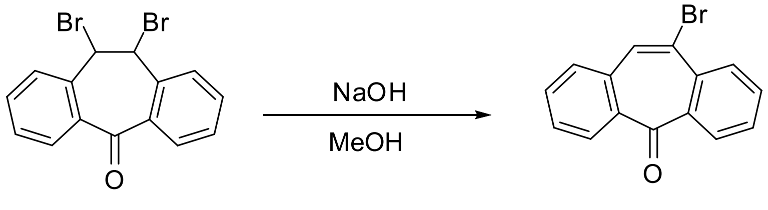
6.4.3 10,11-Dibromo-10,11-dihydro-5H-dibenzo[a,d]cyclohepten-5-one[239]



4 mL of bromine in 50 mL of glacial acetic acid was added dropwise to a suspension of 5H-dibenzo[a,d]cyclohepten-5-one(10 g, 0.049 mol) in 80 mL glacial acetic acid. The solution was allowed to stir at room temperature over night, filtered and the resulting colorless crystals washed with 3 x 15 mL diethylether. The product was confirmed by presence of peaks at 5.79 ppm and 52.8 ppm in the ^{1}H- and ^{13}C-NMR, respectively.

Yield: 51% (9.46 g, 0.026 mol)

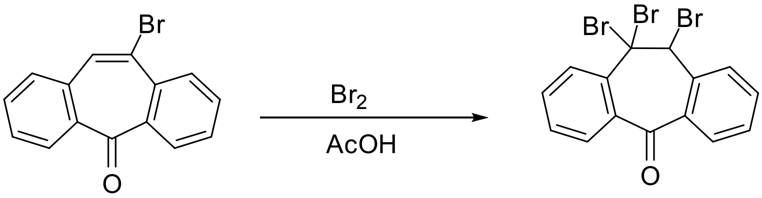
6.4.4 10-bromo-5H-dibenzo[a,d]cyclohepten-5-one[239]



8 g (0.022 mol) of 10,11-Dibromo-10,11-dihydro-5H-dibenzo[a,d]cyclohepten-5-one was refluxed in 175 mL methanol with 2.6 g of NaOH for 3 hours. The solution was filtered while hot and then allowed to cool to room temperature. After removing the solvents under reduced pressure, the residue was recrystallised from methanol to yield the desired ketone. Successful conversion was confirmed by NMR.

Yield: 82 % (5.12g, 0.018 mol)

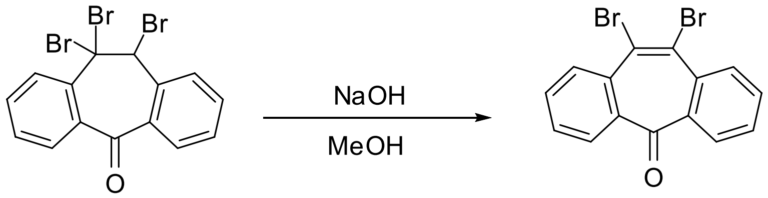
6.4.5 10,10,11-Dibromo-11-hydro-5H-dibenzo[a,d]cyclohepten-5-one[239]



4 mL of bromine in 50 mL of glacial acetic acid was added dropwise to a suspension of 10-bromo-5H-dibenzo[a,d]cyclohepten-5-one (10 g, 0.035 mol) in 80 mL glacial acetic acid. The solution was allowed to stir at room temperature over night. After filtration the resulting colorless crystals were washed with 3 x 15 mL diethylether. The synthesis was confirmed by ^{13}C-NMR in the appearance of two new peaks at 67.4 and 64.7 ppm corresponding to the bromo substituted carbons.

Yield: 81% (12.67g, 0.028 mol)

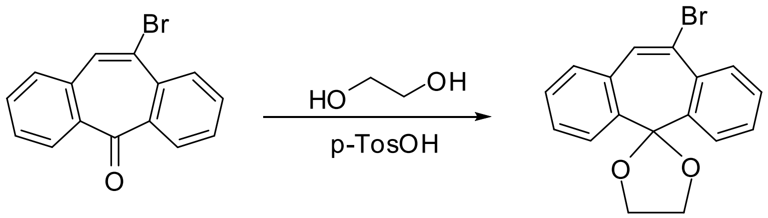
6.4.6 10,11-Dibromo-5H-dibenzo[a,d]cyclohepten-5-one[239]



A mixture of 8 g (0.018 mol) of 10,10,11-tribromo-11-hydro-5H-dibenzo[a,d]cyclohepten-5-one and 2.6 g of NaOH was refluxed in 175 mL methanol for 3 hours. The solution was filtered while hot, upon cooling the volatiles were removed under reduced pressure and the powder was recrystallised from methanol to yield the pure product. Successful conversion was confirmed by NMR.

Yield: 36 % (2.4 g, 0.0065 mol)

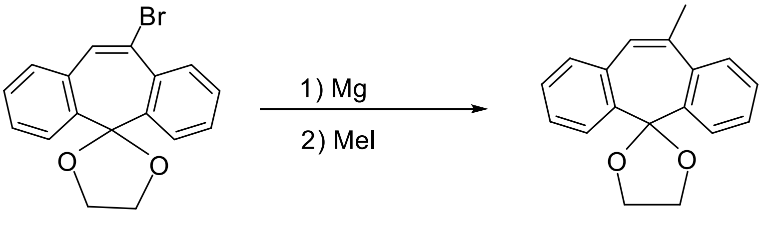
6.4.7 10-Bromo-5H-dibenzo[a,d]cyclohepten-5-acetal[240]



9.0 mL ethelene glycol, and 0.180 g p-toluenesulphonic acid were added to a solution of 2.50 g (8.8 mmol) 10-Bromo-5H-dibenzo[a,d]cycloheptene-5-one in 180 mL benzene. The reaction mixture was then refluxed, in an apparatus fitted with a dean stark apparatus, for 3 days, allowed to cool to room temperature, then neutralized with 2.5 mL of triethyl amine. The organic solution was washed with 3 x 50 mL distilled water, and the organic products were extracted with 200 mL dichloromethane. Combined organic layers were dried over sodium sulphate, filtered and the solvent was removed under reduced pressure. The crude product, an off white powder was further purified by sublimation (160 ºC at 0.5 mbar) to yield a colourless crystalline product. ^{13}C- and ^{1}H-NMR spectra confirm the successful synthesis of the target compound, where ^{1}H NMR of the products confirmed the presence of the protecting group (seen in the appearance of a new chemical shift at 3.72 ppm and 4.18 ppm) and the disappearance of the carbonyl carbon in the ^{13}C-NMR due to the formation of an acetal.

Yield: 50 % (1.43 g, 4.4 mmol)

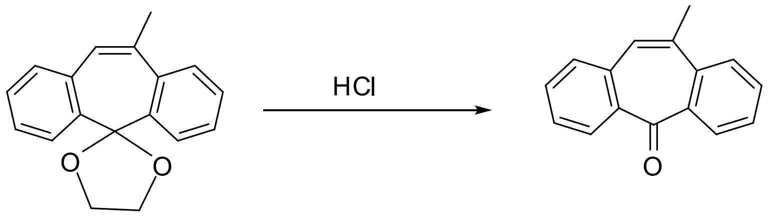
6.4.8 10-Methyl-5H-dibenzo[a,d]cyclohepten-5-acetal[240]



0.4 g of magnesium turnings were placed in a round bottomed Schlenk flask and heated whilst stirring for two hours to remove all moisture. Once the flask was cooled the, two crystals of iodine were added and the flask was evacuated and briefly heated. 20 mL of freshly distilled THF were added, followed by the dropwise addition of 1.43 g (4.4 mmol) of 10-Bromo-5H-dibenzo[a,d]cyclohepten-5-acetal in 30 mL THF. The suspension was stirred for a 3 hours at 50 °C, then filtered, treated with 0.5 methyl iodide and allowed to stir overnight. The solvent was removed under reduced pressure, and the residue dissolved in a mixture of 50 mL THF and 50 mL H_2O. After extracting the product with 200 mL diethylether, and drying the combined organic layers over sodium sulphate, the solvents were removed to yield pale orange crystals. ^{13}C-NMR spectra of the product show the incorporation of a methyl group in the presence of a new signal at δ = 24.7 ppm.

Yield: 82 % (0.886 g, 3.6 mmol)

6.4.9 10-Methyl-5H-dibenzo[a,d]cyclohepten-5-one[240]

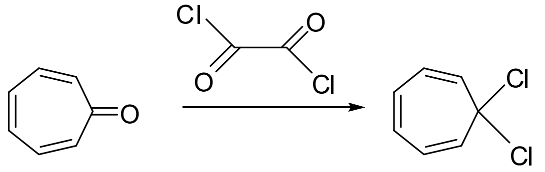


15 mL 6 M hydrochloric acid was added to a solution containing 10-Methyl-5H-dibenzo[a,d]cyclohepten-5-acetal (0.85 g, 3.4 mmol) dissolved in 30 mL THF. The mixture was refluxed for 12 hours, allowed to cool to room temperature and neutralized with a 20 % aqueous solution of sodium hydroxide. Ethyl acetate was used to extract the product from the aqueous phase. The combined organic layers were dried over sodium sulphate before

removal of the solvent under reduced pressure. The resulting dark brown oil was distilled under reduce pressure to yield a very small amount of 10-Methyl-5H-dibenzo[a,d]cyclohepten-5-one confirmed by ^{13}C-NMR in the observation of the carbonyl carbon. As yield was extremely low, this method was not repeated and instead chlorination from the acetal was done directly.

Yield: trace

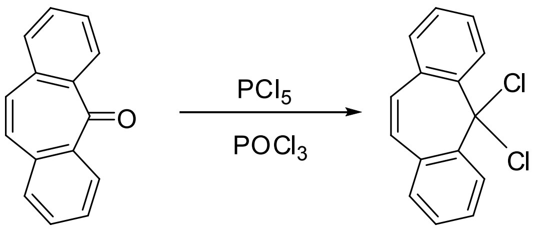
6.4.10 7,7-Dichlorocycloheptatriene[242]



This compound was prepared according to literature methods, in combination with in house standard operating procedure, communicated by Christian Taubmann. 1 mL (1.09 g, 11 mmol) tropone was added dropwise to a solution of 1.20 mL (1.77 g, 14 mmol) oxalyl chloride in 20 mL of dichloromethane at -50 ºC. The solution was stirred and allowed to warm to room temperature over the course of 3 hours. Removal of the solvent under reduced pressure afforded the yellow powder which was further purified by recrystallization from dichloromethane/hexanes.

