TECHNISCHE UNIVERSITÄT MÜNCHEN
Anorganisch-Chemisches Institut

Synthesis and Catalytic Applications of Carbene-Functionalized Hybrid Catalysts

Alexandrina Doina Rusu

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

Doktors der Naturwissenschaften

genehmigten Dissertation.

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

Prüfer der Dissertation:

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

Die Dissertation wurde am 26.05.2009 bei der Technischen Universität München eingereicht und durch die Fakultät für Chemie am 25.06.2009 angenommen.

Die vorliegende Arbeit entstand in der Zeit von Januar 2006 bis Juni 2009 am Anorganisch-Chemischen Institut der Technischen Universität München

Mein besonderer Dank gilt meinem verehrten Lehrer

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

für die Aufnahme in den Arbeitskreis, für das uneingeschränkte Vertrauen das er mir von Anfang an entgegenbrachte, die große Freiheit, die mir beim Erstellen dieser Arbeit gewährt wurde und für sein persönliches Interesse am Gelingen dieser Arbeit.

Diese Arbeit wurde durch ein Stipendium von dem Internationalen Doktoranden Kolleg **NanoCat** gefördert.

To Radu

and my parents

"Chance favors only the prepared mind."

- Louis Pasteur

Acknowledgements

My very special thanks go to **Prof. Dr. Fritz E. Kühn** for his help and constant support over the last three years.

I am very grateful to **Dr. Öfele** for his continuous advises and helps during the "carbene-seminar" meetings. My "carbene-group" mates and all past and present members of the Prof. Herrmann's group are acknowledged for helpful discussions and fruitful collaborations.

I am grateful to **Dr. Eberhardt Herdtweck** for recording numerous X-ray data and for refining X-ray structures included in this work.

I am also very thankful to **Mrs. Ulrike Ammari** and **Mr. Thomas Tafelmaier** for the elemental analysis. **Mrs. Rodica Dumitrescu** for the mass spectroscopy analysis. **Mrs. Georgeta Krutsch** is acknowledged for her readily and cheerfully assistance in the numerous NMR measurements.

Dr. Mirza Cokoja and **MSc. Kavita Jain** are acknowledged for proof reading of this thesis.

I would like to thank my fellow lab mates **Sandra Zinner**, **Alexander Raith**, **Philipp Altmann** and **Claudia Straubinger (geb. Linninger)** for making my experience in the lab enjoyable. It is quit an achievement that we are still friends after seeing each other constantly for all this time.

A big thanks goes to my truly friends, **Monica Pop** and **Iulius Markovits**. Their help and constant presence during all this time was invaluable.

My **Mom** and **Dad**, all that I have accomplished in my life is the result of their love and support. I cannot imagine, how my life would be like without my loving husband **Radu.** Thanks for all your support, understanding, and love during all this time. You have made my life a wonderful and positive experience.

Table of contents

Abbreviations and acronyms

Å	Angstrom
Acac	Acetylacetonate $[CH_3C(O)CHC(O)CH_3]^-$
Ar	Aromatic substituen
Cy	Cyclohexyl-Rest
CCDC	Cambridge Crystallographic Data Centre
CIF	Crystallographic information file
COSY	Correlation spectroscopy (NMR)
δ	chemical shift
DMAc	*N,N*-Dimethylacetamide
DMSO	Dimethylsulfoxide
FAB-MS	Fast atom bombardment mass spectroscopy
GC	Gaschromatography
HMBC	Heteronuclear multiple-bond correlation (2D $^{1}H/^{13}C$ NMR)
HMQC	Heteronuclear multiple quantum coherence (2D $^{1}H/^{13}C$ NMR)
Hz	Hertz
J	Coupling constant
m	multiplet (NMR), medium (IR)
MS	Mass spectroscopy
MHz	Megahertz
NHC	N-heterocyclic carbene
NOESY	Nuclear Overhauser enhancement spectroscopy
OAc	Acetat-Rest
ppm	Parts per million
RT	Room temperature
s	Singlet (NMR), strong (IR)
sept	Septet (NMR)
t	Triplet (NMR)
TOF	Turnover frequency
TON	Turnover number

1 Introduction

1.1. *N*-Heterocyclic carbenes (NHCs)

1.1.1 Historical perspective

Since the pioneering work of *Doering* in 1954, carbenes have been recognized as a unique type of intermediates with characteristics distinct from radicals already known in the organic chemistry.[1] Since then, research on carbenes has rapidly expanded, but for a long time they seemed too reactive to be isolated. First attempts to stabilize carbenes were made in 1980s when *Tomioka* started to study persistent triplet diarylcarbenes.[2]

Although NHCs have been known since the pioneering work of *Wanzlick,* who observed their dimerisation [3] and was able to trap them to form mercury-salt carbene complexes, [4] thirty years went by before the first NHC was isolated. In the following years, stabilization by heteroatoms seemed the most promising way to stabilize carbenes. The first isolable carbenes were reported in 1988 by *Bertrand* [5] and 1991 by *Arduengo*.[6]

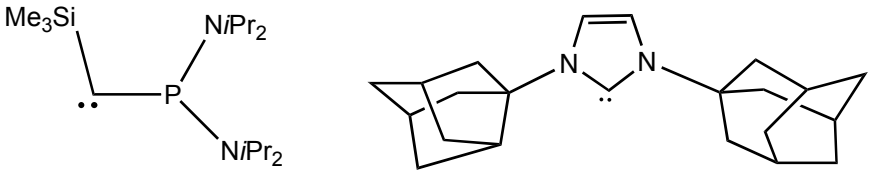


Figure 1. The first stable isolated carbenes.

The phosphinocarbene can be even distilled at 80-85 °C/10^{-2} Torr and N-heterocyclic carbene (NHC) is a crystalline solid that melts above 240-241 °C without decomposition! (Figure 1).

The stability of the NHCs made them very popular, and during the following years further analogues were synthesized (Figure 2). In 1995, *Arduengo* proved using NHC that aromaticity was not needed for stabilization, and in 1996 *Alder* isolated first acyclic NHC**.**[7] This research area has been continually expanded with the isolation of four-membered carbene by *Grubbs* [8], alkyl carbene and three membered carbene by *Bertrand* in 2004 and 2006. [9]

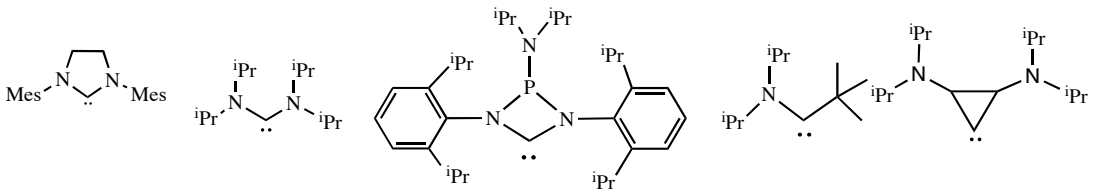


Figure 2. Novel stable NHCs.

However, several new "bottable carbenes" are not only air stable, but can also "survive a humid night in Willington" in solution and crystalline state (Figure 3).[10]

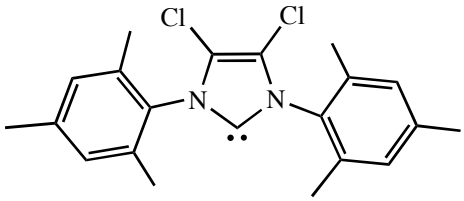
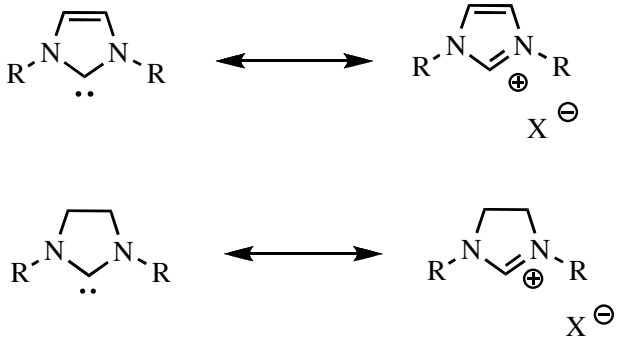


Figure 3. "Bottable carbene" with high stability.

1.1.2 Nomenclature

For the sake of homogeneity, the following nomenclature will be used throughout this work. NHCs**,** which are related to an imidazoline structure**,** will be called *1,3-di-R-imidazolin-2-ylidenes* and NHCs with a saturated C-C double bond will be described as *1,3-di-R-imidazolidin-2-ylidenes*. Corresponding formamidinium salts will be called imidazolium and imidazolinium salts (Scheme 1).



Scheme 1. Nomenclature of the various NHCs and formamidinium salts.

1.1.3 General characteristics

Carbenes are neutral compounds containing divalent carbon with only six electrons in their valence shell. Both non-bonding orbitals can be occupied in two ways. In triplet carbene, both electrons are arranged in different orbitals with parallel spins. In singlet carbene on the other hand, electrons with paired spins occupy the same orbital (Figure 4). In singlet ground state, carbenes are electronically comparable to carbenium ions R_3C^+, while in triplet state to free radicals $\cdot CR_3$. Carbene can show either linear or angular structure in the dependence on the hybridization of the carbene atom. If the carbon atom is sp^2-hybridized, the carbene has nonlinear structure.

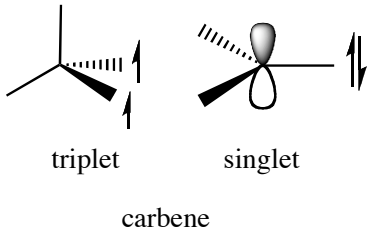


Figure 4. Triplet and singlet carbenes.

Experimental evidence suggests nonlinear structure with triplet ground state for most carbenes.[11] Dihalogencarbenes and carbenes with oxygen, sulfur and nitrogen substituents with their singlet ground state, represent an important exception from this rule. With two nitrogen substituents next to the C-carbene atom, the NHCs are predicted to stabilize their singlet state (two paired electrons in the σ orbital) by a push-pull effect (Figure 5).[12] First, the σ-electron withdrawing nitrogen inductively stabilizes the σ-nonbonding orbital by increasing its s-character. Second, the energy of the vacant p_π-orbital is increased by interaction with the symmetric combination of the nitrogen lone pairs. Combination of the two effects increases the σ-p_π gap and therefore favors the singlet state. Moreover, the pseudo sp^2-hybridization adopted by the C-carbene atom in its singlet state, matches the bent geometry of the NHC five-membered ring.

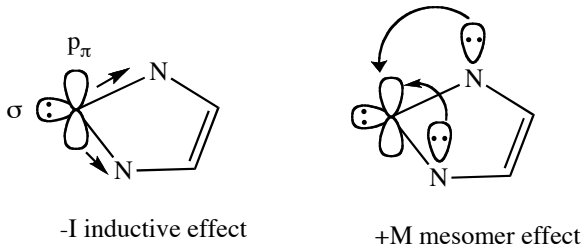


Figure 5. Electronic stabilization of NHCs.

The interaction of the nitrogen lone pair with the p-orbital of the carbene is reflected by a N-C-carbene bond length of 1.365 Å, which is consistent with double bond character. An accurate assessment of the π-backbonding was found by analyzing the dynamic ^{1}H-NMR behavior of bis-(diisopropylamine)carbene.[13] Since the major part of this process involves rotation about the N-C-carbene bond, the measured barrier to rotation of 53 kJ/mol was mostly attributed to the substantial π-component of these bonds.

Dimerisation of NHCs has been known since the first attempts to isolate them. [3] Alder showed that dimerization is thermodynamically unfavorable for imidazolin-2-ylidenes (singlet/triplet gap of 354 kJ/mol), but very likely to happen for imidazolidin-2-ylidenes due to lack of aromaticity and acyclic NHCs due to loss of conjugation through twisting around the N-C-carbene bond.[14] The ^{13}C-NMR chemical shifts ranges from 210-220 ppm downfield from TMS for aromatic imidazolin-2-ylidenes, to 235-245 ppm for imidazolidin-2-ylidenes and acyclic NHCs.[15]

1.1.4 Preparation of the free diaminocarbene

Four principal methods were successfully used for the generation of free diaminocarbenes (Scheme 2):

1 deprotonation of imidazolium salts or formamidinium salts,[6]

2 desulfurization of thioureas,[19]

3 thermolysis of methanol adducts of type,[20]

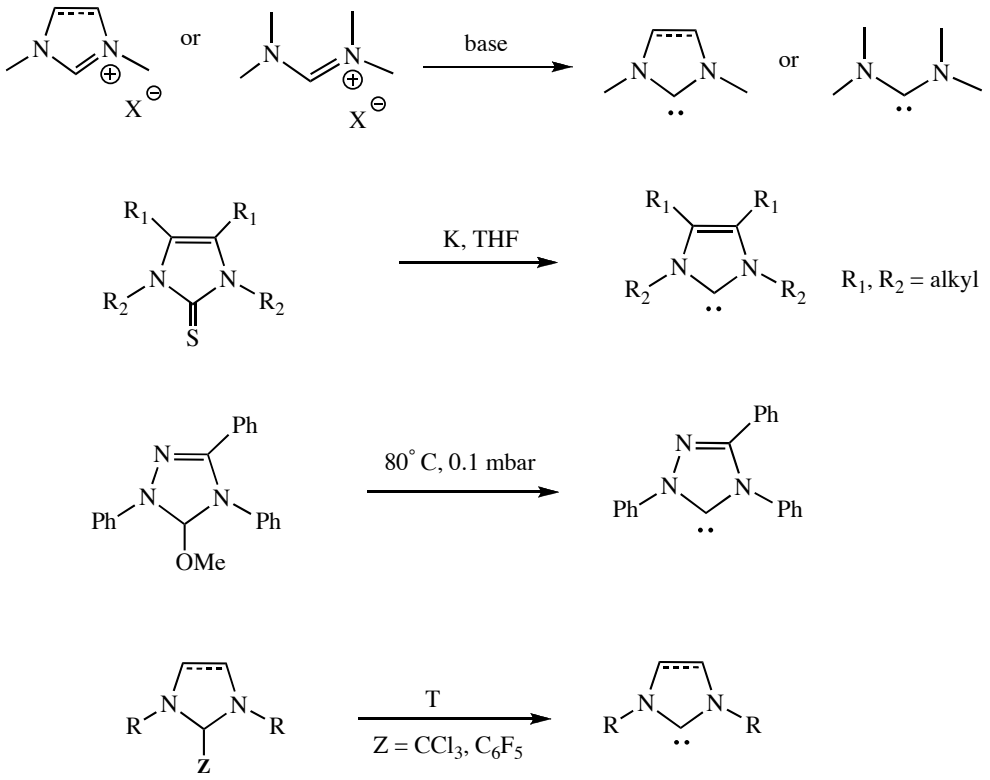
4 thermolysis of chloroform and pentafluorobenzaldehyde adducts,[21]

Alder has measured the pKa value for diisopropyl-imidazolin-2-ylidene on the DMSO

scale and found to be 24.[16] For di-*tert*-butyl-imidazolin-2-ylidene *Streitwieser* found a pKa of 20 in THF.[17] Therefore, it is not surprising that the principal method used for NHCs synthesis is deprotonation of the corresponding imidazolium or formamidinium salts. For the isolation of the first NHC, *Arduengo's* group used NaH/KH in THF in the presence of KO^{t}Bu and DMSO.[6] *Herrmann* showed that milder conditions such as sodium amide in liquid ammonia and THF at -40 °C, were also efficient.[18] With a pKa increased by 2 to 6 units, formamidinium salts underwent nucleophilic addition of the base rather than deprotonation.[16] This problem was solved by the use of hindered alkali amide bases such as lithium diisopropylamide or potassium hexamethyldisilazide.
In 1993, *Kuhn* and *Kratz* reported another pathway to imidazolin-2-ylidene by reduction of the corresponding thiourea using metallic potassium.[19] This heterogeneous reaction, which has proved difficult to reproduce, is attractive because the only other product is potassium sulfide, which is insoluble in THF.

Another successful method was established by *Enders* who synthesized a triazol-2-ylidene by thermolysis of its methanol adduct in a good yield.[20] One drawback of this methodology is the extreme sensitivity of the methanol adduct.

Finally, thermal elimination of chloroform or pentafluorobenzene from their diamino adducts **18** was recently used by *Nyce et al.* for the synthesis of NHC's. The great advantage of this method is high stability and complete lack of air- and moisture sensitivity of the carbene precursors.[21]



Scheme 2. Four methods for the generation of the free NHC's.

1.1.5 Donor-functionalized carbenes

Donor-functionalized NHCs, contain at least another anionic or neutral $2e^-$ donor atom (*e.g.* C, N, O, S or P), which can act as a polydentate ligand upon coordination to a metal center. The feasibility of attaching functional groups to the nitrogen atoms in N-heterocyclic carbenes makes them particularly suitable to the synthesis of functionalized-NHC chelating ligands. Thus, the intense activity in the design and synthesis of functionalized-NHCs, although undoubtedly motivated by a desire to develop exciting and innovative ligand systems, has also in part been driven by the need to circumvent the decomposition of the metal complex and to develop efficient new catalysts. Many novel and varied ligands have thus been designed. In 199,6 *Herrmann* et al. reported the synthesis of the first donor-functionalized NHCs (Figure 6).[18] N-functionalized carbenes with amine, phosphine, or alkoxy groups were synthesized in liquid ammonia. Additionally, imidazolium salts with carbonyl,[18,22] pyridyl,[23] pyrazolyl,[24] and phosphine substituents [25] at the nitrogen atoms have been described.

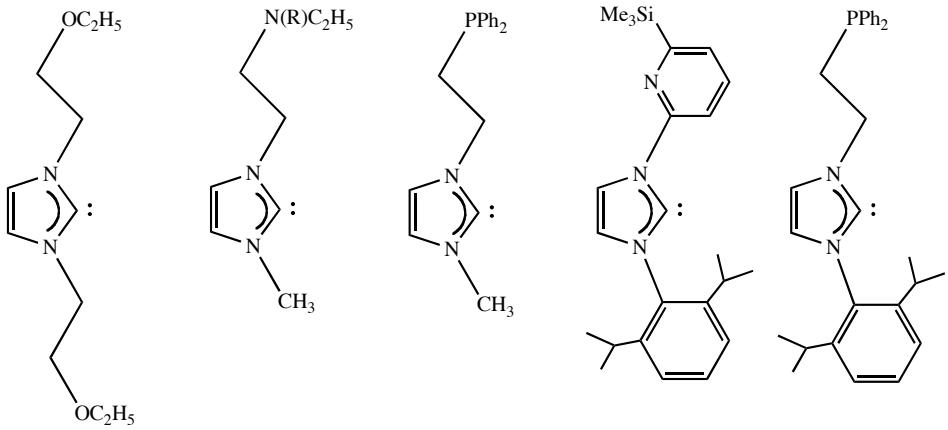
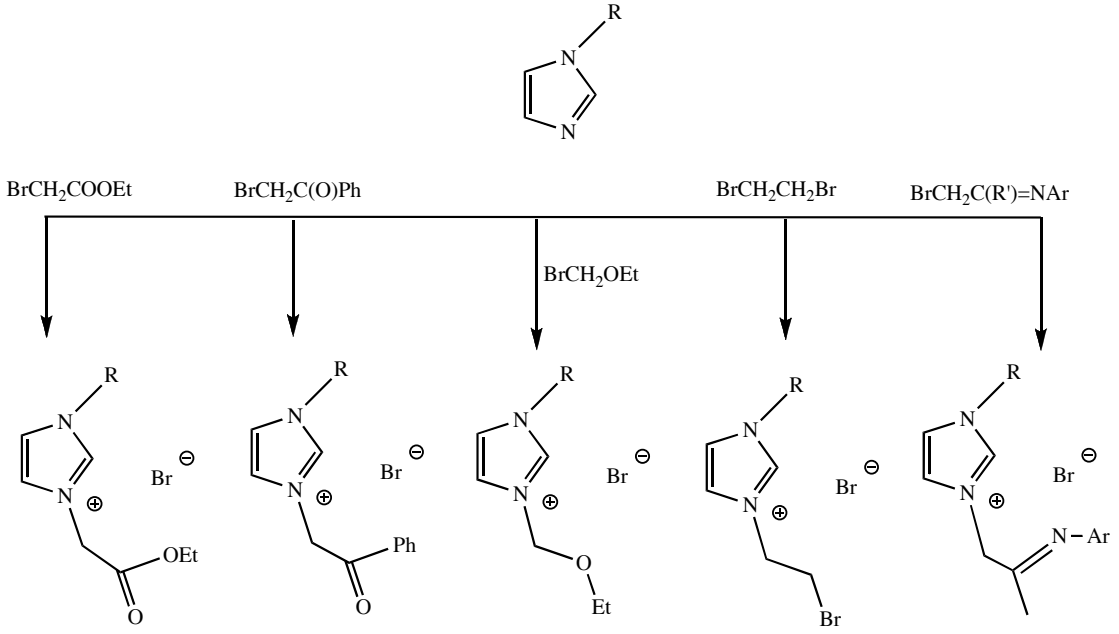


Figure 6. Donor-functionalized N-heterocyclic carbenes

NHC's are synthesized from imidazole, which can be functionalized on both nitrogen atoms. The simplest method to introduce chirality is to use a naturally occurring and commercially available chiral amine in the synthesis of the imidazole ring, or to use a chiral alkyl halide to quarternize the second nitrogen in the synthesis of the imidazolium salt.[26] Functional groups can be introduced in the imidazole side chain by conventional synthetic methods. The hydroxy group can be converted into an ester or ether, or substituted by a halogen [27] and subsequently converted into a phosphine (Scheme 3).[28]



Scheme 3. Functionalization of imidazoles.

Introduction of an amino side group is equally facile.[29] The main limitation for the introduction of functional groups lies in the method of carbene formation. A free NHC is most often synthesized by abstraction of the hydrogen atom bound to the carbon between the two nitrogen atoms. As this hydrogen atom is not very acidic, a strong base is required. Functional groups on the imidazolium ring must therefore be inert to strongly basic conditions, preferably even at elevated temperatures. It is not surprising that the first functional groups introduced into NHC were tertiary amines, ethers, and phosphines, but other groups such as primary and secondary amides as well as alcoholates were soon to follow.

1.2 *N*-heterocyclic carbene metal complexes

1.2.1 Historical perspective

In 1964, transition metal carbene complexes were introduced to inorganic chemistry by the pioneering discovery of *Fisher* and *Maasböl.* The reaction of phenyl lithium with $W(CO)_6$, followed by addition of an acid and subsequent treatment with diazomethane gave complex (Figure 7).[30] A few years later, *Wanzlick* and *Öfele's* first syntheses of NHC metal complexes, extended the Fischer type carbene family.[31,32] In 1974, *Schrock* developed a new type of carbenes, the so-called Schrock carbene with an entirely different reactivity.[33]

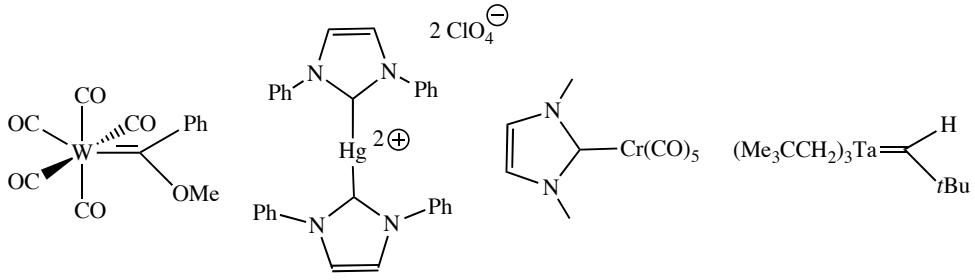
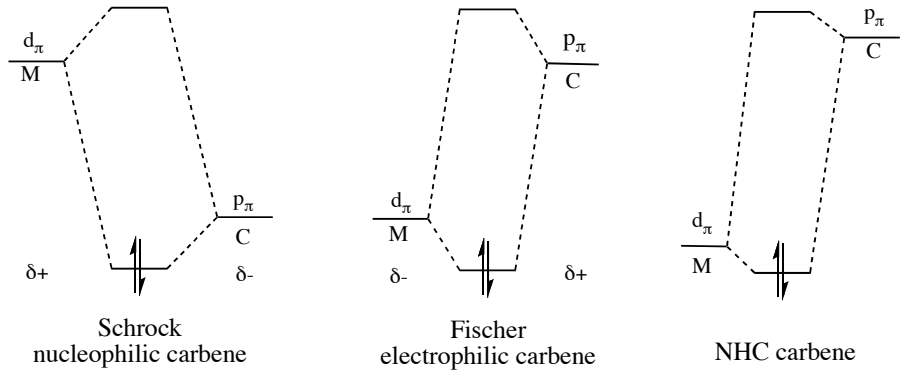


Figure 7: *Fischer, Wanzlick, Öfele* and *Schrock t*ransition metal carbenes complexes.

1.2.2 Properties of carbene ligands

The discovery of the compounds $[(OC)_5W{=}C(Ph)(OMe)]$ by *E.O. Fischer* and $[(Np)_3Ta{=}C(H)(^tBu)]$ by *R. Schrock* has established a novel class of compounds.

[30,32] The chemical behavior of Schrock and Fischer alkylidenes is substantially different, reflecting the different nature of the metal-carbene bonding.



Scheme 4. Partial molecular diagram of *Schrock, Fischer,* and NHC carbene complexes.

Although the metal-carbene bonds in Schrock and Fischer carbene complexes are both described as double bond, they differ by the polarity of the electron density. This difference arises from the difference in energy between the d_π orbital of the metal and the p_π orbital of the carbene. The molecular orbital diagrams (Scheme 4) depict the bonding of Schrock, Fischer and N-heterocyclic carbenes.

A particular example of Fischer carbenes are metal-NHC complexes, where the NHC ligand has a p_π orbital of very high energy since their multiple bonding between the carbene atom and the two nitrogen atoms. As a result, the p_π orbital does not interact well with the d_π, thus preventing almost any π-backbonding from the metal to the carbene. In NHC complexes, the metal carbon bond is therefore best represented by a single bond. The fundamental difference between a typical Schrock alkylidene moiety and an NHC as a ligand is underlined in the crystal structure of $[RuCl_2(NHC)_2(=CHC_6H_4Cl)]$ (NHC = 1,3-diisopropylimidazolin-2-ylidene) where the two types of carbenes are linked to the same metal centre. [34] The ruthenium-carbon bond of the Schrock carbene, generally written as a double bond, has a bond length of 1.821(3) Å, whereas the Ru-C bond length to the NHC (2.107(3) Å and 2.115(3) Å) justifies its representation as a single bond (σ-donor and virtually no π-acceptor). Measurement of IR carbonyl absorption frequencies of NHC carbonyl

metal (Fe, Cr, Rh, Mo and Ir) and their phosphine analogues showed the significantly increased donor capacity of NHC versus phosphines, even to trialkylphosphines. [35,36] Experimental investigations,[37] calorimetric studies [38,39] and experimental calculations [40] have shown that the ligand dissociation energy of NHCs from Ru complexes is higher than for phosphines. Further calculations with other metals such as Au, Cu, Ag, Pd and Pt led to similar conclusions.[41,42] Therefore, *N*-heterocyclic carbenes as ligand on metal center significantly differ from carbene moieties in Fischer and Schrock carbene complexes in respect to their reactivity: imidazolin-2-yliden-metall complexes are exceptionally resistant against nucleophilic and electrophilic attacks, as well other typical carbene decomposition reactions.[43] Because of their properties, classical carbenes are not well suited as ligands for the organometallic catalysis, since they would not survive the common reaction conditions. High thermal and chemical stability of NHCs on the other hand makes this compound class very interesting especially fort he uses in catalysis.

In analogy to the cone angle defined for phosphines by *Tolman*, [44] a method to quantify the steric parameters of NHCs proposed by *Nolan* by describing NHCs as "fences" with "length" and "height".[39] The structural differences of free NHCs and coordinated NHCs are very small. In ^{13}C-NMR, the signals for the free carbene carbon are usually shifted upfield by about 20-30 ppm upon complexation to a transition metal. It has been shown that free NHCs are able to cleave dimeric metallic species such as $[(\eta^4\text{-cod})Rh]_2$,[45] and exchange phosphine [46] or pyridine [47] ligands.

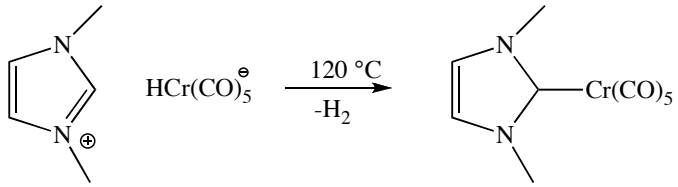
1.2.3 Complexation to metals

Seven synthetic methodologies have been most commonly applied in the literature for the preparation of NHC metal complexes:

1. proton abstraction with bases prior to metallation.[50]
2. *in situ* deprotonation of imidazolium by basic metalates or basic counter-ions.[51]
3. use of an external base in a one pot reaction with the metal precursor.[52]
4. transmetalation via silver complexes.[53]

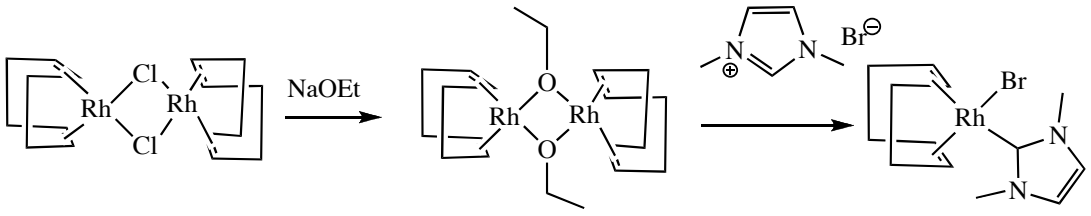
5. oxidative addition of 2-chloro-1,3-disubstituted imidazolinium salts to appropiate metal complexes.[54]
6. metal atom condensation.[55]
7. synthesis of carbene in the cocondensation sphere of metal.[56]

For the synthesis of the very first M-NHC complex an imidazolium salt was in situ deprotonated by an anionic carbonyl hydride complex (Scheme 5). The basic metalate ion $[HCr(CO)_5]^-$ serves as base and ligand acceptors at the same time.



Scheme 5. *Öfele's in situ* deprotonation by a basic metalate ion.

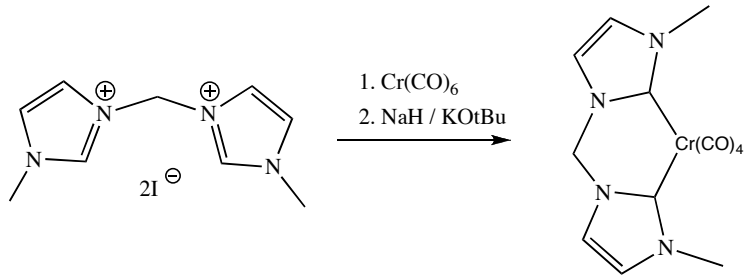
Basic counterions of the metal precursors can also act as deprotonating agents. For example, a convenient method to synthesize NHC-Pd(II) complexes is the treatment of $Pd(OAc)_2$ with a imidazolium salt. In a similar way, $[M(\eta^4\text{-COD})(RO)]$ (M = Rh, Ir) formed *in situ* by adding μ-chloro bridged analogues to a solution of sodium alkoxide in the corresponding alcohol, will deprotonate an imidazolium salt and deliver the corresponding NHC complex (Scheme 6).[48]



Scheme 6. Synthesis of NHC-complexes by deprotonation with basic counter-ions of metal precursors.

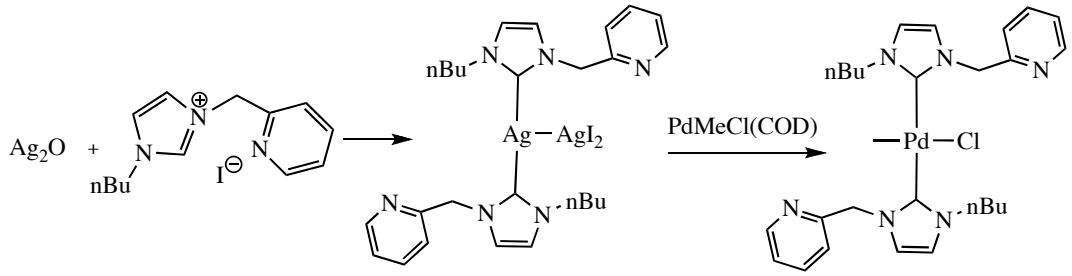
The use of an external base to generate NHCs in the presence of a metal precursor is also an efficient method (Figure 14).[49] A large variety of bases ranging from

triethylamine, [50] lithium diisopropylamide [51] to phosphazene bases [52] have been successfully used over the past years.



Scheme 7. Synthesis of NHC-complexes by deprotonation with external base.

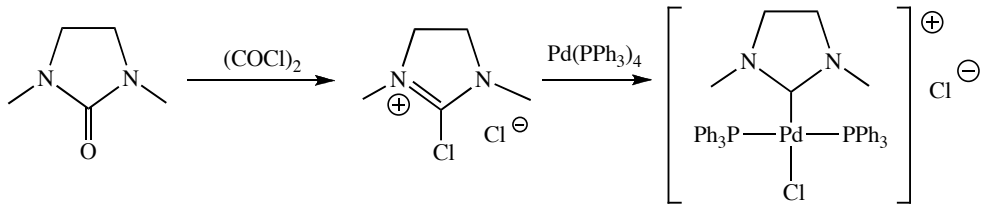
Recently developed a new method for preparing NHC metal complexes via corresponding silver carbene complexes has been developed by Wang et al.[53] Silver NHC complexes are readily prepared upon mixing the corresponding imidazolium salt with Ag_2O in CH_2Cl_2 at room temperature. Subsequent reaction with a chloro-metal precursor gives the desired NHC metal complex that can be easily separated from AgX, the latter being insoluble in THF (Scheme 8).[54]



Scheme 8. Preparation of metal complexes by transmetalation via silver(I) complexes.

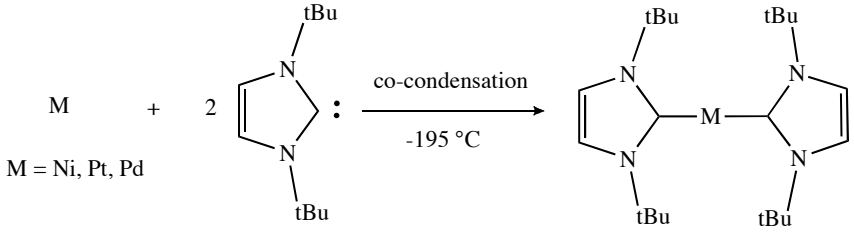
Oxidative addition of 2-chloro-1,3-disubtituted imidazolium salts to a low valent metal was recently used by *Fürstner et al*. for the synthesis of a large number of carbene complexes (Scheme 9).[55] This method has been discovered by *Stone et al.,* who has shown that oxidative addition of 2-chlorothiazolium or 2-chloro-1-methylpyridinium salts to metals afford the corresponding carbene complexes, in excellent yields.[56] Noteworthy, this novel method allows substantial variations,

since the required 2-chloro-1,3-disubstituted imidazolium salts can be easily prepared from cyclic ureas or thioureas on treatment with oxalyl chloride.



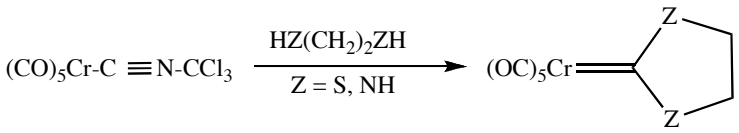
Scheme 9. Synthesis of the NHC-complexes by oxidative addition.

The first stable 14-electron carbene complexes with two-fold coordinated Ni(0) and Pt(0) were synthesized by *DuPont* in 1994 by reaction of isolated carbene with metal precursor in solution.[57] The obtained complexes were however not suitable as catalysts for the C-C coupling reaction type. The synthesis of low-coordinated homoleptic carbene complexes by co-condensation of NHC's with metal vapor was not possible until 1999. [58] An important advantage of this method is the absence of competing ligands from starting material or solvents (Scheme 10).



Scheme 10. Synthesis of NHC-metal complexes by metal atom co-condensation.

Another synthetic strategy for the formation of metal NHC complexes is the nucleophilic addition to metal-coordinated isocyanide ligands. These additions can be carried out either inter- or intramolecular, and represent a very broadly applicable method for the formation of carbene complexes. *Fehlhammer* and coworkers reported that $(CO)_5Cr^*CNCCl_3$ reacts with dithiols and diamines to yield the heterocyclic electron-rich carbene complexes (Scheme 11).[59]



Scheme 11. Synthesis of carbene complexes.

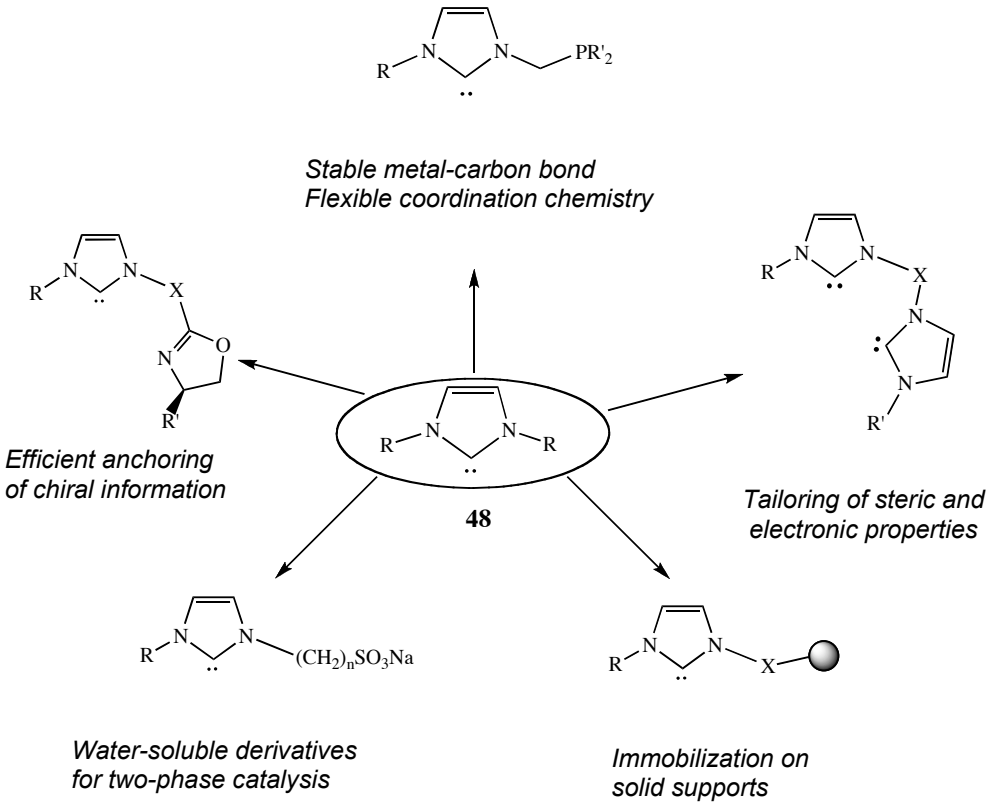
The synthesis of N-heterocyclic carbenes by *Ugi et al.* via an organometallic 4CC-reaction (4CC = four component condensation) of hydroisocyanic acid to metal center, represent new developments of the topic.[60]

1.2.4 N-heterocyclic carbene *vs* phosphine ligands

The first and the greatest advantage of NHCs over phosphines is their ability to build complexes with nearly all metals. Central atoms in NHC-complexes can vary from electron rich transition metals such as Pd(0) and Rh(I) over electron poor main group metal cations such as Be^{2+}, to metals in high oxidation states such as Ti(IV), Nb(V) and Rh(VII).

Because of their pronounced σ-donor ability, NHC's can coordinate to the metals that are not capable of π-backdonation, since the empty p-orbital at the carbene carbon atom is partially filled due to the lone-pair delocalization on nitrogen atoms.[61] Both the syntheses as well the structural data of such complexes lead to the conclusion that they represent donor adducts which resemble amino- and ether-complexes. Much more important is the ability of NHCs to form stable complexes with catalytically active metals e.g. palladium, rhodium, ruthenium.[62]

Since the M-C bond in NHC-complexes is stronger than the P-M bond in phosphine complexes, the problem of the weak ligand-metal bond is avoided. Furthermore, NHC's cannot dissociate from the metal and so, no large excess of the ligand is required.[63]



Scheme 12. Versatile N-heterocyclic carbenes.

Many different synthetic ways, which were shown above, allow convenient access to N-heterocyclic carbenes [64] so, that a large number of substituted, chiral, [67] functionalized, [65] chelating, [68] immobilized, [66] or water soluble, [67] substances are now available for different applications (Scheme 12).

1.3 Applications of NHCs

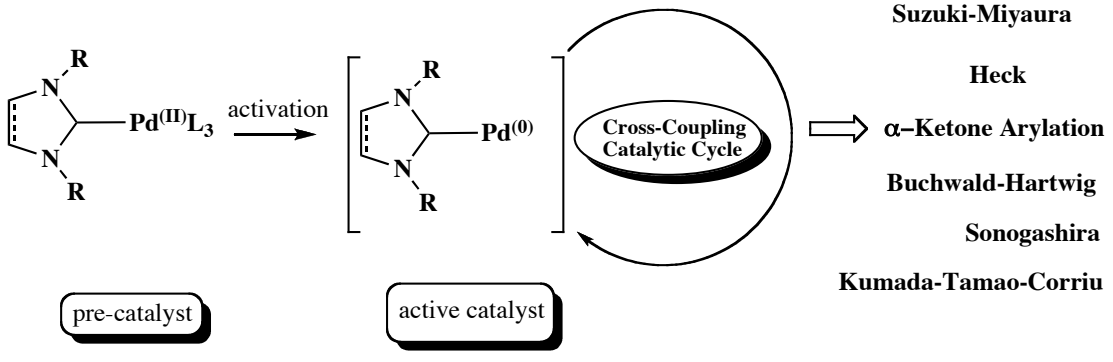
1.3.1 Asymmetric catalysis

The first example of chiral carbenes used in asymmetric catalysis appeared in 1996/1997 with the pioneering work of *Enders* and *Herrmann*. [69,70] Since then, the field has largely expanded.[71] *Enders* successfully applied the NHC and their derivatives in carbene catalyzed asymmetric nucleophilic acylation processes. High asymmetric induction in enantioselective benzoin condensation and enantioselective Stetter reactions were obtained by the use of simple chiral triazolium and thiazolium salt.

Chiral NHC ligands have been used in a large variety of asymmetric reactions. Applications to the following reactions were investigated: Rh-hydrosilylation of ketones, [71,72,73] olefin metathesis, [74] Pd-oxindole reaction, [75-77] Pd-allylic alkylation, [76] Rh(I)- and Ir(I)-transfer hydrogenation of ketones, [76] Cu-catalysed addition of diethylzinc to cyclohexenones, [78-81] Ni-hydroamination of acrylonitrile derivatives [82] and hydrogenation. A logical extension of this development is the application of NHC ligands in stereoselective catalysis. In general, ligand tailoring in asymmetric catalysis is guided by several simple concepts and principles. For instance, the tailoring of chiral catalysts is frequently based on C_2-symmetry in order to reduce the number of diastereomeric intermediates and transition states, which play a role in the catalytic cycle.

1.3.2 Catalysis involving NHCs

The application of *N*-heterocyclic carbenes as ligands for transition metals has led to significant advances in several important catalytic reactions, most notably the metathesis of olefins and Pd catalyzed coupling reactions (e,g, *Heck*-, [83] *Suzuki*-, [84] *Sonogashira*-, [85] *Stille*-, [86] and *Kumada*-couplings [87])**,** *Hartwig-Buchwald*-reactions, [88] α-arylation of amides, [89] hydrogenations, [90] hydrosilylations, [91] and many other (Scheme 13). The ability of NHCs to stabilize low valent Pd species is likely responsible for the enhanced activity observed in these cases.



Scheme 13. General cross-coupling reactions.

Herrmann et al. first reported on the catalytic activity of an NHC-ligated Pd complex in the *Mizoroki-Heck* reaction (Figure 8).[70a]

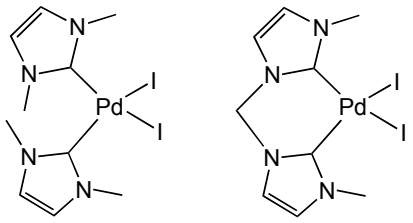
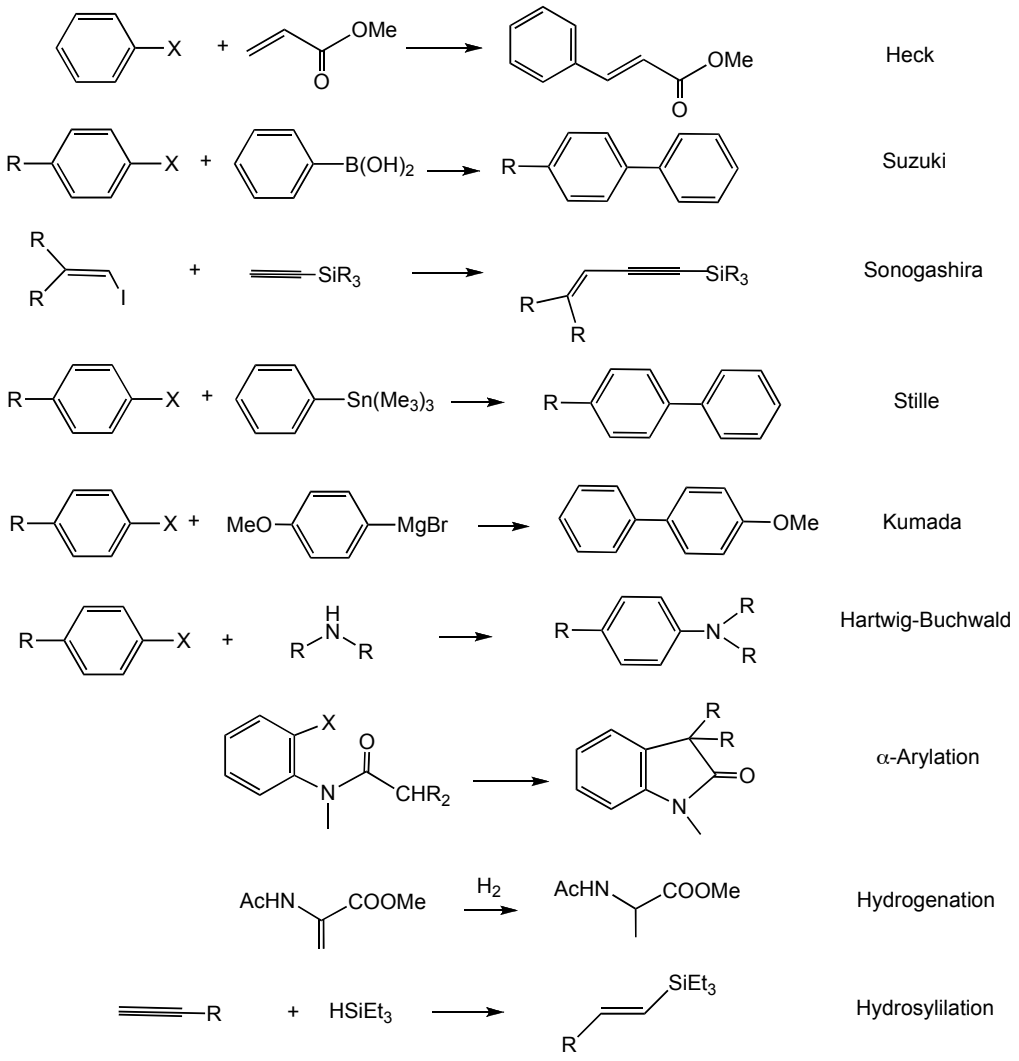


Figure 8. Mono- and biscarbene Pd(II) complexes.

It is assumed that the carbene ligands enhance oxidative addition of the aryl halide because of their strong σ-donating abilities, which enhance the electron density. NHC ligands should also promote the reductive elimination in the more highly substituted complexes formed at the end of the catalytic cycles because of their greater steric hindrance. Recent reports document the preparation of N-heterocyclic carbene complexes anchored to solid or reusable supports by virtue of the NHC ligand.[40]



Scheme 14. Overview of literature examples for coupling reactions catalyzed by M-NHC complexes on organic solution.

Despite the fact that NHCs generally confer greater thermal and oxidative stability on their metal complexes than phosphines, presumably because of decreased ligand lability, it is yet important to be aware of the potential decomposition pathways of NHC ligands. This is especially crucial in cases where the kinetic stability of the metal–ligand bond is important, for example chiral NHCs for asymmetric catalysis, or supported versions of NHC complexes.

1.4 Objectives of this work

The success of *Bedford's ortho*-metallated triaryl phosphite chloro palladium complex **1b**, which was found to be a highly active catalyst in biaryl coupling reactions, [92] prompted us to start our work with the synthesis of the analogous acetate complex **1a** [93, 94] and their unsaturated N-heterocyclic carbene adducts of both chloro- and acetato-ortho-palladated phosphite complexes [94] (Figure 9).

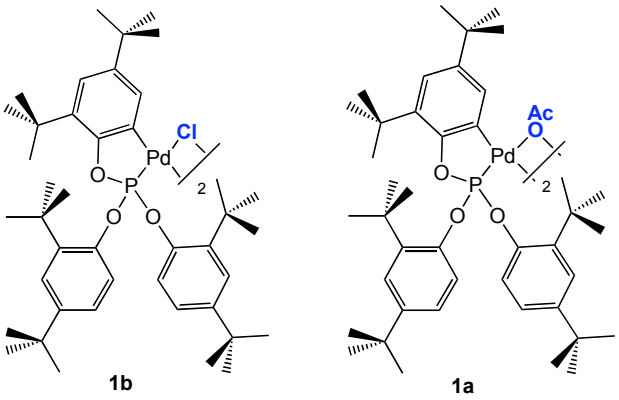


Figure 9. *ortho*-metallated-palladated phosphite complexes.

Because of the high stability of these acetato- and chloro- NHC-phosphitepalladacycles, the project of this work is the variation of the carbenes and the palladacycles to investigate their chemical properties. Acetylacetonate complexes of phospha- and phosphitepalladacycles have been synthesized and fully characterized. It was found that they show excellent air and thermal stability even at elevated temperatures. Their catalytic activities in Suzuki-Miyaura coupling of aryl halides with arylboronic acids have been investigated.

Another important objective is the development of bidentate functionalized-NHC ligands, by incorporation of functional donor groups (e.g. pyridine-benzenimidazoline- and phthalimidine-) in their structure (Figure 10). Various heterobitopic NHC-Pd(II) complexes were synthesized. Their dissymmetry was proved by single crystal X-ray diffraction. The possibility of introducing a new functionality via direct N-alkylation of both heteroatoms of the imidazolium ring is a highly attractive strategy,[95] and makes it suitable for the generation of hemilabile

ligands.[96] The hemilabile arm in such ligands is capable of reversible dissociation from the metal center. Such dynamic behavior produces vacant coordination sites that allow complexation of substrates during the catalytic cycle, and at the same time the strong donor moiety remains connected to the metal center.

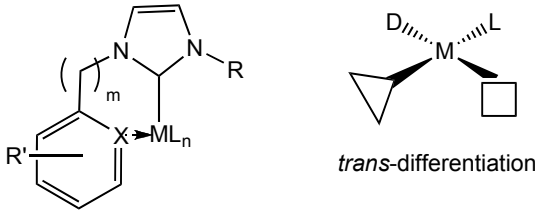


Figure 10. General formula of functional-donor N-heterocyclic carbene ligands.

Both examples of chelating or bridging behavior and complexes in which the donor group is uncoordinated ("dangling") have been obtained. In general, it is important to prepare compounds that exhibit novel reactivity and catalytic behavior. Because of their expected hemilability and tailored *trans*-effect, excellent selectivity for transformations such as C-C and C-heteroatom bond formation with the proposed dissymmetric novel palladium (NHC^amine) complexes can be expected.

2 Phospha/phosphite-Palladacycle Catalysts

2.1. Theoretical background

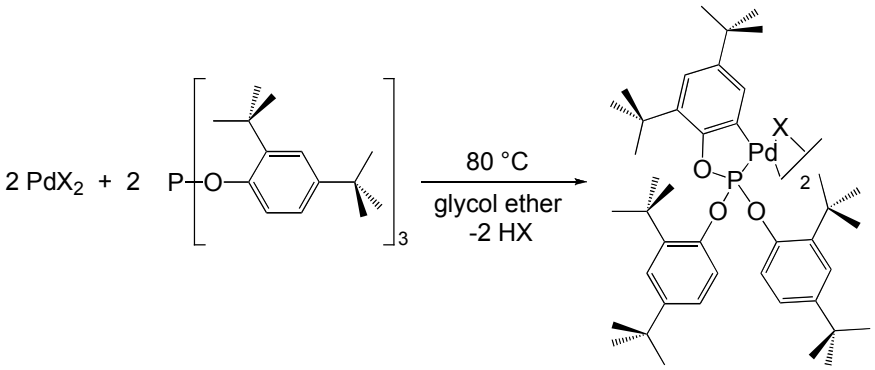
The combination of a palladacycle framework with an NHC was reported first in 1997 by *Herrmann* et al [97-100, 101], and became an important class of novel NHC-substituted palladium complexes for catalysis. The catalyst with unsaturated NHC ligands was found to be effective in the coupling of aryl chloride substrates with arylalkenes [102,103]. NHC substituted phosphapalladacycles combine the advantageous stability of phosphapalladacycles with the steric bulk and high σ-donor strength of N-heterocyclic carbenes [99].

2.2 Preparation of the palladium complexes

Bedford and co-workers published in 1998 an *ortho*-metallated triaryl phosphite chloro palladium complex, which was found to be a highly active catalyst in biaryl coupling reactions [101]. The analogous acetate complex was synthesized in 2004 [102]. Almost simultaneously *Bedford* et al. reported on saturated N-heterocyclic carbene adducts of ortho-palladated triarylphosphite complexes and their catalytic activities in the Suzuki–Miyaura coupling [103]. Because of the high stability of these acetato and chloro NHC-phosphitepalladacycles, we extended our previous work [100] by varying the carbenes and the palladacycles to investigate their chemical properties.

2.2.1 *Ortho*-metallated dimeric complex

The acetate-bridged phosphitepalladacycle dimer **1a** is prepared in a similar way to those of Bedford and co-workers for the analogous chloride complex **1b** [104]. When $Pd(OAc)_2$ or $PdCl_2$ is treated with the sterically demanding tris-(2,4-di-tert-butylphenyl)phosphite in monomethylglycol ether at 80 °C, the colorless complexes **1a** and **1b** are formed in high yields (93–96%) (Scheme 15) [103,104].



1b: X = Cl
1a: X = OAc

Scheme 15. Preparation of *Bedford*-type phosphitepalladacycles **1b** and **1a**

Complex **1a** could be identified as a mixture of *cis*- and *trans*-isomers in solution, with two signals in the ^{31}P NMR spectrum (126.7 and 124.8 ppm; intensity = 1:1), in agreement with the published values of complex **1b** (119.2 and 118.7 ppm) [100,101]. The remarkable air, moisture, and thermal stability of complex **1a** are comparable to the analogous chloride complex **1b**. Complex **1a** has been characterized by spectroscopic methods and elemental analysis. Suitable single crystals of complex **1a** for X-ray diffraction by slow evaporation of a saturated dichloromethane solution were obtained. The solid state structure of the complex **1a**, is shown in Figure 11; selected bond lengths and angles are given in Table 2.

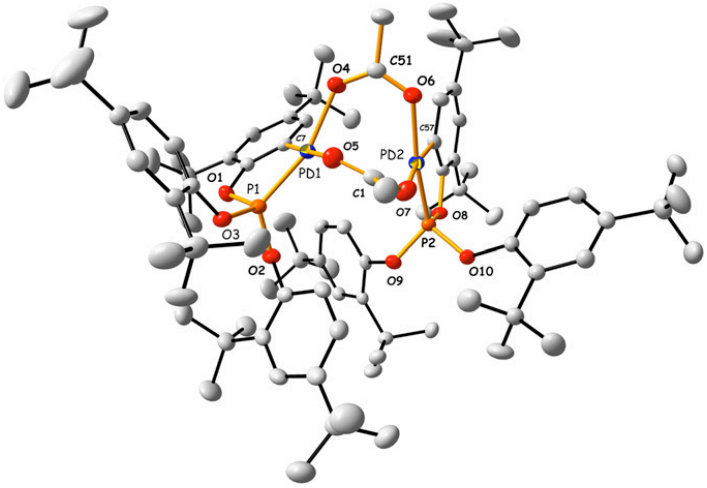


Figure 11. ORTEP plot [118] of compound **1a** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Most of the crystal structures of *ortho*-palladated triaryl-phosphite dimers indicate that in the solid state, the *trans* isomer crystallizes preferentially, where the two phosphorus atoms are coordinated *trans* to each other at the palladium center, although in our case the solid state structure of **1a** depicts the *cis* isomer, in contrast to previously reported ortho-palladated triarylphosphane dimers. [102,107] The two Pd atoms in **1a** adopt square planar geometry and are connected by two bridging acetate ligands. The angles around the palladium center deviate from 90° due to the bite angle of the cyclometalated ligand [P1–Pd1– C7 79.21(6)°; P2–Pd2–C57 80.86(6)°]. No significant differences of the bond lengths between the coordinated atoms and the palladium center were observed compared to other published palladaphosphites [101,103].

2.2.2 NHC-substituted phosphite-palladacycles

Nowadays it is possible to synthesize NHC-palladacycle complexes in two different ways. Firstly we used the ‘‘free carbene’’ route [99] for highly sterically hindered carbene ligands (Scheme 16), or without isolation of the free carbene the *‘‘in situ’’* method, when palladium acetate is used as the starting material [104] (Scheme 17). Reaction of the bulky *ortho*-palladated triarylphosphite complexes **1a** and **1b** with the free carbene ligands (**2–7**), in THF at room temperature gave the mono- and disubstituted complexes **2a**–**7b**. When the palladacycles **1a** and **1b** were treated with 2.1 equiv. of a less sterically hindered carbene such as 1,3-dicyclohexylimidazolin-2-ylidene (**6**), the acetate and chloride products with two NHC ligands were formed (**6a,b**) (Scheme 17). The coordination of two carbenes at one metal center is a good illustration that NHCs are much stronger ligands than the acetate. These complexes were purified by extraction of the obtained residue with *n*-hexane and toluene to remove traces of unreacted free carbene (**6**). By using bulky groups on the carbene ligand, e.g. tert-butyl, only monocarbene substituted complexes (**2a,b**, **3a–5b** and **7a,b**) were obtained, in accordance with previously published results [99,104]. The monocarbene-substituted complexes are obtained in most cases as a mixture of *cis* and *trans* isomers. The reaction of **1b**, **1a** with the free carbene **7** gave a mixture of mono- and di-substituted carbene compounds, if the stoichiometry was held at 2:1 and 1:1, as determined by FAB mass spectrometry and ^{31}P NMR spectra. When the reaction was repeated and the free carbene **7** was added very slowly to a highly diluted metal

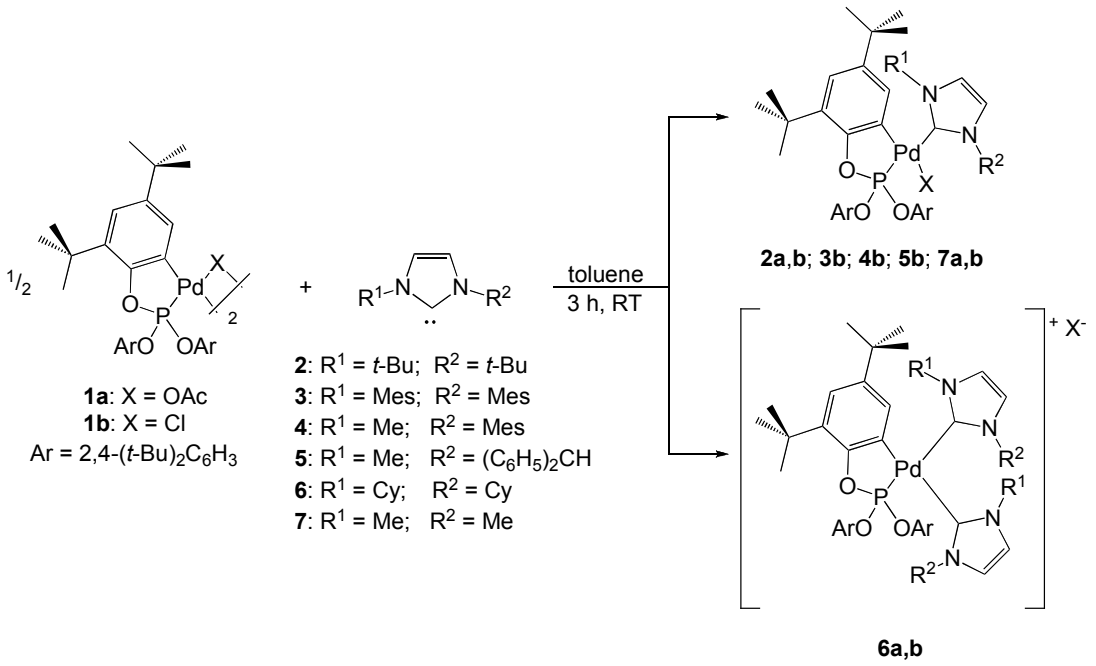
precursor toluene solution, at very low temperatures (-90 °C), the ^{31}P NMR spectra showed two signals in the region for monocarbene *cis/trans* products **7a,b**. Under these conditions the formation of the mono-substituted NHC complexes **7a,b** over the expected di-substituted complexes is favored.

The formation of a mono-substituted NHC complex shows that the coordination of two NHCs to the palladium center is not always necessary, especially when the steric demand of the ligand would disfavor such a conformation. The acetate-bridged phosphapalladacycle **1a** reacts with azolium salts (**8**, **9**) in dimethyl sulfoxide at elevated temperatures bearing weakly coordinating anions like BF_4^- or PF_6^- via deprotonation to form the corresponding carbene complexes (**3a** and **5a**) [97,105,106]. An additional base (NaOAc) is necessary for the complete deprotonation of the azolium salts. For this reaction a temperature dependency was observed; best results were obtained at reaction temperatures between 75 and 90 °C [111]. For the complexes **2a-7b** the ^{13}C NMR signals of the carbene carbon are in the expected range of 176–190 ppm for imidazolin-2-ylidene complexes (Table 1).
The carbene signals in complexes 5a,b could not be differentiated in the ^{13}C NMR spectra, but the ^{31}P NMR spectra show clearly two signals for the phosphorus, suggesting a *cis/trans* product mixture. In the case of dicarbene complex 6a, the two coordinated carbene carbon atoms should be inequivalent, but only one signal was observed for both carbenes. In contrast to complex **6a**, two carbene signals were obtained in the ^{13}C NMR spectra of **6b** (175.1 and 173.0 ppm).

Table 1. ^{13}C NMR carbene signals of complexes **2a-7b**.

Complex	$^{13}C_{carbene}$ (ppm)
2a / 2b	175.7 / 177.5
3a / 3b	182.1 / no carbene signal was obtained
- / 4b	- / 186.2
5a / 5b	185.2 / 186.1
6a / 6b	178.4 / 175.1 and 173.0
7a / 7b	178.3 / 178.2

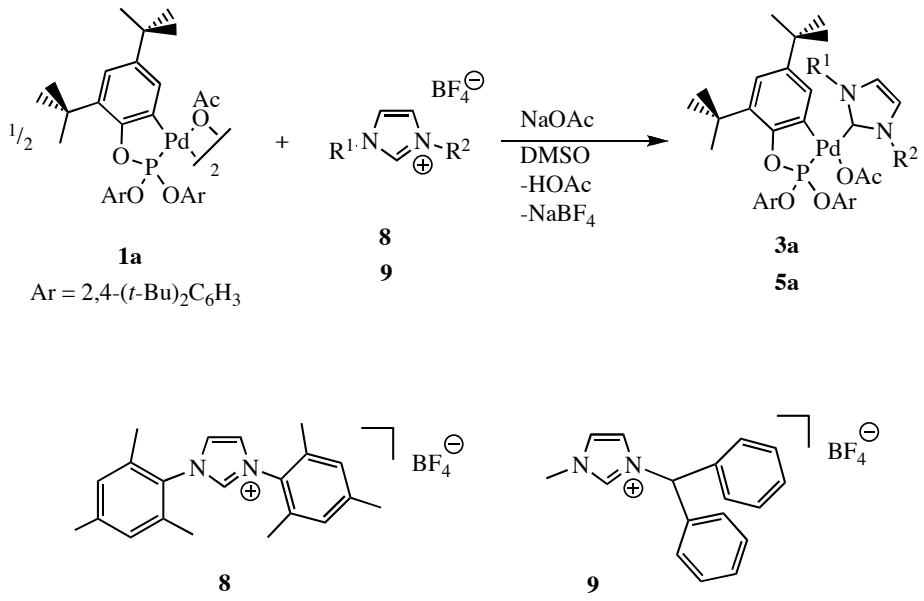
As expected, the ^{31}P NMR spectrum of **6a** shows only one signal, because no *cis/trans* isomerization is possible for these complexes.



Complex	R_1	R_2	X	Yield [%]
2a / 2b	*t*-Bu	*t*-Bu	OAc / Cl	50 / 59
3a / 3b	Mes	Mes	- / Cl	- / 72
- / 4b	Me	Mes	- / Cl	- / 86
5a / 5b	Me	$(C_6H_5)_2CH$	- / Cl	- / 63
6a / 6b	Cy	Cy	OAc / Cl	49 / 60
7a / 7b	Me	Me	OAc / Cl	79 / 75

Scheme 17. Synthesis of mono- and disubstituted NHC-phosphitepalladacycles via the ‘‘*free carbene’’* route.

In the ^{13}C NMR spectra most of the prepared complexes show $^1J_{PC} > 16$ Hz and $^2J_{PC}$ 5–16 Hz for the carbene carbon nuclei. Colorless crystals of complex **7b** suitable for X-ray diffraction were obtained by slow evaporation of a saturated CH_2Cl_2/*n*-pentane solution (Figure 11).



Scheme 18. *In situ* method for the preparation of the complexes **3a** and **5a**.

The palladium center reveals a slightly distorted square-planar structure [Cl1(2)–Pd1(2)–C1(51) 88.91(7)°, 87.31(7)°; Cl1(2)–Pd1(2)–C7(57) 94.26(7)°, 93.89(7)°; P1(2)–Pd1(2)–C1 (51) 98.64(7)°, 99.50(7)°; P1(2)–Pd1(2)–C7(57) 79.11(7)°, 79.42(7)°]. In contrast to the known saturated carbene-substituted phosphitepalladacycles,[113] the NHC ligand in complex **7b** is *cis* coordinated to the phosphorus atom [112]. The Pd1(2)–C7(57) bond length of the orthometallated phosphite ligand is slightly longer (2.052(2), 2.063(2)A ˚) compared to complex **1a** (1.995(2), 2.005(2)A ˚) and **1b** (1.998(6)A ˚). In contrast, the Pd–P bond length is shorter in complex **7b** (2.1590(7), 2.1554(7) Å) compared to **1a** (2.1630(6), 2.1535(6) Å) and **1b** (2.1668 (17)Å). The Pd–C(1) bond lengths for complex **7b** are within the end for carbene-substituted phosphitepalladacycles. The heterocyclic five-membered ring in complex **7b** [Pd1(2)– C7(57)–C8(58)–O1(4)–P1(2)] adopts an envelope conformation, with bond angles similar to those observed in the saturated carbene complexes [118].

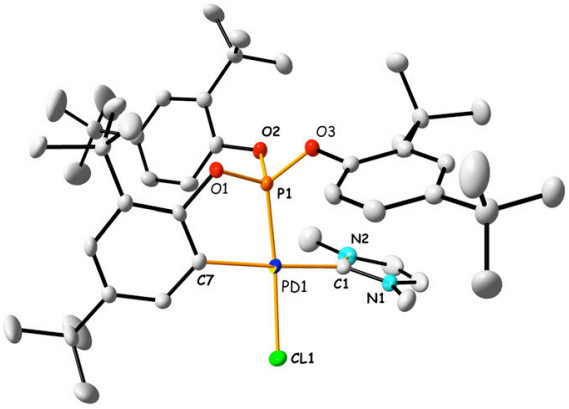
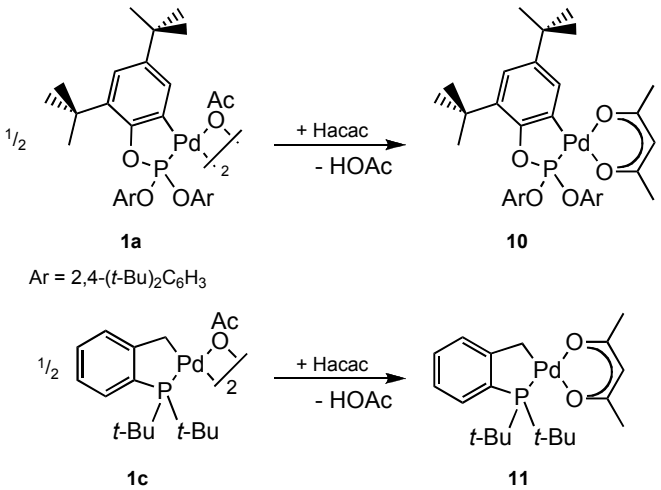


Figure 12. ORTEP plot [118] of compound **7b** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

2.2.3 Acetylacetonates of phospha- and phosphite-palladacycles

It is well established that acetylacetonate substituted palladacycles show very high turnover numbers (TONs) in the Mizoroki-Heck coupling reactions of iodobenzene with styrene, therefore the preparation and characterization of new phospha- and phosphitepalladacycles has been performed in this work.

The acetylacetonate phospha/phosphitepalladacycles were prepared by treatment of the acetate bridged palladacycles **1a** and **1c** with 2,4 pentanedione (acetylacetone, Hacac) in dichloromethane to afford the acetylacetonate products **10** and **11** in nearly quantitative yields according to established methods [91,99,114] (Scheme 19).



Scheme 19. Synthesis of acetylacetonate phospha- **11** and phosphitepalladacycles **10**.

In a previous report it was mentioned that the acetylacetonate substituted palladacycle **11** (Figure 13) shows high TONs of 3500 [mol product per mol 108] in Mizoroki–Heck coupling reactions for the coupling of chlorobenzene with styrene [99].

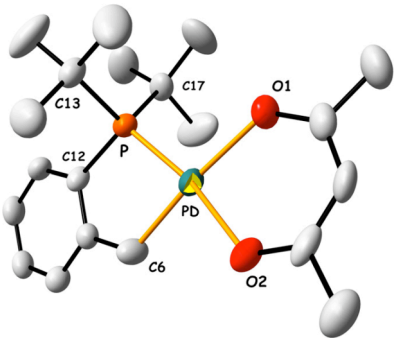


Figure 13. ORTEP plot of compound **11** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

The compounds **10** and **11** show broad ^{1}H NMR signals at 25 °C [116]. Acetylacetonate complexes of phospha- and phosphitepalladacycles show excellent air and thermal stability even at elevated temperatures. The structure of complex **11** was determined by single-crystal X-ray diffraction studies. Suitable single crystals were grown from dichloromethane by slow evaporation of the solvent at ambient temperature (Figure 13). According to previously described solid-state structures of acetylacetonate-substituted palladacycles [117], we found that for complex **11** the two Pd–O distances differ significantly. The oxygen atom O(1) coordinated trans to the carbon atom shows a slightly longer bond length (2.111(4)A˚) compared to the oxygen atom O(2) coordinated trans to the phosphine (2.092(4) Å), because of the donating effect of the carbanion. This behavior was observed for the first time for the di-ortho-tolyl-substituted palladacycle complex ($C_{26}H_{27}O_2PPd$) with bond lengths of 2.112 and 2.078 Å [118].

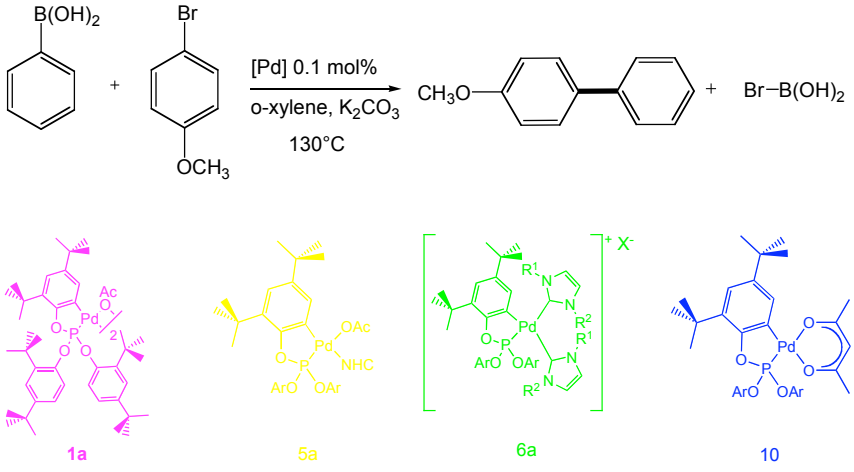
The compounds **1b**, **1a** make versatile precursors for the generation of both mono- and di-substituted carbene adducts of phosphitepalladacycles in good yields. New NHC-substituted phosphitepalladacycles were prepared using a similar procedure to that of the synthesis of NHC substituted phosphine complexes, in order to investigate their chemical properties. Acetylacetonate complexes of phospha- and

phosphitepalladacycles show excellent air and thermal stability even at elevated temperatures. The structural identity of three compounds was clarified by single-crystal X-ray diffraction studies.

2.3 Suzuki-Miyaura *CC*-coupling reactions

There is considerable interest in the development of new, high-activity catalysts that can be used in low loadings [119] in the coupling of the aryl halides with aryl boronic acids. Suzuki-Miyaura reaction, [120] and palladacyclic complexes [121] are playing a significant role in this regard. In this context, the isolation of the acetate-bridged phosphitepalladacycle dimer **1a** and its corresponding mono- (**5a**) and di-substituted (**6a**) carbene adducts [122] represents an important subject in the context of catalysis. Our ongoing efforts include the exploration and optimization of these new classes of catalysts, together with their extensive evaluations in C-C coupling reactions.

Scheme 20. Suzuki-Miyaura C-C coupling reaction of *p*-bromoanisole with phenylboronic acid.



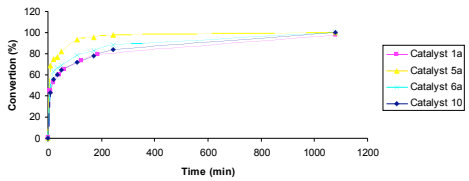


Figure 14. Conversion-time plot for the Suzuki-Miyaura coupling of p-bromoanisole with phenylboronic acid; catalysts **1a**, **5a**, **6a**, **10** (0.1 mol %) are compared. After 12h.

Table 3. Results of the Suzuki-Miyaura C-C coupling reactions.

Entry	R	X	Pd (mol%)	Catalyst	Yield (%)[a]	TON
1	*C*(O)CH_3	Br	0.01	**1a**	100	10^4
2	*C*(O)CH_3	Br	0.001	**1a**	82	8.2 x 10^4
3	*C*(O)CH_3	Br	0.0001	**1a**	23	2.3 x 10^5
4	*C*(O)CH_3	Br	0.01	**5a**	100	10^4
5	*C*(O)CH_3	Br	0.01	**6a**	99	9.9 x 10^3
6	*C*(O)CH_3	Br	0.01	**10**	100	10^4
7	OCH_3	Br	0.01	**1a**	100	10^4
8	OCH_3	Br	0.001	**1a**	63	6.3 x 10^4
9	OCH_3	Br	0.0001	**1a**	21	2.1x 10^5
10	OCH_3	Br	0.01	**5a**	98	9.8 x 10^3
11	OCH_3	Br	0.01	**6a**	100	10^4
12	OCH_3	Br	0.01	**10**	97	9.7 x 10^3
13	H	Br	0.01	**1a**	92	9.2 x 10^3
14	H	Br	0.001	**1a**	80	8.0 x 10^4
15	H	Br	0.0001	**1a**	22	2.2 x 10^5
16	H	Br	0.01	**5a**	90	9.0 x 10^3
17	H	Br	0.01	**6a**	100	10^4
18	H	Br	0.01	**10**	82	8.2 x 10^3
19	*C*(O)CH_3	Cl	0.1[b]	**1a**	62	6.2 x 10^2
20	*C*(O)CH_3	Cl	0.1[b]	**5a**	66	6.6 x 10^2
21	*C*(O)CH_3	Cl	0.1[b]	**6a**	93	9.3 x 10^2
22	*C*(O)CH_3	Cl	0.01[b]	**6a**	55	5.5 x 10^3
23	*C*(O)CH_3	Cl	0.1[b]	**10**	61	6.1 x 10^2

[a]GC yield with diethylene glycol di-n-butyl ether as the internal standard. [b]Cs_2CO_3 as base.

A range of phosphitepalladacycles and their carbene adducts have been prepared in high yields. [123] Using these new classes of catalysts, TONs of approximately 10^6 after a reaction time of 18 h can be achieved. Deactivated bromoarenes could also be coupled efficiently, using extremely low amount of catalyst (0.0001 mol %). Even aryl chlorides can be coupled: TONs of approximately 5500 can be reached after only 18 h without any detectable catalyst deterioration using only 0.01 mol % of the catalyst.

3 Palladium complexes with pyridine-functionalized imidazolin-2-ylidene

3.1 Theoretical background

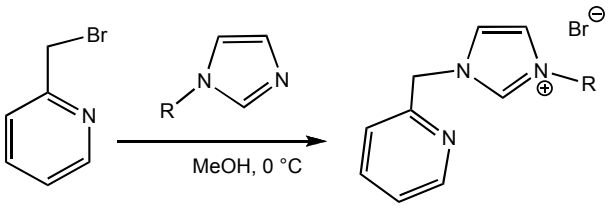
Mono- and dimethyl Pd(II) complexes of bridged bis-imidazole and mixed imidazole-N-heterocycle (py, pz) ligands have been prepared by Canty et al. and their dynamic behavior has been studied with variable temperature NMR spectroscopy. [124] Potentially hemilabile carbene ligands containing both strong and weak donor groups have found widespread use in homogeneous catalysis. The hemilabile part in such ligands is capable of reversible dissociation from the metal center. Such dynamic behavior is known to produce vacant coordination sites that allow complexation of substrates during the catalytic cycle, at the same time the strong donor moiety remains connected to the metal center. [125]

3.2 Pyridine-substituted *N*-heterocyclic carbene ligands

The synthesis and structural characterization of Pd(II) complex **19** bearing imidazole moieties is reported. The corresponding Pd (II) complexes of *N*-functionalized heterocyclic carbene ligands **23-24** have been synthesized through a route involving carbene transfer from an Ag (I) carbene precursor.

3.2.1 Synthesis of the picolyl-imidazolium salts

The *N*-functionalized imidazolium salts **12-17** were prepared by reaction of the corresponding halides with 1-monosubstitutedimidazole according to Scheme 21. Attempts to prepare the free carbene by deprotonation of the imidazolium salt failed due to the high acidity of the methylene protons in these salts. The white-yellow solids obtained were characterized by analytical and spectroscopic methods.



R = Me **(12),** R = Cy **(17),**

R = iPr **(14),** R = Mes **(15)**

R = Dipp **(16)**

Scheme 21. Syntheses of the picolyl-functionalized imidazolium salts.

The reaction of the imidazolium salt **17** with 2 equiv of Ag_2O in refluxing DCM for 2 days yields an *trans*-$[Ag(NCyIm)_2]^+$ species with the imidazole rings bound directly to the N1 atom (Scheme 22). The ^1H NMR data of the silver complex **18** show equivalent cyclohexyl and imidazole protons, but no signal corresponding to the methylene linker group was detected. First, it was assumed that the compound obtained could be a result of the unreacted 1-cyclohexylimidazole present in the original ligand precursor **17**, but this possibility was excluded by elemental analysis and mass spectrometry. The two Ag-coordinated N-cyclohexylimidazole ligands originate from the cleavage of the ligand precursor **17**. It was observed that under mild conditions in N-heterocyclic carbene precursors a splitting of the C-N bond, occurs, yielding the N-alkylimidazole fragments and free pyridine. [123,126] The formation of the bis-N-imidazole silver complex **18** is in contrast to previous studies on C-H bond activation in imidazolium systems, which have so far always, led to the usual C_2 NHC silver complexes. [125,127]

3.2.2 Synthesis of Ag(I) and Pd(II) complexes bearing imidazol moieties

The silver complex **18** reacts smoothly with the Pd(II) precursor $[PdCl_2(MeCN)_2]$ to yield the corresponding *trans*-$[PdCl_2(NCyIm)_2]$ palladium complex **19**. In a typical reaction, the Ag complex was stirred with the Pd precursor in DCM solution for 1h before being filtered to remove the precipitated AgBr. Subsequent workup of the solution afforded the complex in 86 % yield. The crystal structure of **19** has been determined by X-ray diffraction analysis. The ORTEP drawing of **19** is shown in Figure 15.