Yield: 47 % (0.82 g, 5.2 mmol)

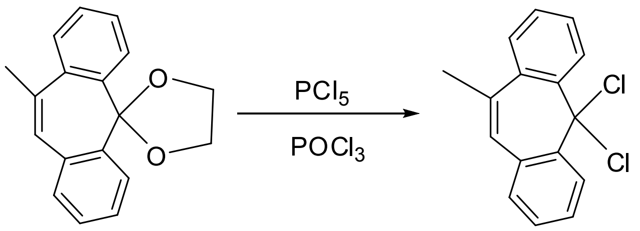
6.4.11 5,5-Dichloro-5H-dibenzo[a,d]cycloheptene[243]



5.0 g (24 mmol) of 5H-dibenzo[a,d]cyclohepten-5-one and 5.0 g PCl_5 were dissolved in 25 mL $POCl_3$. The solution was heated at 120 ºC for 4 hours and then cooled to room temperature. The solvent was removed to minimum volume (~ 3 mL) and the product precipitated as a white crystalline solid upon the addition of petroleum ether and cooling at – 40 ºC overnight. Product synthesis was confirmed by ^{13}C-NMR in the disappearance of the carbonyl carbon signal and the appearance of a new signal at 67.9 ppm which corresponds to the carbon bearing two chlorines.

Yield : 70 % (4.42 g, 17.0 mmol)

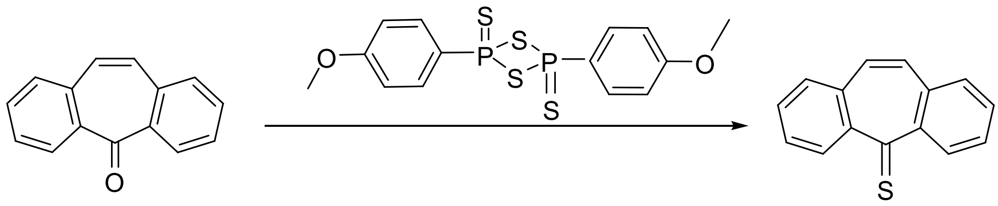
6.4.12 5,5-Dichloro-10-methyl-5H-dibenzo[a,d]cycloheptene



This compound was prepared via the procedure shown above using 2.0 g (7.5 mmol) of 10-Methyl-5H-dibenzo[a,d]cyclohepten-5-acetal and 2.0 g PCl_5 and 20 mL $POCl_3$. Product synthesis was confirmed by ^{13}C-NMR in the disappearance of the carbonyl carbon signal, and the lack of protons corresponding to the acetal functionality in the ^{1}H-NMR.

Yield : 20% (0.41 g, 1.5 mmol)

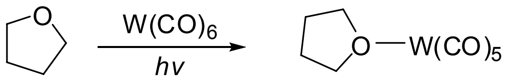
6.4.13 5 -Thioxo-10,11-dihydro-5H-dibenzo[a,d]cycloheptene[241]



0.5 g of Lawesons reagent was added to a solution containing 5.0 g (24 mmol) of dibenzo[a,d]cyclohepten-5-one dissolved in 100 mL toluene. This mixture was then refluxed for 4.5 hours changing in colour over the course of the reaction from white/colourless to black/green. After cooling to room temperature the precipitate which had formed was filtered and washed with 3 x 15 mL hot toluene. The solvent was removed from the combined toluene layers under reduced pressure to yield a green residue which was purified via column chromotography (silica gel, CH_2Cl_3:C_6H_6). Product synthesis was confirmed by ^{13}C-NMR which showed a loss of the signal for the carbonyl and the appearance of a chemical shift at 128.6 ppm.

Yield: 18 % (0.971 g, 4.4 mmol)

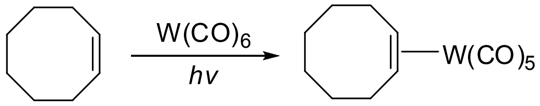
6.4.14 Pentacarbonyl(tetrahydrofuran)tungsten[244]



2.0 g (5.7 mmol) tungsten hexacarbonyl was added to 500 mL of freshly distilled THF in a reaction flask fitted with a mercury lamp. The reaction progress was tract via the carbonyl stretching frequencies. The solution was irradiated for one hour at room temperature. The IR indicated complete conversion after one hour with no visible decomposition products (observed by IR, V_{co}/cm^{-1}: 2077(w), 1928(vs), 1890(m)).

Yield: quantitative (2.25g, 5.7 mmol)

6.4.15 Pentacarbonyl(cyclooctene)tungsten[245]



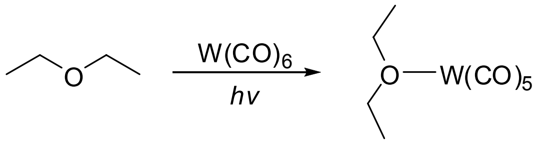
2.0 g (5.7 mmol) tungsten hexacarbonyl and 1.5 mL cyclooctene (6.0 mmol) (passed over an Al_2O_3) were added to 500 mL of freshly distilled hexane in a closed reaction flask fitted with a mercury lamp. The solution was cooled with an ice bath and irradiated for four hours. After irradiation the solution was filtered to remove insoluble side products and then cooled to –

78 ºC, to afford the pentacarbonyl product (observed by IR, V_{co}/cm^{-1}: 2078(w), 1958(vs), 1946(m)) with small amounts of $[W(CO)_4(COE)_2]$ as impurities.

Yield: 55 % (1.37 g, 3.1 mmol)

An alternative synthesis, starting from $[W(CO)_5(THF)]$ tungsten, was the addition of equimolar cyclooctene resulted, but in a mixture of products including the retrosynthetic precursor tungsten hexacarbonyl. As such this synthetic route was abandoned.

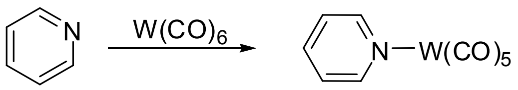
6.4.16 Pentacarbonyl(diethylether)tungsten [246]



1.0 g (2.9 mmol) tungsten hexacarbonyl was added to 220 mL of diethyl ether in a reaction flask fitted with a mercury lamp at -20 ºC. The solution was irradiated for eight hours. The IR spectra indicated complete conversion after eight hours with no visible decomposition products. Product formation confirmed by IR (observed by IR, V_{co}/cm^{-1}: 2073(w), 1928(vs), 1893(m)).

Yield: quantitative (1.13 g, 2.9 mmol)

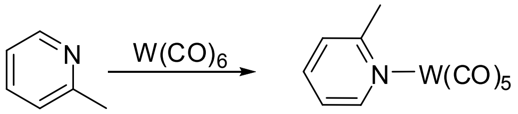
6.4.17 Pentacarbonyl(pyridine)tungsten [247, 248]



1.0 g [$W(CO)_6$] (2.9 mmol) was refluxed in 10 mL pyridine. In a closed vessel for 2 hours, monitoring the volume of gas evolved the reaction mixture changed from colourless to yellow, then to dark red within 30 minutes of heating. The reaction progress was also monitored using infrared spectroscopy in the carbonyl stretching region. When one molar equivalent of CO gas had been displaced, the reaction was stopped. Product formation confirmed by IrV_{co}/cm^{-1}: 2075(s),1929(vs).

Yield: 78 % (0.91 g, 2.3 mmol)

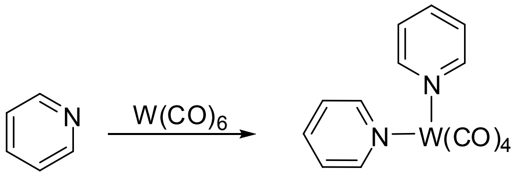
6.4.18 Pentacarbonyl(2-picoline)tungsten [247, 248]



1.0 g (2.9 mmol) [$W(CO)_6$] was refluxed in 10 mL pyridine for 2 hours. In a closed vessel, monitoring the volume of gas evolved, the reaction mixture changed from clear to yellow, then to dark red within 30 min of heating. The reaction progress was also monitored using infrared spectroscopy in the carbonyl stretching region. When one molar equivalent of CO gas had been displaced, the reaction was stopped. Product formation confirmed by IR, V_{co}/cm^{-1}: 2071(s),1927(vs).

Yield: 76 % (0.92 g, 2.2 mmol)

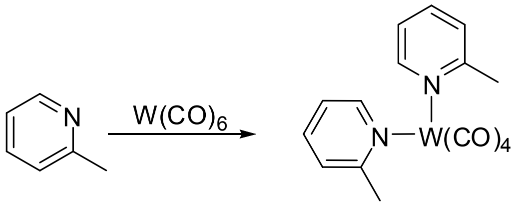
6.4.19 Tetracarbonyl di(pyridine)tungsten[247, 248]



1.0 g (2.9 mmol) [$W(CO)_6$] was refluxed in 10 mL pyridine for 6 hours. The reaction mixture changed from colorless to yellow, then to dark red within 30 minutes of heating. The reaction progress was monitored using infrared spectroscopy in the carbonyl stretching region. Upon completion of the reaction, 20 mL of hexane was added, precipitating pentacarbonyl(pyridine)tungsten as orange crystals. V_{co}/cm^{-1}: 2008(m), 1876(s), 1868(sh), 1828(m).