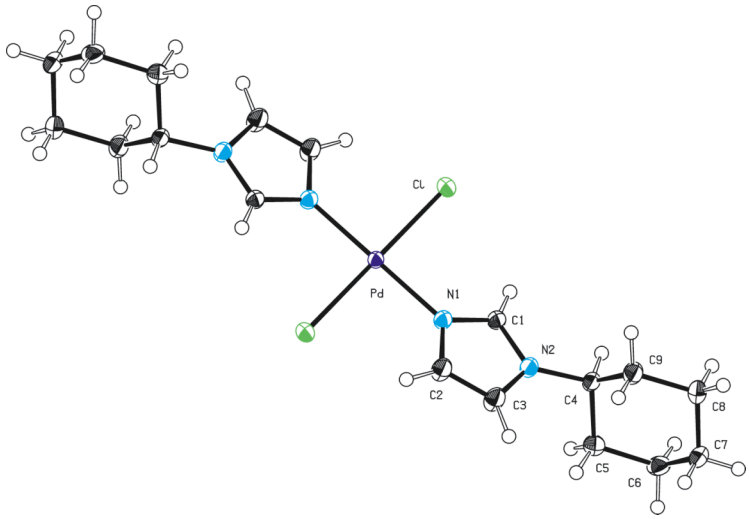


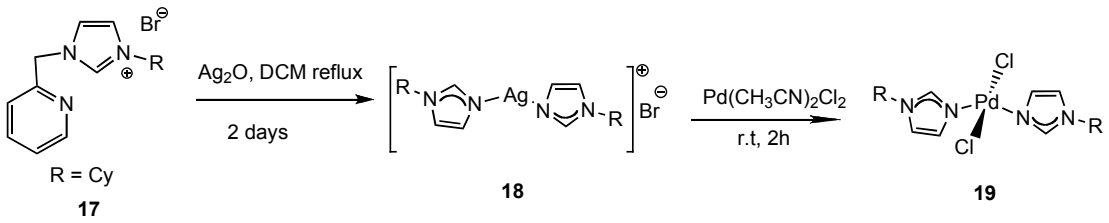
Figure 15. ORTEP style representation of compound **19** in the solid state.

Thermal ellipsoids are drawn at the 50 % probability level. The molecule shows a crystallographic C_i symmetry and an operator for generating equivalent atoms of (1-x, 1-y, 1-z).

The complex consists of monomeric $Pd(NCyIm)_2Cl_2$ units. Most of the crystal structures of corresponding dihalide-bis(1-alkylimidazole)-palladium(II) indicate that in the solid state the *trans* isomer crystallizes preferentially (Scheme 22). The two-imidazole ligands are coordinated *trans* to each other at the palladium center. The imidazole ligands were found to coordinate to the metal via the electronic 'pair' of the N1. The Pd atom in **19** is coordinated in a square-planar fashion to the Cl and N atoms. The Pd–Cl and Pd–N1 bond lengths of the palladium complex **19** are slightly longer [2.310(4) and 2.016(1) Å] as compared to the previous published imidazole complex [2.307(1) and 2.011(2) Å]. [128] The dihedral angle between the plane of imidazole ring and the square plane around the Pd is 27.57(8)°.

3.2.3. Synthesis and characterization of picolyl-functionalized carbene of Pd(II) complexes

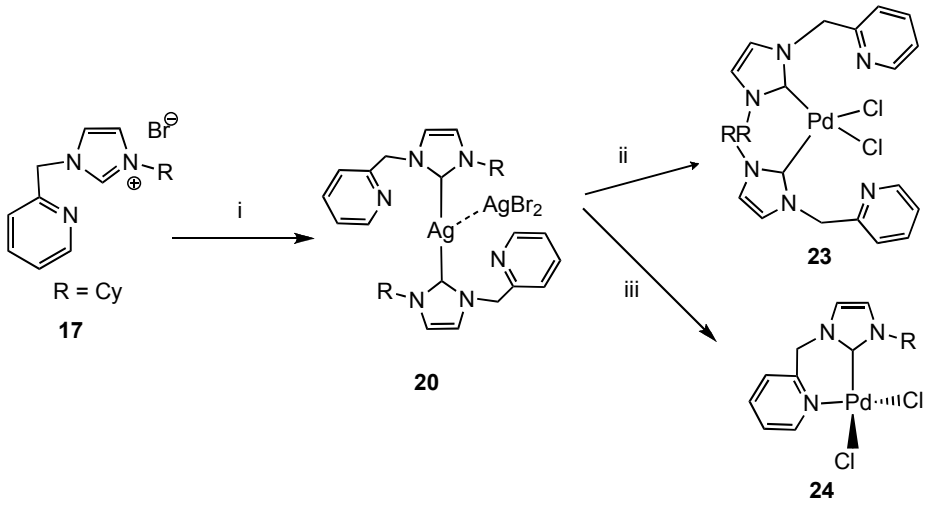
The silver carbene complex **20** was prepared by interaction of the imidazolium salt **17** with Ag_2O in DCM at room temperature for 2 h. It was not possible to prepare the desired silver complex at higher temperatures in DCM as reported by Danopoulos et al. [122b] The silver carbene complex **20** was characterized by a means of analytical and NMR spectroscopy.



Scheme 22. Synthesis of Pd(II) complexes bearing imidazol moieties.

The formation of the carbene complex was found by the presence of a peak at (^{13}C) δ = 180.9 ppm, which was assigned to the C_2-imidazol-2-ylidene carbon atom, and by

the absence of the downfield peak for the 2*H*-imidazolium proton in the ^{1}H NMR spectra usually observed in aprotic solvents below (^{1}H) δ = 9 ppm.



(i) Ag_2O, DCM, 20°C, 2h (ii) $Pd(CH_3CN)_2Cl_2$, DCM, 2h; (iii) 2 $Pd(COD)Cl_2$, DCM, 40 min

Scheme 23. Synthesis of Pd(II) with picolyl-functionalized imidazolin-2-ylidene.

The ^{1}H NMR spectrum of **20** shows a singlet at (^{1}H) δ = 5.32 ppm corresponding to the CH_2 linker group. A dichloromethane solution of the corresponding silver carbene precursor **20**, was added dropwise to a solution of $[PdCl_2(CH_3CN)_2]$ to yield the palladium complex **23** containing two carbene ligands (Scheme 23). Both carbene ligands are coordinated to the Pd center and the donor groups remain dangling with the N atom uncoordinated to the metal center. The complex was obtained as a pale yellow air-stable solid and characterized by spectroscopic and analytical methods. At room temperature the ^{1}H NMR signals sharpen and two sets of peaks, corresponding to the *cis* and *trans* isomers are observed.

Subsequently, the silver complex **20** was stirred with $[Pd(COD)Cl_2]$ in DCM solution for 1 h to yield the palladium complex **24**, containing the donor-functionalized carbene ligand. The ^{1}H NMR spectrum reported here shows very broad, merged signals at room temperature. Fluxional behavior was observed at elevated temperatures. At ambient temperature a broad singlet peak is observed for the diastereotopic methylene protons in the ^{1}H NMR spectrum, resulting from dynamic conformational flipping of the six-membered chelate ring. When cooling the solution to -30 °C, two sharp doublets at (^{1}H) δ = 5.88 and 5.03 ppm are observed with

geminal coupling constants of 14.68 Hz. No additional splitting or broadening of other signals in the spectrum is observed at this lower temperature.

For comparative purposes, the neutral chelating mono-carbene palladium(II) complex [$PdCl_2$(*py*-C^N)] **21** was prepared from the hybrid C/N-functionalized pyridine precursor **15** following a procedure similar to that used by Danopoulos and coworkers.[122b] The structure of **21** was determined by X-ray crystallography and is shown in Figure 16. The chelating ligand is coordinated to the square planar palladium centre with the carbene end disposed *trans* to the bromide. The carbene plane forms an angle of 64.2° with the square plane of the palladium. The resulting six-membered ring is puckered to release conformational strain.

As expected, the spectroscopic properties of compound **24** matches with those reported for the related compound **21** described independently by Danopoulos et al. [122,129]

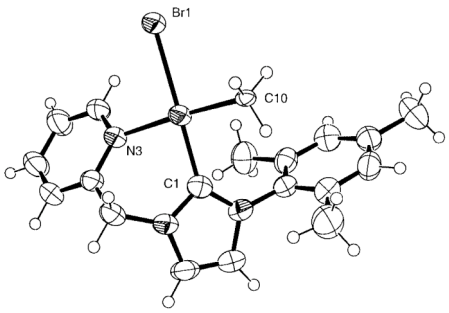
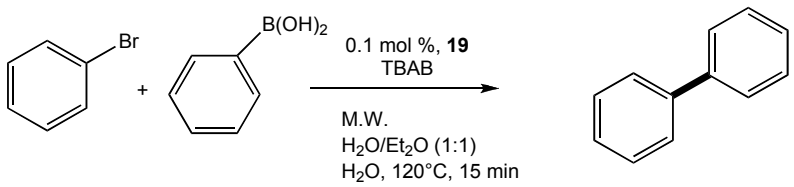


Figure 16. Molecular structure of **21**. Selected bond lengths (Å) and angles (°): Pd1–C1 1.964(4), Pd1–C10, 2.147(3), Pd11–N3 2.183(3), Pd1–Br1 2.4969(6); Br1–Pd1–C1 177.5(1), Br1–Pd1–C10 90.51(8), Br1–Pd1–N3 92.59(8).[130]

3.3 Suzuki-Miyaura coupling catalyzed by Pd(II) complexes

Microwave-assisted Suzuki–Miyaura cross-coupling of bromobenzene and phenylboronic acid in aqueous medium. In this second part of the work, the possible catalytic activity for that reaction of our representative Pd (II) complexes **19** was tested. Pd(II) complexes with two N-coordinated ligands are known to act as catalysts for the selective construction of carbon–carbon bonds. Complex **19** shows a very high catalytic activity for the standard Suzuki–Miyaura system (1 equiv. of bromobenzene

(PhBr) and 1.1 equiv of phenylboronic acid ($PhB(OH)_2$)) (Scheme 24).



Scheme 24. Suzuki-Miyaura coupling reaction catalyzed by **19.**

Table 4. Catalytic activity of complex **19** for the microwave-assisted Suzuki–Miyaura cross-coupling reaction of bromobenzene and phenylboronic acid in aqueous medium.[a]

Entry	Catalyst (mmol)	*t*/min	Base	Solvent	Yield[b] (%)	TON[c]	TOF[d]/min^{-1}
1	**5 x 10^{-5}**	15	K_2CO_3	H_2O-EtOH	96	3.8 x 10^4	2.5 x 10^3
2	**5 x 10^{-5}**	15	K_2CO_3	H_2O	61	2.4 x 10^4	1.6 x 10^3
3	**5 x 10^{-6}**	15	K_2CO_3	H_2O-EtOH	65	2.6 x 10^5	1.7 x 10^4
4	**5 x 10^{-6}**	15	K_2CO_3	H_2O	49	1.9 x 10^5	1.2 x 10^4

[a] PhBr (2.0 mmol) + $PhB(OH)_2$ (2.2 mmol) + base (4.0 mmol) + catalyst + TBAB (2.0 mmol) + H_2O (4 mL) or 1 : 1 mixture of water–ethanol instead of TBAB/water combination; the system was heated under focused microwave irradiation at 120 °C. [b] Mol of biphenyl per 100 mol of PhBr. [c] Turnover number (mol of biphenyl per mol of catalyst). [d] Turnover frequency (mol of biphenyl per mol of catalyst per min).

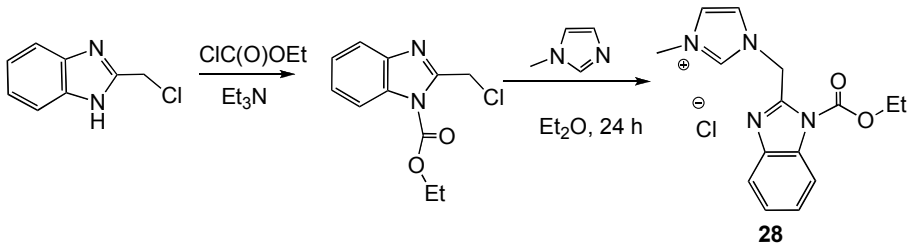
High isolated yields of biphenyl (up to 96 %) were achieved under focused microwave irradiation at 120 °C, using 1 : 1 water–ethanol as a solvent mixture or 1 equiv, of the phase-transfer catalyst tetrabutylammonium bromide (TBAB) in water (Table 3), with turnover numbers (TON) up to 2.6 x 10^5 mol of biphenyl per mol of catalyst, and turnover frequencies (TOF) up to 1.7 x 10^4 mol of biphenyl per mol of catalyst per minute. These results are within the best ones so far reported in the field.[131,132]

4 Palladium and rhodium complexes with “chelating” ligands

4.1 Theoretical background

4.1.1 Synthesis of new benzimidazole-functionalized imidazolium salts

1-carboethoxy-2-chloromethyl-benzimidazole was prepared starting from the commercially available 2-chloromethyl-1-*H*-benzimidazole with ethylchloro-formate in triethylamine. In order to prevent self-condensation, it was necessary to block the 1-position of 2-chloromethylbenzimidazole.[133] The synthesis of the imidazolium ligand precursor of the new C/N-bidentate ligand was carried out by direct N-alkylation of *N*-methylimidazole with 1-carboethoxy-2-chloromethyl-benzimidazole, which in turn was obtained as a white solid via a one-step procedure in 75 % yield (Scheme 25).



Scheme 25. Synthesis of hybrid C/N-functionalized benzimidazolium precursor.

The formation of the benzimidazoyl-functionalized imidazolium salt **28** was confirmed by a characteristic downfield signal in the ^{1}H NMR spectrum at δ = 9.30 ppm for the NC*H*N proton and a base peak in the FAB mass spectrum at *m*/*z* = 285 for the H[*bz*C^N]$^{+}$ fragment.[134] Crystals of **28** suitable for single-crystal X-ray diffraction were grown from a mixture of acetonitrile and diethyl ether. An ORTEP view of the molecular structure is shown in Figure 17.

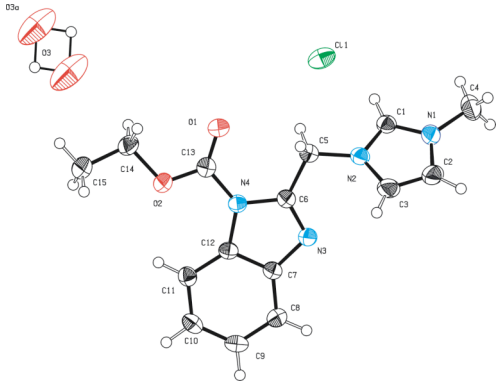
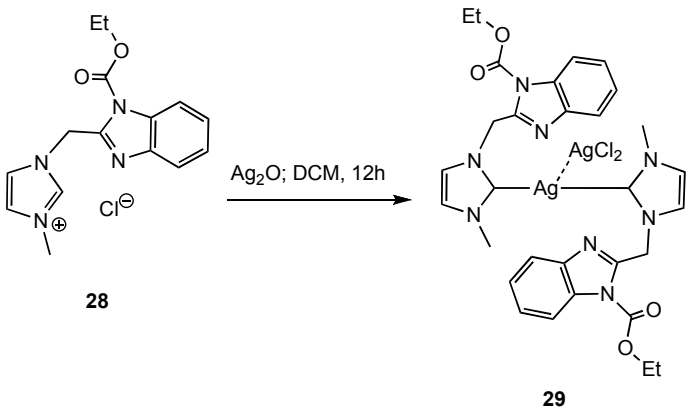


Figure 17. ORTEP view of the molecule salt **28** with 50% thermal ellipsoids and labeling scheme.

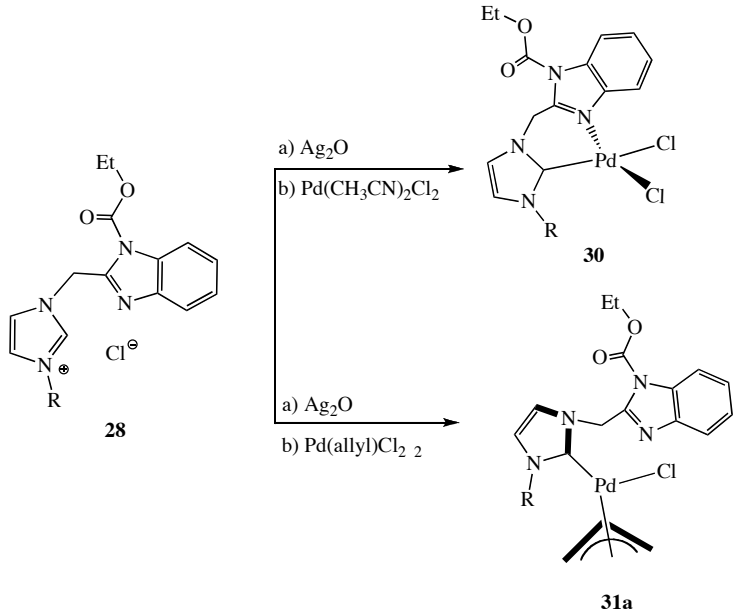
4.1.2 Synthesis and characterization of Ag(I) and neutral Pd(II) complexes

Compound **28** essentially serves as a carbene precursor that delivers the NHC to palladium and rhodium *via* silver in a transmetalation method.[135] Mixing the imidazolium salt **28** with Ag_2O in CH_2Cl_2 at r.t. for 12 h afforded the silver NHC complex $[Ag_2(bz\text{-}N\hat{}C)_2Cl_2]$ **29** (Scheme 26) which was isolated in high yield (76 %).



Scheme 26. Synthesis of Ag(I) intermediate **29.**

The FAB mass spectrum of **29** shows a molecular ion peak at m/z = 678, which corresponds to the silver bis(carbene) monocation, $[Ag(bz\text{-}N\hat{}C)_2]^+$. The Ag-NHC coordination was established by the ^{13}C NMR shift at δ 177.56 ppm, assignable to the 2C-imidazol-2-ylidene carbon, and absence of the ^1H resonance for the 2H-imidazolium proton. [135] For comparative purposes, the neutral chelating mono-carbene Pd(II) complex $[PdCl_2(bz\text{-}C\hat{}N)]$ **30** was prepared from the hybrid C/N-functionalized benzimidazolium precursor **28** following a procedure similar to that used by Hor and coworkers in the synthesis of the related compound $[PdCl_2(\eta\text{-}C\hat{}N)]$ (Figure 18).[136] As expected, the spectroscopic properties of compound **30** match with those reported for the related compound described independently by Hor et al. Complex **29** undergoes transmetalation with $[PdCl_2(CH_3CN)_2]$ by giving the corresponding chelating benzimidazole-carbene palladium(II) complex **30**, in 74 % yield (Scheme 27).



Scheme 27. Synthesis of the neutral Pd(II) dichloride **30** and η^3-Pd-allyl chloride **31** complexes**.**

The use of other palladium precursors (such as $[PdCl_2(COD)]$) is possible but would not improve the yields significantly. FAB mass spectral analysis gives a m/z = 461 peak that could be assigned to $\{[Pd(bz\text{-}N\hat{}C)]^+\}$. ^{13}C and ^1H NMR NMR analysis is consistent with a mononuclear $[PdCl_2(bz\text{-}N\hat{}C)]$ complex with NHC carbene and benzimidazole coordination at nitrogen. Chelation of the hybrid ligand imposes a hindered ligand rotation, thereby differentiating the two hydrogen atoms on the unique carbon that links the NHC to benzimidazole (C_5 in the ^1H NMR).

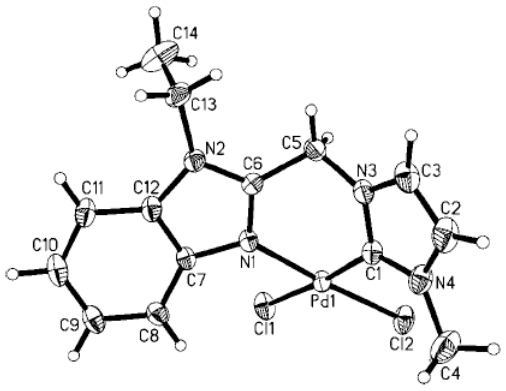


Figure 18. ORTEP view of the molecular structure of $[PdCl_2(\eta\text{-}C\hat{}N)]$ [136] with 30 % thermal ellipsoids and labeling scheme.

The molecular structure of the similar complex [$PdCl_2$(η-C^N)] (Figure 18) was determined by X-ray single crystal diffraction. It shows the expected chelating benzimidazole derivatized NHC at an essentially square-planar Pd(II) (C1-Pd1-N1, 85.6(2)°; C1-Pd1-Cl2, 92.04(15)°; N1-Pd1-Cl1, 91.5(1)°; Cl2-Pd1-Cl1, 90.76(6)°). The Pd1-Cl1 bond [2.376(17) Å] *trans* to the carbene is significantly longer than that *trans* to the benzimidazole-N donor atom [2.300(15) Å], which indicates the strong *trans* influence of the N-heterocyclic carbene ligand. This is consistent with previous structural studies on related complexes.[137]

The imidazolium salt **2** was also successfully applied as the carbene precursor for the synthesis of (NHC)Pd(η^3-allyl)Cl complex **31a** using the silver transmetalation method (Scheme 28). Silver carbene complexes **29** rapidly reacted with 0.5 equiv. [Pd(η^3-allyl)Cl]$_2$ in CH_2Cl_2 to give the complex **31a**. NMR spectroscopy shows that complex **31a** has fluxionality to different extents in the NMR time scale depending on the bulk of the R substituent (wing tip groups). The following common features were observed for the ^{1}H and ^{13}C spectra (room temperature, $CDCl_3$) of **31a** (R = Me): (a) there is simply one set of signals in both the ^{1}H and ^{13}C spectra; (b) the protons of the methylene linkers resonate as a singlet, which has been reported for other PdCl(allyl)(NHC) complexes;[138,139] and (c) three sharp signals and two broad signals are observed for the five allyl protons, with the broad signals attributed to the *syn* and *anti* protons at the allyl terminus *trans* to the chloride (Figure 19).

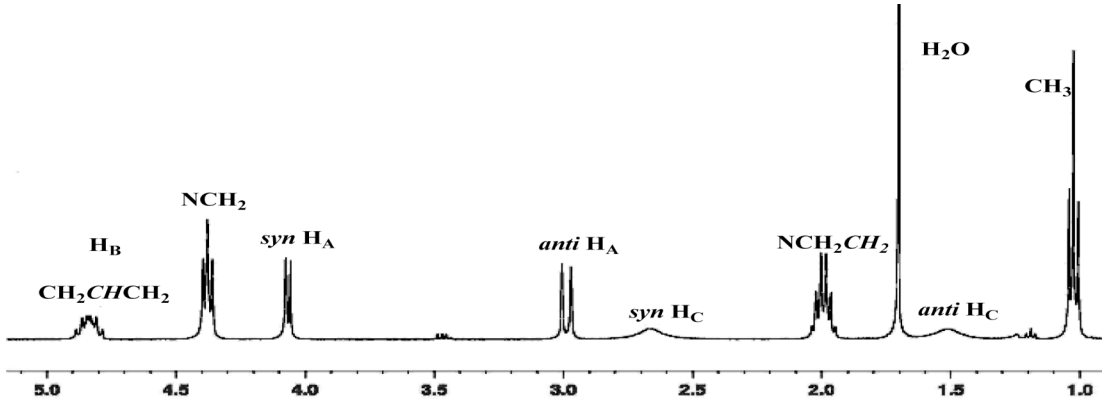
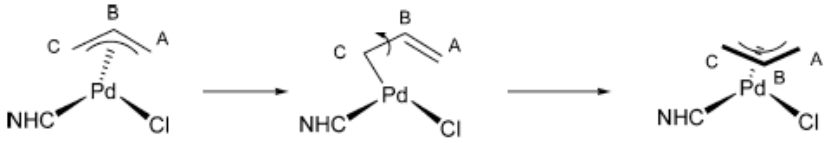


Figure 19. Part of the ^{1}H NMR spectrum of complex **31a**.

The broadening pattern of the allyl groups in complexes **31a** suggests that there is syn/anti exchange only between the protons on C atom. This is consistent with a selective η^3 to η^1 rearrangement of the allyl ligand, possibly under electronic control.

The η^1-allyl intermediate then undergoes C-C bond rotation followed by reformation of the η^3-complex (Scheme 28). The fact that the CH_2 linker protons are equivalent in solution can be accounted for by this selective η^3 to η^1 rearrangement together with free Pd-$C_{carbene}$ rotation. If only the NHC ring rotates, the complex remains chiral and the CH_2 remain diastereotopic.

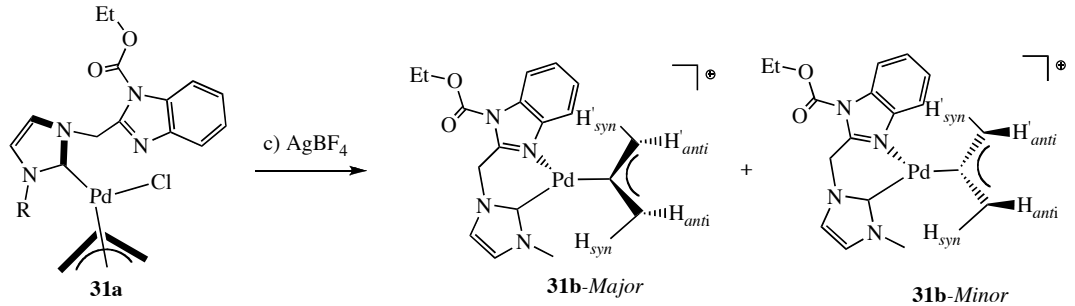


Scheme 28. Mechanism of η^3-η^1-η^3 isomerization in complex **31a**.

However, the concurrent η^3-η^1-η^3 rearrangement process should lead to enantiomerization of this complex and to the equivalence of the CH_2 protons. This type of selective syn/anti exchange has been observed on many occasions and this process could be associative or dissociative in mechanism. [138-143]

4.1.3 Synthesis of the cationic palladium NHC allyl complex

The chloride complex **31a** readily underwent halide abstraction with $AgBF_4$ to afford ionic complex **31b** respectively (Scheme 29). The isolated product was characterized by elemental analysis and NMR spectroscopy. $CDCl_3$ solutions of **31b** show dynamic structures in the NMR time scale.



Scheme 29. Synthesis of the cationic Pd-allyl complex **31b.**

Complex **31b** is studied by one- and two-dimensional NMR in order to determine its structure in solution. Complex **31b** displays duplicated signals for all allyl protons and for some of the protons on the benzimidazol ligand. This effect can be attributed to isomerism of the allyl fragment, which can adopt two orientations (Scheme 29). The isomers are able to interconvert *via* a formal π-rotation involving a η^3-η^1-η^3 isomerization. Previously, it was found that this isomerization is selective in other bidentate ligands containing different nitrogen donor atoms [144], involving opening of only one Pd-C bond of the allyl fragment. In order to establish if such selectivity is also present in complex **31b**, phase-sensitive ^{1}H 2D NOESY experiment was carried out (Figure 20). The spectrum shows exchange peaks (blue) for the central proton H_2 of both isomers and their selective NOE contacts (red) with the syn protons within each isomer. The two sets of proton peaks were observed together with diasteretopic CH_2 linker protons in each conformer. Two sets of peaks were also observed in the ^{13}C NMR spectra. The identity of the solvents ($CDCl_3$, CD_2Cl_2, and DMSO-d_6) has no significant effect on the relative amounts of these two species. The lack of solvent effects suggests that the two species are probably not examples of κ^2-C,N (bidentate) versus κ^2-C (monodentate) isomers.[29] The five allyl protons and the methylene linker protons are all well resolved in ^{1}H NMR spectroscopy.

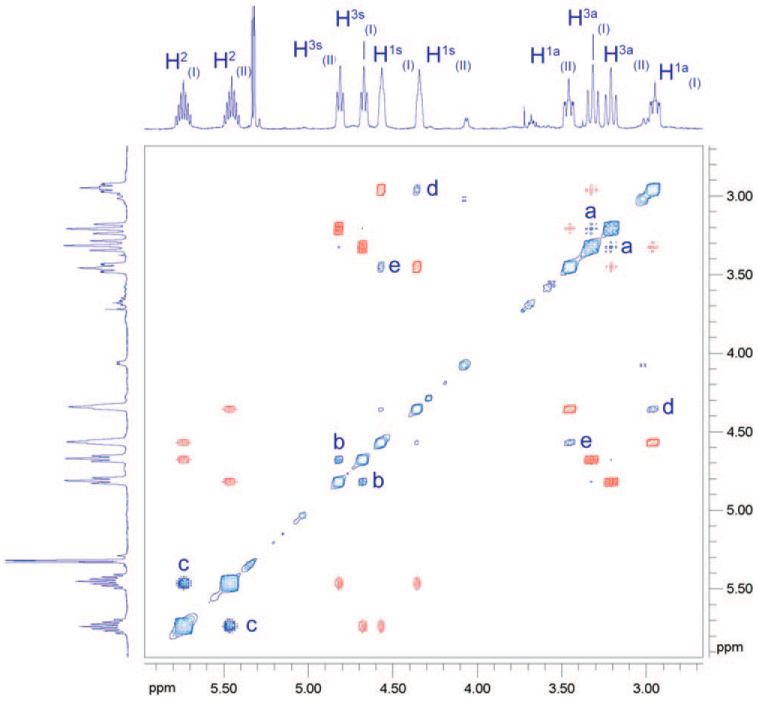
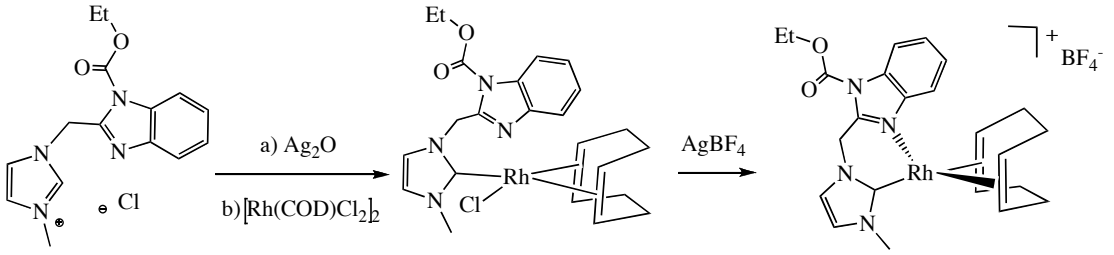


Figure 20. Section of the phase-sensitive ^{1}H 2D NOESY spectrum ($CDCl_3$, 400 MHz, 298 K) for complex **31b**.

In cationic complex [Pd(NHC-N)(allyl)]BF_4, boat-to-boat conversion of the 6-membered ring via a dissociative mechanism is proposed as the mechanism of the solution dynamics on the basis of NOESY spectroscopy.[139]

4.2 Synthesis of neutral and cationic rhodium(I) complexes containing hemilabile NHCs

The treatment of $[Rh(COD)Cl]_2$ with the silver carbene complex **29** in dichloromethane at ambient temperature gave the desired Rh complex **32a** as yellow crystalline solid in quantitative yield (Scheme 30). The structure of this rhodium complex was determined by spectroscopic analyses. A signal of doublet at 182.0 ($J_{Rh–C}$ = 51 Hz) on the $^{13}C\{^1H\}$ NMR spectrum is assigned as the Rh–$C_{carbene}$ resonance, indicating the success of carbene transfer from Ag to Rh. The methylene linker between imidazole and benzimidazole ring exhibited two sets of doublet at 6.19 and 5.86 with the coupling constant of 14.6 Hz, showing two non-equivalent natures of these protons.



28 **32a** **32b**

Scheme 30. Preparation of the Rh (I) carbene complexes**.**

The coordination of the benzimidazole fragment of the hemilabile NHCs in complexes **32b** could be induced by abstraction of the chloro ligand (Scheme 30).[142] Thus, the reaction of complex **32a** with 1 equiv. $AgBF_4$ in acetonitrile/acetone at 0 °C resulted in the precipitation of AgCl and the formation of yellow solutions from which the cationic complexes [Rh(COD)(*bz*C^N)][BF_4] was isolated as microcrystalline yellow solid in good yield. The FAB mass spectra gave peaks at *m*/*z* 526.5 **32b** that correspond to the cation $[Rh(cod)(bzC^{\wedge}N)]^+$. Further evidence for the coordination of the benzimidazole group to the rhodium center comes

from the ^{1}H NMR, as no coordinated solvent was detected when the reaction was conducted in the presence of diverse coordinating solvents as acetone or acetonitrile. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compound **32b** are consistent with a chelating coordination mode (κ^2-C,N) of the NHC ligand that results in the formation of a six-membered metallacycle (Scheme 30). The most relevant features of the NMR spectra are the significant reduction in the magnitude of the $J_{C\text{-}Rh}$ of the carbenic atom, only observed for compound **32b** at δ 179.63 ppm ($J_{C\text{-}Rh} \approx 28$ Hz), and the downfield shifting of ca. 1 ppm of the methylenic -CH_2N resonance relative to the related neutral complex, which is observed as a broad triplet and could be a diagnostic for the coordination of the -NMe_2 fragment.[143] The Rh(COD) complex **32a** obtained from silver transmetalation are consistently monodentate NHC complexes with a pendant benzimidazole moiety, from which chloride abstraction by $AgBF_4$ can cleanly give the corresponding ionic chelating complex **32b**.

The Rh(COD) complexes were characterized by means of NMR spectroscopy, elemental analysis and mass spectrometry. In the ^{1}H NMR spectra, all linker methylene protons are diastereotopic, indicating that there is a hindered rotation along the M-$C_{carbene}$ bond and complexes **32a** and **32b** are all C_1 symmetrical.[144] ^{1}H NMR spectra also show that the differences in the chemical shifts of these two diastereotopic protons are more significant in chelating NHC□N complex **32b**, possibly due to the endo and exo orientation of these two protons with respect to the six-membered metallacycle. The carbene C_2 atoms resonate characteristically in the range δ 172-183.

The 2-benzenimidazole imidazolium salt **2** is a readily accessible precursor for a new chelating C/N ligand system. Its coordination capabilities and its structural chemistry have been established in the synthesis of Ag(I), Pd(II) and Rh(I) complexes.

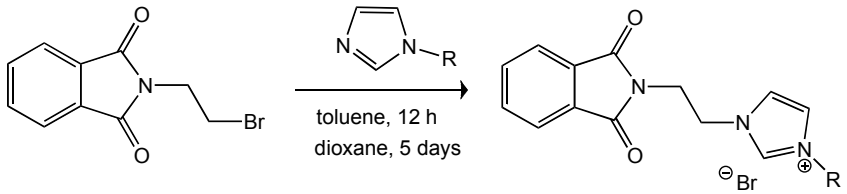
5 Palladium and rhodium complexes with "dangling" ligands

5.1. Theoretical background

Early reports show that certain types of water-soluble quaternary bromide salts have been used as available readily precursors for the preparation of imidazolium based task specific ionic liquids (TSILs) that contain an ethylaminediacetic acid (EDA) as a chelating moiety.[145] The use of these ligand systems in ionic liquids based on imidazolium salts also offers an interesting approach to forming stable complexes and catalysts. We are interested in the functionalization of sterical demanding NHC ligands with phthalimido-groups as well as studies conducted on their coordination chemistry on the palladium center. The synthesis, structures, and catalytic activities of novel palladium complexes with phthalimido-tethered NHC ligands are described.

5.1.1 Synthesis of phthalimido-functionalized imidazolium salts

The imidazolium salts **33-35** functionalized with the phthalamido group were easily obtained by quaternization of alkyl- or aryl-imidazoles with *N*-(2-bromoethyl)-phthalimide. The phthalamido-functionalized imidazolium bromide, [Me-(C^phthaloylH)$^{+}$Br^{-}] **33** has been synthesized according to published procedures.[[146]] In order to examine the differences in the reactivity and gain a better understanding of the functional group, some sterically demanding substituents on the heterocyclic ring were used, yielding [R-(C^phthaloylH)$^{+}$Br^{-}] {**34** R = (Mes = 2,4,6-tri-*tert*-butylphenyl) and **35** (Dipp = 2,6-di-isopropylphenyl)} (Scheme 31). The quaternization of aryl-imidazoles with *N*-(2-bromoethyl)-phthalimide proceeded with excellent yields in dioxane at 140 ° C.



33 R = Me, 84%

34 R = Mes, 72%

35 R = Dipp, 89%

Scheme 31. Synthesis of phthalimido-functionalized imidazolium salts

The hybrid salts **33-35** are air stable powders and were characterized by elemental analysis, high-resolution mass spectrometry (FAB), and ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy. The ^{1}H NMR spectrum of **33-35** showed a very low field resonance in the range δ 10.4 - 10.5 ppm characteristic of the NC*H*N imidazolium proton. The bulky substituents bound to the imidazolium ring, should give sterically demanding ligand systems. An important point concerning these sterically demanding substituents is particularly observed in the ^{1}H NMR spectrum of **35**, were two doublets at δ 1.12 and 1.25 ppm, are attributed to the diastereotopic methyl groups of the arylic-^{i}Pr substituents and only one signal belongs to the two methine groups (Figure 21). This observation suggests that the rotation around the N(Im)-C(Aryl) single bond is severely restricted. The molecular structures of the hybrid precursors **33** and **34** have been determined by single crystal X-ray diffraction studies. An ORTEP view of **33**, **34** is shown in Figure 22 and Figure 23.

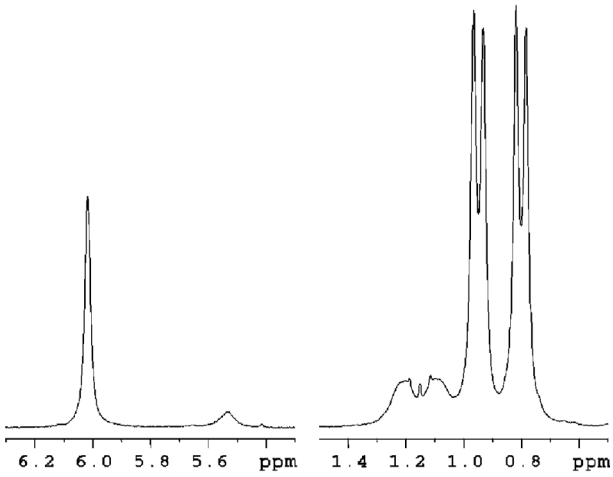


Figure 21. Part of the ^{1}H NMR spectrum of **35**.

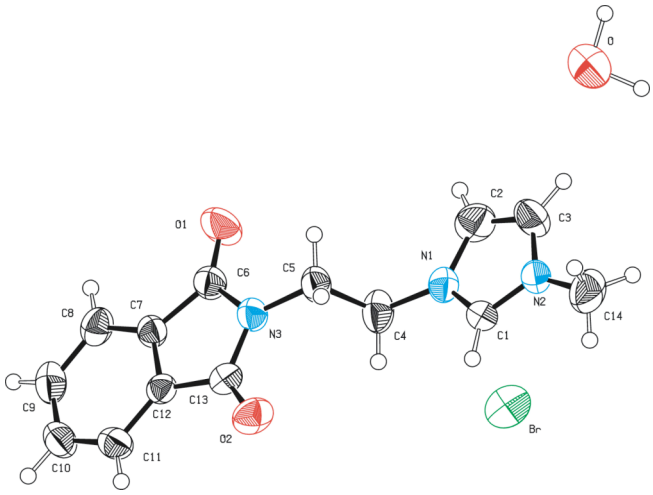


Figure 22. ORTEP [154] style plot of compound **33** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)-N(1) = 1.320(5); C(1)-N(2) = 1.313(5); C(6)-O(1) = 1.210(4); C(13)-O(2) = 1.210(5); N(2)-C(1)-N(1) = 109.8(3); O(1)-C(6)-N(3) = 124.3(4).

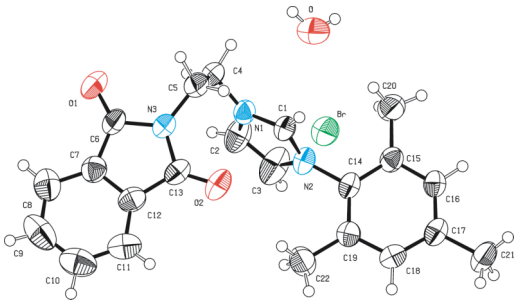


Figure 23. ORTEP[154] style plot of compound **34** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: C(1)-N(1) = 1.326(3); C(1)-N(2) = 1.323(3); C(6)-O(1) = 1.204(3); C(13)-O(2) = 1.209(3); N(2)-C(1)-N(1) = 108.9(2); O(1)-C(6)-N(3) = 123.4(2).