Yield: 78 % (1.03 g, 2.3 mmol)

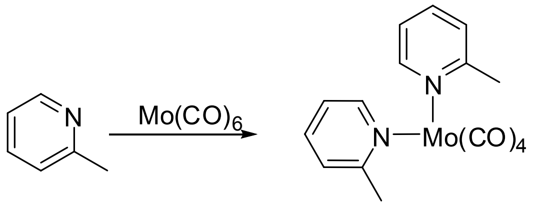
6.4.20 Tetracarbonyl di(2-picoline)tungsten[247]



1.0 g (2.9 mmol) $[W(CO)_6]$ was refluxed in 10 mL picoline for 3.5 hours. The reaction mixture changed from colorless to yellow, then to dark orange within 30 minutes of heating. The reaction progress was monitored using infrared spectroscopy in the carbonyl stretching region. Upon completion of the reaction, 20 mL of hexanes were added, precipitating pentacarbonyl(2-picoline)tungsten as yellow crystals. V_{co}/cm^{-1}: 2006(m), 1870(s), 1870(sh), 1825(m). Elemental analysis: actual: 39.86 2.93 5.81 found: 39.68 2.90 5.73

Yield: 70% (0.95g, 2.0 mmol)

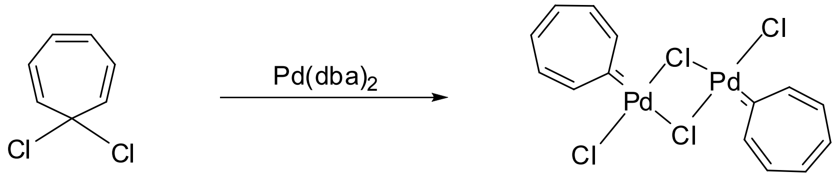
6.4.21 Tetracarbonyl di(2-picoline)molybdenum[247]



1.0 g (3.8 mmol) $[Mo(CO)_6]$ was refluxed in 10 mL picoline for 3.5 hours. The colorless reaction mixture turned from yellow to dark orange within 30 minutes of heating The reaction progress was monitored using infrared spectroscopy in the carbonyl stretching region. Upon completion of the reaction, 20 mL of hexanes were added, to precipitate pentacarbonyl(2-picoline)tungsten as yellow crystals. V_{co}/cm^{-1}: 2006(m), 1870(s), 1870(sh), 1825(m). Elemental analysis: actual 48.06 3.58 7.11 found 47.75 3.55 6.64

Yield: 28 % (0.43 g, 1.1 mmol)

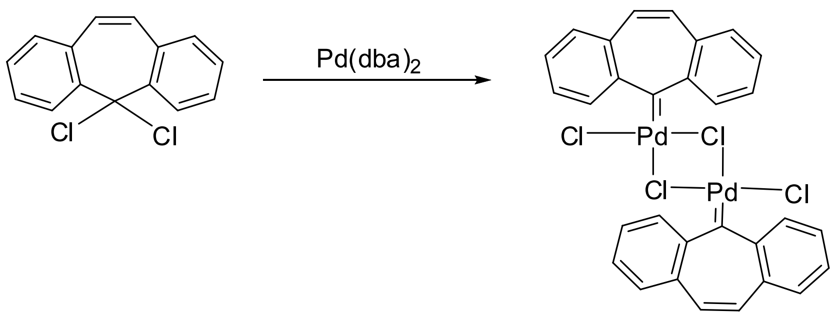
6.4.22 *bis*-Dichlorocycloheptatrienylidenepalladium[115]



60 mg (0.38 mmol) 7,7-Dichlorocycloheptatriene was added to a cooled solution of 0.200 g (0.35 mmol) [Pd(dba)$_2$] in toluene at – 60 ºC. The solution was allowed to warm to room temperature and stirred overnight. The resulting yellow precipitate was separated from the mother liquor, washed with 2 x 5 mL cold toluene and dried under reduced pressure to yield the desired product.

Yield: 70 % (0.130 g, 0.24 mmol)

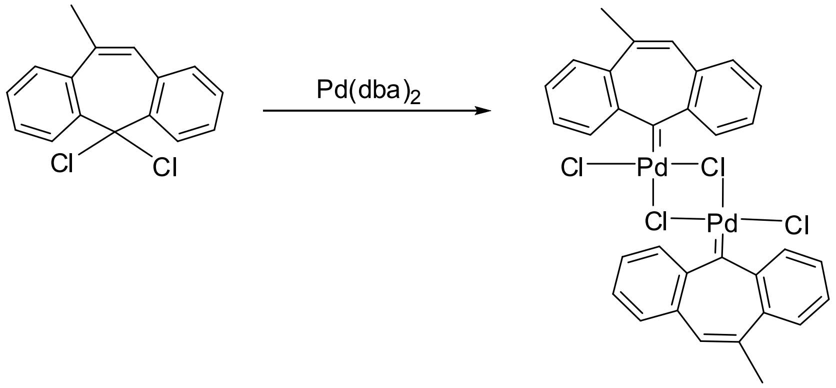
6.4.23 *bis*-(Dichloro(5H-dibenzo[a,d] cycloheptenylidene) palladium)[115]



0.085 g (0.32 mmol) 5,5-dichloro-5H-dibenzo[a,d]cycloheptene was added to a dark purple solution containing 0.170 g (0.30 mmol) [Pd(dba)$_2$] dissolved in 10 ml dry benzene. After stirring for 5 minutes the color of the solution changed to dark red/brown and a precipitate formed. The solution was allowed to stir for an additional 12 hours and then the precipitate was separated by filtration and washed with 2 x 2mL of benzene and 2 x 2mL of diethylether. After drying on under reduced pressure for 2 hours the sample was weighed. The product was found to be insoluble in hydrocarbon solvents as well as dichloromethane and decomposed in DMSO to give the retrosynthetic subterone. Although the product was, slightly soluble in acetonitrile, however attempts to obtain an adequate, observing the carbene carbon signal, ^{13}C-NMR were not successful. Values obtained by elemental analysis (expected: C: 49.00 H: 2.74 found: C: 46.99 H:2.39) suggest that there may be palladium black present in the sample.

Yield: 38 % (0.088g, 0.12 mmol)

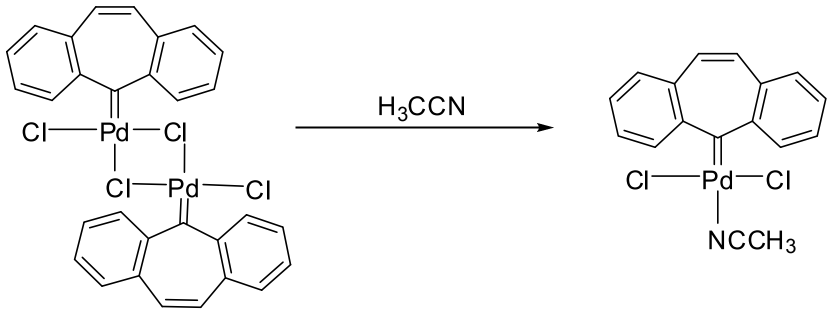
6.4.24 *bis*-(Dichloro(10-methyl-5H-dibenzo[a,d]cycloheptenylidene) palladium)[115]



0.100 g (0.17 mmol) [Pd(dba)$_2$] was dissolved in 10 ml benzene. To this dark purple solution, 0.050 g (0.18 mmol) 5,5-dichloro-10-methyl-5H-dibenzo[a,d]cycloheptene was added, and after stirring for 5 minutes the solution turned to a dark red/brown color and a precipitate formed. The solution was allowed to stir for an additional 12 hours and then the precipitate was separated by filtration and washed with 2 x 2mL of benzene and 2 x 2mL of diethylether. After drying on the under reduced pressure for 2 hours the sample was weighed. The product was found to be insoluble in hydrocarbon solvents as well as dichloromethane and decomposed in DMSO to give the retrosynthetic subterone. The product was also insoluble in acetonitrile.

Yield: 21 % (0.0291 g, 0.04 mmol)

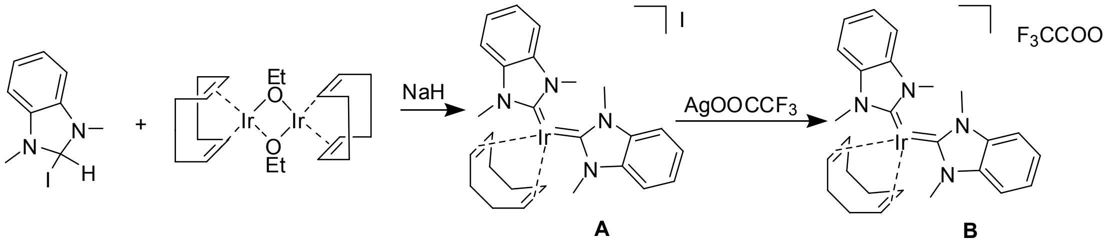
6.4.24 Dichloro(5H-dibenzo[a,d]cycloheptenylidene)acetonitrile palladium



0.20 mg (0.028 mmol) *bis*-(dichloro(5H-dibenzo[a,d] cycloheptatrienylidene) palladium) was dissolved in 1 L dry acetonitrile. Upon dissolving the brown powder changed the solution to a pale red color. After filtration via canula, the solvent was removed under reduced pressure yielding a dark red powder. Synthesis of the product was confirmed by elemental analysis (Expected: C:49.4 H:3.21 Found C:49.43 H:3.39)

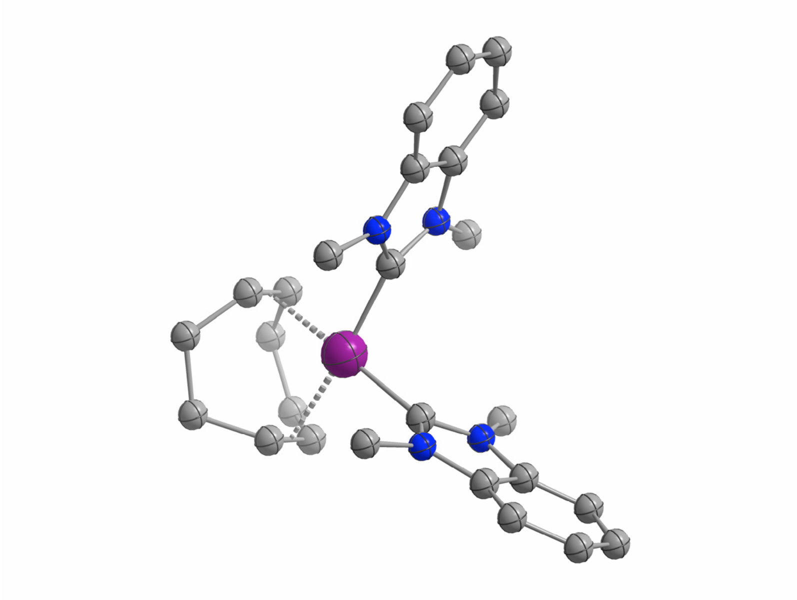
Yield: 64 % (14.7 mg, 0.036 mmol)

6.4.25 (η^4-1,5-Cyclooctadiene)*bis*(1,3-dimethylbenzimidazol-2-ylidene)iridium(I) trifluoroacetate



A solution of sodium hydride (0.6 mmol) in 3 ml EtOH was added drop wise to a suspension of $[Ir(COD)Cl]_2$ (0.15 mmol) in 2 mL EtOH and the resulting mixture was stirred for 45 minutes. After addition of 1.2 mmol azolium salt the suspension was stirred for an additional 12 hours and 1.2 mmol NaI is added. After stirring for another 12 h the volatiles were removed under reduced pressure and the crude product purified by column chromatography (silica gel, 4:1 → 2:1 dichloromethane / acetone) to yield product **A**. In 5 mL acetonitrile 0.1 mmol iridium iodide complex **A** is dissolved and 0.1 mmol of the silver salt [AgTFA] is added, resulting in the formation of [AgI]. The resulting suspension was stirred for 30 minutes at room temperature and the orange-red product solution is filtered off. Volatiles are removed in vacuum, and the resulting red-orange viscous oil is redissolved in dichloromethane. The product is precipitated with pentane and the resulting orange solid dried under reduced pressure. The product was then recrystallized and characterized ^{1}H-NMR and ^{13}C-NMR which corresponded to previously reported signals[236] for this complex and novel X-ray crystallographic findings are shown below.