5.1.2 Synthesis of Ag(I) and neutral bis(carbene)-Pd(II) complexes

Imidazolium salts are frequently used as precursors for metal *N*-heterocyclic carbene complexes. Stirring a mixture of the water-soluble imidazolium salts **33-35** and Ag_2O in acetonitrile gave a clear solution of silver carbene complexes **36-38**, which could be isolated with yields ranging between 43-66 %.[134] The palladium complexes of

phthalimido-functionalized imidazolium bromides, **98-100** were synthesized using the silver transmetalation method.[147] Consistent with the formation of the silver complexes **36-38**, the ^{1}H NMR spectra show the absence of imidazolium C_2-*H* resonances, due to the loss of the acidic imidazolium proton of the salts.

Formation of the silver NHC compounds as a result of the reaction of imidazolium salts with Ag_2O, along with the appearance of diagnostic silver-bound carbene C_2-Ag peaks ranging between δ 177.03 - 180.13 ppm, are observed. The results of ^{13}C-chemical shifts of the C_2 carbene carbons of Ag(I) and bis(carbene) Pd(II) complexes are presented in Table 5. The high-resolution mass spectra (FAB) of the silver complexes display the molecular ion peak at *m*/*z* = 827 (**36**) and *m*/*z* = 911 (**38**), which correspond to the Ag(I) bis(carbene) ion. The data from elemental analysis are in agreement with a “$[AgL_2][AgBr_2]$“ composition. [134]

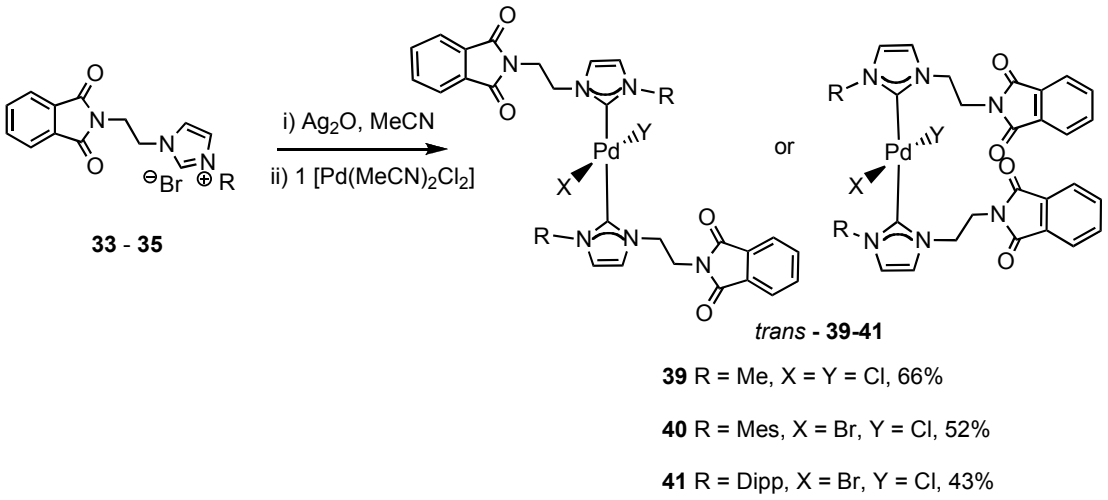
Previous reports demonstrated that monocarbene- and bis(carbene) Pd(II) complexes with donor-functional groups potentially chelating,[148] can be selectively generated simply by adjusting the molar ratio of carbene and Pd precursors. Treating the silver complexes **36-38** with two equiv of $[Pd(MeCN)_2Cl_2]$ led to the neutral phthalimido-carbene-palladium(II) complexes (**39-41**) [Pd{3-R-1-(2’-phthalamidoethyl)-imidazolin-2-ylidene)$_2$XY] (**39** R = Me, X = Y = Cl , **40** R = Mes, X = Br, Y = Cl and **41** R = Dipp, X = Br, Y = Cl) with yields ranging between 43–67 % (Scheme 32). Hence, three new palladium complexes **38-41** were synthesized; they have been also characterized by ^{1}H and ^{13}C{^{1}H} NMR, high-resolution mass spectrometry (FAB), and elemental analysis.

The elemental analysis of **39** showed that there are two phthalimido-carbene ligands attached to palladium, in accordance with the observed reaction stoichiometry. The mass spectrum displays a molecular ion peak with a *m*/*z* value which is corresponding to $[Pd(NHC)_2Cl]^+$ moiety. Information on the solution structure of **39** was obtained from the solution NMR spectra. Here one set of signals was observed in the ^{1}H NMR spectrum in d_6-DMSO. The presence of one set of peaks was also evident in the ^{13}C NMR spectrum with one characteristic C_2 - Pd carbene signal at δ 170.3 ppm (Table 5).

Table 5. ^{13}C-chemical shifts of the C_2 carbene carbons of Ag(I) and bis(carbene) Pd(II) complexes.

Complex	$^{13}C_{carbene}$ (δ ppm)
36	180.1
37	177.0
38	170.3
39	171.0
40	172.8
41	191.8

Since the difference of chemical shifts of the carbene carbon between *trans* or *cis* palladium bis(carbene) complexes was shown to be generally important, it is worth mentioning that the C_2 - Pd carbene peak of **39** falls well within the range observed for other reported *trans*-[Pd(NHC)$_2$] complexes.[156-158] Instead, addition of an equimolar amount of [Pd(MeCN)$_2$Cl$_2$] to a acetonitrile solution of silver complexes **37-38** was found to result in a statistical scrambling of Br / Cl atoms together with the coordination of two phthaloyl-carbene ligands to the metallic center, yielding non-symmetrical bis(carbene) Pd(II) complexes (**40-41**). This stoichiometry was confirmed by mass spectrometry (FAB), indicating *m/z* values corresponding to the [Pd(NHC)$_2$]$^+$ moiety. In case of **40**-41, which differs from **39** in having bulkier substituents (**40** R = Mes and **41** R = Dipp), rather than a methyl group attached to the imidazolium ring and mixed halides attached to the metallic center, notable changes in both ^{1}H and ^{13}C{^{1}H} NMR spectra are seen. The ^{1}H NMR spectra of **40**-41 were as anticipated based on the previously described spectrum for **39**. Whereas **39** exhibits one well defined set of signals, the expected signals for **40-41** are accompanied by an additional minor set of signals. The two sets appear in a molar ratio of approximately 1: 0.2.



Scheme 32. Synthesis of neutral bis.carbene Pd(II) complexes **39-41**.

The relative intensities of the two sets were invariant to the purification process used (repeated washing with pentane and repeated recrystallizations from a acetonitrile/pentane mixture), essentially ruling out that one set arises from the non-symmetrical *trans*-[Pd(NHC)$_2$BrCl] product.

The previous NMR and elemental analysis could not unambiguously establish whether the structures of **39-41** are mixture of palladium halides [149] or isomers of the same product, whether they are of the [(NHC)$_2$PdX$_2$] or [(NHC)$_2$PdXY] (X = Br or/and Y = Cl) type, neither in solution nor in the solid state. Crystals of compound **40** which were suitable for X-ray crystal structure determination were obtained during the purification process. Surprisingly, the novel non-symmetrical *trans*-[Pd{3-Mesityl-1-(2’-phthalamidoethyl)-imidazolin-2-ylidene)$_2$BrCl] (**40**) is isolated as main stable product (Figure 24).

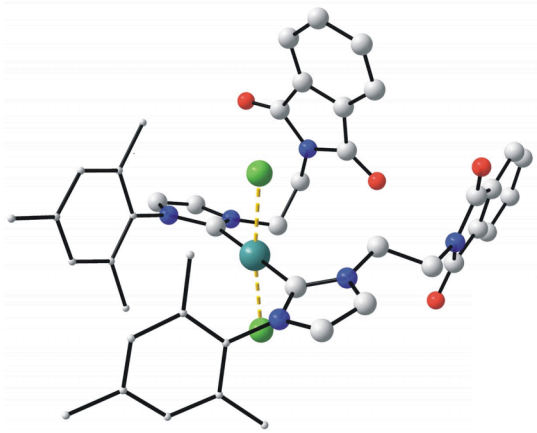


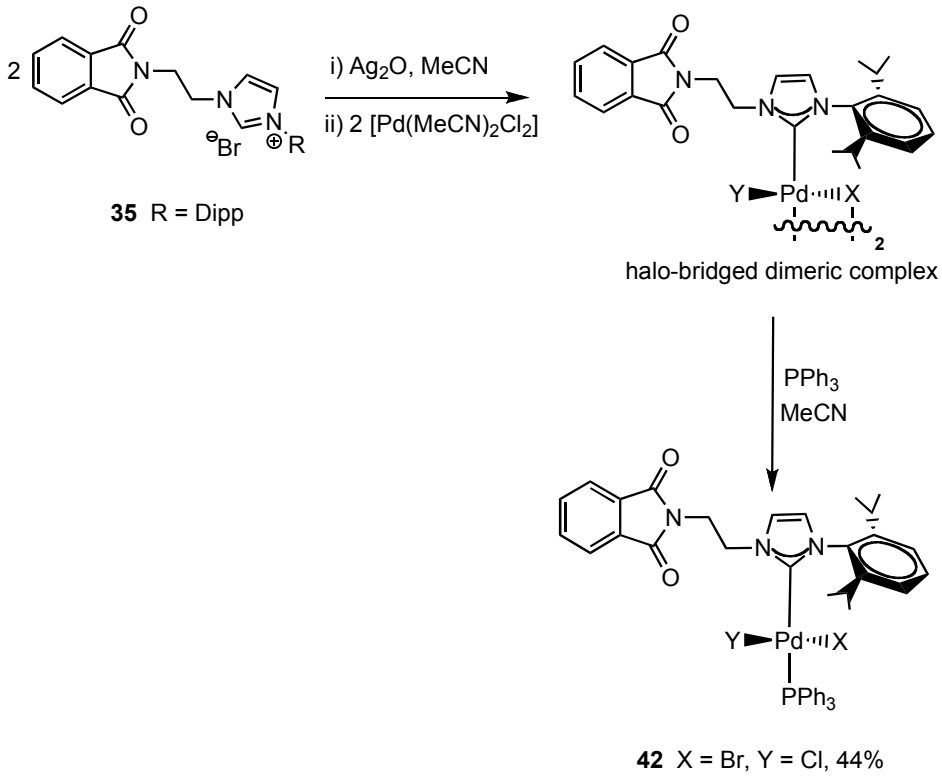
Figure 24. DIAMOND[154] ball and stick plot of compound **40** in the solid state. Hydrogen atoms are omitted for clarity; dashed lines indicate a disorder.

In fact, compound **40** is air stable in the solid state and remains unchanged for several days when exposed to lab atmosphere. New NMR measurements of the stable crystalline products **40-41** revealed one well defined set of signals at room temperature. As is apparent in the molecular structure shown in (Figure 23), the palladium complex was formed as *trans* isomer. Within the square planar coordination geometry the two different halide ligands are tilted away from the sterically demanding mesityl rings. In the solid state, the molecule adopts a conformation in which the two phthaloyl rings are *trans* disposed, with phthalamido-carbene units located on the same side of the coordination plane.[150] As observed in structure **40**, the phthalamido groups of the functionalized sidearm do not chelate palladium and are found to be pointing away from the metal. The preference for the formation of **40** and thus its stability under these conditions is unexpected. Although halide scrambling has been observed in the synthesis of rhodium and iridium NHC complexes *via* silver transmetalation,[134] only few other reports on halide scrambling in the synthesis of palladium NHC halide complexes are known.[149] A similar behaviour of halide scrambling in the synthesis of donor-functionalized palladium NHC halide complexes has been recently reported by Li et al.[153] However, when this reaction was carried out in similar conditions, the authors observed that the product was obtained as a mixture of palladium halides [$(NHC)_2PdCl_2$, $(NHC)_2PdBrCl$, and $(NHC)_2PdBr_2$], instead of simply $(NHC)_2PdCl_2$,

with various overlapping peaks in ^{1}H and ^{13}C NMR spectra and a specific stoichiometry confirmed by Electrospray Ionization Mass Spectrometry (ESIMS).

5.1.3 Synthesis of a mixed phosphine-carbene Pd(II) complex

In order to evaluate whether the phthalimido functionality can coordinate to the palladium center or if the halide scrambling process can be still observed, the ratio of the carbene and palladium was adjusted to 1:1. When the silver compound **35** was treated with two equiv of $[Pd(MeCN)_2Cl_2]$, a halo-bridged dimeric complex is formed (Scheme 33), which is unstable both in the solid state and in solution.



Scheme 33. Synthesis of the mixed NHC-phosphine palladium complex **42.**

During these investigations, the halide scrambling process and the mechanistic implications of the phthalimido functionality group were followed and examined. However it cannot be excluded that the high instability of the halo-bridged dimeric complex in solution could be due to the coexistence of a mixture of $\{(NHC)_2PdXY\}_2$ or {(NHC)PdXY} (X = Br or/and Cl) species. However, the latter one can be explained, as the bridge splitting of the dimeric complex followed by a weak

interaction between the carboxylic group and palladium in a chelate ring system. To clarify this, an equimolar amount of PPh_3 (with respect of Pd) was added to the acetonitrile solution at 25 °C. The strong phosphine ligand is expected to cleave both the halo-bridged dimeric $\{(NHC)_2PdXY\}_2$ as well as the weaker Pd-*C*O(R) bond of {(NHC)PdXY} species. The obtained pale-yellow crystalline solid was also air and moisture stable and was purified by silica gel chromatography to remove possible traces of PPh_3 and other residual palladium complexes. Indeed, the addition of PPh_3 leads to a clean and well-resolved ^{1}H NMR spectrum corroborating the formation of the mixed phosphine-carbene complex **42** as the only product. Two doublets are observed at δ 1.00 and 1.09 ppm for the diastereotopic methyl groups of the ^{i}Pr substituents, as well as one septet at δ 2.78 ppm for the methine protons. The $^{13}C\{^1H\}$ NMR signal for the C_2-carbenoic carbon appears at δ 191.8 ppm. In the ^{31}P NMR spectrum the phosphine donor resonance appers at δ 23.7 ppm. In the high-resolution mass spectrum (FAB) of *trans*-**42** complex, two strong signal groups are observed around *m*/*z* 850 and 804, corresponding to $[M^+ - Cl]$ and $[M^+ - Br]$ for the **42** complex. Single crystals obtained from a saturated CD_3Cl solution were subjected to an X-ray diffraction analysis, and the molecular structure of **42** is shown in Figure 25.

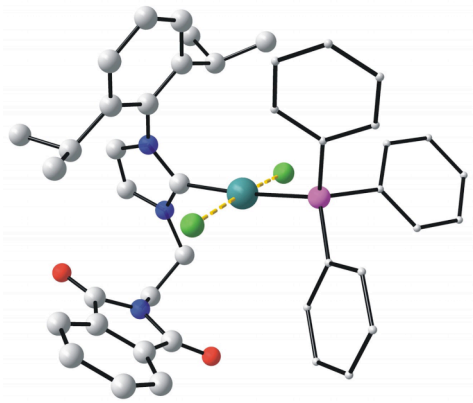
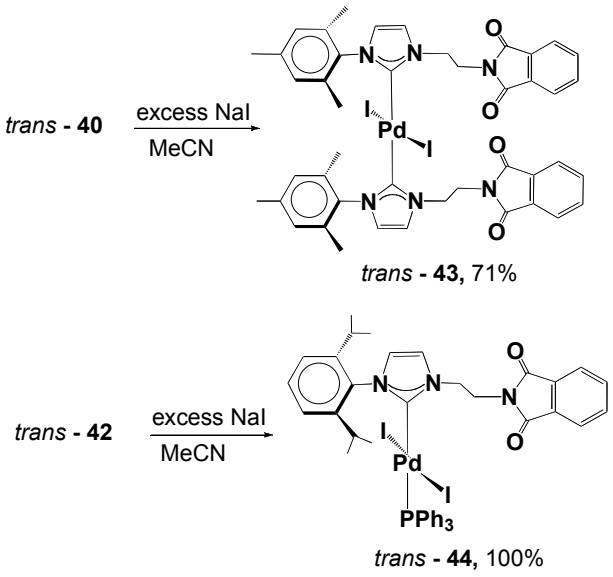


Figure 25. DIAMOND[154] ball and stick plot of compound **42** in the solid state. Hydrogen atoms are omitted for clarity; dashed lines indicate a disorder.

The metal center is coordinated by one phthalimido-carbene, one phosphine and two Br / Cl ligands in a distorted square planar fashion. The former two are found in a *trans* arrangement, coordination that is thermodynamically favored. Although the formation of the non-symmetrical palladium complexes **40-41** and **42** was not anticipated, this process probably occurs due to the influence of the bulky substituents

on the reactivity of the metallic center, when the imidazolium salts and the metallic precursors, bearing different anions are used. To the best of our knowledge, no X-ray structural characterization of the non-symmetrical palladium analogues has been reported before, in spite of the fact that the mixed phosphine-carbene Pd(II) complexes of similar type as well as bis(carbene) Pd(II) complexes are well known.[154] It is noteworthy that complexes **40-41** and **42** represent novel structural types bearing scrambled halide ligands. The observed preference for *trans* configuration seems to be due to the bulky *N*-aryl substituents in these palladium complexes.

Although structural characterization of the novel non-symmetrical compounds **40** and **42** has been possible, to exchange the scrambled halides with symmetrical ones additional reactions have been performed. The solution of **40** and **42** was almost quantitatively transformed into the *trans*-diiodo complexes **43** and **44** by treatment with an excess of sodium iodide in acetonitrile at 20 °C (Scheme 34).[149]



Scheme 34. Synthesis of symmetrical bis(carbene) and NHC-phosphine palladium diiodide complexes **43** and **44.**

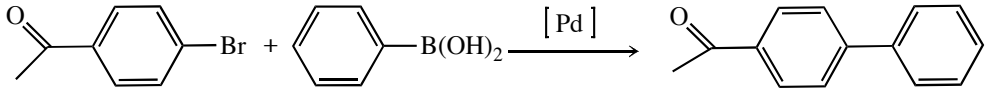
This halide exchange at room temperature allowed the one step synthesis of the symmetrical *trans*-diiodo complexes **43** and **44** which have been identified by ^{1}H NMR spectroscopy, elemental analysis and mass spectrometry. The high-resolution mass spectrometry (FAB) of **43** and **44**, indicated *m/z* values corresponding to $[(NHC)Pd]^{+}$ and $[(NHC)PdI]^{+}$ ions. One set of signals in the ^{1}H NMR spectra and one

phosphine donor resonance at δ 16.3 ppm in the ^{31}P NMR spectrum of **44** has been observed.

5.2 Suzuki-Miyaura coupling reaction

The Suzuki cross-coupling reaction of aryl bromides with arylboronic acids catalyzed by Pd-NHC complexes is well documented.[155] The palladium complexes **39**, **44** and **43** have been found to be efficient catalyst precursors for the Suzuki-Miyaura cross-coupling reaction. The activity and stability of these catalysts was first tested in the classical Suzuki coupling of phenylboronic acid with 4-bromoacetophenone. The reaction performed at 110 °C in toluene, in the presence of 1 mol % of **39**, **43** and **44** catalysts loading (Table 6, entries 1-3) led to 4-acetobiphenyl in moderate yields after 12 h. The solubility of the reactants and catalysts in the solvent is crucial for the success of the coupling reaction. Traditionally, solvents as THF, dioxane and toluene are used in the Suzuki reaction, but the low solubility of the catalysts in these usual solvents tempted us to use xylene as solvent. To probe the long-term stability of these catalysts, the catalyst concentration was reduced (0.01 and 0.001% mol). Higher yields have been reached after 12 h at 130 °C. The bis(carbene) palladium complex **43** with sterically demanding substituents was more efficient than the less sterically methyl-substituted carbene complex **39**, for promoting the coupling of 4-bromoacetophenone with phenylboronic acid (Table 6, entries 4-5).

Table 6. Selected results of Suzuki–Miyaura C-C coupling reactions of 4-bromoacetophenone with phenylboronic acid catalyzed by **39**, **43** and **44**[a]



entry	Catalyst	mol % [Pd]	Solvents	*T* [°C]	Yield [%][b]
1	**98**	1	toluene	110	32
2	**102**	1			53
3	**103**	1			72
4	**98**	0.01	xylene	130	44
5	**102**	0.01			86
6	**103**	0.01			100
7	**102**	0.001	xylene		98
8	**103**	0.001			100

[a] Reaction conditions: 2.0 mmol 4-bromoacetophenone, 2.4 mmol phenylboronic acid, 3 mmol K_2CO_3, 5 mL organic solvent, mol % of catalysts, 12 h. [b] Determined by GC using diethylene glycol di-*n*-butyl ether as an internal standard. [c] After 6 h.

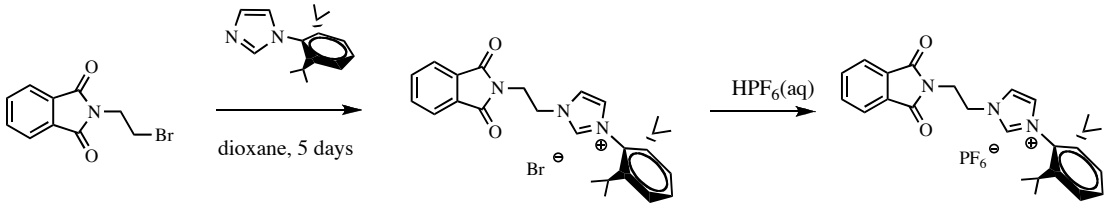
This result can be explained by the strong effect of the bulky substituents on the metal environment. Using the mixed phosphine-carbene complex **44**, the reaction proceeded rapidly at 130 °C with no traces of Pd metal deposit (Table 6, entry 6). After 6 h at 130 °C, excellent yields were obtained, demonstrating the stability and the great efficiency of these catalysts under the conditions described (Table 6, entry 8). It is well known that the use of mixed NHC-phosphine catalysts strongly enhances the activity of such cross-coupling reactions, especially in the Suzuki reaction.[165] The formation of aryl dehalogenation and aryl-aryl coupling products can be a problem in Suzuki coupling reactions using other catalyst systems. However, no side products were observed during catalysis with these carbene complexes.

The synthesis and structural characterization of new phthalimido-functionalized *N*-heterocyclic carbene Pd(II) complexes derived from water-soluble quaternary bromide salts is described. These compounds are easily accessible *via* the Ag–carbene

transfer method. Studies of the L: Pd molar ratio determines either the formation of the neutral *trans*-bis(carbene) **39-41** or dimeric palladium complexes. The latter can be easily cleaved by a stronger phosphine ligand forming a mixed phosphine-carbene complex **42**. To the best of our knowledge, these are the first examples of stable non-symmetrical bis(carbene) and mixed phosphine-carbene Pd(II) complexes that have been structurally characterized. In our case, the sterically demanding environment of the ligand systems strongly influences the structural and conformational behaviour of the formed metal complexes **40-41** and **42** having a statistical halide scrambling of Br / Cl at room temperature as consequences. Three of the symmetrical palladium complexes **39**, **43** and **44** effectively catalyze Suzuki-Miyaura types cross coupling of phenylboronic acid and 4-bromoacetophenone in very good yields.

5.3 Synthesis and characterization of neutral rhodium(I) complexes

Two neutral rhodium complexes [Rh(Dipp-C^phthaloyl)(η^4-1,5-COD)X] (**45** X = Cl, **46** X = Br) have been synthesized either *via* silver transmetalation or by deprotonation of the imidazolium salt (**35**) by $[Rh(acac)(COD)]_2$ (acac = acethylacetonate), which increases the yield of the formed product and avoids multi-step reactions (Scheme 35).

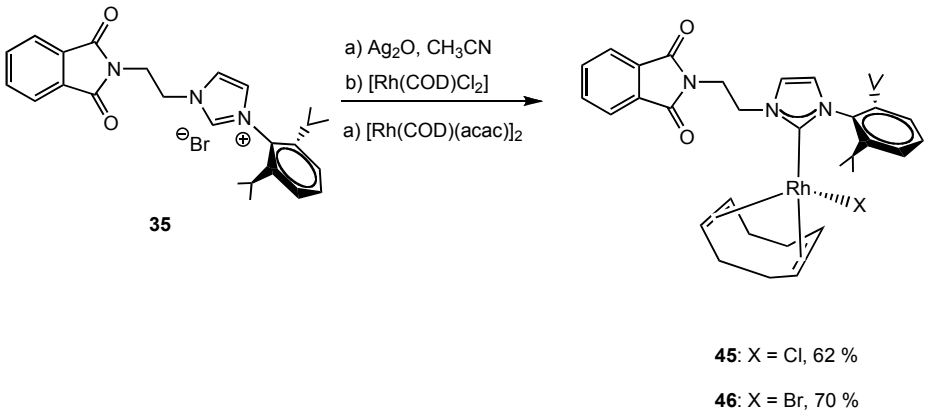


35 **35a**

Scheme 35. Synthesis of the phthaloyl-imidazolium salt **35a**.

The neutral rhodium(I) complex (**45**) of the ligand precursor [(Dipp-C^phthaloyl)·HBr] (**35**) was synthesized by Lin’s method of transmetalation from intermediate silver(I) complex $[Ag(Dipp\text{-}C\text{^}phthaloyl)_2(AgBr_2)]$ (**38**) Metalation of the phthalamido-functionalized imidazolium salt **35** using Ag_2O was monitored by ^1H NMR spectroscopy. Alternatively, $[Rh(COD)Cl]_2$ (COD = 1,5 - cyclooctadiene), was

added directly to a dichloromethane solution of [Ag(Dipp-C^phthaloyl)$_2$(AgBr$_2$)] (**38**). Precipitation of AgCl was observed immediately, but the mixture was allowed to stir at room temperature for 1 h before workup. The rhodium complex [Rh(Dipp-C^phthaloyl)(η^4-1,5-COD)Cl] **45**, was isolated as yellow crystalline solid in 62 % yield. The structure of this rhodium complex was determined by spectroscopic analyses. In the ^{13}C NMR spectrum a doublet at 180.5 ppm with a coupling constant ($J_{Rh–C}$ = 55 Hz), is assigned to the diagnostic Rh–C_2 resonance, indicating the carbene transfer from Ag to Rh. The formation of carbene complex **45** was corroborated by a base peak in the CI mass spectrum at m/z = 540.09 for [Rh(Dipp-C^phthaloyl) Cl]$^+$ fragment.

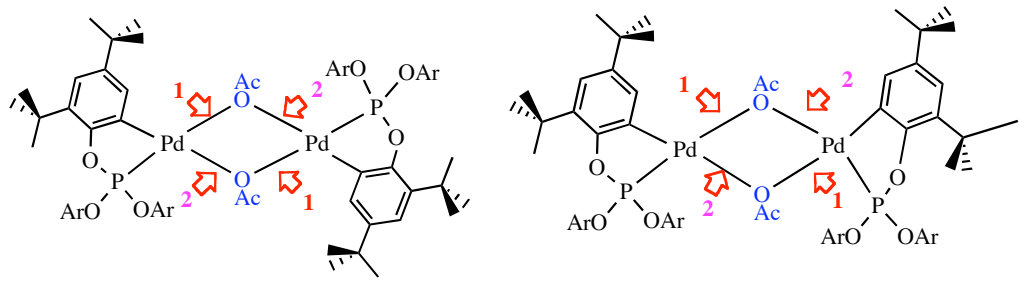


Scheme 36. Synthesis of the neutral Rh(I) complexes **45** and **46**.

The rhodium bromide derivative [Rh(Dipp-C^phthaloyl)(1,5-COD)Br] **46** was prepared by the direct reaction of the imidazolium precursor **35** with [Rh(acac)(COD)]$_2$ in THF at room temperature.[165] The synthesis is based on the protonation of the acetylacetonate by the imidazolium precursor and on trapping the resulting carbene by coordination to the metal. The rhodium complex **46** was characterized by elemental analysis, high-resolution mass spectrometry (FAB), and ^{1}H and ^{13}C NMR studies. The ^{13}C NMR spectrum displays the carbene carbon Rh–*C*(2) resonance at δ 186.6 ppm with the coupling constant (J_{Rh-C} = 56.0 Hz), which is in good agreement with the data reported for an oxazoline-NHC system. This *one-pot* synthesis reaction of the neutral rhodium complex **46** is obtained in a better yield and avoiding multi-step reactions.

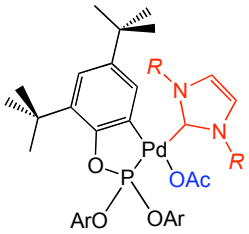
6 Summary

The primary focus of this dissertation is set on the design, synthesis, and catalytic applications of new donor-functionalized *N*-heterocyclic carbene ligands with multiple functionalities, as environmentally friendly water-soluble NHC precursors. In the first part of the thesis, the preparation of unsaturated NHC-substituted phosphitepalladacycles *via* phosphitepalladacycle acetato and chloro precursors and azolium salts with noncoordinating anions in DMSO is reported. With this one-pot synthesis NHC-substituted phosphite-palladacycles are obtained avoiding multi-step reactions. Synthesis of the pyridine- and benzenimidazoline-functionalized *N*-heterocyclic carbenes with the chelating possibility (hemilability) and their palladium and rhodium complexes is represented in the second part of the thesis. In the last part of the thesis the preparation of novel "green" imido-based *N*-heterocyclic carbene ligands and their versatile reactivity and applications in various *C-C* coupling reactions is presented.



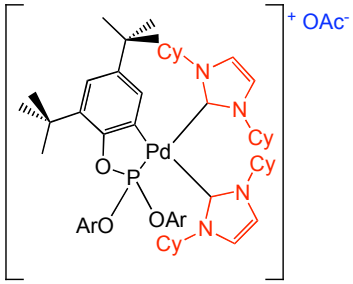
***trans*-1a** Ar = 2,4-(*t*-Bu)$_2$C$_6$H$_3$ ***cis*-1a**

The synthesis of acetate-bridged phosphitepalladacycle dimer **1a** was achieved in a similar way to that synthesized by *Bedford* and co-workers for the analogous chloride complex, by the thermal treatment of $Pd(OAc)_2$ with the sterically demanding tris-(2,4-di-tert-butylphenyl)phosphite in monomethyl-glycol ether at 80 °C. The complex **1a** could be identified as a mixture of *cis*- and *trans*-isomers in solution, with two signals in the ^{31}P NMR spectrum. The complex **1a** has been characterized by spectroscopic methods and elemental analysis. The molecular structure of the acetate-bridged phosphitepallada-cycle dimer **1a** has been determined by single crystal X-ray analysis, showing that the two Pd atoms adopt a square planar geometry and are connected by two bridging acetate ligands.



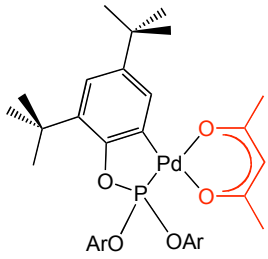
Ar = 2,4-(*t*-Bu)$_2$C$_6$H$_3$

5a



Ar = 2,4-(*t*-Bu)$_2$C$_6$H$_3$

6a



Ar = 2,4-(*t*-Bu)$_2$C$_6$H$_3$

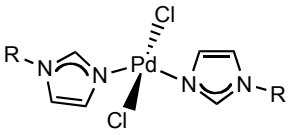
10

Two different routes were employed to synthesize unsaturated NHC-palladacycle complexes. First, the ‘‘free carbene’’ route for the high sterically hindered carbene ligands, or without isolation of the free carbene *‘‘in situ’’* method, when palladium acetate is used as the starting material. When the palladacycle **1a** was treated with 2.1 equiv. of a less sterically hindered carbene such as 1,3-dicyclohexylimidazolin-2-ylidene, the acetate product with two NHC ligands was obtained. The coordination of two carbenes at one metal center is a good illustration that NHC ligands are much stronger ligands than the acetate ligand. The formation of a mono-substituted NHC complex shows that the coordination of two NHCs to the palladium center is not always necessary, especially when the steric demand of the ligands would disfavor such a conformation. The acetylacetonate phospha/phosphitepalladacycles were prepared by treatment of the acetate-bridged palladacycles **1a** with 2,4-pentanedione (Hacac) in dichloromethane to afford the acetylacetonate product **10** in nearly quantitative yield. Using these new classes of catalysts, TONs of approximately 10^6 after a reaction time of 18 h can be achieved. Deactivated bromoarenes could also be coupled efficiently, using extremely low amount of catalyst (10^{-4} mol %). Even aryl chlorides can be coupled, TONs of approximately 5500 can be reached after only 18 h without any detectable catalyst deterioration using only 0.01 mol % of the catalyst.

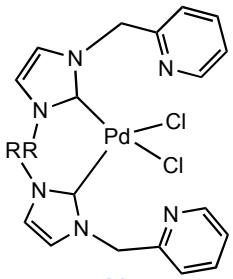
The possibility of direct introduction of new functionalities (or a new C–C bond) via direct C–H bond transformation or oxidative addition is a highly attractive strategy, owing to the ubiquitous nature of C–H bonds in organic substances. Metallacycles represent a challenge to chemists not only in terms of their synthesis but also in terms of their structures, design, and types of ligands metallated. Therefore, our plan was to synthesize another catalysts library**,** where one substituent can be formed from derivatives of any amine functionality**,** thus allowing more variations in direct

proximity to the metal.

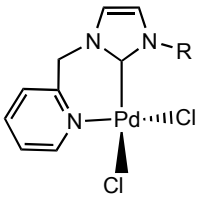
Bidentate ligands have often been prepared from *N*-alkyl or -aryl imidazolium salts. The preparation of the imidazolium precursors is usually straightforward from commercial available products. Pd(II) and Rh(I) complexes of donor-functionalized heterocyclic carbene ligands have been synthesized through a route involving carbene transfer from Ag(I) carbene precursors. The Ag complexes undergo facile reaction with $[PdCl_2(MeCN)_2]$ to yield $[Pd(pyC\hat{}N)_2Cl_2]$ **23** and $[Pd(\eta\text{-}C\hat{}N)Cl_2]$ **24**, (C^N) = 3-cyclohexyl-1-picolylimidazolin-2-ylidene) which presents a monodentate and chelating behavior.



19



23

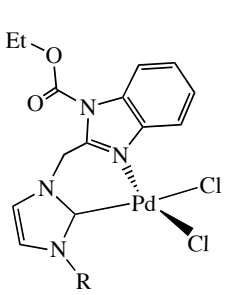


24

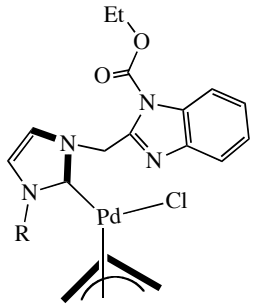
A bis-N-imidazole Pd(II) compound **19** [*trans*-$Pd(NCyIm)_2Cl_2$] with the imidazol ring bound at the N_1 atom not at the C_2 atom was obtained and fully characterized. Under mild conditions in NHC precursors a cleavage of their C-N bonds occurs, yielding the N-alkyl-imidazole fragments. The formation of the bis-N-imidazole Pd(II) complex **19** is in contrast to previous studies on C-H bond activation in imidazolium systems, which have so far, always led to the usual C_2 carbenes silver complexes. The novel Pd(II) complex **19** with *N*-coordinated imidazol ligands show a remarkably high catalytic activity towards the microwave-assisted Suzuki–Miyaura cross-coupling reaction in aqueous medium. The use of focused microwave technology allowed us to isolate the biphenyl product in a short reaction time and in excellent yield.

New benzimidazole-functionalized imidazolium-based NHC complexes of Pd(II) and Rh(I) have been prepared. The hybrid ligand (bzC^N), carrying two heterodonors of benzenimidazole and carbene, can be either monodentate or chelate in both Pd(II) and Rh(I) compounds. The benzenimidazole moiety was attached to the imidazole ring through a methylene group. NHC's with a methylene linker tend to form *trans*

biscarbene complexes in the reaction of $[PdCl_2(MeCN)_2]$, while in our case a chelate (bzC^N-N) Pd(II) complex **30** was formed.

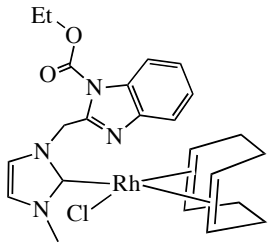


30

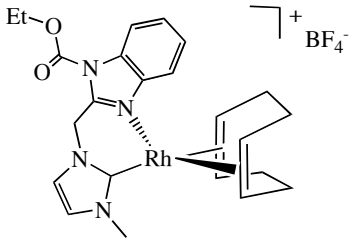


31a

The resultant mononuclear Pd(II) **30** has the desirable heterobidentate C/N chelate and is chemically stable. This new type of carbene precursor also reacts with $[Pd(allyl)Cl]_2$ to give monodentate NHC palladium η^3-allyl chloride [Pd(NHC)(allyl)Cl]. Fluxionality in the NMR time scale was observed for most complexes, and the origin of their dynamic behaviors was discussed for each type of structure. For [Pd(NHC)(allyl)Cl] with a small wing tip group of the NHC, the fluxionality is caused by selective η^3-η^1-η^3 allyl isomerization. For cationic chelating complexes $[Pd(NHC\text{-}N)(allyl)]BF_4$, the dynamic exchange process likely originates from a dissociative boat-to-boat inversion of 6-membered palladacycles.



32a

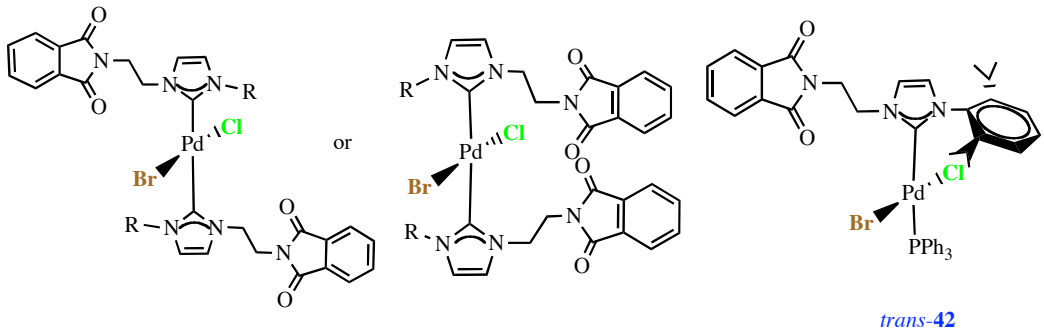


32b

Coordination chemistry of the new benzenimidazole imidazole-2-ylidene ligand (bzC^N) system toward rhodium(I) metal ions has been investigated. The rhodium complex [(bzC^N)RhCl(COD)] **32** (COD = 1,5-cyclooctadiene) was prepared via either the transmetallation from the silver complex or in a one-step reaction of **28** with $[Rh(acac)(CO)_2]$ (acac = acetylacetonate). Upon the abstraction of chloride, the benzimidazole nitrogen coordinated to the metal center and formed [(C,N-

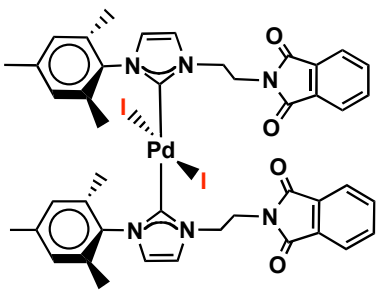
bzC^N)Rh(COD)]BF_4 with the chelation of bzC^N moiety.

A new family of phthalimido-functionalized NHC ligands has been used to prepare new series of neutral bis-carbene palladium complexes **39-41** and mixed carbene-phosphine palladium complex **42**, through the silver transmetalation method. The new hybrid imidazolium precursors **33-35**, upon reaction with Ag_2O yielded the corresponding silver complexes, in which two carbenes are bonded to silver *via* the imidazoline-2-ylidene carbon atom. Addition of the corresponding silver compounds to one equiv of [$PdCl_2(MeCN)_2$] afforded neutral bis-carbene palladium complexes **39-41**. A single-crystal X-ray diffraction study was performed on complex [Pd(Mes-C^phthaloyl)$_2$XY] (Mes-C^phthaloyl) = {3-Mesityl-1-(2'-phthalamidoethyl)-imidazolin-2-ylidene} (X = Br, Y = Cl) revealing that **40** displays a statistical scrambling of the Br / Cl ligands at the central carbene-supported Pd(II).

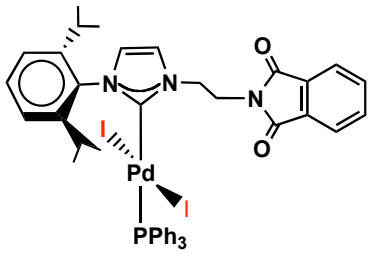


trans - **39-41** *trans*-**42**

A mixed carbene-phosphine palladium complex **42** was obtained from a intermediate dimeric complex with triphenylphosphine ligands, when two equiv of [$Pd(MeCN)_2Cl_2$] are treated with the corresponding silver complex. Like the non-symmetrical bis-carbene complex **40**, compound **42** shows the same halide scrambling. Although the separation and the exact structure determination of **40**, **41** and **42** is possible, the transformation of these non-symmetrical complexes into the diiodo-derivatives **43** and **44** is better performed by the treatment with an excess of sodium iodide in acetonitrile. Complexes **39, 43** and **44** were further evaluated for their efficacy in promoting catalytic Suzuki-Miyaura C-C coupling reactions.



trans-**43**



trans-**44**

The introduction of *green chemistry* framework, mild conditions, and simpler methods even for the most demanding coupling reactions, especially for the deactivated aryl chlorides and bromides, are an ongoing challenge of today's chemistry. Numerous new types of ligands have been designed to further enhance the yields and the selectivity of the reaction. Within this work, one of the main goals was to open up a venue to couple most types of aryl halides with phenyl boronic acids using a green chemistry framework. High activity of the present systems, as well as the possibility to control their design and reactivity justifies further explorations of bidentate ligands based on the same principles.

7 Experimental section

7.1 General Aspects

All syntheses, storage, and characterization of organometallic compounds were performed under argon atmosphere using thoroughly heated Schlenk vessels. Distillation, sublimation, removal of the solvents and drying of the solid materials wes performed under high vacuum (< 0.1 mbar). Sealed equipment was secured against air contact with paraffin security valves. Solvents were dried by standard procedures (THF, *n*-hexane, toluene and Et_2O over Na/benzophenone; CH_2Cl_2 over CaH_2), distilled under nitrogen, and kept over 4 Å molecular sieves. The solvents were also dried with an alumina based solvent purification system. All other materials were obtained from commercial resources (Sigma-Aldrich, Fluka, Acros Organics, Lancaster, Merk) and were used as received, except as noted.

7.2 Characterization of the new compounds

7.2.1 Nuclear magnetic resonance spectroscopy

NMR spectra were recorded on Jeol-JNM-GX-270, Jeol-JNM-GX-400 and Bruker AMX-400 MHz spectrometers operating on following frequencies (Table 7). When needed, the signal were assigned by 2D NMR experiments (APT, DEPT, COSY, HMQC, HMBC and NOESY).

Table 7. NMR spectrometer frequencies

	^{1}H-NMR	^{13}C-NMR	^{19}F-NMR	^{31}P-NMR
Bruker AMX-400	400.13 MHz	100.61 MHz	-	161.98 MHz
Jeol-JNM-GX-270	270.16 MHz	67.93 MHz	-	109.37 MHz
Jeol-JNM-GX-400	399.80 MHz	100.51 MHz	376 MHz	161.83 MHz

The substances were dissolved in pure deuterated solvents purchased by Fa. Deutero GmbH, which were dried, if necessary, over molecular sieve (4Å) and degassed by means of repeating freeze-pump-thaw cycles. The chemical shift δ in ppm is specified comparatively to the working frequency of the spectrometer.

For ^{1}H-NMR and ^{13}C-NMR spectra, solvent signals were used as internal reference:
^{1}H NMR: δ = 7.25 ppm ($CDCl_3$), 2.5 ppm (DMSO-*d*$_6$), 7.15 ppm (C_6D_6-*d*$_6$), 5.32 ppm (CH_2Cl_2).
^{13}C{^{1}H} NMR: δ = 77.2 ppm ($CDCl_3$), 39.52 ppm (DMSO-*d*$_6$), 128.0 ppm (C_6D_6-*d*$_6$), 53.5 ppm (CH_2Cl_2).
For ^{31}P {^{1}H} NMR, shifts are quoted relative to aqueous H_3PO_4 (85 %) as external standard. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad signal. Coupling constants J are given in Hz.

7.2.2 Infrared spectroscopy

IR spectra were recorded on a JASCO FT/IR-4000 spectrometer using KBr pellets. The positions of the bands are given in wave numbers (cm^{-1}).

7.2.3 Mass spectroscopy

Mass spectra were measured on either MAT-90 or MAT-311 instrument of Finnigan. They were used for the characterization using EI-, CI- (isobutene, positive and negative ions) and FAB (using 4-nitrobenzyl alcohol as solvent).

7.2.4 Melting points

Melting points were measured with Fa. (Büchi melting point apparatus) and are not corrected.

7.2.5 Elemental analysis

Elemental analyses were performed in the microanalytical laboratory of Anorganisch-chemisches Institut der Technische Universität München (director: Mr. Barth).

7.2.6 Gas chromatography

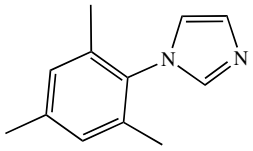
Quantitative analyses of fluid organic mixtures (catalytic runs), GC spectra were measured on a Varian gas chromatograph CP-3800 (column: Factor Four VF-5 ms) equipped with a FID detector.

7.3 Working Procedures

7.3.1 Synthesis of mono- and bis-(alkyl/aryl)imidazolium salts

7.3.1.1 Monosubstituted imidazolium salts

[1-(mesityl)imidazole] (1).



An ammonium chloride solution (5.35 g, 0.10 mol, 20 ml H_2O) was added dropwise over 30 min to a rapidly stirred solution of 100 ml H_2O and 100 ml 1,4-dioxane at 100 °C containing paraformaldehyde (3.00 g, 0.10 mol), mesitylammonium salt (prepared from the addition of phosphoric acid to mesitylamine (13.5 g, 0.10 mol) in 50 ml H_2O until a pH of ca. 2 was reached) and glyoxal (11.5 ml of 40 % aqueous solution, 0.10 mol). During the addition t he solution turns yellow and then rapidly black. The solution is maintained at 100°C for a further 1h (all mesitylamine consumed by GC-MS analysis) and then chilled in an ice bath. Solid NaOH was added at 0 °C until a pH of 12 was obtained and a dark organic layer separated. H_2O (150 ml) was added to the reaction mixture and the product was extracted with 3 x 500 ml hexane. The combined hexane extracts were dried over $MgSO_4$ and evaporated to yield the product as a light brown solid, which was recrystallised from ethyl acetate as a colorless crystalline solid in three crops.

Yield: 7.36 g (40 %).

m.p. = 112–113°C

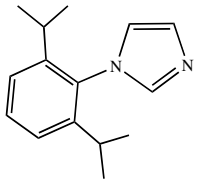
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.98 (6 H, s, *o*-Me), 2.34 (3 H, s, *p*-Me), 6.89 (1 H, bs, CH_{imid}), 6.97 (2 H, s, *m*-CH_{mes}), 7.23, 7.43 (2x1 H, bs, CH_{imid}).

^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) δ = 17.3 (*o*-Me), 21.0 (*p*-Me), 120.0, 128.9, 129.5, 133.4, 135.4, 137.4, 138.8 (3xCH_{imid}), *ipso*-, *o*-, *m*-, *p*-C_{mes}).

MS *m*/*z* = 186 (M^+, 32%).

Anal. Calcd for $C_{12}H_{14}N_2$: C 77.38, H 7.58, N 15.04%, Found C 77.37, H 7.56, N 14.97%.

[1-(2,6-diisopropylphenyl)imidazole] (1').



An ammonium chloride solution (5.35 g, 0.10 mol, 20 ml H_2O) was added dropwise over 30 min to a rapidly stirred solution of 100 ml H_2O and 100 ml 1,4-dioxane at 100 °C containing paraformaldehyde (3.00 g, 0.10 mol), 2,6-diisopropylphenyl ammonium salt (prepared from the addition of phosphoric acid to diisopropylphenylamine (15 g, 0.10 mol) in 50 ml H_2O until a pH of ca. 2 was reached) and glyoxal (11.5 ml of 40 % aqueous solution, 0.10 mol). During the addition the solution turns yellow and then rapidly black. The solution is maintained at 100 °C for a further 1 h (all diisopropylphenylamine consumed by GC-MS analysis) and then cooled in an ice bath. Solid NaOH was added at 0 °C until a pH of 12 was obtained and a dark organic layer separated. H_2O (150 ml) was added to the reaction mixture and the product was extracted with 3 x 500 ml hexane. The combined hexane extracts were dried over $MgSO_4$ and evaporated to yield the product as a light brown solid, which was recrystallized from ethyl acetate as a colorless crystalline solid in three crops.
Yield: 9.36 g (50 %).

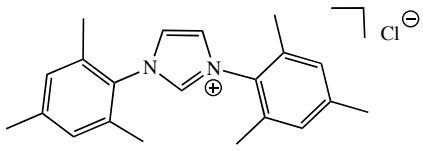
^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.25 (s, Me), 2.34 (2H, sept, CH), 6.89 (1 H, bs, $CH_{(imidazole)}$), 6.97 (2 H, s, *m*-CH(*Ph*)), 7.23, 7.43 (2x1 H, bs, $CH_{(imidazole)}$).

^{13}C{^{1}H}-NMR (100.53 MHz, $CDCl_3$) δ 11.3 (Me), 21.0 (CH), 120.0, 128.9, 129.5, 133.4, 135.4, 137.4, 138.8 (3 x $CH_{(imidazole)}$, *ipso*-, C(*Ph*)).

MS *m*/*z* = 228 (M^+, 50%).

Anal. Calcd for $C_{12}H_{14}N_2$: C 78.38, H 8.83, N 12.27%, Found C 77.97, H 8.56, N 12.17%.

[1,3-Bis-(2,4,6-trimethylphenyl)imidazolium] Chlorides (3).



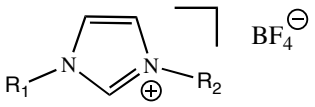
A mixture of 11.21 g (30.3 mmol) of N,N'-bis-(2,4,6-trimethylphenylamino)ethane dihydrochloride,100 ml of triethyl orthoformate, and two drops of 96 % formic acid was heated in a distillation apparatus until the ethanol distillation ceased. The temperature of the reaction mixture reached 130 °C. Upon cooling to 23 °C a colorless solid precipitate which was collected by filtration, and dried *in vacuo***.** In some cases an imidazolinium salthriethyl orthoformiate adduct formed, and purification was achieved by repeated recrystallizations from acetonitrile/ether.
Yield: 8.30 g (80 %).

m.p. > 250 °C

^{1}H NMR (400 MHz, DMSO-d_6): δ 2.28 (s, 6 H, para-CH_3), 2.36 (s, 12 H, ortho-CH_3), 4.48 (s, 4 H, im-H_5), 7.08 (s, 4 H, meta-CH), 9.22 (s, 1 H, im-H_2).

^{13}C{^{1}H} NMR (100 Hz, DMSO-d_6): δ 17.2 (s, ortho-CH$_3$), 20.5 (s, para-CH$_3$), 50.9 (s, im-$C4$-5), 129.3 (s, meta-C), 130.8 (s, ipso-C), 135.3 (s, ortho-C_{aryl}), 139.5 (s, para-C_{aryl}), 160.2 (s, im-C_2).

Anion exchange reactions (8,9)

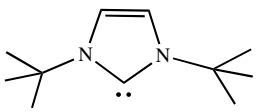


General method. An acetonitrile or water solution of the corresponding silver salt ($AgBF_4$) was added dropwise to a solution of the corresponding imidazolium salts and stirred at room temperature for 2–12 h. After completion, the reaction mixture was filtered, the volatiles were removed under *vacuo* and the resulting solid washed with diethyl ether. Drying under vacuum gave the products as white solids. In most cases, the products obtained at this stage were spectroscopically and analytically pure. If necessary, they were purified by recrystallization from saturated solution of dichloromethane and diethyl ether or by extraction into hot toluene and crystallization by slow cooling to room temperature.

7.3.1.2 General preparation of the free carbenes

Under an inert atmosphere, a round-bottomed flask was charged with 1,3-bis-(alkyl/aryl)imidazolium chlorides and 50 ml THF. The mixture was stirred at 23 °C and potassium tert-butoxide was added in a single portion. The reaction was stirred for 30 min. The mixture was filtered through a Celite pad. The filter cake was extracted with 2x10 ml hexane. The filtrate was concentrated *in vacuo* to afford an oil as the crude free carbene.

[1,3-Bis-(tert-butyl)imidazolin-2-ylidene] (2').



Under an inert atmosphere, a round-bottomed flask was charged with *5* g (23.3 mmol) of 1,3-di-tert-butylimidazolium chloride and 50 ml THF. The mixture was stirred at 23 °C and 2.8 g (24.9 mmol) potassium tert-butoxide was added in a single portion. The reaction was stirred for 30 min. The mixture was filtered through a Celite pad. The filter cake was washed with 20 ml THF. The filtrate was concentrated *in vacuo*

to afford an oil of the crude 2a. The solid was recrystallized by cooling an *n*-hexane solution.

Yield: 3.5 g (84 %).

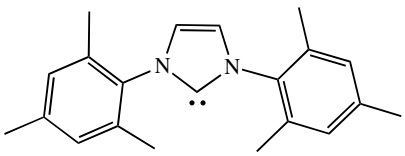
^{1}H-NMR (400 MHz, THF-d_8) δ 1.46 (s, 18H, t-Bu), 6.99 (s, 2H, NCCH); 7.20 (s, NCN).

^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ 31.2 (s, CH_3), 56.8 (s, *C*CH_3), 115.8 (s. im-C4,5), 213.8 (s, im-C_2).

^{15}N NMR (THF-d_8) δ -164.10.

Anal. Calcd for $C_{11}H_{20}N_2$: C, 73.28; H, 11.18; N, 15.54. Found: C, 73.32; H, 10.97; N, 15.54.

[1,3-Bis-(2,4,6-trimethylphenyl)imidazolin-2-ylidene] (3').



To 0.150 g of a ca. 35 % suspension of potassium hydride in mineral oil (corresponding to 1.3 mmol KH) a suspension of 0.381 g (1 mmol) of 1,3-bis-(2,4,6-tri-methylphenyl)jmidazolinium chloride **1a** in 20 ml of THF was added at room temperature. Immediately, a moderate evolution of gas was observed. The mixture was stirred for 3 h at 23 °C until the evolution of gas had ceased, filtered through a frit covered with celite, and evaporated. Recrystallization from *n*-hexane at -25 °C gave **3a** as a colorless solid.

Yield: 0.22 g (72 %).

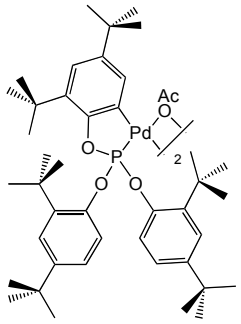
m.p. = 107.9 °C.

^{1}H NMR (400 MHz, C_6D_6): δ 2.16 (s, 6 H, p-C*H*$_3$), 2.29 (s, 12 H, ortho-C*H*$_3$), 3.26 (s, 4 H, im- *H4*), 4.29 (s, 2 H, im-*H*), 6.93 (s, 4 H, meta-C*H*).

^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 18.2 (s, ortho-CH), 21.8 (s, para-CH), 50.8 (s. im-C4), 69.3 (s, im-C)), 129.3 (s, meta-CH), 136.2 (s, para-CH), 136.4 (s, ortho-CH), 139.9 (s, ipso-CH), 243.8 (s, im-C_2).

7.3.2 Ortho-metallated dimeric complexes 1a and 1b

***trans*-di(μ-acetato)-bis[2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP-oxy]-3,5-di-tert-butylphenyl-κC]dipalladium(II) (1a).**



To a solution of 750 mg (3.34 mmol) $Pd(OAc)_2$ dissolved in 50 ml monomethylglycol ether, 2.38 g (3.68 mmol) tri[2,4-di-*tert*-butylphenyl]phosphite was added and heated for 2 h at 80 °C. After 10 min a white product started to precipitate from the solution. The solution was cooled to room temperature and the solvent was removed by filtration, the solid was washed with the same amount of 5 ml monomethylglycol ether, toluene, and *n*-hexane. The obtained product **1a** is well soluble in THF and DCM.

Yield: 252 mg (93 %).

m.p. = 247.1 °C.

^{1}H-NMR (400 MHz, $(CD_3)_2SO$): δ = 7.80 (2H, d, $^3J_{HH}$ = 9.2 Hz), 7.34 (2H, s), 7.23 (2H, t, $^3J_{HH}$ = 8.0 Hz), 7.16 (2H, d, $^3J_{HH}$ = 6.6 Hz), 7.12 (2H, s), 6.97 (2H, t, $^3J_{HH}$ = 9.6 Hz), 6.84 (2H, s), 6.67 (2H, d, $^3J_{HH}$ = 8.4 Hz, CH_{Aryl}), 1.84 (6H, s, CO_2CH_3), 1.40

(18H, s, C(CH_3)$_3$), 1.33 (18H, s, C(CH_3)$_3$), 1.23 (18H, s, C(CH_3)$_3$), 1.21 (18H, s, C(CH_3)$_3$), 1.20 (18H, s, C(CH_3)$_3$), 1.15 (18H, s, C(CH_3)$_3$).

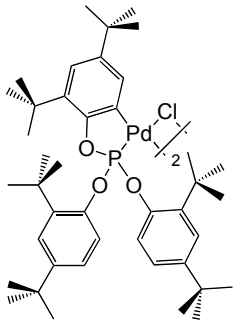
^{13}C {^{1}H}-NMR (100 MHz, d_8-THF): δ = 152.4 (CO$_2$CH$_3$), 148.9 (d, C_{Aryl}, J_{PC} = 5.4 Hz), 147.8, 139.8, 135.5, 133.5, 131.5, 129.7, 128.9, 126.0, 125.5, 124.6, 122.0 (C_{Aryl}), 35.4, 35.2, 32.2, 31.9, 30.9, 29.9 (CH$_3$), 21.5 (CO$_2$$CH_3$).

^{31}P {^{1}H}-NMR (161 MHz, THF-d_8): δ = 126.7 (s), 124.8 (s) (I = 1:1).

MS (CI) m/z (%): 1563.5.2 (65, [M$^+$ - OAc]), 1386.7 (40, [M$^+$ - 2,4-di-*t*-Bu-C$_6$H$_5$O]), 976.3 (35, [M$^+$ - (2,4-di-*t*-Bu-C$_6$H$_5$O)$_3$]), 810.6 (100, [1/2 Palladacycle]), 751 (50,[(2,4-di-*t*-Bu-C$_6$H$_5$O)$_3$PPd]), 441.5 (20, [(2,4-di-*t*-Bu-C$_6$H$_5$O)$_2$P]), 191.3 (10, [2,4-di-*t*-Bu-C$_6$H$_5$]).

Anal. Calcd. for C$_{88}$H$_{130}$O$_{10}$P$_2$Pd$_2$ • THF (1694.86): C, 65.20; H, 8.21. Found: C, 66.20; H, 7.98%.

***trans*-di(μ-chloro)-bis[2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP-oxy]-3,5-di-tert-butylphenyl-κC]dipalladium(II) (1b).**



To a solution of 592 mg (3.34 mmol) $PdCl_2$ dissolved in 50 ml toluene, 2.38 g (3.68 mmol) tri[2,4-di-*tert*-butylphenyl]phosphite was added and heated for 2 h at 80 °C. After 10 min. a white product started to precipitate from the solution. The solution was cooled to room temperature and the solvent was removed by filtration, the solid was washed with the same amount of 5 ml monomethylglycol ether, toluene and *n*-hexane. The obtained product 56 is well soluble in THF and DCM.
Yield: 252 mg (96 %).

m.p. = 256.1 °C.

^{1}H-NMR (400 MHz, ($CDCl_3$): δ = 8.21 (2H, d, $^3J_{HH}$ = 9.2 Hz), 7.40 (2H, s), 7.33 (2H, t, $^3J_{HH}$ = 8.0 Hz), 7.16 (2H, d, $^3J_{HH}$ = 6.6 Hz), 7.04 (2H, s), 6.95 (2H, t, $^3J_{HH}$ = 9.6 Hz), 6.88 (2H, s), 6.67 (2H, d, $^3J_{HH}$ = 8.4 Hz, CH_{Aryl}), 1.66 (6H, s, CO_2CH_3), 1.35 (18H, s, $C(CH_3)_3$), 1.32 (18H, s, $C(CH_3)_3$), 1.22 (18H, s, $C(CH_3)_3$), 1.18 (18H, s, $C(CH_3)_3$), 1.16 (18H, s, $C(CH_3)_3$), 1.12 (18H, s, $C(CH_3)_3$).

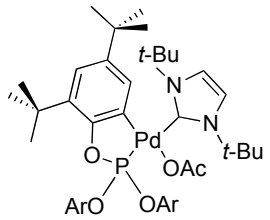
^{31}P {^{1}H}-NMR (161 MHz, d_8-THF): δ = 155.2 and 118.1 ($^2J_{PP}$ = 29.8 Hz) (minor isomer) and 141.4 and 117.3 ($^2J_{PP}$ = 868.4 Hz) (major isomer).

MS (CI) m/z (%): 1538.2 (68, [M^+ - Cl]), 787.6 (100, [1/2 Palladacycle]), 751.0 (50, [(2,4-di-*t*-Bu-$C_6H_5O)_3$PPd]), 441.5 (20, [(2,4-di-*t*-Bu-$C_6H_5O)_2$P]), 191.3 (10, [2,4-di-*t*-Bu-C_6H_5]).

Anal. Calcd. for $C_{84}H_{124}Cl_2O_6P_2Pd_2$(1575.47): C, 64.03; H, 7.93. Found: C, 64.20; H, 7.35%.

7.3.3 NHCs-substituted phosphitepalladacycles

Acetato-(1,3-di-tert-butylimidazolin-2-ylidene){2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) (2a)



Ar = 2,4-(*t*-Bu)$_2$C$_6$H$_3$

To a suspension of 300 mg (0.19 mmol) *trans*-di(*μ*-acetato)-bis[2-[[bis[2,4-bis(1,1-dimethylethyl)phenoxy]phosphino-κP]oxy]-3,5bis(1,1dimethylethyl)phenyl-κC]-dipalladium(II) **1a** in 10 ml toluene, a solution of 100 mg (0.55 mmol) 1,3-di-*tert*-butylimidazolin-2-ylidene **2'** in 7 ml THF was added at -70 °C. The reaction mixture was slowly warmed to room temperature and stirred for 3 h. After 30 min a clear solution was obtained. The solvent was removed *in vacuo* and the residue was washed twice with 5 ml *n*-hexane.

Yield: 245 mg (49 %).

^{1}H-NMR (400 MHz, C_6D_6): δ = 8.44 (1H, s), 8.07 (1H, d, $^3J_{HH}$ = 7.2 Hz), 7.55 (1H, s), 7.45 (1H, s), 7.29 (1H, d, $^3J_{HH}$ = 7.6 Hz), 7.03 (1H, s), 6.66 (1H, s), 6.60 (1H, s), 6.51 (2H, s, NC*H*C*H*N), 2.42 (3H, s, OAc), 1.65 (9H, s, C(CH_3)$_3$), 1.58 (9H, s, C(CH_3)$_3$), 1.43 (9H, s, C(CH_3)$_3$), 1.37 (9H, s, C(CH_3)$_3$), 1.32 (9H, s, C(CH_3)$_3$), 1.31 (9H, s, C(CH_3)$_3$), 1.13 (9H, s, C(CH_3)$_3$), 0.97 (9H, s, C(CH_3)$_3$).

^{13}C{^{1}H}-NMR (100 MHz, C_6D_6): δ = 175.7 (d, N*C*N, J_{PC} = 16.8 Hz), 154.7 (s, C_6H_5), 153.9, 153.7 (s, C_6H_5), 148.4, 148.3 (s, C_6H_5), 146.4, 144.8 (s, C_6H_5), 142.1, 140.3, 138.3 (s, C_6H_5), 135.6, 134.9, 131.8, 131.5 (s, C_6H_5), 131.0 (s, O*C*O), 124.2, 124.0, 123.5, 123.4 (s, C_6H_5), 123.1, 120.3, 119.6, 118.73 (s, C_6H_5), 116.7 (N*C*H*C*HN), 60.0 (N*C*(CH)$_3$), 35.0, 34.9, 34.7, 34.3, 34.2 (s, *C*(CH$_3$)$_3$), 31.2 (d, C(*C*H$_3$)$_3$, J_{PC} = 9.2 Hz),

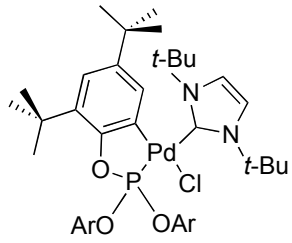
30.4 (s, $C(CH_3)_3$), 30.2 (s, $C(CH_3)_3$), 29.7 (d, $C(CH_3)_3$, J_{PC} = 12.2 Hz), 29.5 (s, $C(CH_3)_3$).

^{31}P {^{1}H}-NMR (161 MHz, C_6D_6): δ = 136.89 (s), 135.93 (s); (I = 5:1).

MS (FAB) m/z (%): 930.2 (100, [M^+ - OAc]), 286.8 (50, [Pd + carbene]), 228.8 (45, [Pd + carbene – *t*-Bu]), 181 (58, [carbene]), 123 (50, [carbene - *t*-Bu]).

Anal. Calcd. for $C_{55}H_{86}N_2O_5PPd$ (992.53): C, 66.55; H, 8.73; N, 2.82. Found: C, 66.37; H, 8.99; N, 2.17%.

Chloro-(1,3-di-tert-butylimidazolin-2-ylidene){2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) (2b).



Ar = 2,4-(*t*-Bu)$_2$C$_6$H$_3$

To a suspension of 300 mg (0.19 mmol) *trans*-di(*μ*-chloro)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) **1b** in 10 ml toluene, a solution of 100 mg (0.55 mmol) 1,3-di-*tert.*-butylimidazolin-2-ylidene **2'** in 7 ml THF was added at -70 °C. The reaction mixture was stirred at room temperature for 3 h. After 30 min a clear solution was obtained. The solvent was removed in vacuo and the residue was washed twice with 5 ml *n*-hexane.
Yield: 273 mg (61 %).

^{1}H-NMR (400 MHz, C_6D_6): δ = 8.34 (1H, s), 8.08 (1H, s), 7.48 (2H, s), 7.43 (2H, s), 7.30 (1H, s), 6.78 (1H, d, $^3J_{HH}$ = 7.6 Hz), 6.51 (2H, s, NC*H*C*H*N), 1.75 (9H, s, $C(CH_3)_3$), 1.61 (9H, s, $C(CH_3)_3$), 1.53 (9H, s, $C(CH_3)_3$), 1.46 (9H, s, $C(CH_3)_3$), 1.39 (9H, s, $C(CH_3)_3$), 1.32 (9H, s, $C(CH_3)_3$), 1.19 (9H, s, $C(CH_3)_3$), 1.07 (9H, s, $C(CH_3)_3$).

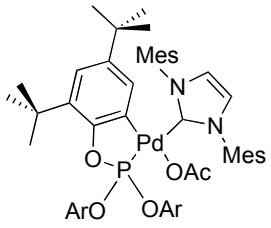
$^{13}C\{^1H\}$-NMR (100 MHz, C_6D_6): δ = 177.5 (d, N*C*N, J_{PC} = 16.8 Hz), 163.7, 161.3, 155.6, 148.9, 146.7, 144.8, 140.7, 138.9, 138.1, 135.1, 133.5, 124.6, 123.9, 122.8, 122.2, 121.2, 120.1, 119.1, 117.4 (N*C*HCHN), 68.1 (N*C*$(CH)_3$), 35.8, 35.1, 35.0, 34.9, 34.5, 34.1, 34.1 (*C*$(CH_3)_3$), 32.5 (d, C(*C*$H_3)_3$, J_{PC} = 7.7 Hz), 31.8, 30.4, 30.1 (d, C(*C*$H_3)_3$, J_{PC} = 9.2 Hz), 30.1 (d, C(*C*$H_3)_3$, J_{PC} = 9.2 Hz).

$^{31}P\ \{^1H\}$-NMR (161 MHz, C_6D_6): δ = 141.1 (s), 135.9 (s); (I = 1:8).

MS (FAB) m/z (%): 931.3 (22, [M^+ - Cl]), 751.1 (7, [1/2 Palladacycle – Cl]), 284.7 (27, [Pd + carbene]), 180.9 (100, [carbene]).

Anal. Calcd. for $C_{53}H_{83}N_2O_3PPdCl$ (967.49): C, 65.69; H, 8.63; N, 2.89. Found: C, 65.28; H, 8.44; N, 2.57%.

Acetato-(1,3-di-mesitylimidazolin-2-ylidene){2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) (3a).



Ar = 2,4-(*t*-Bu)$_2$C$_6$H$_3$

300 mg (0.19 mmol) *trans*-di(*μ*-acetato)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) **1a**, 30 mg (0.36 mmol) sodium acetate and 144 mg (0.37 mmol) 1,3-di-mesitylimidazolium tetrafluoroborat **3'** were suspended in 5 ml DMSO and heated for 2 h at 90 °C. The volatile compounds were removed *in vacuo* and the residue was extracted three times with 4 ml toluene to obtain a yellow product.
Yield: 246 mg (60 %).

^1H-NMR (400 MHz, C_6D_6): δ = 8.15 (2H, dd, $^3J_{HH}$ = 7.9 Hz), 8.04 (1H, s, br), 7.44 (2H, dd, $^3J_{HH}$ = 9.2 Hz), 6.99 (1H, dd, $^3J_{HH}$ = 10.1 Hz, $^4J_{HH}$ = 2.4 Hz), 6.61 (2H, s, br, Mes), 6.65 (2H, br. s, Mes), 6.53 (2H, dd, $^3J_{HH}$ = 10.7 Hz), 3.81 (2H, m, NCHC*H*N),

2.32 (6H, s, $CH_{3,mesityl}$), 2.21 (6H, s, $CH_{3,mesityl}$), 2.03 (6H, s, $CH_{3,mesityl}$), 1.95 (9H, s, $C(CH_3)_3$), 1.78 (18H, s, $C(CH_3)_3$), 1.75 (9H, br. s, $C(CH_3)_3$), 1.44 (9H, s, $C(CH_3)_3$), 1.23 (9H, s, $C(CH_3)_3$).

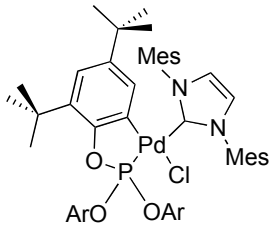
$^{13}C\{^1H\}$-NMR (100 MHz, C_6D_6): δ = 182.1 (s, NCN), 163.6 (d, $C_{metallated,}$ $^2J_{PC}$ = 18.1 Hz), 148.9, 147.6 (s, C_{Aryl}), 139.8, 138.3, 136.9, 136.5, 132.6, 131.6, 130.2 (d, C_{Aryl}, J_{PC} = 7.4 Hz), 126.0, 125.3 (d, C_{Aryl}, J_{PC} = 4.6 Hz), 124.9, 124.8, 124.4 (dd, C_{Aryl}, J_{PC} = 24.4 Hz), 122.5, 121.5, 119.7, 119.6, 115.9 (s, C_{Aryl}), 50.2 (s, NC*H*C*H*N), 40.8, 35.7, 35.6, 35.5, 35.4, 34.8, (s, $C(CH_3)_3$), 32.4, 31.9, 31.7, 30.7, 30.4, 29.8 (s, $C(CH_3)_3$), 21.7, 21.2, 18.5, 18.1 (s, CH_3).

$^{31}P\{^1H\}$-NMR (109 MHz, C_6D_6): δ = 134.1(s), 133.1 (s); (I = 2:1).

MS (FAB) m/z (%): 1115.2 (5, [M^+]), 1101.1 (18, [M^+ - CH_3]), 1086.1 (5, [M^+ - OCH_3]), 1056.4 (19, [M^+ - OAc]), 305.0 (100, [carbene]), 189.0 (45, [2,4-di-*t*-Bu-C_6H_5]).

Anal. Calcd. for $C_{65}H_{89}N_2O_5PPd$ (1115.81): C, 69.97; H, 8.04; N, 2.51. Found: C, 69.40; H, 8.21; N, 2.41 %.

Chloro-(1,3-di-mesitylimidazolin-2-ylidene){2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) (3b).



Ar = 2,4-(t-Bu)$_2$C$_6$H$_3$

To a suspension of 300 mg (0.19 mmol) *trans*-di(*μ*-chloro)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) **1b** in 15 ml toluene, a solution of 152 mg (0.49 mmol) 1,3-di-mesitylimidazolin-2-ylidene **3'** in 10 ml THF was added at -90 °C. The reaction mixture was stirred at room temperature for 2 h. After 30 min a clear solution was obtained. The solvent was removed in vacuo and the residue was washed with 5 ml *n*-hexane and 5 ml *n*-pentane.

Yield: 398 mg (72 %).

^{1}H-NMR (400 MHz, C_6D_6): δ = 7.65 (2H, dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 2.0 Hz), 7.44 (1H, dd, br, $^3J_{HH}$ = 5.59 Hz, $^4J_{HH}$ = 2.3 Hz), 7.03 (2H, dd, $^3J_{HH}$ = 7.9 Hz), 6.92 (1H, dd, $^3J_{HH}$ = 10.7 Hz, $^4J_{HH}$ = 2.0 Hz), 6.74 (2H, s, br, mesityl), 6.65 (2H, br. s, mesityl), 6.34 (2H, dd, $^3J_{HH}$ = 10.7 Hz, $^4J_{HH}$ = 2.3 Hz), 3.59 (2H, m, NC*H*C*H*N), 2.69 (6H, s, CH_3), 2.37 (6H, s, CH_3), 2.12 (6H, s, CH_3), 1.48 (9H, s, C(CH_3)$_3$), 1.28 (18H, s, C(CH_3)$_3$), 1.18 (18H, s, C(CH_3)$_3$), 1.11 (9H, s, C(CH_3)$_3$).

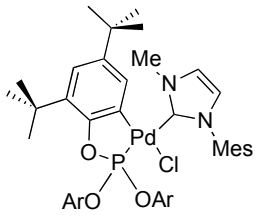
^{13}C{^{1}H}-NMR (100 MHz, C_6D_6): no signal was detected for carbene carbon, δ = 167.5 (s, C_{Aryl}), 163.1, 159.9 (s, C_{Aryl}), 152.3 (d, J_{PC} = 21.2 Hz), 147.1, 146.9, 144.6, 140.2 (d, C_{Aryl}, J_{PC} = 5.4 Hz), 140.0, 139.5 (d, C_{Aryl}, J_{PC} = 4.6 Hz), 148.9, 148.4, 147.5, 146.7, 145.9, 139.2, 136.3, 132.1, 130.8, 129.8, 129.1, 125.5, 124.5, 124.4 (dd, C_{Aryl}, J_{PC} = 24.4 Hz), 121.3, 120.5 (d, N*C*H*C*HN, $^4J_{PC}$ = 6.9 Hz), 35.3, 35.1, 34.6, 34.4, 34.3 (s, *C*(CH_3)$_3$), 31.7, 30.6, 30.5, 29.7 (s, C(*C*H$_3$)$_3$), 24.0, 21.2, 18.0 (s, *C*H$_3$).

^{31}P{^{1}H}-NMR (109 MHz, C_6D_6): δ = 121.3 (s), 133.7(s); (I = 1:2).

MS (FAB) m/z (%): 1057.5 (10, [M^+] - Cl), 751.4 (5, [M^+ - (Cl + carbene)]), 645.4 (5, [P(OC_6H_2-2,4-*t*-Bu_2]), 305.0 (100, [carbene]), 189.0 (45, [2,4-di-*t*-Bu-C_6H_5]).

Anal. Calcd. for $C_{63}H_{86}N_2O_3PPdCl$ (1092.22): C, 69.28; H, 7.94; N, 2.56. Found: C, 69.31; H, 7.93; N, 2.48%.

Chloro-(1-mesityl-3-methylimidazolin-2-ylidene){2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) (4b).



Ar = 2,4-(*t*-Bu)$_2$C$_6$H$_3$

To a suspension of 300 mg (0.19 mmol) *trans*-di(*μ*-chloro)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) **1b** in 15 ml toluene, a solution of 100 mg (0.49 mmol) 1-mesityl-3-methylimidazolin-2-ylidene **4'** in 10 ml THF was added at -85 °C. The reaction mixture was stirred at room temperature for 2 h. After 30 min a clear solution was obtained. The solvent was removed *in vacuo* and the residue was washed twice with 5 ml *n*-pentane.
Yield: 424 mg (86 %).

^{1}H-NMR (400 MHz, C_6D_6): δ = 9.28 (2H, dd, $^3J_{HH}$ = 8.45 Hz), 7.91 (1H, dd, br, $^3J_{HH}$ = 8.56 Hz), 7.46 (2H, dd, $^3J_{HH}$ = 9.6 Hz, $^4J_{HH}$ = 2.4 Hz), 7.33 (1H, t, br, J_{HH} = 4.0 Hz), 6.68 (2H, dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.5 Hz), 6.32 (2H, br. s, mesityl), 3.54 (2H, m, NC*H*CHN), 1.78 (3H, s, CH_3), 1.66 (6H, s, CH_3), 1.52 (6H, s, CH_3), 1.49 (6H, s, CH_3), 1.32 (9H, s, C(CH_3)$_3$), 1.26 (18H, s, C(CH_3)$_3$), 1.13 (18H, s, C(CH_3)$_3$), 0.87 (9H, s, C(CH_3)$_3$).

^{13}C{^{1}H}-NMR (100 MHz, C_6D_6): δ = 186.2. (s, N*C*N), 179.9 (d, J_{PC} = 14.8 Hz), 154.5 (d, J_{PC} = 16.5 Hz), 149.0 (d, C_{Aryl}, J_{PC} = 6.5 Hz), 148.8, 148.0, 147.7, 146.7, 146.3, 144.1, 141.2 (s, C_{Aryl}), 139.6 (d, C_{Aryl}, J_{PC} = 5.5 Hz), 138.5, 138.2, 137.7, 136.1,

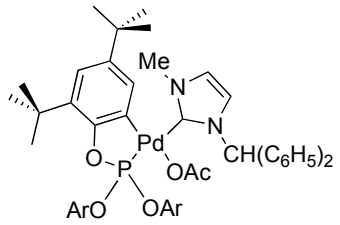
135.2, 134.5, 133.9 (s, C_{Aryl}), 129.8 (d, C_{Aryl}, J_{PC} = 11.4 Hz), 125.6, 124.5, 123.9, 121.8 (s, C_{Aryl}), 121.3 (d, C_{Aryl}, J_{PC} = 6.7 Hz), 120.6, (d, N*C*H*C*HN, J_{PC} = 9 Hz), 35.5, 35.3, 34.5, 34.3 (s, $C(CH_3)_3$), 32.2, 31.9, 31.8, 31.5, 31.3 (s, $C(CH_3)_3$), 21.2, 20.3, 19.6, 19.3, 18.8 (s, $CH_{3,mesityl}$), 14.2 (s, CH_3).

$^{31}P\{^1H\}$-NMR (109 MHz, C_6D_6): δ = 138.5 (s), 137.3 (s); (I = 1: 3).

MS (FAB) m/z (%): 951.5 (10, [M^+] - Cl), 543.2 (5, [(2,4-di-*t*-Bu-C_6H_5-O)$_2$PPd]), 333.2 (8, [carbene + Pd + P]), 306.0 (8, [carbene + Pd]), 199.1 (100, [carbene]), 185.0 (10, [carbene - Me]).

Anal. Calcd. for $C_{55}H_{78}N_2O_3PPdCl$ (988.07): C, 66.86; H, 7.96; N, 2.84. Found: C, 66.07; H, 7.97; N, 2.25%.

Acetato-(1-diphenylmethyl-3-methylimidazolin-2-ylidene){2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) (5a).



Ar = 2,4-(*t*-Bu)$_2$C$_6$H$_3$

354 mg (0.22 mmol) *trans*-di(*μ*-acetato)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]-phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) **1a**, 60 mg (0.73 mmol) sodium acetate and 150 mg (0.30 mmol) imidazoliumtetrafluoroborat salt **5'** were suspended in 5 ml DMSO and heated for 2 h at 80 °C. The volatile compounds were removed *in vacuo* and the residue was extracted with 3x4 ml toluene to obtain a yellow product.

Yield: 273 mg (60 %).