Yield : 69 % (50 mg, 0.07 mmol)



Crystal system	monoclinic
Space group	C2/c
Cell dimensions	
a (Å)	28.255(4)
b (Å)	12.725(2)
c (Å)	16.291(2)
α (°)	90
β (°)	105.067(6)
γ (°)	90
V(Å^3)	5655.28
Calculated density (g/cm^3)	1.392

The crystal structure contains a disorder due to the counter ion which could not be resolved. Therefore the refinement could not be fully completed.

6.5 Standard procedures for catalysis

For catalytic evaluations, established standard protocols were followed to facilitate direct comparison to previously published reports. All solvents were distilled and reaction vessels flame dried and allowed to cool to room temperature in an inert atmosphere before use.

For reactions carried out at TUM, vessels were charged with reactants and solvents in the glove box, sealed and transferred out of the box and reacted. Yield vs. time reactions were carried out in Schlenk apparatus and samples taken at various time intervals maintaining an inert atmosphere in the reaction vessel. These samples were quenched and immediately placed in the – 40 ºC freezer. After reaction all samples were thawed, worked up and tested.

Reactions were carried out in various scales and reaction vessels (2 mL to 20 mL, Schlenk tubes, catalytic carousel reactors, gc vials). To ensure continuity among sample runs (a run is defined as a batch set of reactions where in 12 - 16 reactions are preformed at the same time) a standard catalyst is used. This enables the comparison of results and confirms the reproducibility of a given set of results ensuring that standard reaction conditions have been maintained. To further ensure reproducibility of small scale reactions (2 - 5 mL total volume), these reactions were tested in triplicate and varrience among these reaction subsets was seen to be not greater than ±5 %.

6.5.1 C–N-Coupling

Organometallic palladium precatalysts, base and n-eicosane were suspended in dry toluene. To this mixture the alkyl halide, morpholine, and a solution containing the phosphine were added. The reaction vessel was then sealed and transfered out of the glovebox and heated for the given reaction time (typically 18 hours) at the given reaction temperature (typically 100 ºC). The vessels were then allowed to cool to room temperature and quenched with 20 % total volume water (2 mL water would be added to a reaction mixture with a total volume of 10 mL). Reaction vs yield runs were preformed in a Schlenk apparatus with the reaction time 0 defined at the point when the phosphine had been added. Conversions and yields were determined by GC/FID analysis.

6.5.2 Decarboxylative biaryl synthesis

Solid reactants, palladium precatalyst, copper catalysts (Cu_2O or CuI), potassium nitro benzoate, and phospine ligand were charged into reaction vessels. These vessels were then sealed and evacuated and backfilled with inert gas 3 times. The degassed solvent (NMP) and liquid reagents (aryl chloride, or triflate) were added with a positive stream of inert gas and a vent to the reaction vessel via syringe. The reaction vessels were then placed in a preheated (typically 170 ºC) aluminum block. After reaction for specified times, the solutions were allowed to cool and to this the n-tetradecane standard was added. Reaction vials were then opened and 2 mL 5 M HCl and 2 mL were added to the mother liquor. The solution was well mixed and the organic phase separated and passed through a small column containing cotton, $NaHCO_3$ and $MgSO_4$, then loaded into a GC vial and analysed.

References

1 Anastas, P. and Warner,J. *Green Chemistry: Theory and Practice* (Oxford University Press: New York, **1998**).

2 United Nations General Assembly (**1987**) *Report of the World Commission on Environment and Development: Our Common Future*. Transmitted to the General Assembly as an Annex to document A/42/427

3 Sheldon, R. A. *Green Chem.* **2007,** *9 (12),* 1273.

4 Sheldon R. A. *Pure and Appli. Chem*. **2000,** *72 (7),* 1233.

5 Trost B. M. Angew. Chem. Int. Ed. Engl. **1995,** *34 (3),* 259

6 Tester, J. W.; Drake, E. M.; Driscoll, M. J.; Golay, M. W.; Peters, W. A. *Sustainable Energy: Choosing Among Options* (MIT Press: Cambridge, **2005**)

7 Clegg, B. *Ecologic: The truth and lies of green economics* (Transworld Publishers: London, **2009**)

8 (*a*) Kühn,F. E.; Santos, A. M.; and Abrantes, M. *Chem. Rev.*, **2006**, *106,* 2455; (*b*) Romão, C.C.; Kühn, F. E.; and W. A. Herrmann, *Chem. Rev.*, **1997**, 97, 3197; (*c*) Santos, A. M. and Kühn, F. E. *Homogeneous Multiphase Catalysis*, ed. B. Cornils, W. A. Herrmann, I. T. Horváth, W. Leitner, S. Mecking, H. Olivier-Bourbigou and D. Vogt, Wiley-VCH, Weinheim, **2005**, *2*, 807.

9 (*a*) Kühn, F. E.; Scherbaum, A. and Herrmann, W. A., *J. Organomet. Chem.*, **2004**, *689*, 4149 (*b*) Kühn, F. E.; Santos, A. M. and Herrmann, W. A. *Dalton Trans.*, **2005,** 2483; (*c*) Herrmann, W. A. and Kühn, F.

E., *Acc. Chem. Res.*, **1997**, *30*, 169 ; (*d*) Beattie, I. R. and Jones, P. J. *Inorg. Chem.*, **1979,** *18,* 2318.

10 (*a*) Rost, A. M. J.; Herrmann, W. A. and Kühn, F. E. *Tetrahedron Lett.*, **2007,** 48, 1775; (*b*) Kühn, F. E.; Jain, K. R. and Zhou,M. *Rare Metals*, **2006**, *25*, 411.

11 Herrmann, W. A.; Kuchler, J. G.; Felixberger, J. K.; Herdtweck, E. and Wagner, W., *Angew. Chem.*, **1988**, *100*, 420 (*Angew. Chem., Int. Ed.*, **1988**, 27, 394).

12 Herrmann,W. A.; Kühn, F. E.; Fischer, R. W.; Thiel, W. R. and Romão, C. C. *Inorg. Chem.*, **1992**, *31,* 4431

13 Herrmann, W. A.; Kratzer, R. M. and Fischer, R. W. *Angew. Chem.*, **1997**, *109*, 2767 (*Angew. Chem., Int. Ed.*, **1997**, *36*, 2652) .

14 Herrmann, W. A.; Rost, A. M. J.; Mitterpleininger, J. K. M.; Szesni, N.; Sturm, S.; Fischer, R. W. And Kühn, F. E. *Angew. Chem.*, **2007**, *Angew. Chem., Int. Ed.*, **2007**, DOI:10.1002/anie.200703017.

15 *(a*) Herrmann, W. A.; Romão, C. C.; Fischer, R. W.; Kiprof, P. and Meric de Bellefon, C. *Angew. Chem***.,** **1991**, *103,* 183 (*Angew. Chem., Int. Ed.*, **1991**, 30, 185); (*b*) Herrmann, W. A.;Kühn, F. E.; Romão,C. C.; Tran Huy, H.; Wang, M.; Fischer,R. W.; Scherer, W. and Kiprof, P. *Chem. Ber.*, **1993**, *126*, 45; (*c*) Rost,A. M. J.; Scherbaum, A. ; Herrmann, W. A. and Kühn, F. E. *New J. Chem.*, **2006**, ***30,*** 1559.

16 G. E. Coates and D. Ridley, *J. Chem. Soc.*, **1964**, 1870.

17 Herrmann,W. A.; Zoller, J. P. and Fischer,R. W. *J. Organomet. Chem.* **1999**, *579*, 404.

18 Dale, B. E. *J. Chem. Technol. Biotechnol.* **2003**, *78*, 1093.

19 a)de Nooy, A.; Besemer,A. C.; van Bekkum,H. *Carbohydr. Res.* **1995**, *269*, 89; b) Sorokin, A.B.; Kachkarova-Sorokina, L. S.; Donze, C.; Pinel, C.; Gazelot, P. *Top. Catal.* **2004**, *27*, 67; c) Herrmann,W. A.; Fischer, W. A.and Zoller, A. P *WO 0061639*, **2000**.

20 Weaver,M. O. *Stärke* **1977**, *29*, 414.

21 Ban, W.; Song, J.; Argyropoulos, D. S. and Lucia, L. A. *Ind. Eng. Chem. Res.* **2006**, *45*, 627.

22 a) Besemer, A. C.;de Nooy,A. E. J. *WO 9507303*, **1995**; b) de Nooy,A. E. J.; Besemer,A. C. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 165.

23 a) Besemer, A. C. E. ; de Nooy, A. E. J. *NL 9301172*, **1992**; b) de Nooy, A. E. J. *Dissertation*, Technische Universität Delft, **1997**; c) Painter, T. J. *Carbohydr. Res.* **1977**, *55*, 95; d) Painter, T. J. *Carbohydr. Res.* **1985**, *140*, 61.

24 a) Kühn, F. E. ; Santos, A. M. ; Herrmann, W. A. *Dalton Trans.* **2005**, 2483; b) Kühn, F. E.; Scherbaum, A. Herrmann, W. A. *J. Organomet. Chem.* **2004**, *689*, 4149; c) Herrmann, W. A.; Kühn, F. E. *Acc. Chem. Res.* **1997**, *30*, 169; d) Romão, C. C.; Kühn, F. E. ; Herrmann, W. A. *Chem. Rev.* **1997**, *97*, 3197; e) Herrmann, W. A.; Fischer, R. W. ; Scherer, W.; Rauch, M. U. *Angew. Chem.* **1992**, *105*, 1209; *Angew. Chem. Int. Ed.* **1992**, *32*, 1157; f) Herrmann, W. A; Kühn, F. E.; Fischer, R. W.; Thiel, W. R. and Romão, C. C. *Inorg. Chem.* **1992**, *31*, 4431; g) Herrmann, W. A.; Wagner, W.; Flessner, U. N.; Volkhardt, U.; Komber, H. *Angew. Chem.* **1991**, *103*, 1704; *Angew. Chem. Int. Ed.* **1991**, *30*, 1636; h) Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem.* **1991**, *103*, 1706; *Angew. Chem. Int. Ed.* **1991**, *30*, 1638; i) Herrmann,

W. A.; Wang, M. *Angew. Chem.* **1991**, *103*, 1709; *Angew. Chem. Int. Ed.* **1991**, *30*, 1641.

25 Arts, S. J. H. F.; Mombarg, E. J. M.; van Bekkum, H.; Sheldon, A. *Synthesis* **1997**, 597.

26 Smudde, G.; Bailey, W.; Felker, B.; George, M.; Langan, J. *Corrosion Science* **1995**, *37*, 1931.

27 a) de Nooy, A. Dissertation, *Technische Universiteit Delft*, **1999**; b) B. Feuer, B. Haack, H. J. *DE 19746805*, **1997.**

28 Espenson, J. H.; Zauche, T. H. *Inorg. Chem.* **1998**, *37*, 6827.

29 DIN Deutsches Institut für Normung e.V., *Modified starch – Determination of carboxyl group content of oxidized starch*, *DIN EN ISO 11214*, Beuth Verlag, Berlin, **1996**.

30 a) Jonas, G.; Klimmek,H. *DE 19645240*, **1998**; b) Brueggemann, H.; Dahmen, K. *DE 19505708*, **1996**; c) H. Eschwey, L. Hackler, *DE 3720031*, **1989**; d) Yoshimura, T.; Yoshimura, R.; Seki,C.; Fujioka, R. *Carbohydrate Poly.* **2006**, 345.

31 a) Espenson, J. H. *Chem. Commun.* **1999**, *479*; b) Laurenczy, G. ; Lukacs, F. ; Roulet, R. ; Herrmann, W. A. ; Fischer, W. R. *Organometallics* **1996**, ***15***, 848; c) Abu-Omar, M. M. ; Hansen, P. J. ; Espenson, J. H. *J. Am .Chem. Soc.* **1996**, *118*, 4699.

32 a) Trost, B, M. *Science* **1991**, *254*, 1471; b) Trost, B. M. *Angew. Chem.* **1995**, *107*, 285; *Angew. Chem. Int. Ed.* **1995**, *34*, 259.

33 a) Herrmann, W. A.; Rost, A. M. J. ; Mitterpleininger, J. K. M.; Szesni, N.; Sturm, S.; Fischer, R. W.; Kühn, F. E. *Angew. Chem.* **2007**, *119*, 7440; *Angew. Chem. Int. Ed.* **2007**, *47*, 7301; b) Tosh, E.;

Mitterpleininger, J. K. M.; Rost, A. M. J.; Veljanovski, D.; Herrmann, W. A.; Kühn, F. E. *Green Chem.* **2007**, *9*, 1296.

34 Herrmann, W. A.; Kratzer, R. M.; Fischer, R. W. *Angew. Chem.* **1997**, *109*, 2767; *Angew. Chem. Int. Ed.* **1997**, *36*, 2652.

35 Goldsmith, C. R.; Cole, A. P.; Stack, T. and Daniel, P. *J. Am. Chem. Soc.*, **2005**, *127*, 9904.

36 Chatt, J. and Davidson, J. M. *Chem. Commun*. **1965**, 843.

37 (a) Foley, P. and Whitsides ,G. M. *J. Am. Chem. Soc*. **1979**, *101*, 2732; (b) Green, M. L. H. and Knowles, P. J. *Chem. Commun.* **1970**, 1677; (c) Bennett, M. A and Milner, D. L. *Chem. Commun.* **1967**, 581; (d) Janowicz, A. H. and Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352; (e) Hoyano, J. K. and Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723; (f) Bergman, R. G. *Science* **1984,** *223*, 902; (g) Periana, R. A. and Bergman, R. G. *J. Am. Chem. Soc*. **1986**, *108*, 7332; (h) Jones, W. D. and Dong, L. *J. Am. Chem. Soc.* **1989***, 111*, 8722; (i) Belt, S. T.; Dong, L.; Duckett, S. B.; Jones, W. D.; Partridge M. G. and Perutz, R. N. *Chem. Commun*. **1991**, 266; (j) Jones, W. D.; Partridge, M. G. and Perutz, R. N. *Chem. Commun.* **1991,** 264; (k) Stoutland, P. O. and Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107,* 4581.(l) Crabtree, R. H. *J. Organomet. Chem.* **2004,** *689*, 4083.

38 (a) Muehlhofer, M.; Strassner, T. and Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002***, 41*, 1745; (b) Strassner, T.; Muehlhofer, M.; Zeller, A.; Herdtweck, E.; Herrmann*,* W. A. *J. Organomet. Chem.* **2004***, 689,* 1418.

39 (a) Shilov, A. E.; and Shteinman, A. A. *Coord. Chem. Rev*. **1977***, 24,* 97; (b) Kushch, L. A.; Lavrushko, V. V.; Misharin, Y. S.; Moravskii, A. P. and Shilov, A. E. *Nouveau Journal de Chimie* **1983**, *7*, 729; (c) Stahl, S. S.; Labinger, J. A. and Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961; (e) Periana, R. A.;Taube, D. J.; Gamble, S.; Taube, H.; Satoh,T. and Fujii, H. *Science* **1998**, *280*, 560.

40 (a) Kunin, A. J. and Eisenberg, R. *J. Am. Chem. Soc.* **1986**, *108*, 535; (b) Murai, S.;Kakiuchi, F.; Sekine, S. ; Tanaka, Y. Kamatani, A. Sonoda, M. and Chatani, N. *Nature* 1993, **366**, 529; (c) Kakiuchi, F. Yamamoto, Y. Chatani N. and Murai, S. *Chem. Lett.* **1995**, 681. (d) Chatani, N.;Ishii, Y.; Ie, Y.; Kakiuchi F. and Murai, S. *J. Org. Chem.* **1998**, *63*, 5129; (e) Chatani, N.; Asaumi, T.; Yorimitsu, S.; Ikeda, T.; Kakiuchi,F. and Murai, S. *J. Am. Chem. Soc.* **2001***, 123,* 10935; (f) B. Sezen and D. Sames, *J. Am. Chem. Soc*. **2005**, *127*, 5284; (g) Campeau,L.-C. and Fagnou, K. *Chem. Commun*. **2006**, 1253; (h) Proch, S. and Kempe, R. *Angew. Chem. Int. Ed.* **2007**, *46*, 3135; (i) *Crabtree, R. H. Dalton Trans.* **2003**, 3985.

41 Ishiyama, T. and Miyaura, N. *J. Organomet. Chem.* **2003,** *680*, 3.

42 (a) Suzuki, A. *in Metal-Catalyzed Cross-Coupling Reactions*, ed. Diederich, F. and Stang, P.J. Wiley-VCH, New York, **1998**, pp. 49–97.

43 Pelter, A.; Smith,K.; and Brown, H. C. *in Borane Reagents*, Academic Press, New York, **1988**.

44 Chen, H. and Hartwig, J. F. *Angew. Chem. Int. Ed.* **1999**, *38,* 3391.

45 (a) Iverson,C. N. and Smith III, M. R. *J. Am. Chem. Soc*. **1999**, *121*, 7696; (b) Chen, H.;Schlecht, S.; Semple, T. C. and Hartwig, J. F.

Science **2000**, *287*, 1995; (c) Cho, J.-Y.; Iverson, C. N. and Smith III, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 12868; (d) Tse, M. K.; Cho, J.-Y. and Smith III, M. R. *Org. Lett.,* **2001**, *3*, 2832.

46 Ishiyama, T.;Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R. and Hartwig, J. F. *J. Am. Chem. Soc.,* **2001**, *124*, 390.

47 (a) Ishiyama, T. ; Takagi, J.; Hartwig, J. F. and Miyaura, N. *Angew. Chem. Int. Ed.,* **2002**, *41*, 3056. (b) Herrmann, W. A.; Elison, M.; Fischer, J.;Köcher, C. and Artus, G. R. J. *Angew. Chem. Int. Ed.,* **1995**, *24*, 2371. (c) Herrmann, W. A. and Köcher, C. *Angew. Chem. Int. Ed.,* **1997**, *36*, 2162.

48 Ishiyama, T.; Nobuta, Y.; Hartwig, J. F. and Miyaura, N. *Chem. Commun.*, **2003**, 2925.

49 Chotana, G. A.; Rak, M. A. and Smith III, M. R. *J. Am. Chem. Soc.,* **2005**, *127*, 10539.

50 Boller, T. M.; Murphy, J. M.; Hapke, M.; Miyaura, N. and Hartwig, J. F. *J. Am. Chem. Soc.*, **2005**, *127*, 14263.

51 Mertins, K.; Zapf, A. and Beller, M. *J. Mol. Catal. A: Chem.* **2004**, *207*, 21.

52 (a) Tamura, H.; Yamazaki, H.; Sato, H. and Sakaki, S. *J. Am. Chem. Soc.* **2003**, *125,* 16114

53 Hartwig, J. F.; Cook, K. S.; Hapke, M.; Incarvito, C.; Fan, Y.; Webster, C. E. and Hall, M. B. *J. Am. Chem. Soc.* **2005**, *127*, 2538.

54 Murphy, J. M.; Lawrence, J. D.; Kawamura, K.; Incarvito, C. and Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128,* 13684.

55 Cho, J.-Y.; Tse, M. K.; Holmes, D.; Malezka, R. E. and Smith **III**, M. R. ;*Science* **2002,** *295,* 305.

56 (a) Mkhalid, I. A. I.; Coventry, D. N.; Albesa-Jove, D.; Batsanov, A. S.; Howard, J. A. K.; Perutz, R. N. and Marder, T. B. *Angew. Chem. Int. Ed.* **2006***, 45*, 489; (b) Coventry, D. N.; Batsanov, A. S.; Goeta, A. E.; Howard, J. A. K.; Perutz, R. N. and Marder, T. B. *Chem. Commun.* **2005**, 2172.

57 Frey, G. D.; Rentzsch, C. F.; v. Preysing, D.; Scherg, T.; Mühlhofer, M.; Herdtweck, E. and Herrmann, W. A. *J. Organomet. Chem.* **2006**, *691*, 5725.

58 (a) Herrmann, W. A. *Angew. Chem.* **2002** *114* 1342; *Angew. Chem. Int. Ed*. **2002** *41* 1290; (b) Herrmann, W. A. *in Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, 2nd ed., Wiley-VCH, Weinheim, **2002**, pp. 591-598, 775-793, and 822-828; (c) Glorius, F. *in N-Heterocyclic Carbenes in Transition Metal Catalysis*, Berlin, 2007; (d) Scott, N. M. and Nolan, S. P. *Eur. J. Inorg . Chem.,* **2005**, 1815.