^{1}H-NMR (400 MHz, C_6D_6): δ = 8.57 (1H, dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.2 Hz), 7.91 (1H, dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.2 Hz), 7.56 (2H, s), 7.53 (1H, dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$

= 2.2 Hz), 7.41 (2H, s), 7.29 (1H, s), 7.28 (1H, d, $^4J_{HH}$ = 2.4 Hz), 7.12 – 6.93 (7H, m, C*H*$_{Aryl}$), 6.84 (2H, d, J_{HH} = 1.8 Hz), 6.30 (1H, s, NC*H*), 6.24 (1H, d, $^4J_{HH}$ = 1.0 Hz, NC*H*CHN), 6.05 (1H, s, NC*H*CHN), 3.76 (3H, s, NCH_3), 2.10 (3H, s, CO_2CH_3), 1.52 (9H, s, C(CH_3)$_3$), 1.40 (9H, s, C(CH_3)$_3$), 1.38 (9H, s, C(CH_3)$_3$), 1.21 (9H, s, C(CH_3)$_3$), 1.15 (9H, s, C(CH_3)$_3$), 1.01 (9H, s, C(CH_3)$_3$).

^{13}C{^{1}H}-NMR (100 MHz, C_6D_6): δ = 185.2 (s, N*C*N), 176.5 (s, *C*O_2CH_3), 155.3, 154.8, 154.5, 149.2, 149.0 (d, C$_{Aryl}$, J_{PC} = 6.2 Hz), 147.1, 146.9, 144.6, 140.2 (d, C$_{Aryl}$, J_{PC} = 5.4 Hz), 140.0, 139.5 (d, C$_{Aryl}$, J_{PC} = 4.6 Hz), 139.4, 137.8, 135.1, 129.3, 129.1, 129.1, 128.9, 128.7, 128.5, 128.4, 125.6, 124.8, 124.7, 124.5, 124.1, 123.7, 123.4, 122.2 (d, C$_{Aryl}$, J_{PC} = 24.4 Hz), 121.3, 118.8 (d, N*C*HCHN, J_{PC} = 21.2 Hz), 68.0 (N*C*H), 38.5 (N*C*H_3), 35.4, 35.3, 35.1, 34.6, 34.4, 34.3 (*C*(CH_3)$_3$), 31.8, 31.5, 31.4, 30.6, 30.5, 30.1 (C(*C*H_3)$_3$).

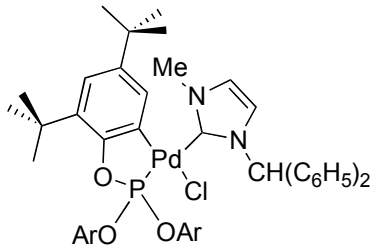
^{31}P {^{1}H}-NMR (161 MHz, $(CD_3)_2SO$): δ = 139.5 (s), 138.3 (s); (I = 1:4).

^{31}P {^{1}H}-NMR (109 MHz, C_6D_6): δ= 139.9 (s), 138.9 (s); (I = 1:4).

MS (FAB) m/z (%): 998.5 (11, [M$^+$]), 353.6 (12, [Pd + carbene]), 246.8 (43, [carbene]), 166.8 (100, [carbene - Ph]).

Anal. Calcd. for $C_{61}H_{81}N_2O_5PPd$ (1059.72): C, 69.14; H, 7.70; N, 2.64. Found: C, 69.34; H, 7.68; N, 2.67%.

Chloro-(1-diphenylmethyl-3-methylimidazolin-2-ylidene){2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) (5b).



Ar = 2,4-(*t*-Bu)$_2$C$_6$H$_3$

To a suspension of 394 mg (0.25 mmol) *trans*-di(*μ*-chloro)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) **1b** in 15 ml toluene, a solution of 200 mg (0.55 mmol) 1-diphenylmethyl-3-methylimidazolin-2-ylidene **5'** in 10 ml THF was added at -90 °C. The reaction mixture was stirred at room temperature for 3 h. After 30 min a clear solution was obtained. The solvent was removed *in vacuo* and the residue was washed twice with 5 ml *n*-hexane.

Yield: 282 mg (63 %).

^{1}H-NMR (270 MHz, C_6D_6): δ = 8.43 (1H, dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.0 Hz), 8.33 (1H, dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.7 Hz), 7.91 (1H, s), 7.53 (2H, dd, $^3J_{HH}$ = 10.6 Hz, $^4J_{HH}$ = 2.0 Hz), 7.40 (2H, dd, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 1.8 Hz), 7.23 (1H, s), 7.12 - 6.93 (10H, m, C*H*$_{Aryl}$), 6.38 (1H, t, $^3J_{HH}$ = 1.7 Hz, NC*H*), 6.20 (1H, s, NC*H*CHN), 6.16 (1H, t, $^3J_{HH}$ = 1.7 Hz, NC*H*CHN), 3.32 (3H, s, NCH_3), 1.70 (9H, s, C(CH_3)$_3$), 1.49 (9H, s, C(CH_3)$_3$), 1.39 (9H, s, C(CH_3)$_3$), 1.21 (9H, s, C(CH_3)$_3$), 1.11 (9H, s, C(CH_3)$_3$), 1.08 (9H, s, C(CH_3)$_3$).

^{13}C{^{1}H}-NMR (100 MHz, C_6D_6): δ = 186.1 (N*C*N), 154.0 (d, C_{Aryl}, J_{PC} = 27.5 Hz), 149.1, 146.8 (d, C_{Aryl}, J_{PC} = 6.7 Hz), 144.5, 139.7, 137.3 (d, C_{Aryl}, J_{PC} = 6.2 Hz), 134.8, 133.7 (d, C_{Aryl}, J_{PC} = 16.6 Hz), 129.8, 128.8, 128.7, 128.6, 128.5, 128.2, 124.5 (d, C_{Aryl}, J_{PC} = 5.7 Hz), 124.2 (d, C_{Aryl}, J_{PC} = 6.2 Hz), 121.6 (N*C*HCHN), 121.2 (N*C*HCHN), 67.6 (N*C*H), 38.0 (N*C*H$_3$), 35.5, 35.4, 35.3, 34.6, 34.5, 34.2 (*C*(CH$_3$)$_3$), 31.8, 31.6, 31.5, 30.8, 30.6, 30.1 (C(*C*H$_3$)$_3$), 23.6 (CO$_2$*C*H$_3$).

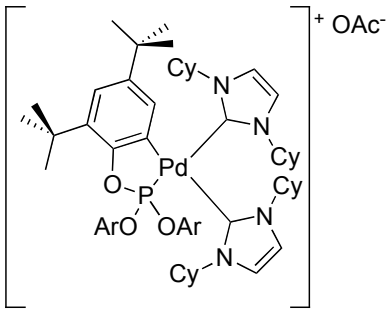
$^{31}P\{^{1}H\}$-NMR (161 MHz, $(CD_3)_2SO$): δ = 140.2 (s).

$^{31}P\{^{1}H\}$-NMR (109 MHz, C_6D_6): δ = 138.8 (s), 137.6 (s); (I = 8.5:1).

MS (FAB) m/z (%): 998.4 (15, [M^+]), 353.6 (15, [Pd + carbene]), 246.8 (59, [carbene]), 166.8 (100, [carbene - Ph]).

Anal. Calcd. for $C_{59}H_{78}N_2O_3PPdCl$ (1036.11): C, 68.39; H, 7.59; N, 2.70. Found: C, 68.23; H, 7.43; N, 2.65%.

Bis-(1,3-di-cyclohexylimidazolin-2-ylidene){2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) acetate (6a).



To a suspension of 300 mg (0.19 mmol) *trans*-di(*μ*-acetato)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) **1a** in 15 ml toluene, a solution of 128 mg (0.55 mmol) 1,3-di-cyclohexylimidazolin-2-ylidene **6'** in 10 ml THF was added at -80 °C. The reaction mixture was stirred at room temperature for 3 h. After 30 min a clear solution was obtained. The solvent was removed *in vacuo* and the residue was washed twice with 5 ml *n*-hexane and 5 ml *n*-pentane.

Yield: 346 mg (49 %).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.28 (2H, d, J_{HH} = 6.4 Hz), 8.49 (1H, bt, t, $^{3}J_{HH}$ = 8.4 Hz), 7.55 (2H, br, dd, $^{3}J_{HH}$ = 9.6 Hz, $^{4}J_{HH}$ = 2.7 Hz, CH_{Aryl}), 7.05 (1H, br, t, $^{3}J_{HH}$ = 8.4 Hz, CH_{Aryl}), 6.68 (2H, br, dd, $^{3}J_{HH}$ = 8.4 Hz, CH_{Aryl}), 6.54 (m, NC*H*C*H*N), 6.41 (m, NC*H*C*H*N), 4.94 (2H, t, $^{3}J_{HH}$ = 10.6 Hz, CH_{Cy}), 4.08 (2H, t, $^{3}J_{HH}$ = 4.7 Hz, CH_{Cy}), 1.78 – 1.41 (br. m, C$H_{2,Cy}$) 1.36 (9H, s, C(CH_3)$_3$), 1.21 (18H, s, C(CH_3)$_3$), 0.61 (18H, s, C(CH_3)$_3$), 0.39 (9H, s, C(CH_3)$_3$).

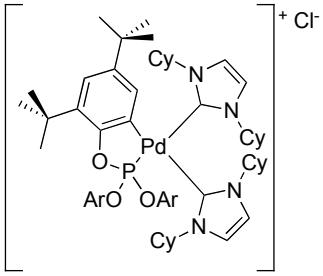
$^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ = 178.4 (s, N*C*N), 176.8 (s, *C*O_2CH_3), 164.1, 161.3, 148.6, 147.0 (s, C_{Aryl}), 146.1 (d, C_{Aryl}, J_{PC} = 3.9 Hz), 145.3 143.1 (s, C_{Aryl}), 138.7 (d, C_{Aryl}, J_{PC} = 5.7 Hz), 136.1, 133.4, 132.4, 132.2, 130.9 (s, C_{Aryl}), 126.7, 126.2, 125.3, 124.3, 121.9 (s, C_{Aryl}), 120.9, (d, C_{Aryl}, J_{PC} = 6.7 Hz), 118.4 (s, C_{Aryl}), 117.4 (s, N*C*HCHN), 116.5 (s, N*C*HCHN), 69.4 (br, N*C*H_{Cy}), 58.1 (br, N*C*H_{Cy}), 34.1, 33.9, 33.7 (s, br, *C*$H_{2,Cy}$), 31.9, 31.6, 30.4, 30.8 (s, *C*$(CH_3)_3$), 29.2, 29.0, 28.7, 28.6, (s, br, C(*C*$H_3)_3$), 25.8 (CO_2*C*H_3), 24.3 - 23.6 (s, br, *C*$H_{2,Cy}$).

$^{31}P\{^1H\}$-NMR (109 MHz, C_6D_6): δ = 139.4 (s).

MS (FAB) m/z (%): 1215.5 (40, [M^+ - OAc]), 983.3 (35, [M^+ - (OAc + 1NHC]), 337.1 (15, [Pd + carbene]), 233.1 (100, [carbene]), 151.8 (42, [carbene - Cy]).

Anal. Calcd. for $C_{74}H_{113}N_4O_5PPd \cdot ½CH_2Cl_2$ (1318.58): C, 67.86; H, 8.71; N, 4.25. Found: C, 68.44; H, 8.83; N, 3.22%.

Bis-(1,3-di-cyclohexylimidazolin-2-ylidene){2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) chloride (6b).



To a suspension of 300 mg (0.19 mmol) *trans*-di(*μ*-chloro)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) **1b** in 15 ml toluene a solution of 128 mg (0.55 mmol) 1,3-di-cyclohexylimidazolin-2-ylidene **6'** in 10 ml THF was added at -80 °C. The reaction mixture was stirred at room temperature for 3 h. The solvent was removed *in vacuo* and the residue was washed twice with 5 ml *n*-hexane and 5 ml *n*-pentane.

Yield: 375 mg (60 %).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.49 (2H, d, $^{3}J_{HH}$ = 4.4 Hz), 8.26 (1H, d, $^{3}J_{HH}$ = 8.4 Hz), 7.85 (2H, d, $^{3}J_{HH}$ = 8.4 Hz), 7.47 (1H, br, t, $^{3}J_{HH}$ = 9.7 Hz, CH_{Aryl}), 6.52 (2H, d, $^{3}J_{HH}$ = 4.8 Hz, CH_{Aryl}), 6.43 (br, s, NC*H*CHN), 4.92 (2H, t, $^{3}J_{HH}$ = 4.7 Hz, CH_{Cy}), 4.63 (2H, t, $^{3}J_{HH}$ = 4.7 Hz, CH_{Cy}), 1.66 (9H, s, C(CH_3)$_3$), 1.46 (18H, s, C(CH_3)$_3$), 1.45 (9H, s, C(CH_3)$_3$), 1.42-1.31(m, 20H, $CH_{2,Cy}$), 1.23 (18H, s, C(CH_3)$_3$), 1.10 (9H, s, C(CH_3)$_3$).

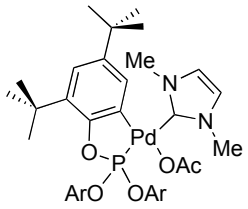
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): δ = 175.1 (s, NCN), 173.0 (s, NCN), 171.0 (d, C_{Aryl}, J_{PC} = 16.7 Hz), 153.5 (d, C_{Aryl}, J_{PC} = 23.9 Hz), 148.2, 147.6, 147.2, 146.6, 146.0, 145.5, (s, C_{Aryl}), 141.5, 138.9, 134.3, 133.6 (s, C_{Aryl}), 133.5 (d, C_{Aryl}, J_{PC} = 5.6 Hz), 124.9, 123.8, 123.2, 122.6 (s, C_{Aryl}), 119.5 (d, C_{Aryl}, J_{PC} = 8.5 Hz), 118.5 (NCHCHN), 60.1 (br, s, C$H_{,Cy}$), 59.3 (s, br, C$H_{,Cy}$), 35.0, 34.8, 34.6, 34.3 (C(CH_3)$_3$), 33.1 - 31.3(C$H_{2,Cy}$), 30.2, 30.1, 29.7, 29.5 (C(CH_3)$_3$), 26.4 (CO_2CH_3), 25.0, 24.9, 24.5, 24.4 (C(CH_3)$_3$).

^{31}P {^{1}H}-NMR (109 MHz, C_6D_6): δ = 141.0 (s).

MS (FAB) m/z (%): 1215.5 (40, [M^+ - Cl]), 983.3 (35, [M^+ - (Cl + 1NHC]), 336.9 (15, [Pd + carbene]), 233.1 (100, [carbene]), 151.8 (42, [carbene - Cy]).

Anal. Calcd. for $C_{72}H_{110}N_4O_3PPdCl$ (1252.52): C, 69.04; H, 8.85; N, 4.47. Found: C, 69.23; H, 8.64; N, 3.98%.

Acetato-(1,3-di-methylimidazolin-2-ylidene){2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) (7a).



Ar = 2,4-(*t*-Bu)$_2$C$_6$H$_3$

To a suspension of 101 mg (0.125 mmol) *trans*-di(*μ*-acetato)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) **1a** in 15 ml toluene, a solution of 48 mg (0.55 mmol) 1,3-di-methylimidazolin-2-ylidene **7'** in 10 ml THF was added at -90 °C. The reaction mixture was stirred at room temperature for 4 h. After 30 min a clear solution was obtained. The solvent was removed *in vacuo* and the residue was washed twice with 5 ml *n*-hexane.
Yield: 198 mg (79 %).

^{1}H-NMR (270 MHz, C_6D_6): δ = 8.45 (2H, d, J_{HH} = 4.3 Hz), 7.91 (1H, t, $^3J_{HH}$ = 6.3 Hz), 7.43 (2H, br, d, $^3J_{HH}$ = 8.6 Hz), 7.31 (1H, br. t, J_{HH} = 2.5 Hz), 6.57 (2H, d, $^3J_{HH}$ = 7.3 Hz), 3.16 (2H, s, NC*H*C*H*N), 1.58 (6H, s, CH_3), 1.42 (9H, s, C(CH_3)$_3$), 1.33 (18H, s, C(CH_3)$_3$), 1.16 (18H, s, C(CH_3)$_3$), 1.08 (9H, s, C(CH_3)$_3$).

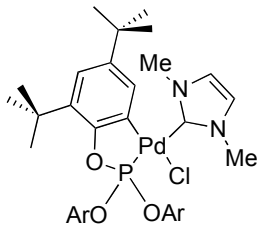
^{13}C{^{1}H}-NMR (100 MHz, C_6D_6): δ = 178.3 (N*C*N), 170.1 (*C*O$_2$CH$_3$), 154.9, 148.6, 147.5 (s, C_{Aryl}), 145.5, 140.6, 139.2, 139.2, 135.1, 132.5, 125.8, 125.4 (s, C_{Aryl}), 124.6 (t, C_{Aryl}, J_{PC} = 7.9 Hz), 124.3, 124.2, 123.8, 123.3 (s, C_{Aryl}), 122.1, 121.5 (s, C_{Aryl}), 121.2 (d, C_{Aryl}, J_{PC} = 10.4 Hz), 116.8 (s, N*C*H*C*HN), 70.8 (N*C*H), 36.7 (N*C*H$_3$), 35.4, 35.3, 35.2, 35.1 (*C*(CH$_3$)$_3$), 31.8, 31.6, 31.5, 31.4 (C(*C*H$_3$)$_3$), 30.4, 30.1, 29.9, 29.8 (C(*C*H$_3$)$_3$).

^{31}P {^{1}H}-NMR (109 MHz, C_6D_6): δ = 128.4 (s), 130.7 (s); (I = 1:1).

MS (FAB) m/z (%): 943.4 (55, [M$^+$ - OAc]), 847.3 (100, [M$^+$ - (OAc + NHC)]), 831.3 (10, [M$^+$- (OAc + NHC + CH$_3$)]), 439.2 (5, [2,4-di-*t*-Bu-C$_6$H$_5$OPPd + carbene]).

Anal. Calcd. for $C_{49}H_{73}N_2O_5PPd$ (907.51): C, 64.67; H, 8.11; N, 3.09. Found: C, 64.74; H, 8.22; N, 2.10 %.

Chloro-(1,3-di-methylimidazolin-2-ylidene){2-[[bis[2,4-di-tert-butylphenoxy]phosphino-κP]oxy]-3,5-di-tert-butylphenyl-κC}palladium(II) (7b).



Ar = 2,4-(*t*-Bu)$_2$C$_6$H$_3$

To a suspension of 200 mg (0.13 mmol) *trans*-di(*μ*-chloro)-bis[2-[[bis[2,4-di-*tert*-butylphenoxy]phosphino-κP]oxy]-3,5-di-*tert*-butylphenyl-κC]dipalladium(II) **1b** in 15 ml toluene, a solution of 48 mg (0.55 mmol) 1,3-methylimidazolin-2-ylidene **7'** in 10 ml THF was added at -90 °C. The reaction mixture was stirred at room temperature for 4 h. After 30 min a clear solution was obtained. The solvent was removed *in vacuo* and the residue was washed twice with 5 ml *n*-hexane.
Yield: 185 mg (75 %).

^{1}H-NMR (270 MHz, C_6D_6): δ = 8.31 (2H, d, $^3J_{HH}$ = 9.8 Hz), 7.68 (1H, d, J_{HH} = 7.3 Hz), 7.39 (2H, br. d, $^3J_{HH}$ = 9.1 Hz), 7.34 (1H, br. t, J_{HH} = 3.1 Hz), 7.18 (2H, d, $^3J_{HH}$ = 7.3 Hz), 3.74 (1H, m, NC*H*CHN), 3.21 (1H, d, $^3J_{HH}$ = 10.8 Hz, NCHC*H*N), 1.76 (6H, s, CH_3), 1.42 (9H, s, C(CH_3)$_3$), 1.32 (18H, s, C(CH_3)$_3$), 1.26 (18H, s, C(CH_3)$_3$), 1.03 (9H, s, C(CH_3)$_3$).

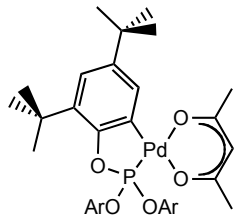
^{13}C{^{1}H}-NMR (100 MHz, C_6D_6): δ = 178.2 (d, J_{PC} = 14.5 Hz, N*C*N), 154.8 (t, J_{PC} = 23.9 Hz, C_{Aryl}), 148.6, 147.4, 145.8, 145.4, 140.9 (s, C_{Aryl}), 139.1 (d, C_{Aryl}, J_{PC} = 5.2 Hz), 134.9, 134.2 (s, C_{Aryl}), 132.3 (d, C_{Aryl}, J_{PC} = 18.4 Hz), 129.2, 125.6, 125.1, 124.9, 123.8, 122.13 (s, C_{Aryl}), 120.6 (d, J_{PC} = 10.2 Hz, N*C*H*C*HN), 67.5 (N*C*H), 36.4 (N*C*H$_3$), 35.2, 34.9, 34.4, 34.3 (*C*(CH$_3$)$_3$), 32.0, 31.8, 31.5, 31.3 (C(*C*H$_3$)$_3$), 30.5, 30.2, 29.9, 29.8 (C(*C*H$_3$)$_3$).

^{31}P {^{1}H}-NMR (109 MHz, C_6D_6): δ = 132.4 (s), 135.4 (s); (I = 1:2).

MS (FAB) m/z (%): 847.3 (100, [M^+ - (OAc + NHC)]), 645.5 (10, [(2,4-di-*t*-Bu-$C_6H_5O)_3P$]), 202.1 (8, [Pd + NHC]).

Anal. Calcd. for $C_{47}H_{70}N_2O_3PPdCl$ (883.92): C, 63.77; H, 8.09; N, 3.17. Found: C, 63.72; H, 8.40; N, 3.58%.

Acetylacetonato-{[bis[2,4-di-tert-butylphenoxy]phosphino-P]oxy]-3,5-di-tert-butylphenyl-C}- dipalladium(II) (10).



Ar = 2,4-(*t*-Bu)$_2$C$_6$H$_3$

To a solution of 405 mg (0.25 mmol) acetate bridged dimer **1a** in 20 mL dichloromethane 150 mg (1.50 mmol) acetylacetone was added and the reaction mixture was stirred for 1 h at room temperature. The solvent was removed in *vacuo* and the residue was washed with cold diethyl ether. The product was recrystallized from dichloromethane as a pale yellow solid.
Yield: 821 mg (97 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (1H, d, J_{HH} = 8.1 Hz, H_{Aryl}), 7.72 (2H, d,J_{HH} = 8.6 Hz, H_{Aryl}), 7.51 (2H, d, J_{HH} = 8.2 Hz, H_{Aryl}), 7.12 (1H, br. t, J_{HH} = 5.2 Hz), 7.03 (2H, m, H_{Aryl}), 5.27 (1H, s, CH_{acac}), 2.06 (3H, s, $CH_{3,acac}$), 1.66 (3H, s, $CH_{3,acac}$), 1.36 (9H, s, $C(CH_3)_3$), 1.29 (18H, s, $C(CH_3)_3$), 1.25 (18H, s, $C(CH_3)_3$), 1.03 (9H, s, $C(CH_3)_3$).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 187.9 (s, CO_{acac}), 186.9 (s, CO_{acac}), 148.2 (d, C_{Aryl}, J_{PC} = 19.3 Hz), 146.8 (s, C_{Aryl}), 144.8 (s, C_{Aryl}), 139.0 (d, J_{PC} = 5.4 Hz, C_{Aryl}), 127.3 (s, C_{Aryl}), 124.4 (d, C_{Aryl}, J_{PC} = 17.3 Hz), 123.7 (d, C_{Aryl}, J_{PC} = 12.1 Hz), 122.0

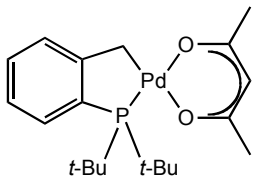
(s, C_{Aryl}), 119.8 (d, C_{Aryl}, J_{PC} = 8.9 Hz), 99.6 (s, CH_{acac}), 53.1 (s, $CH_{3,acac}$), 45.9 (s, $CH_{3,acac}$), 35.1, 35.0, 34.9, 34.5 ($C(CH_3)_3$), 31.8, 30.3, 29.7, 28.1 ($C(CH_3)_3$).

$^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ = 127.5 (s).

MS (FAB) m/z (%): 850.4 (38, [M^+]), 751.4 (100, [M^+ - acac]), 692.3 (17, [M^+-(acac + *t*-Bu])), 636.7 (41, [M^+ - (acac + *2t*-Bu])).

Anal. Calcd. for $C_{47}H_{69}O_5PPd$ (851.44): C, 66.30; H, 8.17; P, 3.64; Pd 12.46. F
ound: C, 66.21; H, 8.13; P, 3.78; Pd 12.80%.

Acetylacetonato-[o-(di-t-butylphosphino)-benzyl]palladium(II) (11).



To a solution of 401 mg (0.5 mmol) acetate bridged dimer **1c** in 20 ml dichloromethane, 150 mg (1.5 mmol) acetylacetone was added and the reaction mixture was stirred for 1 h at room temperature. The solvent was removed *in vacuo* and the residue was washed with cold diethyl ether. The product was recrystallized from dichloromethane as a colorless solid.
Yield: 440 mg (100 %).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (1H, t, $^3J_{HH}$ = 7.1 Hz, H_{Aryl}), 7.3–7.2 (2H, m, H_{Aryl}), 7.11 (1H, t, $^3J_{HH}$ = 6.7 Hz, H_{Aryl}), 5.23 (1H, s, CH_{acac}), 3.30 (2H, d, J_{HH} = 4.2 Hz, $PdCH_2$), 1.93 (3H, s, $CH_{3,acac}$), 1.36 (18H, d, J_{HH} = 14 Hz, CH_3,t-Bu).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 189.0 (s, CO_{acac}), 187.9 (s, CO_{acac}), 160.9 (d, C_{Aryl}, J_{PC} = 25 Hz), 134.8 (d, C_{Aryl}, J_{PC} = 43 Hz), 133.2 (s, C_{Aryl}), 132.0 (s, C_{Aryl}), 130.2 (d, C_{Aryl}, J_{PC} = 21 Hz), 126.1 (d, C_{Aryl}, J_{PC} = 7 Hz), 100.6 (s, CH_{acac}), 38.2 (s, $CH_{3,acac}$), 38.0 (s, $CH_{3,acac}$), 31.4 (s, CH_3,t-Bu).

$^{31}P\{^{1}H\}$ NMR (161 MHz, $CDCl_3$): δ = 89.3 (s).

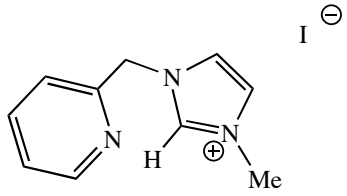
MS (FAB) m/z (%): 439.7 (12, [M^+]), 340.7 (100, [M^+- acac]), 284.7 (17, [M^+-(acac+t-Bu])), 240.7 (41, [M^+-(acac+2t-Bu])).

Anal. Calcd. for $C_{20}H_{31}O_2PPd$ (440.84): C, 54.49; H, 7.09; P, 7.03; Pd 24.14. Found: C, 54.40; H, 7.10; P, 7.10; Pd 24.60 %.

7.4 Picolyl-functionalized imidazolin-2-ylidene of Pd(II) and Pt(II) complexes

7.4.1 [3-R-1-(2'-picolyl)imidazolium] salts

[3-Methyl-1-(2'-picolyl)imidazolium] iodide (12)



To a solution of picolyl chloride (5.85 mmol, prepared by basifying 0.96 g of picolyl chloride hydrochloride) in 20 ml acetone 1-methylimidazole (0.470 mL, 5.89 mmol) and NaI (0.88 g, 5.9 mmol) were added. After stirring for 48 h, the solution was filtered through Celite and the solvent removed *in vacuo* to afford thick brown oil. The oil was redissolved in 15 ml DCM and the solution filtered to remove residual NaCl. Addition of 25 ml Et_2O caused an oily second phase. The solvent was decanted off, the oil taken up in 8 ml DCM. Subseuently, 20 ml Et_2O were added to precipitate the product. The oily solid that formed was triturated for 2 h and the resultant powder washed with 10 ml Et_2O. Drying *in vacuo* overnight yielded a light orange solid.
Yield: 1.22 g (69 %).

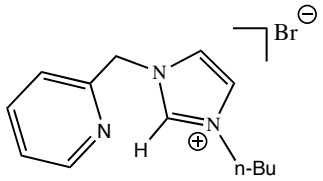
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.27 (s, 1H, NC(*H*)N), 8.56 (m, 1H, pyridyl *H*6), 7.91 (m, 1H, pyridyl *H*4), 7.80 (s, 1H, *H*CC*H*), 7.76 (s, 1H, *H*CC*H*), 7.52 (m, 1H, pyridyl *H*3), 7.41 (m, 1H, pyridyl *H*5), 5.60 (s, 2H, NCH_2), 3.91 (s, 3H, NCH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 153.9 (pyridyl C_2), 149.9 (pyridyl C_6), 137.8, 137.5 (pyridyl C_4, N*C*N), 123.9, 123.4, 122.8 (pyridyl C_3, pyridyl C_5, N*CC*N), 53.2 (N*C*H$_2$), 36.2 (N*C*H$_3$).

MS (FAB): *m*/*z* (174, [M]$^+$, 100%).

Anal. Calcd for $C_{10}H_{12}N_3I$: C, 39.89; H, 4.02; N 13.95. Found: C, 39.60; H, 3.91; N, 13.76.

[3-*n*Butyl-1-(2'-picolyl)imidazolium] bromide (13).



A modification of the procedure of Tulloch et al. was used. 2-(Bromomethyl) pyridine hydrobromide (4 g, 16 mmol) was neutralized using a saturated aqueous solution of sodium carbonate. The liberated 2-(bromomethyl) pyridine was extracted into diethyl ether (3 x 30 ml) at 0 °C, dried with magnesium sulfate, and filtered. 1-Butylimidazole (1.95 g, 16 mmol) in methanol (100 mL) was added at 0 °C, the ether removed under reduced pressure, and the solution stirred at room temperature for 12 h. The methanol is evaporated under reduced pressure, and the formed oil was purified by repetitive precipitation from CH_2Cl_2 / Et_2O mixtures. The resulting oily product was dried *in vacuo*.
Yield: 4.52 g (95 %).

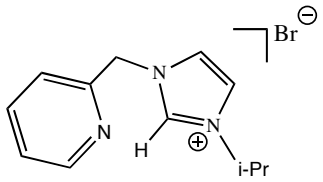
^{1}H NMR (400 MHz, $CHCl_3$): δ = 10.44 (s, 1H, NCHN), 8.49 (d, 1H, $^3J_{HH}$ = 5.0 Hz, H_{py}), 7.80 (d, 1H, $^3J_{HH}$ = 7.7 Hz, H_{py}), 7.74-7.69 (m, 1H, H_{py}), 7.67 (s, 1H, H_{im}), 7.42 (s, 1H, H_{im}), 7.28-7.24 (m, 1H, H_{py}), 5.77 (s, 2H, CH2), 4.27 (t, 2H, $^3J_{HH}$ = 7.5 Hz, CH_2), 1.91-1.82 (m, 2H, CH_2), 1.39-1.29 (m, 2H, CH2), 0.91 (t, 3H, $^3J_{HH}$ = 7.5 Hz, CH_3).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 152.32 (C_{py}), 149.52 (C_{py}), 137.80 (C_{py}), 136.98 (N*C*N), 124.08 (C_{py}), 123.99 (C_{py}), 122.80 (C_{im}), 121.56 (C_{im}), 53.61 (CH_2),

49.86 (CH_2), 31.92 (CH_2), 19.36 (CH_2), 13.33 (CH_3).

Anal. Calcd for $C_{13}H_{18}BrN_3$ (296.21) · $1.5H_2O$: C, 48.31; H, 6.55; N, 13.00. Found: C, 47.85; H, 6.54; N, 12.96.

[3-Isopropyl-1-(2-picolyl)imidazolium] bromide (14).



2-(Bromomethyl)pyridine hydrobromide (1.01 g, 4 mmol) was neutralized using a saturated aqueous solution of sodium carbonate. The liberated 2-(bromomethyl)-pyridine was extracted into diethyl ether (3 x 30 ml) at 0 °C, dried with magnesium sulfate, and filtered into a solution of 1-isopropylimidazole (0.44 g, 4 mmol) in 1,4-dioxane (30 ml). The ether was removed under reduced pressure and the solution refluxed for 12 h. The volatiles were removed *in vacuo*, and the formed oil was purified by repetitive precipitation from MeOH/Et_2O and finally recrystallized from CH_2Cl_2/Et_2O to give colorless crystals.
Yield: 680 mg (60 %).

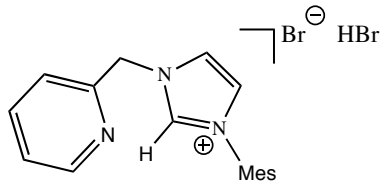
m.p. = 85-86 °C.

^{1}H NMR (400 MHz, $CHCl_3$): δ= 10.97 (s, 1H, NCHN), 8.56-8.52 (m, 1H, Hpy), 7.93 (d, 1H, $^3J_{HH}$ = 7.8 Hz, Hpy), 7.75 (dt, 1H, $^4J_{HH}$= 1.7 Hz, $^3J_{HH}$ = 7.5 Hz, Hpy), 7.65 (t, 1H, $^3J_{HH}$ = 1.5 Hz, Him), 7.31- 7.24 (m, 1H, Hpy), 7.22 (t, 1H, $^3J_{HH}$ = 1.5 Hz, Him), 5.81 (s, 2H, CH_2), 4.74 (septet, 1H, $^3J_{HH}$ = 6.7 Hz, CH), 1.63 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH_3).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 152.57 (C_{py}), 149.72 (C_{py}), 137.80 (C_{py}), 136.80 (NCN), 124.60 (C_{py}), 124.06 (C_{py}), 122.78 (C_{im}), 118.65 (C_{im}), 53.86 (CH_2), 53.43 (CH), 23.09 (2xC, CH_3).

Anal. Calcd for $C_{12}H_{16}BrN_3$ (282.18)· H_2O: C, 48.01; H, 6.04; N, 14.00. Found: C, 48.33; H, 5.81; N, 14.10.

[3-Mesityl-1-(2-picolyl)imidazolium] bromide hydrate (15).



This was obtained following a procedure similar to that described by Tulloch et al., using 2-bromomethylpyridine hydrobromide (3 g, 1.2 mmol) and 1-mesitylimidazole (2.2 g, 1.2 mmol).

Yield: 2.9 g (70 %).

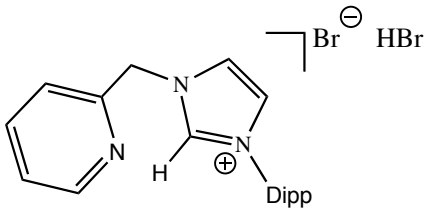
m.p. = 210 °C (decomp).

MS (FAB): *m/z* 278 (M^+).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.0 (6H, s, *o*-mesityl CH_3), 2.3 (3H, s, *p*-mesityl CH_3), 6.1 (2H, s, CH_2), 6.9 (2H, s, mesityl CH), 7.0 and 8.0 (2 x 1H, s, 4,5-imidazolium CH), 7.2 (1H, m, 5-CH of py), 7.7 (1H, t, 4-CH of py), 7.9 (1H, d, 3-CH of py), 8.5 (1H, m, 6-CH of py) and 10.4 (1H, s, 2-imidazolium CH).

Anal. Calcd for $C_{18}H_{22}BrN_3O$ requires C, 57.45; H, 5.89; N, 11.17 %, (Found: C, 56.42; H, 5.42; N, 11.03).

[3-(2,6-Diisopropylphenyl)-1-(2-picolyl)imidazolium] bromide hydrate (16).



This was obtained following a similar procedure for **15**, using 2-bromomethylpyridine hydrobromide (3 g, 1.2 mmol) and 1-(2,6-diisopropylphen yl)imidazole (2.75 g, 1.2 mmol).

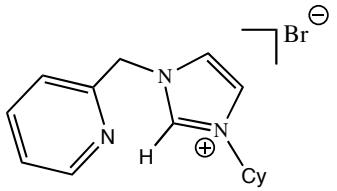
Yield: 3.4 g (70 %).

m.p. = 220 °C (decomp).

^{1}H NMR ($CDCl_3$) δ = 1.1 and 1.2 (2 x 6H, d, $CH(CH_3)_2$), 2.3 [2H, septet, $CH(CH_3)_2$], 6.2 (2H, s, CH_2), 7.1 and 8.3 (2 X 1H, s, 4,5-imidazolium CH), 7.3 (2H, d, 3,5-^{i}Pr $_2C_6H_2$H), 7.3 (1H, m, 5-CH of py), 7.5 (1H, t, 4-^{i}Pr$_2C_6H_2H$), 7.8 (1H, t, 4-CH of py), 8.0 (1H, d, 3-CH of py), 8.5 (1H, d, 6-CH of py) and 10.1 (1H, s, 2-imidazolium CH).

MS (FAB): *m/z* 320 ([M^+], 100 %).

[3-Cyclohexyl-1-(2-picolyl)imidazolium] bromide (17).



2-(Bromomethyl)pyridine hydrobromide (1 g, 4 mmol) was neutralized using a saturated aqueous solution of sodium carbonate. The liberated 2-(bromomethyl) pyridine was extracted into diethyl ether (3 x 10 ml) at 0 °C, dried with magnesium sulfate, and filtered. 1-Cyclohexylimidazole (0.60 g, 4 mmol) in 100 mL methanol was added at 0 °C, the ether removed under reduced pressure, and the solution stirred at room temperature for 12 h. The methanol was evaporated under reduced pressure, and the formed oil was purified by repetitive precipitation from CH_2Cl_2/Et_2O mixtures. Evaporation of the volatiles under reduced pressure left compound **17** as a yellow solid.

Yield: 790 mg (74 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.72 (s, 1H, NCHN), 8.50 (d, 1H, $^3J_{HH}$ = 4.4 Hz, H_{py}), 7.89 (d, 1H, $^3J_{HH}$ = 8.0 Hz, H_{py}), 7.71 (t, 1H, H_{py}), 7.62 (s, 2H, H_{im}), 7.27-7.25 (m, 1H, H_{py}), 5.82 (s, 2H, CH_2), 4.27 (m, 1H, CH_{Cy}), 2.22 - 1.39 (m, 10H, $CH_{2,Cy}$).

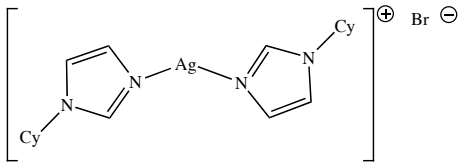
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 152.87 (C_{py}), 149.88 (C_{py}), 137.59 (C_{py}), 136.06 (NCN), 135.22 (C_{py}), 123.73 (C_{py}), 122.75 (C_{im}), 120.69 (C_{im}), 60.23 (CH_2), 56.84 (CH_{Cy}), 33.93 ($CH_{2,Cy}$), 25.18 ($CH_{2,Cy}$).

MS (FAB): *m/z* 242.3, $[M\text{-}Br]^+$ (100 %).

Anal. Calcd for $C_{15}H_{21}BrN_3 \cdot HBr$ (401.01): C, 44.69; H, 5.25; N, 10.42. Found: C, 43.95; H, 4.48; N, 10.26.

7.4.2 Ag(I) and Pd(II) complexes containing imidazole moieties

[Ag(1-cyclohexyl-imidazole)$_2$]Br (**18**).



A clear solution of **17**(1.13 g, 3.5 mmol) in 30 ml dichloromethane and Ag_2O (0.4 g, 1.75 mmol) was heated to 40 °C for 2 days. The solution was filtered through Celite and the solvent removed under reduced pressure. The yellow powder obtained was washed with ether and dried *in vacuo*.
Yield: 925 mg (61 %).

^{1}H NMR ($CDCl_3$, 298 K): δ = 8.15 (s, 2x1H, NCHN), 7.04 (s, 2H, H_{im}), 6.95 (s, 2H, H_{im}), 4.02 (m, 1H, CH_{Cy}), 2.12 - 1.24 (m, 10H, $CH_{2,Cy}$).

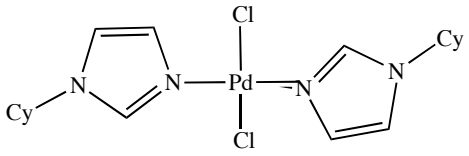
^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ = 155.29 (NCN), 135.26 (C_{im}), 117.13 (C_{im}), 57.05 (CH_{Cy}), 34.45 ($CH_{2,Cy}$), 25.35 ($CH_{2,Cy}$).