59 (a) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C. and Artus, G. R. J. *Chem. Eur. J.* **1996,** *2*, 772; (b) Denk, K.; Sirsch, P.; Herrmann, W. A. *J. Organomet. Chem***.,** **2002**, *649*, 219. (c) Herrmann, W. A.; Frey, G. D.; Herdtweck, E. and Steinbeck, M. *Adv. Synth. Catal.,* **2007**, *349,* 1677; (d) Köcher, C. and Herrmann, W. A. *J. Organomet. Chem.,* **1997**, *532*, 265; (e) Schütz, J.; Herrmann, W. A. *J. Organomet. Chem*., **2004**, *689*, 2995.

60 Herrmann, W. A.; Schütz, J.; Frey, G. D. And Herdtweck, E. *Organometallics*, **2006,** *25*, 2437.

61 (a)Perry, M. C.; Cui, X.; Hou, D. and Reibenspies, J. H. *J. Am. Chem. Soc.,* **2003,** *125,* 113; Lee, M.; Jiang, T.; Stevens, E. D. and Nolan, S. P. *Organometallics*, **2001,** *20,* 1255. (b) Albrecht, M.; Mieczinkowski, J. R. ; Samuel, A.; Faller, J. W. and Crabtree, R. H. *Organometallics*, **2002**, *21*, 3596. (c) Vazquez-Serrano, L. D.; Owens, B. T. and Buriak, J. M. *Inorganica Chimica Acta*, **2006***, 359,* 2786. (d) Leuthhäußer, S. ; Schwarz, D. and Plenio, H. *Chem. Eur. J.*, **2007**, *13*, 7195. (e) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W. and Crabtree, R. H. *Organometallics,* **2003**, *22*, 1663. (f) Mas-Marza, E.; Poyatos, M.; Sanau,M and Peris,E. *Inorg. Chem.*, **2004**, *43*, 2213. (g) Viciano, M.; Mas-Marza, E.; Sanau, M. and Peris,E. *Organometallics***, 2006,** *25,* 3063.

62 Viciano, M.; Poyatos, M.; Sanau, M.; Peris, E.; Rossin, A.; Ujaque, G. and Lledos, A. *Organometallics,* **2006***, 25*, 1120.

63 (a) Kappe, C.O. *Angew. Chem.,* **2004**, *116*, 6408; (b) Hayes, B. L. *in Microwave Synthesis: Chemistry at the Speed of Light*, CEM Publishing, Matthews NC, **2002**.

64 Mata, J. A.; Chianese, A. R.; Miecznikowski, J. R.; Poyatos, M.; Peris, E.; Faller, J. W.; and Crabtree, R. H. *Organometallics,* **2004**, *23*, 1253.

65 Young, K. J. H.; Meier, S. K.; Gonzales, J. M. Oxgaard, J. Goddard III, W. A. and Periana, R. A. *Organometallics,* **2006**, *25,* 4734.

66 (a) Steudel, R. *in Chemie der Nichtmetalle*, 2nd edn., de Gruyter, Berlin, **1998**, p. 195. (b) Hendrickson, J. B.; Cram, D. J.; Hammond, G.

S. *in Organic Chemistry*, 3rd edn., McGraw Hill, New York, **1970**, pp. 303-307 (c) Macintyre, J. E. *in Dictonary of Inorganic Compounds*, 1st edn., Chapman & Hall, London **1992,** vol 1, p. 145.

67 (a) Littke, A. F. and Fu, G. C. *Angew. Chem.,* **2002**, *114*, 4350 (*Angew. Chem. Int. Ed.* **2002,** *41*, 4176 (b) Gossage, R. A. and Van Koten, G. *Activation of Unreactive Bonds and Organic Synthesis*, ed. Murai,S. Springer-Verlag, Berlin, **1999**, 3.

68 Fu, K. S. Y.; Li, J.-N.; Liu, L. and Guo,Q.-X. *Tetrahedron*, **2007**, *63,* 1568.

69 (a) Chin, R. M.; Dong,I.; Duckett, S. B.; Partridge, M. G.;. Jones W. D. and Perutz, R. N. *J. Am. Chem. Soc*. **1993,** *115*, 7685; (b) Jones, W. D. and Feher, F. J. *J. Am. Chem. Soc.,* **1984**, *106*, 1650.

70 (a) Tenn, W. J.; Young, K. J. H.; Oxgaard, J.; Nielsen, R. J.; Goddard III, W. A. and Periana, R. A. *Organometallics.,* **2006,** *25,* 5173 (b) Young, K. J. H.; Meier,S. K.; Gonzales, J. M.; Oxgaard, J.; Goddard III, W. A. and Periana, R. A. *Organometallics,* **2006**, *25*, 4734.

71 Ben-Ari, E.; Cohen, R.; Gandelman, M.; Shimon, L. J. W.; Martin, J. M. L. and Milstein, D. *Organometallics*, **2006**, *25,* 3190.

72 Voutchkova, A. M.; Appelhans, L. N.; Chianese, A. R. and Crabtree, R. H. *J. Am. Chem. Soc.* 2005, **127**, 17624

73 Wanzlick, H. M.; Schönherr, H. J. *Angew. Chem.* **1968**, *80*, 154.

74 Öfele, K. *J. Organomet. Chem.* **1968**, *12*, P42.

75 a) Herrmann, W. A.; Weskamp, T.; Böhm, V. P. W. *Adv. Organomet. Chem.* **2002**, *48,* 1; b) Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290.

76 Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.

77 Herrmann, W. A.; Köcher, C. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162.

78 Jones, W. M. *J. Am. Chem. Soc.* **1967**, *89*, 3069.

79 Öfele, K. *J. Organomet. Chem.* **1970**, *22*, C9.

80 Öfele, K. *Angew. Chem.* **1968**, *80*, 1032.

81 Lavallo, V.; Ishida, Y.; Donnadieu, B.; Bertrand, G. *Angew. Chem. Int. Ed.* **2006**, 45, 6652.

82 Lavallo, V.; Canac, Y.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Science* **2006**, *312*, 722.

83 Allison, N. T.; Kawada, Y.; Jones, W. M. *J. Am. Chem. Soc.* **1978**, *100*, 5224.

84 Öfele, K. *Angew. Chem.* **1969**, *22*, 936.

85 Konishi, H.; Matsumoto, S.; Kamitori, Y.; Ogoshi, H.; Yoshida, Z.-I. *Chem. Lett.* **1978**, 241.

86 Yoshida, Z.-I. *Pure Appl. Chem.* **1982**, *54,* 1059.

87 Taubmann, C.; Tosh, E.; Öfele, K.; Herdtweck, E.; Herrmann, W. A. *J. Organomet. Chem.,* **2008**, *693*, 2231.

88 Kawada, Y.; Jones, W. M. *J. Organomet. Chem.* **1980**, *192*, 87.

89 Öfele, K. *Angew. Chem.* **1968**, *24*, 1032.

90 Kirchgässner, U.; Piana, H.; Schubert, U. *J. Am. Chem. Soc* **1991**, *113*, 2228.

91 Kirchgässner, U.; Schubert, U. *Organometallics* **1988**, *7*, 784.

92 Juneau, K. N.; Hegedus, L. S.; Röpke, F. W. *J. Am. Chem. Soc* **1989**, *111*, 4762.

93 Rees, C. W.; v. Angerer, E. *J. Chem. Soc., Chem. Commun.* **1972**, 420.

94 Holschumacher, D.; Hrib, C. G.; Jones, P. G.; Tamm, M. *Chem. Commun.* **2007**, 3661.

95 Yoshida, Z.-I.; Konishi, H.; Kamitori, Y.; Ogoshi, H. *Chem. Lett.* **1977**, 1341.

96 Schumann, H.; Glanz, M.; Girgsdies, F.; Hahn, F. E.; Tamm, M.; Grzegorzewski, A. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*.

97 Kuchenbeiser, G.; Donnadiew, B.; Bertrand, G., *J. Organomet. Chem.* **2008**, *693*, 899.

98 Bruce, M. I.; Swincer, A. G.; Thomson, B. J.; Wallis, R. C. *Aust. J. Chem.* **1980**, *33*, 2605.

99 Bruce, M. I.; Swincer, A. G. *Aust. J. Chem.* **1980**, *33*, 1477.

100 Ting, P.-C.; Lin, Y.-C.; Lee, G.-H.; Cheng, M.-C.; Wang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6433.

101 Gade, L. H.; Memmler, H.; Kauper, U.; Schneider, A.; Fabre, S.; Bezougli, I.; Lutz, M.; Galka, C.; Scowen, I. J.; McPartlin, M. *Chem. Eur. J.* **2000**, *6,* 692.

102 Caskey, S. R.; Stewart, M. H.; Johnson, M. J. A.; Kampf, J. W. *Angew. Chem. Int. Ed.* **2006**, *45*, 7422.

103 Manganiello, F. J.; Radcliffe, M. D.; Jones, W. M. *J. Organomet. Chem.* **1982**, 273.

104 Lisko, J. R.; Jones, W. M. *Organometallics* **1986**, *5*, 1890.

105 Lu, Z.; Jones, W. M.; Winchester, W. R. *Organometallics* **1993**, *12*, 1344.

106 Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *J. Am. Chem. Soc.* **1980**, *102*, 2458.

107 Tamm, M.; Hartl, H. *Chem. Commun.* **1997**, 2227.

108 Tamm, M.; Grzegorzewski, A.; Brüdgam, I.; Hartl, H. *J. Chem. Soc., Dalton Trans.* **1998**, *20*, 3523.

109 Nemeh, S.; Flesher, R. J.; Gierling, K.; Maichle-Mössmer, C.; Mayer, H. A.; Kaska, W. C. *Organometallics* **1998**, 2003.

110 Winter, A. M.; Eichele, K.; Mack, H.-G.; Kaska, W. C.; Mayer, H. A. *Organometallics* **2005**, 1837.

111 Lu, Z.; Abboud, K. A.; Jones, W. M., *J. Am. Chem. Soc.* **1992**, *114*, 10991.

112 Herrmann, W. A.; Plank, J.; Kriechbaum, G. W.; Ziegler, M. L.; Pfisterer, H.; Atwood, J. L.; Rogers, R. D. *J. Organomet. Chem.* **1984**, *264*, 327.

113 Dötz, K. H., Pfeiffer, J. *Chem. Commun.* **1996**, 895.

114 Pfeiffer, J.; Dötz, K. H. *Organometallics* **1998**, *17*, 4353.

115 Herrmann, W. A.; Öfele, K.; Schneider, S. K.; Herdtweck, E.; Hoffmann, S. D. *Angew. Chem. Int. Ed.* **2006**, *45*, 3859.

116 Vilinskaya, V. S.; Burshtein, R. Kh.; Tarasevich, M. R. *Elektrokhimiya* **1970**, *6*, 1497.

117 Schneider, S. K., Ph.D. Thesis, Technische Universität München, **2005**.

118 Föhlisch, A., Ph.D. Thesis, Technische Universität München, **1968**.

119 Tamm, M.; Kunst, A.; Herdtweck, E. *Chem. Commun.* **2005,** 13, 1729.

120 Bartole-Scott, A.; Braunschweig, H.; Kupfer, T.; Lutz, M.; Manners, I.; Nguyen, T.-I.; Radacki, K.; Seeler, F. *Chem. Eur. J.* **2006**, *12*, 1266.

121 Yao, Q.; Zabawa, M.; Woo, J.; Zheng, C. *J. Am. Chem. Soc.* **2007**, *129*, 3088.

122 Winchester, W. R.; Jones, W. M. *Organometallics* **1985**, *4*, 2228.

123 Winchester, W. R.; Gawron, M.; Palenik, G. J.; Jones, W. M. *Organometallics* **1985**, *4*, 1894.

124 (a)Feher, F. J.; Gergens, D.; Ziller, J. W. *Organometallics* **1993**, *12*, 2810. (b)Sanders, A.; Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V. *J. Am. Chem. Soc.* **1973**, *95*, 5430.

125 Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Weidenhammer, K. *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 777.

126 Zhang, J.; Gandelman, M.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2008**, *27*, 3526.

127 Otsuka, S.; Nakamura, A.; Koyama, T.; Tatsuno, Y. *Liebigs Ann. Chem.* **1975**, 626.

128 Werner, H.; Schwab, P.; Bleuel, E.; Mahr, N.; Steinert, P.; Wolf, J. *Chem. Eur. J.* **1997**, *3*, 1375.

129 Herrmann, W. A.; Plank, J.; Hubbard, J. L.; Kriechbaum, G. W.; Klacher, W.; Koumbouris, B.; Ihl, G.; Schäfer, A.; Ziegler, M. L.; Pfisterer, H.; Pahl, C.; Atwood, J. L.; Rogers, R. D. *Z. Naturfosch.* **1983**, *38b,* 1392.

130 Schanz, H.-J.; Edwin, L. J.; Stevens, D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5187.

131 Fürstner, A.; Grabowski, J.; Lehmann, C. W. *J. Org. Chem.* **1999**, *64*, 8275.

132 Fürstner, A.; Guth, O.; Düffels, A.; Seidel, G; Liebl, M.; Gabor, B.; Mynott, R. *Chem. Eur. J.* **2001**, *7*, 4811.

133 Shaffer, E. A.; Chen, C.-L.; Beatty, A. M.; Valente, E. J.; Schanz, H. J. *J. Organomet. Chem.* **2007**, *692*, 5221.

134 Castarlenas, R.; Vovard, C.; Fischmeister, C.; Dixneuf, P. H. *J. Am. Chem. Soc.* **2006**, *128*, 4079.

135 Castarlenas. R; Dixneuf, P. H. *Angew. Chem. Int. Ed.* **2003**, *42*, 4524.

136 Bauer, D.; Härter, P.; Herdtweck, E. *Chem. Commun.* **1991**, 829.

137 Fischer, H.; Podschadly, O.; Früh, A.; Troll, C.; Stumpf, R.; Schlageter, A. *Chem. Ber.* **1992**, *125*, 2667.

138 Fischer, H.; Leroux, F.; Roth, G.; Stumpf, R. *Organometallics* **1996**, *15*, 3723.

139 Davison, A.; Solar, J. P. *J. Organomet. Chem.* **1978**, *155*, C8.

140 Kolobova, N. Y.; Skripkin, V. V.; Alexandrov, G. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1979**, *169*, 293.

141 Weng, W.; Bartik, T.; Johnson, M. T.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1995**, *14*, 889.

142 Scherer, W.; Tafipolsky, M.; Öfele, K. *Inorg. Chim. Acta* **2008**, *361*, 513.

143 Huttner, G.; Schelle, S.; Mills, O. S. *Angew. Chem. Int. Ed. Engl* **1969**, *8*, 515.

144 Tamm, M.; Grzegorzewski, A.; Hahn, F. E. *J. Organomet. Chem.* **1995**, *501*, 309.

145 Kawada, Y.; Sugawara, T.; Iwamura, H. *J. Chem. Soc., Chem. Commun.* **1979**, 291.

146 Yoshida, Z.-I.; Kamitori, Y. *Chem. Lett.* **1978**, 1341.

147 Miki, S.; Ohno, T.; Iwasaki, H.; Maeda, Y.; Yoshida, Z.-I. *Tetrahedron* **1988**, *44*, 55.

148 Wilson, R. D.; Kamitori, Y.; Ogoshi, H.; Yoshida, Z.-I.; Ibers, J. A. *J. Organomet. Chem.* **1979**, *173*, 199.

149 W. A. Herrmann; K. Öfele; Taubmann, C.; Herdtweck, E.; Hoffmann, S. D. *J.Organomet. Chem.* **2007**, *692*, 3846.

150 Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.***1996**, *118*, 1535.

151 Johnson, R. P. *Chem. Rev.* **1989**, 89, *1111*.

152 Aboud, J. *Acta Cryst.* **1992**, *c48*, 909.

153 Klosin, J.; Zheng, X.; Jones, W. M. *Organometallics* **1996,** *15*, 3788.

154 Oon, S. M.; Koziol, A. E.; Jones, W. M.; Palenik, G. J., *J. Chem. Soc., Chem. Commun.* **1987**, 491.

155 Herrmann, W. A.; Plank, J.; Kriechbaum, G. W.; Ziegler, M. L.; Pfisterer, H. Atwood, J. L.; Rogers, R. D. *J. Organomet. Chem.* **1984**, *264*, 327.

156 Odden, P. Y. *Acta Cryst.* **1984**, *c40,* 524.

157 Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *Inorg. Chem.* **1982**, 21, 1321.

158. Abboud, J. *Acta Cryst.* **1996**, *c52*, 1101.

159. Tamm, M.; Kunst, A.; Bannenberg, T.; Randoll, S.; Jones, P. G. *Organometallics* **2007**, *26*, 417.

160 Tamm, M., *Chem Commun.* **2008**, *27,* 3089.

161 Sanders, A.; Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V. *J. Am. Chem. Soc.* **1973**, *95*, 5430.

162 Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V.; Sanders, A. *J. Organomet. Chem.* **1974**, *65*, C57.

163 Sanders, A.; Bauch, T.; Magatti, C. V.; Lorenc, C.; Giering, W. P. *J. Organomet. Chem.* **1976,** *107*, 359.

164 Gamble, A. S.; Birdwhistell, K. R.; Templeton, J. L. *Organometallics* **1988,** *7*, 1046.

165 Bruce, M. I. *Chem. Rev.* **1991,** *91*, 197.

166 Tenorio, M. A. J.; Tenorio, M. J.; Puerta, M. C.; Valerga, P. *Organometallics* **2000**, *19*, 1333.

167 Crespi, A. M.; Shriver, D. F. *Organometallics* **1985**, *4*, 1830.

168 Díez, J.; Gamasa, M. P.; Gimeno, J.; Lastra, E.; Villar, A. *Organometallics* **2005**, *24*, 1410.

169 Díez, J.; Gamasa, M. P.; Gimenoa, J.; Lastra, E.; Villar, A. *J. Organomet. Chem.* **2006,** *691*, 4092.

170 Alvarez, P.; Lastra, E.; Gimeno, J.; Bassetti, M.; Falvello, L. R. *J. Am. Chem. Soc.* **2003**, *175*, 2386.

171 Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Weidenhammer, K. *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 777.

172 Otsuka, S.; Nakamura, A.; Koyama, T.; Tatsuno, Y. *Liebigs Ann. Chem.* **1975**, 626.

173 Fischer, E. O.; Held, W.; Kreissl, F. R.; Frank, A.; Huttner, G. *Chem. Ber.* **1977**, *110*, 656.

174 Forman, G. S.; Bellabarba, R. M.; Tooze, R. P.; Slawin, A. M. Z.; Karch, R.; Winde, R. *J. Organomet. Chem.* **2006**, *691*, 5513.

175 Jafarpour, L.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18,* 5416.

176 Monsaert, S.; Drozdzak, R.; Dragutan, V.; Dragutan, I.; F., V. *Eur. J. Inorg. Chem.* **2008**, 432.

177 Burtscher, D.; Lexer, C.; Mereiter, K. W., R.; Karch, R.; Slugovc, C. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 4630.

178 Cheng, C.-W.; Kuo, Y.-C.; Chang, S.-H.; Lin, Y.-C.; Liu, Y.-H.; Wang, Y. *J. Am. Chem. Soc.* **2007,** *129*, 14974.

179 Herrmann, W. A.; Plank, J.; Hubbard, J. L.; Kriechbaum, G. W.; Klacher, W.; Koumbouris, B.; Ihl, G.; Schaefer, A.; Ziegler, M. L.; Pfisterer, H.; Pahl, C.; Atwood, J. L.; Rogers, R. D., *Z. Naturforsch.* **1983,** *38b*, 1392.

180 Gilchrist, T. L.; Livingston, R.; Rees, C. W.; Angerer, E. v.; Robinson, R. *J. Chem. Soc., Perkin I* **1973**, 2535.

181 de Meijere, A.; Müller, S.; Labahn, T. *J. Organomet. Chem* **2001**, *617-618*, 318.

182 Cetinkaya, B.; Cetinkaya, E.; Lappert, M. F. *J. Chem. Soc. Dalton Trans.* **1973**, 906.

183 O’Brien, C. J.; Kantchev, E. A. B.; Valente, C.; Hadei, N.; Chass, G. A.; Lough, A.; Hopkinson, A. C.; Organ, M. G. *Chem. Eur. J.* **2006**, *12*, 4743.

184 Organ, M. G.; Avola, S.; Dubovyk, I.; Hadei, N.; Kantchev, E. A. B.; O’Brien, C. J.; Valente, C. *Chem. Eur. J.* **2006**, *12*, 4749.

185 Organ, M. G.; Abdel-Hadi, M.; Avola, S.; Hadei, N.; Nasielski, J.; O'Brien, C. J.; Valente, C., *Chem. Eur. J.* **2007**, *13*, 150.

186 Boeda, F.; Clavier, H.; Nolan, S. P. *Chem. Commun.* **2008**, 2726.

187 Bieniek, M.; Michrowska, A.; Usanov, D. L.; Grela, K. *Chem. Eur. J.* **2008**, *14*, 806.

188 Wass, D. F.; Haddow, M. F.; Hey, T. W.; Orpen, A. G.; Russell, C. A.; Wingad, R. L.; Green, M. *Chem. Commun.* **2007**, 2704.