IR (KBr): 2930, 2859 ($\nu_{C\text{-}H\ aromatic}$); 1500 ($\nu_{C=N}$), 1444, 1271, 1233, 1107, 1081, 988 ($\nu_{C\text{-}H\ aliphatic}$) cm^{-1}.

MS (FAB): *m/z* 409.1, $[M\text{-}Br]^+$ (100 %), 257.0, $[M\text{-}Br\text{-}CyIm]^+$ (90 %).

Anal. Calcd for $C_{18}H_{30}AgBrN_4 \cdot CH_2Cl_2$ (563.07): C, 40.49; H, 5.61; N, 9.74. Found: C, 41.00; H, 4.97; N, 9.50.

***trans*-[Pd(1-cyclohexyl-imidazole)$_2$]Cl$_2$ (19)**.



A mixture of **18** (0.5 g, 1.0 mmol) and [Pd(MeCN)$_2$Cl$_2$] (0.13 g, 0.5 mmol) was dissolved in 5 ml DCM and stirred for 1 h. The solution was filtered through Celite, and the solvent was removed *in vacuo* to give a white powder.
Yield: 415 mg (86 %).

IR (KBr): 2930, 2859 ($\nu_{\text{C-H aromatic}}$); 1514 ($\nu_{\text{C=N}}$), 1453, 1351, 1262, 1121, 1050, 997 ($\nu_{\text{C-H aliphatic}}$) cm^{-1}.

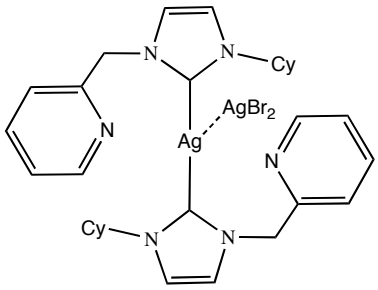
^{1}H NMR ($CDCl_3$, 298 K): δ 8.21 (s, 1H, NCHN), 7.35 (s, H_{im}), 7.26 (s, H_{im}), 4.0 (m, 1H, CH_{Cy}), 2.14 - 1.23 (m, 10H, $CH_{2,Cy}$).

^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 138.54 (NCN), 128.94 (C_{im}), 117.77 (C_{im}), 57.83 (CH_{Cy}), 33.77 ($CH_{2,Cy}$), 33.57 ($CH_{2b,Cy}$), 25.35 ($CH_{2,Cy}$).

Anal. Calcd for $C_{18}H_{30}Cl_2N_4Pd$ (479.78): C, 45.06; H, 6.30; N, 11.68. Found: C, 44.38; H, 6.05; N, 10.85.

7.4.3 Ag(I) and Pd(II) complexes bearing picolyl-functionalized imidazolin-2-ylidene

[Ag(3-cyclohexyl-1-picolylimidazolin-2-ylidene)$_2$] [AgBr$_2$] (**20**).



A mixture of **17** (0.5 g, 1.5 mmol) and Ag_2O (0.18 g, 0.7 mmol) was dissolved in 30 ml dichloromethane and the mixture stirred for 2 hours at room temperature. The solution was filtered through Celite and the solvent removed *in vacuo* to give a yellow solid. The product was recrystallized from DCM/ diethylether, collected by filtration, and washed with 10 ml diethylether. After drying *in vacuo* a yellow powder was obtained.

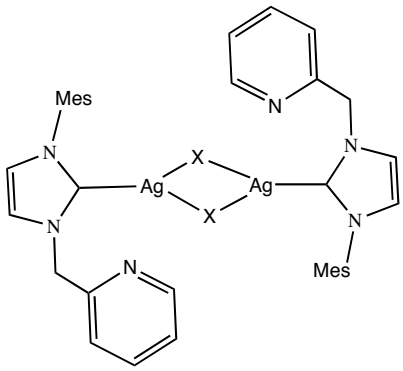
Yield: 500 mg (60 %).

^{1}H NMR ($CDCl_3$, 298 K): 8.55 (dd, 1H, $H_{py,6}$), 7.69 (dt, 1H, $H_{py,4}$), 7.28 (d, 1H, $H_{py,3,5}$), 7.23 and 7.14 (d, 2x1H, H_{im}), 5.32 (s, 2H, CH_2), 4.26 (m, 1H, CH_{Cy}), 2.03 - 1.23 (m, 10H, $CH_{2,Cy}$).

^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 180.9 (NCN), 155.51 (C_{py}), 149.52 (C_{py}), 137.21 (C_{py}), 123.25 (C_{py}), 122.64 (C_{im}), 121.60 (C_{im}), 118.22 (C_{py}), 61.72 (CH_2), 56.68 (CH_{Cy}), 34.65 ($CH_{2,Cy}$), 25.41 ($CH_{2,Cy}$).

Anal. Calcd for $C_{31}H_{43}Ag_2Br_2N_6$ (871.00): C, 42.54; H, 4.95; N, 9.60. Found: C, 42.46; H, 5.01; N, 9.64.

[1-Mesityl-3-(2'-picolyl)imidazol-2-ylidene]silver bromide (21).



To a solution of compound **15** (0.4 g, 1.07 mmol) in dichloromethane (30 mL) was added Ag_2CO_3 (0.17 g, 0.64 mmol) and the mixture heated to 40 °C for two days. Work up as described for **21** gave a pale yellow solid.
Yield: 100 %.

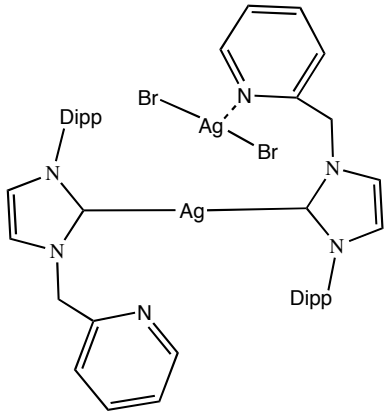
^{1}H NMR ($CDCl_3$): δ = 1.9 (6H, s, *o*-mesityl CH_3), 2.3 (3H, s, *p*-mesityl CH_3), 5.4 (2H, m, CH_2), 6.9 (2H, s, *m*-mesityl H), 7.2 and 7.3 (2 x 1H, d, 4,5-imidazol-2-ylidene H), 7.2 (2H, m, 3,5-H of py), 7.7 (1H, dt, 4-H of py), and 8.6 (1H, d, 6-H of py).

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 17.8 (*o*-mesityl CH_3), 21.2 (*p*-mesityl CH_3), 57.4 (CH_2), 121.9, 122.5, 123.1, 123.7, 129.6, 134.8, 137.7, 140.1 and 150.1 (mesityl, pyridyl and 4,5-imidazol-2-ylidene C) and 173.9 (2-imidazol-2-ylidene C_2).

MS (FAB): *m/z* 427, $[Ag(ligand)]^+$; 663, $[Ag(ligand)_2]^+$.

Anal. Calcd. for $C_{18}H_{19}AgBrN_3$**:** C, 46.48; H, 4.12; N, 9.03%. Found: C, 47.70; H, 4.22; N, 8.94.

[1-(2,6-Diisopropylphenyl)-3-(2-picolyl)imidazolin-2-ylidene]silver bromide (22).



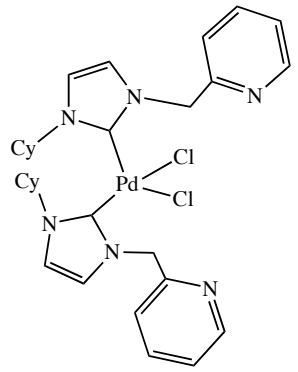
Prepared by method B using compound **16** (0.340 g, 0.17 mmol) and Ag_2CO_3 (0.117 g, 0.09 mmol) in dichloromethane (50 mL) and heating to 40 °C for two days, quantitative yield of a white solid.
Yield: 30 mg (96 %).

^{1}H NMR ($CDCl_3$): δ = 1.1 and 1.2 [2 x 6H, d, $CH(CH_3)_2$], 2.4 [2H, septet, $CH(CH_3)_2$], 5.5 (2H, s, CH_2), 7.0 and 7.3 (2 x 1H, d, 4,5-imidazol-2-ylidene H), 7.2–7.4 (4H, m, 3,5-H of py, H of *m*-^{i}Pr$_2$C$_6$H$_3$), 7.5 (1H, t, H of *p*-^{i}Pr$_2$C$_6$H$_3$), 7.8 (1H, dt, 4-H of py) and 8.6 (1H, d, 6-H of py).

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 24.2 and 24.6 ($CH(CH_3)_2$), 28.3 ($CH(CH_3)_2$), 56.9 (CH_2), 122.1, 122.2, 123.3, 124.1, 124.2, 130.3, 134.6, 137.3, 145.6, 149.7 and 154.9 (^{i}Pr$_2$*C*$_6$H$_3$, pyridyl, 4,5-imidazol-2-ylidene C). The carbene carbon was not observed.

MS (FAB): *m/z* 469, [Ag(ligand)]$^+$; 748, [Ag(ligand)$_2$]$^+$.

***cis*-[Pd(3-cyclohexyl-1-picolylimidazolin-2-ylidene)$_2$] Cl$_2$ (23)**.



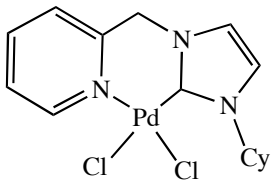
A mixture of Pd(MeCN)$_2$Cl$_2$ (21.9 mg,0.77 mmol) and **20** (0.37 g, 0.42 mmol) was dissolved in 50 ml DCM. The mixture was stirred for 1 h, and then filtered through Celite to remove precipitated silver bromide. The solvent was removed in vacuo until ca. 5 ml remained, and 10 ml hexane were added. The product was recrystallized from a DCM/diethylether mixture (5 ml/10 ml) followed by two washings with 10 ml hexane and dried *in vacuo* to afford a yellow powder.
Yield: 193 mg (69 %).

^{1}H NMR (DMSO-d_6, two isomers in a 1:2 ratio (a:b)): δ = 8.52 (m, 2H, $H_{py,6b}$), 8.34 (m, 2H, $H_{py,6a}$), 8.0-7.7 (m, 2H, $H_{py,4a+b}$), 7.5-7.1 (m, 8H, $H_{py,3a+b}$, $H_{py,5a+b}$), 6.6 ($HCCH_{a+b}$), 5.72 (s, 2H, NCH_{2a}), 5.51 (s, 2H, NCH_{2b}), 4.13 (m, 2H, NC$H_{Cy,a+b}$), 1.92-1.15 (m, 20H, NC$H_{2Cy,a+b}$).

^{13}C{^{1}H} NMR (DMSO-d_6): δ 180.2 (N*C*N), 161.9, 148.5, 137.9 (C_{py}), 129.1, 122.7, 120.9, 117.8 (C_{py}, N*CC*N), 57.5 (N*C*H$_2$), 33.6(CH$_{Cy}$), 25.3 (CH$_{2,Cy}$).

MS (FAB): *m*/*z* 593.2, [M - 2Cl]$^+$ (20%); 441.3, [M - 2Cl - CyIm] $^+$ (40 %); 242.3, [ylidene] $^+$ (100 %).

[Pd(3-cyclohexyl-1-picolylimidazolin-2-ylidene)]Cl_2 (24).



A dichloromethane solution of the corresponding silver carbene complex **20** (0.3 g, 0.34 mmol) was added dropwise to a solution of $Pd(COD)Cl_2$ (0.19 g, 0.66 mmol) and stirred at room temperature for 40 min, then it was filtered through Celite to remove precipitated silver bromide. The remaining solid residue was washed with diethyl ether and dried *in vacuo*. The product was recrystallized from a DCM/diethylether mixture (5 ml/10 ml) followed by two washings with 10 ml hexane and dried *in vacuo* to afford a yellow powder.
Yield: 0.105 g (81 %).

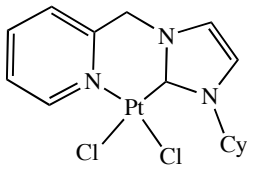
^{1}H NMR (CD_2Cl_2, -30 °C): δ = 9.26 (br d, $1H_{py}$), 7.88 (dt, $1H_{py}$), 7.48 (d, $2H_{py}$), 7.36 (m, $1H_{py}$), 7.12 (d, 1H, *H*CCH), 6.88 (d, 1H, HCC*H*), 5.88 (d, 1H, NC*H*H), 5.03 (d, 1H, NCH*H*), 3.92 (m, 1H, CH_{Cy}), 2.54 - 1.12 (m, 10H, $CH_{2,Cy}$).

^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 182.8 (N*C*N), 156.7, 155.6, 133.8 (C_{py}), 124.8, 123.7, 121.9, 112.2 (C_{py}, N*CC*N), 56.7 (N*C*H2), 34.2(CH_{Cy}), 31.3($CH_{2,Cy}$), 25.5 ($CH_{2,Cy}$).

Anal. Calcd for $C_{15}H_{20}Cl_2N_3Pd$ (418.01): C, 42.93; H, 4.80; N, 10.01. Found: C, 41.86; H, 5.41; N, 10.64.

7.5 Pt(II) complexes bearing picolyl-functionalized imidazolin-2-ylidene

[Pt(3-Cyclohexyl-1-picolylimidazolin-2-ylidene)]Cl_2 (25).



A dichloromethane solution of the corresponding silver carbene complex **20** (0.1 g, 0.12 mmol) was added dropwise to a solution of [Pt(COD)Cl_2] (0.86 g, 0.23 mmol) and stirred at room temperature for 40 min, than it was filtered through Celite to remove precipitated silver bromide. The remaining solid residue was washed with diethyl ether and dried *in vacuo*. The product was recrystallized from a DCM/diethylether mixture (5 ml/10 ml) followed by two washings with 10 ml hexane and dried *in vacuo* to afford a yellow powder.
Yield: 51 mg (86 %).

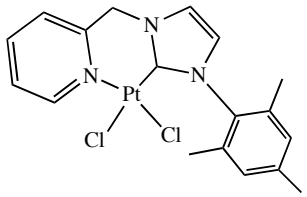
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 - 8.52 (dd, ^{4}J = 14.6 Hz, ^{2}J = 2.4 Hz, $1H_{py,6}$), 7.95 (d, ^{3}J = 7.6 Hz, H_{py}), 7.71-7.60 (dt, $1H_{py}$), 7.24 (d, 1H, *H*CCH), 7.23 (d, $2H_{py}$), 7.16 (m, $1H_{py}$), 7.00 (d, 1H, HCC*H*), 5.84 (d, 1H, NCH_2), 5.30 (d, 1H, NCH_2), 4.25 (sept, 1H, CH_{Cy}), 2.20 - 1.41 (m, 10H, $CH_{2,Cy}$).

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 208.9 (N*C*N), 155.1, 153.1, 138.9 (C_{py}), 128.6, 126.0, 122.9, 121.2, 117.9 (C_{py}, N*CC*N), 100.31 (C_{ipso}), 58.7 (NCH_2), 54.7 (NCH_2), 34.2 (CH_{Cy}), 28.3 ($CH_{2,Cy}$), 25.1 ($CH_{2,Cy}$).

MS (FAB): *m*/*z* 434.1, $[M - 2Cl]^+$ (100 %).

Anal. Calcd for $C_{15}H_{19}Cl_2N_3Pt$ (507.31): C, 35.51; H, 3.77; N, 8.28. Found: C, 35.94; H, 3.45; N, 8.73.

[Pt(3-mesityl-1-picolylimidazolin-2-ylidene)]Cl_2 (26).



A dichloromethane solution of the corresponding silver carbene complex **21** (0.317 g, 0.35 mmol) was added dropwise to a solution of $Pt(COD)Cl_2$ (0.255 g, 0.68 mmol) and stirred at room temperature for 2h, than it was filtered through Celite to remove precipitated silver bromide. The remaining solid residue was washed with diethyl ether and dried *in vacuo*. The product was recrystallized from an acetonitrile/hexane mixture (5 ml/10 ml) followed by two washings with 10 ml hexane and dried *in vacuo* to afford a yellow powder.
Yield: 96 mg (52 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.44 - 9.42 (dd, ^4J = 14.5 Hz, ^2J = 2.4 Hz, $1H_{py,6}$), 8.90 (d, ^3J = 7.6 Hz, H_{py}), 8.64 (d, ^3J = 7.6 Hz, H_{Mes}), 7.94-7.91 (dt, $1H_{py}$), 7.84 (d, 1H, *H*CCH), 7.34 (d, 2 x H_{Mes}), 7.03 (d, $2H_{py}$), 6.96 (m, $1H_{py}$), 6.90 (d, 1H, HCC*H*), 5.57 (br s, 1H, NCH_2), 2.35 (s, 1H, $CH_{3,Mes}$), 1.97 (s, 2 x $CH_{3,Mes}$).

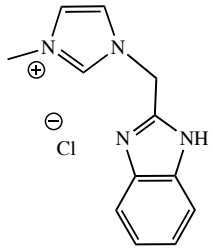
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 177.3 (N*C*N), 139.1, 138.4, 137.8 (C_{py}), 136.7, 130.6, 128.1, 121.9, 121.2, 112.9 (C_{py}, N*CC*N), 99.6 (C_{ipso}), 44.8 (N*C*H_2), 30.2 ($CH_{3,Mes}$), 16.8 (2 x $CH_{3,Mes}$).

MS (FAB): *m*/*z* 473.1, [M^+ - 2Cl] (100 %).

Anal. Calcd for $C_{18}H_{20}Cl_2N_3Pt$ (544.36): C, 39.72; H, 3.70; N, 7.72. Found: C, 39.52; H, 3.44; N, 7.2

7.6 Benzimidazole-functionalized imidazolin-2-ylidene and their metallic derivatives

7.6.1 [3-Alkyl/aryl-1-(2-methylbenzoyl)imidazolium salts [3-Methyl-1-(1*H*-2-methylbenzoyl)imidazolium chloride] (27).



To a solution of 2-chloromethyl benzimidazole (2.43 g, 15 mmol) in Et_2O (50 mL) was added 1-methylimidazole (1.0 g, 12 mmol). The mixture was stirred overnight at room temperature. Then the resultant yellow powder was collected and washed with 10 ml Et_2O three times. yielding 2.5 g (2 %). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a MeOH solution of the product.
Yield: 2.5 g (80 %).

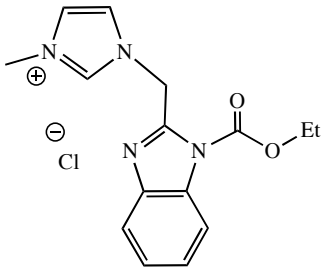
^{1}H NMR (400 MHz, d_6-DMSO) δ = 9.36 (s, 1H, NC(*H*)N), 7.89 (d, $^3J_{(H,H)}$ = 1.7, 1H, *H*CCH), 7.76 (d, $^3J_{(H,H)}$ = 1.6, 1H, HCC*H*), 7.55 (m, 2H, phenyl H), 7.19 (m, 2H, phenyl H), 6.97 (s, 2H, C$H_{backbond}$), 5.78 (s, 2H, CH_2N), 3.91 (s, 3H, NCH_3), 3.68 (s, N*H*).

^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) δ = 156.76 (s, N*C*N), 150.52, 148.87, 138.39, 124.53, 124.14, 123.14, 122.84, 122.92 (s, Ar-*C*), 47.18 (s, *C*H_2N), 36.80 (s, *C*H_3).

MS (FAB): *m/z*= 213.3 [M^+-Cl].

Anal. Calcd. for $C_{12}H_{13}ClN_4$: C, 57.95; H, 5.27; N, 22.53. Found: C, 57.68; H, 5.76; N, 22.70.

[3-Methyl-1-(1-carboethoxy-2-methylbenzoyl)imidazolium chloride] (28).



To a solution of 1-carboethoxy-2-chloromethyl benzimidazole (2.38 g, 10 mmol) in Et_2O (50 ml) 1-methylimidazole (1.64 g, 20 mmol) was added. The mixture was stirred overnight at room temperature and then the solution was reduced to 5 ml by vacuum pump and 10 ml pentane was added to precipitate the product. Then the resultant white powder was collected and washed with 3x10 ml Et_2O. Crystals suitable for X-ray diffraction were obtained by slow evaporation of CH_3CN solution of the product.

Yield: 2.4 g (75 %).

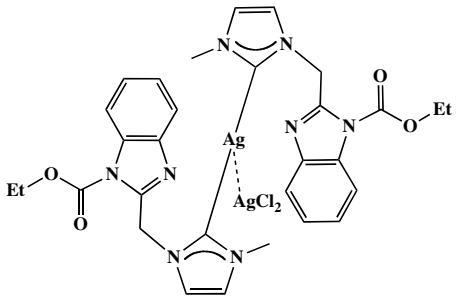
^{1}H NMR (400 MHz, d_6-DMSO) δ = 9.30 (s, 1H, NC(*H*)N), 7.98 (d, $^3J_{(H,H)}$ = 1.7, 1H, *H*CCH), 7.81 (d, $^3J_{(H,H)}$ = 1.6, 1H, HCC*H*), 7.69–7.64 (m, 2H, phenyl H), 7.45–7.37 (m, 2H, phenyl H), 6.94 (s, 2H, C$H_{backbond}$), 6.04 (s, 2H, CH_2N), 4.58 (q, 2H, OCH_2CH$_3$), 3.96 (s, 3H, NCH_3), 1.47 (t, $^3J_{(H,H)}$ = 7.2, 3H, OCH$_2$CH_3).

^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) δ = 150.31 (s, N*C*N), 141.92, 138.75, 133.15, 125.82, 123.61, 122.92, 120.62, 120.23, 115.12 (s, Ar-*C*), 64.68 (s, *C*H$_2$N), 39.44 (s, O*C*H$_2$CH$_3$), 33.36 (s, *C*H$_3$), 14.18 (s, OCH$_2$*CH$_3$*).

MS (FAB): *m/z*= 285.1 [M$^+$-Cl].

Anal. Calcd. for $C_{15}H_{17}ClN_4O_2$: C, 55.99; H, 5.64; N, 17.41. Found: C, 55.71; H, 5.89; N, 16.76.

[Ag{3-methyl-1-(1-carboethoxy-2-methylbenzoyl)imidazolin-2-ylidene}$_2$][AgCl$_2$] (29).



A solution of **28** (320 mg, 1 mmol) and Ag_2O (116 mg, 0.5 mmol) in CH_2Cl_2 was stirred overnight at room temperature. Filtration of the reaction mixture through Celite gave a colorless solution, which was then concentrated to about 5 ml. Upon addition of Et_2O to the crude reaction mixture, complex **29** was precipitated and isolated as a white solid.

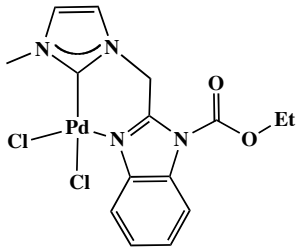
Yield: 652 mg (76 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 (d, $^3J_{(H,H)}$ = 1.7, 1H, *H*CCH), 7.76 (d, $^3J_{(H,H)}$ = 1.7, 1H, HCC*H*), 7.42–7.37 (m, 2H, phenyl H), 7.28 (s, 2H, C*H*$_{backbond}$), 5.19 (s, 2H, C*H*$_2$N), 4.59 (q, 2H, OC*H*$_2$CH$_3$), 3.54 (s, 3H, NC*H*$_3$), 1.55 (t, $^3J_{(H,H)}$ = 7.2, 3H, OCH$_2$*CH*$_3$).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 177.56 (s, N*C*N), 165.7 (s, *C*O), 150.32, 147.42, 145.65, 144.67, 141.89, 126.09, 124.61, 122.94, 120.65, 114.89 (s, Ar-C), 64.75 (s, *C*H$_2$N), 39.52 (s, OCH$_2$CH$_3$), 30.34 (s, *C*H$_3$), 14.04 (s, OCH$_2$*C*H$_3$).

MS (FAB): *m*/*z* = 678.1 (30%, $[Ag(C\text{-}N)_2]^+$), 392.04 (60%, $[Ag(C\text{-}N)]^+$).

[Pd{3-methyl-1-(1-carboethoxy-2-methylbenzoyl)imidazolin-2-ylidene}Cl_2] (30).



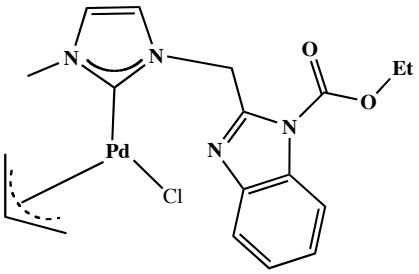
To a solution of **29** (215 mg, 0.25 mmol) in 20 mL of CH_2Cl_2 a CH_3CN suspension of [Pd(CH_3CN)Cl_2] (130 mg, 0.5 mmol) was added. After stirring overnight at room temperature, the solution was filtered through Celite to remove precipitated AgCl. The solvent was removed *in* v*acuo* to ca. 5 ml, followed by addition of Et_2O (10 ml), causing a yellow precipitate to form. The product was re-crystallized from CH_3CN / Et_2O to give a yellow crystalline solid.
Yield: 85 mg (74 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78–8.75 (d, 1H, Ar-H), 8.06–7.94 (d, 1H, Ar-H), 7.63–7.61 (m, 3H, Ar-H), 7.09 (s, 1H, Ar-H), 6.02 (d, $^2J_{(H,H)}$ = 1.60, 2H, *C*H_2), 4.66 (q, 2H, O*CH*$_2$CH$_3$), 3.81 (s, 3H, *C*H_3), 1.59 (t, 3H, OCH$_2$*CH*$_3$).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 177.38 (N*C*N), 166.45 (*C*O), 152.34, 149.68, 141.88, 133.14, 125.97, 124.96, 120.96, 120.46, 115.25 (s, Ar-C), 64.74 (s, *C*H_2N), 39.52 (s, O*CH*$_2$CH$_3$), 14.23 (s, OCH$_2$*C*H$_3$).

MS (FAB): *m*/*z* = 460.9 (20%, [M^+]), 391.0 (40%, [Pd(C-N)]$^+$), 285.1 (80%, [C-N]$^+$).

[Pd{3-methyl-1-(1-carboethoxy-2-methylbenzoyl)imidazolin-2-ylidene}(η^3-allyl)]chloride (31a).



To a solution of **29** (200 mg, 0.42 mmol) in 20 mL of CH_2Cl_2 a CH_3CN suspension of $[Pd(allyl)Cl]_2$ was added (92 mg, 0.24 mmol). After stirring at room temperature for 1h, the solution was filtered through Celite to remove precipitated AgCl. The solvent was removed *in* v*acuo* to ca. 5 ml, followed by addition of Et_2O (10 ml), causing a pale yellow precipitate to form. The product was recrystallized from CH_2Cl_2 / Et_2O to give a yellow crystalline solid.
Yield: 156 mg (76 %).

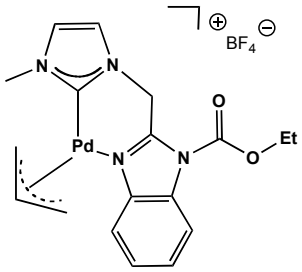
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.94-8.92 (m, 1H, N-CH benzimidazole), 8.18-8.16 (m, 1H), 7.80-7.76 (m, 2H), 7.52-7.43 (m, 2H), 7.13 (d, 1H, J = 1.5 Hz, $CH_{imidazole}$), 6.88 (d, 1H, J =1.5 Hz, $CH_{imidazole}$), 6.07 (s, 2H, CH_2 linker), 5.24 (m, 1H, HB), 4.26 (d, 1H, J = 7.5 Hz, syn HA), 4.20-4.16 (br m, 2H, NCH_2), 3.30 (br s, 1H, syn HC), 3.24 (d, 1H, J =13.6 Hz, anti HA), 2.23 (br d, 1H, J = 11.6 Hz, anti HC), 1.81 (m, 2H, NCH_2CH_2), 1.36 (m, 2H, OCH_2CH_3), 0.94 (t, 3H, J = 7.3 Hz, CH_3).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 179.6 (carbene), 149.9, 146.1, 136.4, 134.9, 130.1, 128.2, 128.1, 126.4, 122.2, 121.4, 120.5, 114.6 (CB), 72.7 (br, CA), 51.0 (CH_2, linker), 50.4 (NCH_2), 48.1 (br, CC), 33.1 (OCH_2CH_3), 19.9 (OCH_2CH_3), 13.8 (CH_3).

MS (FAB): m/z = 430.7 (100%, $[M^+$-Cl]), 391.0 (40%, $[Pd(C\text{-}N)]^+$), 285.3 (80%, $[C\text{-}N]^+$).

Anal. Calcd. for $C_{19}H_{28}ClN_4O_2Pd$ (486.32): C, 45.92; H, 5.80; N; 11.52. Found: C, 46.52; H, 5.02; N, 11.85.

[Pd{3-methyl-1-(1-carboethoxy-2-methylbenzoyl)imidazolin-2-ylidene}(η^3-allyl)]BF_4 (31b).



To a solution of **29** (215 mg, 0.25 mmol) in 20 ml CH_2Cl_2 a CH_3CN suspension of $[Pd(allyl)Cl]_2$ was added (46 mg, 0.12 mmol). After stiring at room temperature for 3 h, a solution of $AgBF_4$ (24.3 mg, 0.12 mmol) in CH_2Cl_2 was added and stirred for a further 0.5 h in the dark. The solution was filtered through Celite to remove precipitated AgCl. The solvent was removed *in vacuo* to ca. 5 ml, followed by addition of Et_2O (10 ml), causing a pale yellow precipitate to form. The product was recrystallized from CH_2Cl_2 / Et_2O to give a yellow crystalline solid.
Yield: 106 mg (94 %).

The ^{1}H NMR spectrum of **11c** shows two sets of peaks in a ratio of 1.00:0.98 and they were disentangled by the 1H-1H COSY.
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.48-9.46 (m, 1H, set a or set b, N-CH benzimidazole), 9.25 (dd, 1H, *J* = 4.8 and 1.0 Hz, set a or set b, N-CH benzimidazole), 8.39-8.37 (m, 2H, set a and set b), 8.17 (d, 1H, *J* = 6.7 Hz, set a or set b), 8.11 (d, 1H, *J* = 6.7 Hz, set a or set b), 7.96-7.92 (m, 2H, set a and set b), 7.68-7.56 (m, 4H, set a and set b), 7.40 (d, 1H, *J* = 1.4 Hz, CH imidazole), 7.35 (d, 1H, *J* = 15.0 Hz, set a or set b, exo diastereotopic CH_2 linker), 7.32 (d, 1H, *J* = 1.4 Hz, CH_{im}), 7.01-6.97 (m, 3H, 2 imidazole CH + 1 exo diastereotopic CH_2 linker), 5.86 (m, 1H, HB set a), 5.70 (m, 1H, HB set b), 5.62 (d, 1H, *J* = 14.9 Hz, endo diastereotopic CH_2 linker, coupled with the signal at 7.35), 5.40 (d, 1H, *J* = 15.0 Hz, endo diastereotopic CH_2 linker, coupled with a signal in 7.01-6.97), 4.42 and 4.66 (q, 2H, O*C*$H_2$$CH_3$, syn HA set b), 4.20 (d, 1H, *J* = 7.6 Hz, syn HA set a), 3.91 (d, 1H, *J* = 6.6 Hz, syn HC set b), 3.81 (s, 3H, *C*H_3), 3.74 (d, 1H, *J* = 6.6 Hz, syn HC set a), 3.64 (d, 1H, *J* = 13.6 Hz, anti HA set a), 3.55 (d, 1H, *J*) 13.5 Hz, anti HA set b), 2.94 (d, 1H, *J* = 12.3 Hz, anti HC set a), 2.83 (d, 1H, *J* = 11.8 Hz, d, 1H, anti HC set b), 1.45 and 1.41 (t, 3H,

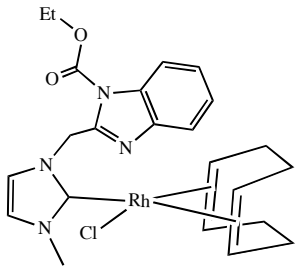
$OCH_2\mathit{CH_3}$).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 173.8 (carbene), 173.2 (carbene), 155.9, 155.4, 145.7, 145.6, 140.35, 140.31, 135.0, 134.9, 131.4, 131.3, 131.0, 130.9, 127.82, 127.80, 121.8, 121.7, 120.5, 120.2, 120.0, 119.3, 118.9 (CB), 117.4 (CB), 75.3 (CA), 74.7 (CA), 57.9 (CH_2 linker), 54.1 (CH_2 linker), 39.34 and 38.66 (s, $O\mathit{CH_2}CH_3$), 31.4 (CH_3), 31.3 (CH_3), 14.12 and 13.98 (s, $OCH_2\mathit{C}H_3$).

MS (FAB): *m*/*z* = 450.8 (100%, $[M^+\text{-}BF_4]$), 391.0 (40%, $[Pd(C\text{-}N)]^+$), 285.3 (80%, $[C\text{-}N]^+$).

Anal. Calcd. for $C_{22}H_{36}BF_4N_4O_2Pd$ (581.77): C, 45.41; H, 6.24; N; 9.63. Found: C, 45.45; H, 6.76; N, 9.85.

[Rh{3-methyl-1-(1-carboethoxy-2-methylbenzoyl)imidazolin-2-ylidene}(η^5-COD)Cl] (32a).



To a solution of complex **28** (200 mg, 0.62 mmol) in CH_2Cl_2, Ag_2O (72 mg, 0.31 mmol) was added. The mixture was stirred for 1 h in the dark. Filtration of this mixture gave a clear solution, to which $[Rh(COD)Cl]_2$ was added (122 mg, 0.25 mmol) in one portion. The mixture was stirred for another 1 h. After filtration, the solvent was removed and the residue was washed with hexane twice to give **32a** as a yellow solid product.

Yield: 257 mg (78 %).

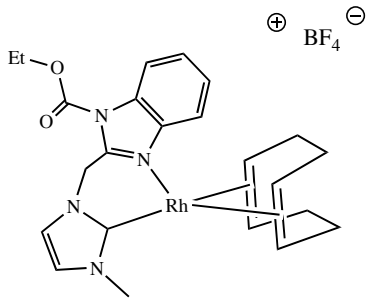
^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 8.54 (d, 1H, J = 4.1 Hz, Ar-H), 7.98 (dd, 1H, J = 8.2 and 1.4 Hz, Ar-H), 7.60 (d, 1H, J = 7.3 Hz), 7.54 (d, 1H, J = 8.0 Hz), 7.55 (t, 1H, J = 7.6 Hz, Ar-H), 7.13 (s, 1H, $CH_{(imidazole)}$), 6.96 (s, 1H, $CH_{(imidazole)}$), 6.19 (d, 1H, J = 14.5 Hz, diastereotopic CH_2(linker)), 5.86 (d, 1H, J = 14.6 Hz, diastereotopic CH_2(linker)), 4.65 (br, 2H, 2CH(COD)), 4.60-4.59 (m, 2H, O*CH*$_2$), 4.53 (br, 1H, CH(COD)), 4.06 (s, 3H, NCH_3) 3.36 (br, 1H, CH(COD)), 2.47-2.14 (m, 4H, $2CH_2$(COD)), 1.85-1.57 (m, $2CH_2$(COD)), 1.50 (t, 3H, J = 7.3 Hz, OCH_2*CH*$_3$).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 182.0 (d, J_{Rh-C} = 51 Hz), 159.1, 155.8, 138.0, 137.0, 136.6, 135.7, 135.1, 133.9, 129.1, 127.9, 127.7, 123.5, 122.6, 121.4, 120.9, 97.0 (d, J_{Rh-C} = 6.9 Hz), 96.9 (d, J_{Rh-C} = 7.6 Hz), 68.8 (d, J_{Rh-C} = 14.5 Hz), 67.5 (d, J_{Rh-C} = 14.4 Hz), 56.8, 34.1, 31.8, 29.4, 28.3, 21.4, 20.6, 20.1, 18.0.

MS (CI): m/z = 524.9 (100 %, [M^+]).

Anal. Calcd. for $C_{23}H_{25}ClN_4O_2Rh \cdot CH_2Cl_2$ (611.23): C, 47.04; H, 4.44; N; 9.14. Found: C, 47.32; H, 4.82; N, 9.14.

[Rh{3-methyl-1-(1-carboethoxy-2-methylbenzoyl)imidazolin-2-ylidene}(η^5-COD)][BF_4] (32b).



$AgBF_4$ (47 mg, 0.24 mmol) was added to a solution of complex **32a** (100 mg, 0.24 mmol) in acetonitrile/acetone. After 6 h of stirring a 0 °C the solid formed was separated by filtration. The resulting yellow solution was concentrated to ca. 1 mL and treated with diethyl ether to give a yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried *in vacuo*.
Yield: 102 mg (62 %).

^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 7.54 (d, 1H, J = 4.1 Hz, Ar-H), 7.08 (dd, 1H, J = 8.2 and 1.4 Hz, Ar-H), 6.60 (d, 1H, J = 7.3 Hz), 6.54 (d, 1H, J = 8.0 Hz), 6.35 (t, 1H, J = 7.6 Hz, Ar-H), 6.13 (s, 1H, $CH_{(imidazole)}$), 6.06 (s, 1H, $CH_{(imidazole)}$), 6.03 (d, 1H, J = 14.5 Hz, diastereotopic CH_2(linker)), 5.86 (d, 1H, J = 14.6 Hz, diastereotopic CH_2(linker)), 4.45 (br, 2H, 2CH(COD)), 4.30-4.25 (m, 2H, OCH_2), 4.13 (br, 1H, CH(COD)), 3.96 (s, 3H, NCH_3) 3.56 (br, 1H, CH(COD)), 2.47-2.14 (m, 4H, $2CH_2$(COD)), 1.85-1.57 (m, $2CH_2$(COD)), 1.43 (t, 3H, J = 7.3 Hz, OCH_2CH_3).

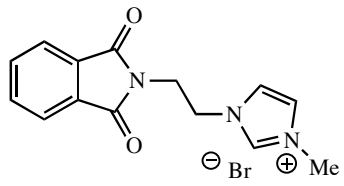
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 179.63 (d, $J_{C\text{-}Rh}$ = 28.8, C_2), 125.86, 123.99 (CH), 100.40 (d, $J_{C\text{-}Rh}$ = 8.4, CH cod), 100.21 (d, $J_{C\text{-}Rh}$ =7.8, CH cod), 77.33 (d, $J_{C\text{-}Rh}$ = 13.5, CH cod), 72.45 (m, CH cod), 65.13 (NCH_2), 51.51 (NMe), 49.35 (NCH_2), 39.21 (NMe_2), 35.79 (CH_2), 32.14, 31.60, 29.67, 27.86 (CH_2 cod).

MS (CI): m/z = 526.5 (100 %, [M^+-BF_4]).

Anal. Calcd for $C_{17}H_{29}BF_4N_3Rh$: C, 43.90; H, 6.28; N, 9.03. Found: C, 44.10; H, 6.17; N, 9.09.

7.7 Phthalimido-functionalized imidazolin-2-ylidene and their metallic derivatives

7.7.1 Phthalimido-functionalized imidazolin-2-ylidene [3-Methyl-1-(2'-phthalamidoethyl)imidazolium] bromide (33).



To a solution of *N*-(2-bromoethyl)-phthalimide (1.05 g, 3.93 mmol) in toluene (5 ml) 1-methylimidazole (0.32 g, 3.93 mmol) was added. After stirring the solution for at room temperature 1 h, the reaction mixture was refluxed for another 16 h. After cooling to room temperature the resulting precipitate was filtered off and washed twice with 5 ml hot hexane. Evaporation of the solvent under reduced pressure gives compound **33** as a white solid. The product was recrystallized from methanol / hexane, yielding light white crystals.
Yield: 1.12 g (84 %).

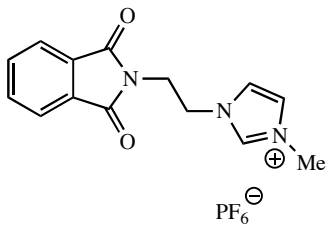
^{1}H NMR (400 MHz, d_6-DMSO): δ = 10.57 (s, 1H, NC*H*N), 7.80–7.73 (m, 4H, C*H* $_{Phth}$), 7.32 (s, 2H, *H*CC*H*), 4.46 (t, 2H, $^{3}J_{HH}$ = 1.8 Hz, N-CH_2), 4.00 (t, 2H, $^{3}J_{HH}$ = 1.5 Hz, CH_2-NIm), 3.84 (s, 3H, NCH_3) ppm.

^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO): δ = 167.79 (s, N*C*O), 138.25, 134.56 (s, N*C*N), 131.49, 123.74, 123.37, 122.61, 48.70 (s, N-*C*H_2), 38.52 (s, *C*H_2-NIm), 36.89 (s, N*C*H_3) ppm.