189 Wass, D. F.; Hey, T. W.; Rodriguez-Castro, J.; Russell, C. A.; Shishkov, I. V.; Wingad, R. L.; Green, M. *Organometallics* **2007**, *26*, 4702.

190 Pinter, B.; Veszpremi, T. *Organometallics* **2008**, in press.

191 Schubert, J.; Mock, S.; Schubert, U. *Chem. Ber.* **1993**, *126,* 657.

192 Gompper, R.; Bartmann, E. *Liebigs Ann. Chem.* **1979**, 229.

193 Miki, S.; Ohno, T.; Iwasaki, H.; Yoshida, Z.-I. *J. Phys. Org. Chem.* **1988,** *1*, 333.

194 Winter, A. M.; Eichele, K.; Mack, H.-G.; Kaska, W. C.; Mayer, H. A. *Dalton Trans.* **2008**, 527.

195 Alexandrov, G. G.; Skripkin, V. V.; Kolobova, N. E.; Struchkov, Y. T., *Koord. Khim.* **1979**, *5*, 453.

196 Berke, H.; Härter, P.; Huttner, G.; Zsolnai, L. *Z. Naturforsch.* **1981**, *36b*, 929.

197 Fischer, H.; Leroux, C. C.; Strumpf, R.; Roth, G. *Chem. Ber.* **1996**, *129*, 1475.

198 Fischer, H.; Volkland, H.-P.; Früh, A.; Stumpf, R. *J. Organomet. Chem.* **1995**, *491*, 267.

199 Fischer, H.; Podschadly, O.; Roth, G.; Herminghaus, S.; Klewitz, S.; Heck, J.; Houbrechts, S.; Meyer, T. *J. Organomet. Chem.* **1997**, *541*, 321.

200 Roth, G.; Reindl, D.; Gockel, M.; Troll, C.; Fischer, H. *Organometallics* **1998**, *17*, 1393.

201 Leroux, F.; Stumpf, R.; Fischer, H., *Eur. J. Inorg. Chem.* **1998**, 1225.

202 Karl, C. C.; Joneleit, S.; Weißenbach, K.; Fischer, H. *J. Organomet. Chem.* **2001**, *617-618*, 464.

203 Ipaktschi, J.; Mohseni-Ala, J.; Dülmer, A.; Steffens, S.; Wittenburg, C.; Heck, J., *Organometallics* **2004**, *23*, 4902.

204 Díez, J.; Gamasa, M. P.; Gimenoa, J.; Lastra, E.; Villar, A. *J. Organomet. Chem.* **2006**, *691*, 4092.

205 Harlow, K. J.; Hill, A. F.; Winton-Ely, J. D. E. T. *J. Chem. Soc., Dalton Trans.* **1999**, 285.

206 Thayer, A. M. *Chem. Eng. News* **2007**, *85*, 37.

207 Dorta, R.; Kelly, R. A.; Nolan, S. P. *Adv. Synth. Catal.* **2004**, *346*, 917.

208 Boeda, F.; Clavier, H.; Jordaan, M.; Meyer, W. H.; Nolan, S. P. *J. Org. Chem.* **2008**, *73*, 259.

209 Randl, S.; Gessler, S.; Wakamatsu, H.; Blechert, S. *Synlett* **2001**, 430.

210 Puentener, K.; Scalone, M. *PCT Int. Appl., WO 2006111491,* **2006**.

211 Opstal, T.; Verpoort, F. *New J. Chem.* **2003**, *27*, 257.

212 Clavier, H.; Nolan, S. P. In *Metathesis Chemistry*; Imamoglu, Y.; Dragutan, V., Eds.; NATO ASI 243; Springer: Dordrecht, **2007**, 29.

213 Clavier, H.; Petersen, J. L.; Nolan, S. P. *J. Organomet. Chem.* **2006**, *691*, 5444.

214 *Drozdzak*, N.; Ledoux, B.; Allaert, I.; Dragutan, V.; Verpoort, F. *Cent. Eur. J. Chem.* **2005**, *3*, 404.

215 Opstal, T.; Verpoort, F. *Angew. Chem. Int. Ed.* **2003**, *42*, 2876.

216 Reetz, M. T.; Becker, M. H.; Liebl, M.; Fürstner, A. *Angew. Chem. Int. Ed.* **2000**, *39*, 1236.

217 Fischer, H.; Karl, C. C.; Roth, G. *Chem. Ber*. **1996**, *129*, 615.

218 Opstal, T.; Verpoort, F. *Synlett* **2002**, *6*, 935.

219 a) Louie,J.; Hartwig,J. F.; Tetrahedron Lett. **1995,** *36,* 3609.

b) Guram, A. S.; Rennels,R. A.; Buchwald, L. S. *Angew. Chem., Int. Ed*. **1995**,*34,* 1348.

220 a) Schlummer, B.; Scholz, U. *Adv. Synth. Catal*. **2004** ,*346*, 1599;

b) de Meijere, A.; Diederich, F. (Eds.), Metal-Catalyzed Cross-Coupling Reactions, 2nd ed., Wiley-VCH, Weinheim, Germany, **2004**.

c) Hartwig, J. F. in: Negishi, E. (Ed.), Handbook of Organopalladium Chemistry for Organic Synthesis, Wiley, New York, **2002**, 1051.

221 Reetz, M. T., de Vries, J. G. *Chem. Commun.* **2004** 1559.

222 (a) Kantchev, E.A.B. ; O'Brien, C. J. ; Organ, M. G. *Angew. Chem., Int. Ed.* **2007** *46* 2768 (b) Farina,V. *Adv. Synth. Catal*. **2004** *346* 1553.(c) Herrmann, W. A.; Öfele, K.; v. Preysing, D.; Schneider, S. K.; *J. Organomet. Chem.* **2003** ,*687,* 229; d) Bedford, R. B. *Chem. Commun.* **2003** 1787.(e) Herrmann,W. A. *Angew. Chem*. **2002**, *114,* 1342; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002,** *41,* 1290;

223 (a) Weiss, R.; Priesner, C. *Angew. Chem.* **1978,** *90,* 491; Weiss, R.; Priesner,C. *Angew. Chem. Int. Ed. Engl.* **1978,** *17,* 457(b)

Manganiello, F. J.; Radcliffe, M. D.; Jones, W. M. *J. Organomet. Chem*. **1982** *228* 273

224 Hartwig, J. F.; Kawatsura, M.; Hauck, S. I.; Shaughnessy, K. H.; Alcazar-Roman, L. M. *J. Org. Chem*. **1999**, *64,* 5575.

225 (a) Stauffer, S. R.; Lee, S.; Stambuli, J. P.; Hauck, S. I.; Hartwig, J. F. *Org. Lett.* **2000**, *2,* 1423 (b) Wolfe, J. P.; Buchwald, L. S. *Angew. Chem., Int. Ed***. 1999,** *38,* 2413.

226 Miyaura, N.; Top. Curr. Chem. **2002**, *219*, 11.

227 (a) Kosugi, M.; Sasazawa, K.; Migita, T. *Chem. Lett*. **1977***, 6*, 301. (b) Stille, J. *Angew. Chem. Int. Ed. Engl*. **1986,** *25,* 508

228 (a) Negishi, E. I*. Acc. Chem. Res*. **1982,** *15*, 340. (b) Knochel, P.; Singer, R. *Chem. Rev*. **1993**, *93,* 2117.

229 Lipshutz, B. H.; Siegmann, K.; Garcia, E.; Kazser, F. *J. Am. Chem. Soc.* **1993,** *115,* 9276

230 (a) Hiyama, T.; Hatanaka, Y. *Pure Appl. Chem*. **1994***, 66*, 1471 (b) Denmark, S. E.; Sweis, R. F*.; Acc. Chem. Res*. **2002**, *35,* 835.

231 (a) Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374 (b) Corriu, R. J. P.; Masse, J. P. *J. Chem. Soc. Chem. Comm.* **1972**, 144

232 (a) Goossen, L. J.; Deng, G., Levy, L. M. *Science* **2006**, *313,* 662 (b) Goossen, L. J.; Rodriguez, N.; Melzer, B.; Linder, C.; Deng, G.; Levy, L.M. *J. Am. Chem. Soc***. 2007**, *129*, 4824

233 Goossen, L. J.; Rodríguez, N.; Melzer, B.; Linder, C. *J. Am. Chem. Soc.*, **2008**, *130,* 15248

234 Goossen, L. J.; Thiel, W. R.; Rodríguez, N.; Linder, C.; Melzer, B. *Adv. Synth. Catal.* **2007**, *349*, 2241.

235 Hermann,W. A.; Rost, A. M. J.; Tosh, E.; Riepl, H.; Kühn, F. E. *Green Chem.* **2008,** *10,* 442.

236 Rentzsch, C. F.; Tosh, E.; Kühn, F. E. and Herrmann, W. A. has been submitted to Green Chemistry

237 Schuster,O.; Stander-Grobler, E.; Tosh, E. Krueger,A.; Raubenheimer, H. at the XVI International Symposium on Homogeneous Catalysis, Florence, July 6-11 2008

238 Berti, G., *Gazzetta Chemica Itallia*, **1957**, *87,* 293

239 Taljaard, B.; Taljaard, J. H.; Imrie, C.; Caira, M. R. *Eur. J. Org. Chem*. **2005**, *12*, 2607.

240 Deblon, S.; Ruegger, H.; Schonberg, H.; Loss, S.; Gramlich, V.; Grutzmacher, H. *New J. Chem*. **2001,** *25,* 83.

241 Hegab, M. I.; El-Gazzar, A. B. A.; Farag, I. S.; Gad, F. A. *Sulfur Lett.* **2002**, *25,* 79-85.

242 Kolthoff, I. M.; Chantooni, M. K. *J. Am. Chem. Soc.* **1969,** *91*, 23

243 Looker, J. J. *J. Org. Chem*. **1966**, *31*, 3599

244 Kusama, H.; Funami, H.; Shido, M.; Hara, Y.; Takaya, J.; Iwasawa, N. J. Am. Chem. Soc. **2005**, *127*, 2709.

245 Toma, J. M. D. R.; Toma, P. H.; Fanwick, P. E.; Bergstrom, D. E.; Byrn, S. R. *J. Crys. Spec. Res.* **1993**, *23,* 41

246 Abd-Elyaher, M. M.; Fischer, H. *J.Organomet. Chem*. **1999,** *588,* 235.

247 Tosh, E. *M. Sc. Thesis*, University of Regina, **2006**.

248 Kraihanzel, C. S.; Cotton, F. A. *Inorg. Chem.* **1963**, *2,* 533