MS (FAB) *m/z* (%): 256.0 (100, [M^+ - Br]).

Anal. Calcd. for $C_{14}H_{14}BrN_3O_2 \cdot H_2O$ (354.20): C, 47.47; H, 4.55, N, 11.86 Found: C, 47.29; H, 4.44, N, 11.61.

[3-(Methyl)-1-(2'-phthalimidoethyl)imidazolium] hexafluorophosphate (**33a**).



To a solution of **33** (0.80 g, 2.24 mmol) in water (10 ml) HPF_6 was added (0.16 g, 1.02 mmol). The solution was stirred for 1 h in an ice bath. Removal of the water followed by addition of Et_2O gave an off-white solid, which was further washed with Et_2O (2 x 5ml) and dried *in vacuo* giving the desired imidazolium salt **33a**
Yield: 0.53 mg (66 %).

^{1}H NMR (400 MHz, d_6-DMSO): δ = 9.21 (s, 1H, NC*H*N), 7.84–7.68 (m, 4H, C*H* $_{Phth}$), 7.21 (s, 2H, *H*CC*H*), 4.44 (t, 2H, $^3J_{HH}$ = 1.8 Hz, N-CH_2), 4.00 (t, 2H, $^3J_{HH}$ = 1.5 Hz, CH_2-NIm), 3.81 (s, 3H, NCH_3) ppm.

^{31}P{^{1}H} NMR (161 MHz, DMSO-d_6): δ 57.4 (sept, J = 714 Hz).

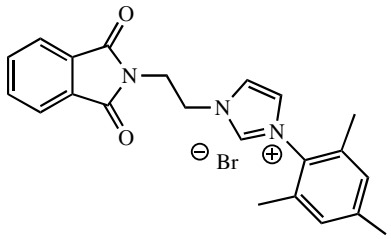
MS (FAB) *m/z* (%): 255.3 (100, [M^+ - PF_6]).

Anal. Calcd. for $C_{14}H_{14}BrN_3O_2 \cdot H_2O$ (401.24): C, 41.91; H, 3.57, N, 10.46 Found: C, 42.29; H, 3.44, N, 10.45.

General procedure for the synthesis of sterical demanding imidazolium salts 34 and 35.

To a solution of *N*-(2-bromoethyl)-phthalimide in dry dioxane (10 ml) x 1-aryl imidazole was added. The solution was charged in an ACE pressure tube, sealed and heated at 140 °C for 5 days in a thermostated oil bath. Removal of dioxane followed by addition of Et_2O gave white solids, which were further washed with Et_2O (2 × 5mL) and dried *in vacuo*.

[3-Mesityl-1-(2'-phthalamidoethyl)imidazolium] bromide (34).



N-(2-bromoethyl)-phthalimide (1.0 g, 3.93 mmol) and 1-mesitylimidazole (733 mg, 3.93 mmol) were heated in dry dioxane at 140 °C for 5 days. A white solid was obtained following the workup procedure described above, giving the desired imidazolium salt **34.**

Yield: 1.25 g (72 %).

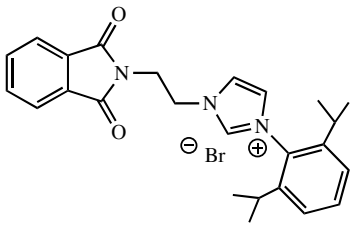
^{1}H NMR (400 MHz, C*D*Cl$_3$): δ = 10.35 (s, 1H, NC*H*N), 7.85–7.75 (m, 2H, C*H* $_{Phth}$), 7.75–7.65 (m, 2H, C*H* $_{Phth}$), 7.04 (s, *H*CC*H*), 6.94 (s, 2H, C*H* $_{mes}$), 5.12 (t, 2H, $^{3}J_{HH}$ = 7.7 Hz, N-C*H*$_2$), 4.11 (t, 2H, $^{3}J_{HH}$ = 1.8 Hz, C*H*$_2$-NIm), 2.31 (s, 3H, C*H*$_3$ $_{mes}$, 1.93 (s, 6H, C*H*$_3$ $_{mes}$) ppm.

^{13}C{^{1}H} NMR (100 MHz, C*D*Cl$_3$): δ = 167.73 (N*C*O), 141.35, 135.23 (s, N*C*N), 131.49 (s, *C*H $_{mes}$), 123.74, 123.37 (N*CC*N), 122.61, 49.61 (s, N-*C*H$_2$), 39.02 (s, *C*H$_2$-NIm), 21.05 (s, *p*-*C*H$_3$ $_{mes}$), 17.61 (s, *o*-*C*H$_3$ $_{mes}$) ppm.

MS (FAB) *m/z* (%): 360.1 (100, [M$^+$ - Br]).

Anal. Calcd. for $C_{22}H_{22}BrN_3O_2 \cdot H_2O$ (458.35): C, 57.65; H, 5.28, N, 9.17 Found: C, 57.70; H, 5.19, N, 9.27.

[3-(2,6-Diisopropylphenyl)-1-(2'-phthalimidoethyl)imidazolium]bromide (35).



N-(2-bromoethyl)-phthalimide (1.67 g, 6.57 mmol) and 1-(2,6-diisopropylphenyl)imidazole (1.79 g, 7.84 mmol) were heated in dry dioxane at 140 °C for 5 days. An off-white solid was obtained following the workup procedure described above, giving the desired imidazolium salt **35**.

Yield: 2.83 g (89 %).

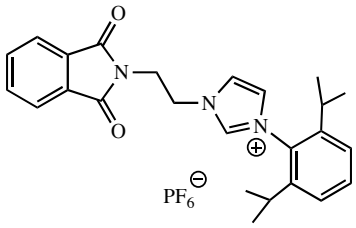
^{1}**H NMR** (400 MHz, C*D*Cl$_3$): δ = 10.53 (s, 1H, NC*H*N), 7.86–7.84 (m, 2H, C*H* $_{Phth}$), 7.80–7.73 (m, 2H, C*H* $_{Phth}$), 7.51 (t, 5H, $^{3}J_{HH}$ = 8.0 Hz, HCC*H*), 7.28 (m, C*H* $_{dipp}$), 5.25 (s, 2H, N-C*H*$_2$), 4.37 (s, 2H, C*H*$_2$-NIm), 2.37 (sept, J_{HH} = 6.9 Hz, C*H* $_{dipp}$), 1.23 and 1.12 (d, 6H each, $^{3}J_{HH}$ = 7.2 Hz, C*H*$_{3\ dipp}$) ppm.

^{13}C{^{1}H} NMR (100 MHz, C*D*Cl$_3$): δ = 167.79 (s, N*C*O), 141.62, 138.73 (s, N*C*N), 134.44, 131.87 (s, *C*H $_{dipp}$), 131.64 (s, *C*H $_{dipp}$), 130.19 (s, *C*H $_{dipp}$), 124.64, 123.93 (NC*C*N), 123.60, 123.47, 123.32, 49.64 (s, N-*C*H$_2$), 39.15 (s, *C*H$_2$-NIm), 28.50 (s, *C*H $_{dipp}$), 24.48 and 24.31 (s, *C*H$_{3\ dipp}$) ppm.

MS (FAB) *m/z* (%): 402.2 (100, [M$^+$ - Br]).

Anal. Calcd. for $C_{25}H_{28}BrN_3O_2 \cdot H_2O$ (500.43): C, 60.00; H, 6.04, N, 8.40 Found: C, 60.37; H, 5.71, N, 8.30.

[3-(2,6-Diisopropylphenyl)-1-(2'-phthalimidoethyl)imidazolium] hexafluorophosphate (**35a**).



To a solution of **35** (0.40 g, 0.84 mmol) in water (10 mL) HPF_6 was added (0.16 g, 1.02 mmol). The solution was stirred for 1h in an ice bath. Removal of the water followed by addition of Et_2O gave an off-white solid, which was further washed with Et_2O (2 x 5ml) and dried *in vacuo* giving the desired imidazolium salt **35a**.
Yield: 42.8 mg (91 %).

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.55 (s, 1H, NC(H)N), 8.26–8.04 (m, 2H, CH $_{Phth}$), 7.80–7.76 (m, 2H, CH $_{Phth}$), 7.59 (t, 5H, $^3J_{H\text{-}H}$ = 2.0 Hz, NCCN), 7.39 (m, CH $_{dipp}$), 4.58 (s, 2H, PhthN-CH_2), 4.13 (s, 2H, CH_2-NIm), 2.37 (sept, $J_{H\text{-}H}$ = 6.9 Hz, CH $_{dipp}$), 1.11 and 1.02 (dd, $^3J_{H\text{-}H}$ = 7.2 Hz, $CH_{3\ dipp}$) ppm.

^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 168.57 (NCO), 145.70, 138.88 (NCN), 135.14, 131.99 (C $_{dipp}$), 130.94 (C $_{dipp}$), 129.99 (C $_{dipp}$), 124.91, 123.68 (NCCN), 49.46 (PhthN-CH_2), 38.15 (CH_2-NIm), 28.42 (s, CH $_{dipp}$), 24.52 and 24.44 (s, $CH_{3\ dipp}$) ppm.

^{31}P{^{1}H} NMR (161 MHz, DMSO-d_6): δ -143.5 (sept, J = 714 Hz).

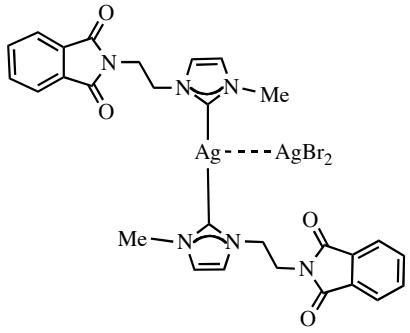
Anal. Calcd. for $C_{25}H_{28}F_6N_3O_2P$ (547.18): C, 54.85; H, 5.16; F, 20.82; N, 7.68; Found: C, 55.02; H, 5.48; F, 20.80; N, 7.31.

7.7.2 Ag(I), Pd(II) and Rh(I) Complexes bearing phthaloyl-functionalized imidazolin-2-ylidene

General procedure for the synthesis of Ag(I) complexes.

A solution of imidazolium salt (**33-35**) and Ag_2O in MeCN was stirred at room temperature overnight with exclusion of light. Filtration of the reaction mixture through Celite gave a colourless solution, which was then concentrated to about 5 ml. Upon the addition of Et_2O to the crude reaction mixture, complexes **36-38** were precipitated and isolated as white solids.

[Ag{3-methyl-1-(2'-phthalamidoethyl)-imidazolin-2-ylidene}$_2$][AgBr$_2$] (36).



A solution of **33** (500 mg, 1.48 mmol) and Ag_2O (170 mg, 0.74 mmol) in MeCN was stirred at room temperature for 12 h. Compound **36** was obtained as an analytically pure product.

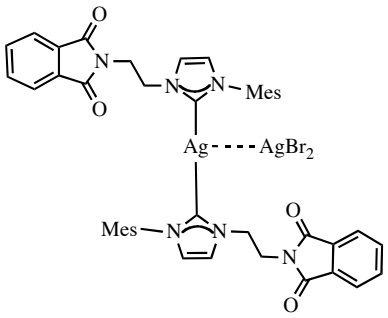
Yield: 850 mg (65 %).

^{1}H NMR (400 MHz, d_6-DMSO): δ = 7.79–7.55 (m, 4H, CH_{Phth}), 7.11 (s, 2H, HCC*H*), 4.43 (t, 2H, $^3J_{HH}$ = 8.0 Hz, N-CH_2), 4.03 (t, 2H, $^3J_{HH}$ = 7.8 Hz, CH_2-NIm), 3.72 (s, 3H, NCH_3) ppm.

^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO): δ = 180.13 (s, N*C*N-Ag), 167.90 (s, N*C*O), 134.90, 131.86, 122.42, 122.35, 49.50 (s, N-*C*H$_2$), 38.54 (s, *C*H$_2$-NIm), 30.22 (s, N*C*H$_3$) ppm.

Anal. Calcd. for $C_{28}H_{28}Br_2N_6O_4Ag_2$ (888.10): C, 37.87; H, 3.18, N, 9.46 Found: C, 37.41; H, 2.94, N, 9.73.

[Ag{3-mesityl-1-(2'-phthalamidoethyl)-imidazolin-2-ylidene}$_2$][AgBr$_2$] (37).



A solution of **34** (500 mg, 1.13 mmol) and Ag_2O (131 mg, 0.56 mmol) in MeCN was stirred at room temperature for 16 h. Compound **37** was obtained as a white analytically pure product.

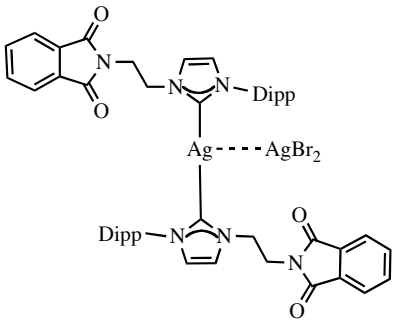
Yield: 635 mg (51 %).

^{1}H NMR (400 MHz, d_6-DMSO): δ = 7.89–7.85 (m, 2H, C*H* $_{Phth}$), 7.74–7.71 (m, 2H, C*H* $_{Phth}$), 6.95 (s, C*H* $_{mes}$), 6.87 (s, C*H* $_{mes}$), 6.79 (s, 2H, HCC*H*), 4.55 (br, 2H, N-CH_2), 4.16 (br, 2H, CH_2-NIm), 2.31 (s, 3H, CH_3 $_{mes}$), 1.99 (s, 6H, CH_3 $_{mes}$) ppm.

MS (FAB) *m/z* (%): 827.3 (100, [M^+ - $AgBr_2$]), 466.0 (85, $[Ag(NHC)]^+$), 360.1 (75, $[NHC]^+$).

Anal. Calcd. for $C_{44}H_{44}Br_2N_6O_4Ag_2$ (1091.99): C, 48.20; H, 4.04, N, 7.67 Found: C, 48.38; H, 4.45, N, 7.65.

[Ag{3-(2,6-diisopropylphenyl)-1-(2'-phthalamidoethyl)-imidazolin-2-ylidene}$_2$][AgBr$_2$] (38).



A solution of **35** (500 mg, 1.03 mmol) and Ag_2O (119 mg, 0.52 mmol) in MeCN was stirred at room temperature for 16 h. Compound **38** was obtained as an off-white analytically pure product.

Yield: 513 mg (42 %).

^{1}H NMR (400 MHz, *d*$_6$-DMSO): δ = 7.83–7.76 (m, 2H, C*H* $_{Phth}$), 7.74–7.71 (m, 2H, C*H* $_{Phth}$), 7.40 (br, C*H* $_{dipp}$), 7.19 (d, 2H, $^2J_{HH}$ = 1.7 Hz, C*H* $_{dipp}$), 6.91 (s, 1H, HCC*H*), 4.57 (br, 2H, N-C*H*$_2$), 4.18 (br s, 2H, C*H*$_2$-NIm), 2.27 (sept, J_{HH} = 6.7 Hz, C*H* $_{dipp}$), 1.08 and 1.04 (d, 6H each, $^3J_{HH}$ = 7.0 Hz, C*H*$_3$ $_{dipp}$) ppm.

^{13}C{^{1}H} NMR (100 MHz, *d*$_6$-DMSO): δ = 177.03 (s, N*C*N-Ag), 167.63 (s, N*C*O), 145.68, 134.45, 134.40, 131.53 (s, *C*H $_{dipp}$), 130.52 (s, *C*H $_{dipp}$), 124.19 (s, *C*H $_{dipp}$), 123.84, 123.70 (s, 2 x NC*C*N), 50.07 (s, N-*C*H$_2$), 38.84 (s, *C*H$_2$-NIm), 28.15 (s, *C*H $_{dipp}$), 23.31 and 22.98 (s, *C*H$_3$ $_{dipp}$) ppm.

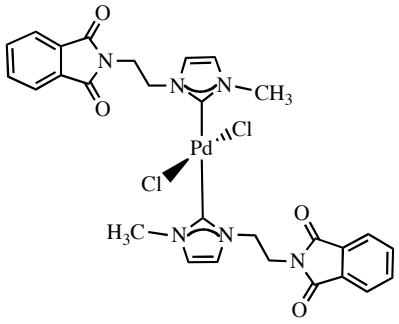
MS (FAB) *m/z* (%): 911.4 (100, [M$^+$- AgBr$_2$]), 508.1 (80, [Ag(NHC)]$^+$), 402.2 (65, [NHC]$^+$).

Anal. Calcd. for $C_{50}H_{56}Br_2N_6O_4Ag_2$ (1076.08): C, 50.87; H, 4.78, N, 7.12 Found: C, 50.83; H, 4.58, N, 7.15.

General procedure for the synthesis of Pd(II) complexes.

To a solution of **36-38** in acetonitrile (20 ml) a suspension of $[Pd(MeCN)_2Cl_2]$ in acetonitrile was added. After stirring overnight at room temperature, the solution was filtered through Celite to remove precipitated AgCl. The solvent was removed *in* v*acuo* to ca. 5 ml, followed by addition of pentane (10 ml), causing a precipitate to form.

trans-[Pd{3-methyl-1-(2'-phthalamidoethyl)-imidazolin-2-ylidene}$_2$]Cl_2 (39).



A solution of $[Pd(MeCN)_2Cl_2]$ (122 mg, 0.47 mmol) in acetonitrile (5 mL) was canulated to a solution of **36** (0.33 g, 0.47 mmol) in acetonitrile under exclusion of light. After stirring for 12 h at room temperature the solution was filtered through Celite, the solvent was concentrated to ca. 5 ml, followed by addition of pentane (10 ml) to yield a dark-yellow solid **39**. The product was recrystallized from a mixture of acetonitrile and pentane (1:5 ml), yielding light yellow crystals.

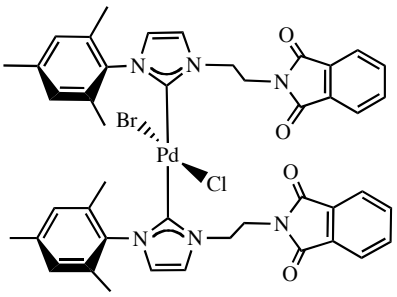
Yield: 135 mg (66 %).

^{1}**H NMR** (400 MHz, d_6-DMSO): δ = 7.89–7.86 (m, 4H, CH_{Phth}), 7.67 (s, 2H, HCC*H*), 3.98 (t, 2H, $^3J_{HH}$ = 7.7 Hz, N-CH_2), 3.71 (t, 2H, $^3J_{HH}$ = 7.8 Hz, CH_2-NIm), 3.33 (s, 3H, NCH_3) ppm.

^{13}**C{^{1}H} NMR** (100 MHz, d_6-DMSO): δ = 170.31 (s, N*C*N-Pd), 168.04 (s, N*C*O), 147.84, 132.09, 131.93, 131.86, 122.42, 122.35, 48.58 (s, N-*C*H$_2$), 38.59 (s, *C*H$_2$-NIm), 30.52 (N*C*H$_3$) ppm. MS (FAB) *m/z* (%): 398.8.4 (40, [Pd(NHC)Cl$^+$]), 256.1 (100, [NHC]$^+$).

Anal. Calcd. for $C_{28}H_{28}Cl_2N_6O_4Pd \cdot H_2O$ (706.07): C, 47.51; H, 4.27, N, 11.87 Found: C, 47.41; H, 4.17, N, 11.73.

trans-[Pd{3-mesityl-1-(2'-phthalamidoethyl)-imidazolin-2-ylidene}$_2$BrCl] (Br: Cl = 50 : 50 %) **(40).**



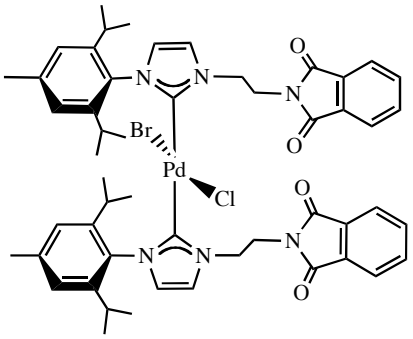
A solution of [Pd(MeCN)$_2$Cl$_2$] (107 mg, 0.41 mmol), in MeCN (5 mL) was added to a solution of **37** (450 mg, 0.41 mmol) in CH_2Cl_2 (5 mL) and stirred at r.t. under exclusion of light. After 16 h the mixture was filtered through Celite to remove the silver salt formed. The solution was concentrated to ca. 5 ml, followed by addition of pentane (10 ml) to yield a pale yellow powder. The product is recrystallized from a mixture of acetonitrile and pentane (1:7 ml), yielding light yellow crystals.
Yield: 115 mg (52 %).

^{1}H NMR (400 MHz, d_6-DMSO) δ = 7.81–7.72 (m, 2H, CH_{Phth}), 7.63–7.60 (m, 2H, CH_{Phth}), 7.12 (s, 1H, HCC*H*), 7.07 (s, CH_{mes}), 6.64 (m, CH_{mes} + 1H, HCC*H*), 5.06 (t, 2H, $^3J_{HH}$ = 7.7 Hz, N-CH_2), 4.37 (t, 2H, $^3J_{HH}$ = 7.6 Hz, CH_2-NIm), 2.41 (s, 3H, C$H_{3\ mes}$), 1.74 (s, 6H, C$H_{3\ mes}$) ppm.

^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) δ = 171.05 (s, N*C*N-Pd), 168.24 (s, N*C*O), 137.49 (s, *C*H $_{Phth}$), 135.83 (s, *C*H $_{Phth}$), 134.65 (s, *C*H $_{mes}$), 132.43 (*C*H $_{mes}$), 128.86 (s, *C*H $_{mes}$), 123.33 (s, NC*C*N), 120.5 (s, N*C*CN), 49.86 (s, N-*C*H$_2$), 39.30 (s, *C*H$_2$-NIm), 21.45 (s, *C*H$_{3\ mes}$), 18.71 (s, *C*H$_{3\ mes}$) ppm.

MS (FAB) *m/z* (%): 825.6 (100, [Pd(NHC)]$_2^+$]), 465.4 (60, [Pd(NHC)$^+$]), 360.7 (85, [NHC]$^+$).

trans-[Pd{3-(2,6-diisopropylphenyl)-1-(2'-phthalamidoethyl)-imidazolin-2-ylidene}$_2$BrCl] (Br : Cl = 50 : 50 %) **(41).**



This complex was prepared in a manner analogous to that described for **40**, using [Pd(MeCN)$_2$Cl$_2$] (66.17 mg, 0.25 mmol) and **41** (300 mg, 0.25 mmol) to yield a white powder. The product is recrystallized from a mixture of acetonitrile and pentane (1:7 ml), yielding light white crystals.
Yield: 107 mg (43 %).

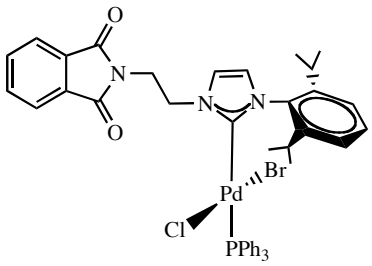
^{1}H NMR (400 MHz, d_6-DMSO) δ = 7.85–7.76 (m, C*H* $_{Phth}$), 7.75–7.62 (m, C*H* $_{Phth}$), 7.70 (m, 2H, C*H* $_{Phth}$), 7.56 (m, 2H, C*H* $_{dipp}$), 7.01 (br s, 1H, HCC*H*), 5.01 (br, 2H, N-C*H*$_2$), 4.29 (br, 2H, C*H*$_2$-NIm), 2.31 (m, C*H* $_{dipp}$), 0.90 and 0.59 (d, 6H each, $^3J_{HH}$ = 1.2 Hz, C*H*$_3$ $_{dipp}$) ppm.

^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO) δ = 172.85 (s, N*C*N-Pd), 168.50 (s, N*C*O), 147.03 (s, *C*H $_{Phth}$), 135.23 (s, *C*H), 134.35, 132.98 (d, $^{2/3}J_{PC}$ = 11.0 Hz, *C*H $_{dipp}$), 130.41 (*C*H $_{dipp}$), 127.71 (*C*H $_{dipp}$), 125.54 (s, *C*H), 124.16 (s, NC*C*N), 123.20 (s, N*C*CN), 49.65 (N-*C*H$_2$), 38.61 (s, *C*H$_2$-NIm), 28.24 (s, *C*H $_{dipp}$), 26.53 and 23.40 (s, *C*H$_3$ $_{dipp}$) ppm.

MS (FAB) *m/z* (%): 909.4 (45, [Pd(NHC)$_2$]$^+$), 507.3 (30, [Pd(NHC)]$^+$), 402.2 (100, [NHC]$^+$).

Anal. Calcd. for $C_{50}H_{56}BrClN_6O_4Pd \cdot H_2O$ (1042.24): C, 57.48; H, 5.60, N, 8.04 Found: C, 57.31; H, 5.32, N, 7.83.

trans-[Pd{3-(2,6-diisopropylphenyl)-1-(2'-phthalamidoethyl)-imidazolin-2-ylidene)(PPh_3)}BrCl] (Cl: Br = 50 : 50 %) **(42)**.



The dimeric complex one equiv (based on Pd) of a stronger phosphine ligand PPh_3 (65.57 mg, 0.25 mmol) in acetonitrile (10 ml) was stirred at room temperature overnight in the absence of light and then filtered off through a pad of Celite. After filtration, the solvent was removed *in vacuo* to ca. 5 ml, followed by addition of pentane (10 ml) to yield a pale yellow solid. The light pale yellow solid obtained was purified by silica gel chromatography (petrol ether / AcOEt; 95: 5) to give the product as light yellow crystalline solid.

Yield: 98.5 mg (44 %).

^{1}H NMR (400 MHz, C*D*Cl_3): δ = 7.79–7.62 (m, 19H, C*H* $_{Phth}$), 7.53–7.37 (m, 2H, C*H* $_{Phth}$), 7.26 (d, 2H, $^3J_{HH}$ = 7.9 Hz, C*H* $_{dipp}$), 6.98 (br s, 1H, HCC*H*), 5.02 (t, 2H, $^3J_{HH}$ = 7.6 Hz, N-CH_2), 4.28 (t, 2H, $^3J_{HH}$ = 7.7 Hz, CH_2-NIm), 2.78 (m, C*H* $_{dipp}$), 1.09 and 1.00 (d, 6H each, $^3J_{HH}$ = 7.2 Hz, CH_3 $_{dipp}$) ppm.

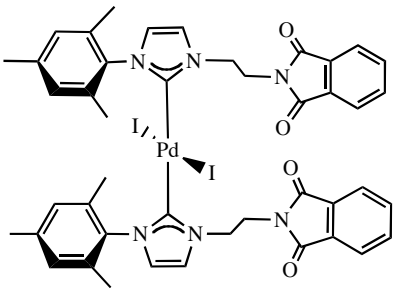
^{13}C{^{1}H} NMR (100 MHz, C*D*Cl_3): δ = 191.86 (s, N*C*N-Pd), 168.03 (s, N*C*O), 146.98 (*C*H $_{Phth}$), 134.75 (s, *C*H), 134.35 (d, $^{2/3}J_{PC}$ = 11.0 Hz, *C*H), 133.34 (s, *C*H $_{dipp}$), 130.46 (s, *C*H $_{dipp}$), 129.40 (s, *C*H $_{dipp}$), 127.84 (d, $^{1/3}J_{PC}$ = 35.7 Hz, *C*H), 123.42 (d, $^{4/3}J_{PC}$ = 2.7 Hz, *C*H), 120.15 (s, NC*C*N), 50.65 (s, N-*C*H_2), 30.34 (s, *C*H_2-NIm), 28.27 (s, *C*H $_{dipp}$), 22.61 and 22.56 (s, *C*H_3 $_{dipp}$) ppm.

^{31}P NMR (C*D*Cl_3): δ = 23.7 (s).

MS (FAB) *m/z* (%): 850.1 (10, $[Pd(NHC)(PPh_3)Br]^+$), 804.4 (15, $[Pd(NHC)(PPh_3)Cl]^+$), 508.2 (10, $[Pd(NHC)]^+$), 402.2 (100, $[NHC]^+$).

Anal. Calcd. for $C_{43}H_{43}BrClN_3O_2PPd$ (884.10): C, 58.25; H, 4.89, N, 4.74; P, 3.49. Found: C, 58.53; H, 5.22, N, 4.39; P, 3.30.

trans-[Pd{3-mesityl-1-(2'-phthalamidoethyl)-imidazolin-2-ylidene}$_2$I$_2$] (43).



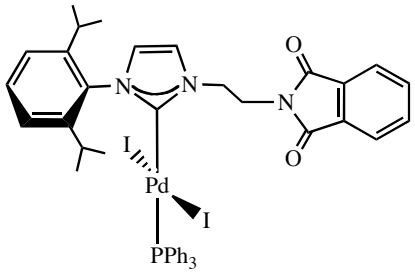
To a solution of **40** (63 mg, 0.07 mmol), in acetonitrile (5 ml) an excess of NaI was added (100 mg, 0.7 mmol) and stirred overnight at room temperature. Subsequently, the mixture was filtered through a pad of Celite to remove the white precipitate formed. The solvent was removed and the dark yellow solid was washed several times with methanol (5 ml) to yield a pale-yellow powder.
Yield: 54 mg (71 %).

^{1}H NMR (400 MHz, *d*$_6$-DMSO): δ 7.48–7.46 (m, 2H, C*H* $_{Phth}$), 7.41–7.39 (m, 2H, C*H* $_{Phth}$), 6.93 (s, 1H, HCC*H*), 6.50 (m, C*H* $_{mes}$ + 1H, *H*CCH), 4.68 (t, 2H, $^3J_{HH}$ = 7.5 Hz, N-C*H*$_2$), 4.10 (t, 2H, $^3J_{HH}$ = 7.6 Hz, C*H*$_2$-NIm), 2.34 (s, 3H, C*H*$_3$ $_{mes}$), 1.73 (s, 6H, C*H*$_3$ $_{mes}$) ppm.

MS (FAB) m/z (%): 1098.3 (20, {[M$^+$] + H$_2$O}), 948.7 (60, {[M$^+$]- I$^-$}), 822.2 (25, {[M$^+$]- 2I$^-$}), 402.1 (100, [NHC]$^+$).

Anal. Calcd. for $C_{44}H_{44}I_2N_6O_4Pd \cdot H_2O$ (1098.35): C, 48.08; H, 4.22, N, 7.65. Found: C, 48.07; H, 3.98, N, 8.10.

trans-[Pd{3-(2,6-diisopropylphenyl)-1-(2'-phthalamidoethyl)-imidazolin-2-ylidene)(PPh_3)}I_2] (44).



To a solution of **42** (25 mg, 0.03 mmol) in MeCN (5 mL) an excess of NaI was added (43 mg, 0.3 mmol). After stirring at overnight r.t., the solution was filtered through a pad of Celite. The solvent was concentrated to ca. 1 ml, followed by addition of pentane (7 ml) to yield an orange solid**.**

Yield: 29 mg (100 %).

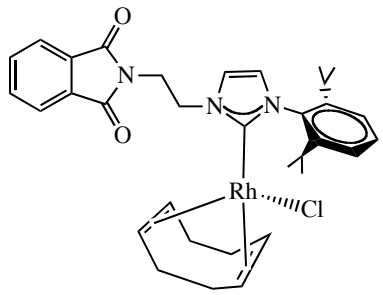
^{1}H NMR (400 MHz, C*D*Cl_3): δ = 7.75–7.62 (m, 19H, C*H*), 7.44–7.42 (m, 2H, C*H* $_{Phth}$), 7.29 (d, 2H, $^3J_{HH}$ = 6.7 Hz, C*H* $_{dipp}$), 7.10 (s, 1H, HCCH), 4.80 (t, 2H, $^3J_{HH}$ = 7.7 Hz, N-CH_2), 4.34 (t, 2H, $^3J_{HH}$ = 7.7 Hz, CH_2-NIm), 3.07 (sept, C*H* $_{dipp}$), 1.2 and 1.01 (d, 6H each, $^3J_{HH}$ = 7.2 Hz, CH_3 $_{dipp}$) ppm.

^{31}P NMR (C*D*Cl_3): δ 16.3 (s).

MS (FAB) *m/z* (%): 761.9 (15, [M^+]- PPh_3), 635.3 (10, [Pd(NHC)$^+$I$^-$]), 402.2 (80, [NHC]$^+$).

Anal. Calcd. for $C_{43}H_{43}I_2N_3O_2PPd$ (1025.02): C, 50.39; H, 4.23, N, 4.10. Found: C, 50.53; H, 4.22, N, 3.89.

[Rh{3-(2,6-diisopropylphenyl)-1-(2'-phthalamidoethyl)-imidazol-2-ylidene)}(η^4-1,5-COD)Cl] (45).



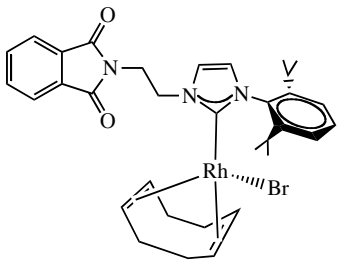
To a solution of the silver carbene complex **38** (96.5 mg, 0.09 mmol) in dichlomethane (10 mL) $[Rh(COD)Cl]_2$ was added (43.85 mg, 0.09 mmol). The mixture was stirred for 1 h in the absence of light and then filtered off through a Celite plug. After filtration, the solvent was removed *in vacuo* to ca. 5 ml, followed by addition of hexane (10 ml) to yield a yellow solid product.
Yield: 38.6 mg (62 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.80 (m, 2H, C*H*$_{pht}$), 7.74–7.71 (m, 2H, C*H*$_{pht}$), 7.36 (br s, C$_{dipp}$), 7.14 (d, 2H, $J_{H\text{-}H}$ = 7.6 Hz, C*H*$_{dipp}$), 6.73 (br s, 1H, C*H*$_{imid}$), 4.91 (br s, 2H, PhtN-C*H*$_2$), 4.84 (br s, 2H, C*H*$_2$-NIm), 4.36-4.24 (br m, 2H, *2*C*H*$_{cod}$), 3.55 (m, *CH*$_{dipp}$), 3.42 (br s, *CH*$_{cod}$), 2.85 (br, *CH*$_{cod}$), 2.33-2.22 (m, *CH*$_2$ $_{cod}$), 1.95-1.92 (m, *CH*$_2$ $_{cod}$), 1.69-1.57 (m, *CH*$_2$ $_{cod}$), 1.55-1.41 (m, *CH*$_2$ $_{cod}$), 1.14 (m, *CH*$_2$ $_{cod}$) 1.13 and 1.00 (d, 12H, *CH*$_3$ $_{dipp}$) ppm.

^{13}C{^{1}H} NMR (100 MHz, C*D*Cl_3): δ = 180.53 (d, $J_{C\text{-}Rh}$ = 55.2 Hz, N*C*N-Rh), 167.88 (N*C*O), 147.57, 145.75 (*C*H $_{pht}$), 134.43, 134.40 (*C*H $_{pht}$), 131.93 (*C*H $_{dipp}$), 125.27 (*C*H $_{dipp}$), 124.81, 123.39, 122.72, 120.87 (CH $_{imid}$), 97.5 (br m, *CH* $_{cod}$), 68.7 (br, *CH* $_{cod}$), 50.16 (N-*C*H$_2$), 43.61 (*C*H$_2$ $_{cod}$), 38.64 (*C*H$_2$-NIm), 28.81 (*C*H$_2$ $_{cod}$), 28.20 (*C*H $_{dipp}$), 28.00, 25.80 (*C*H$_2$ $_{cod}$), 22.86 and 21.89 (*C*H$_3$ $_{dipp}$) ppm.

MS (CI) m/z (%): 540.09 (20, $[M]^+$- COD), 492.6 (40, $[M]^+$ - {COD + ^{i}Pr}).

[Rh{3-(2,6-diisopropylphenyl)1-(2'-phthalamidoethyl)-imidazol-2-ylidene} (η^4-**1,5-COD)Br] (46).**



The solid $[Rh(acac)(COD)]_2$ (112 mg, 0.205 mmol) precursor and 101 mg (0.205 mmol) of the imidazolium salt **35** were weighed in a Schlenk tube in the glovebox. Dry THF (10 ml) was then canulated, and the color of the solution immediately turned yellow. After stirring for 30 minutes at room temperature, the solvent was removed *in vacuo*, and the crude product was washed twice with Et_2O, giving the rhodium complex as a yellow solid.

Yield: 95 mg (70 %).

^{1}H NMR (400 MHz, C*D*Cl_3): δ = 7.84–7.82 (m, 2H, C*H*$_{pht}$), 7.73–7.71 (m, 2H, C*H*$_{pht}$), 7.37 (br, C$_{dipp}$), 7.13 (d, $J_{H\text{-}H}$ = 7.9 Hz, C*H*$_{dipp}$), 6.75 (br, C*H*$_{imid}$), 5.01 (br, 2H, N-C*H*$_2$), 4.85 (br, 2H, C*H*$_2$-NIm), 4.30-4.28 (m, 2H, *2*C*H*$_{cod}$), 3.60 (m, *CH*$_{dipp}$), 3.56 (br, *CH*$_{cod}$), 2.97 (br, *CH*$_{cod}$), 2.53-2.32 (m, *CH*$_2$ $_{cod}$), 2.05-1.92 (m, *CH*$_2$ $_{cod}$), 1.85-1.52 (m, *CH*$_2$ $_{cod}$), 1.51-1.43 (m, *CH*$_2$ $_{cod}$), 1.23 (m, *CH*$_2$ $_{cod}$), 1.02 and 0.94 (d, 12H, *CH*$_3$ $_{dipp}$).

^{13}C{^{1}H} NMR (100 MHz, C*D*Cl_3): δ = 186.64 (d, $J_{C\text{-}Rh}$ = 56.0 Hz, N*C*N-Rh), 167.81 (s, N*C*O), 148.52, 145.56 (*C*H$_{pht}$), 134.29, 134.13 (*C*H$_{pht}$), 131.83 (*C*H$_{dipp}$), 125.20 (*C*H$_{dipp}$), 124.81, 123.38, 123.13, 122.99 (*C*H $_{imid}$), 100.05 (m, *C*H$_{cod}$), 69.97 (br, *CH*$_{cod}$), 50.86 (N-*C*H$_2$), 45.25 (*C*H$_2$ $_{cod}$), 40.23 (*C*H$_2$-NIm), 31.51 (*C*H$_2$ $_{cod}$), 29.04 (s, *C*H$_{dipp}$), 28.00, 26.44 (*C*H$_2$ $_{cod}$), 23.97 and 22.70 (s, *C*H$_3$ $_{dipp}$).

MS (FAB) m/z (%): 691.8 (20, $[M]^+$), 611.1 (80, ($[M]^+$ - Br), 502.3 (85, $[Rh(NHC)]^+$), 402.2 (100, $[NHC]^+$).

Anal. Calc. for $C_{33}H_{38}BrN_3O_2Rh$ (691.48): C, 57.32; H, 5.54, N, 6.08 Found: C, 57.25; H, 6.03, N, 5.49.

7.8 Catalysis

An oven dried Schlenk flask was charged with potassium carbonate (3.0 mmol), aryl halide (2.0 mmol), phenylboronic acid (2.4 mmol), and the internal standard diethylene glycol di-*n*-butyl ether (100 mg). Then degassed solvent (2 ml) was added in an argon stream, and the reaction mixture was heated at temperature given in the specific tables. When the reaction temperature was reached the catalyst solution was added against a stream of argon. At the end of the reaction solution was cooled to 25 °C, treated with water (3 ml), and extracted with diethyl ether (3 x 2 ml). The organic phase was dried over $MgSO_4$. The yields were determined by GC analysis. Catalyst solutions: A solution of catalyst (0.02 mmol) in DMF (10 ml) was stored in the freezer. The concentration was selected such that 0.1 mL of the solution corresponds to a catalyst/substrate ratio of 0.01 mol % catalyst. For experiments with extremely low catalyst concentrations the catalyst solution was diluted further.

7.8.1 Microwave-assisted Suzuki–Miyaura cross coupling of bromobenzene and phenylboronic acid in aqueous medium

Bromobenzene (0.314 g, 2.00 mmol), phenylboronic acid (0.268 g, 2.20 mmol), base (K_2CO_3) (4.00 mmol), 1 ml of freshly prepared (see below) acetone solution of catalyst containing 5 x 10^{-4}–5 x10^{-6} mmol of complex **19** (2.5 x 10^{-2}–2.5 x10^{-4} mol% Pd relatively to bromobenzene), the phase transfer catalyst tetrabutylammonium bromide (TBAB) (0.645 g, 2.00 mmol) and water (4 ml) or a 1 : 1 mixture of water–ethanol instead of TBAB,were added to a cylindrical Pyrex tube which was then placed in the focused microwave reactor. The system was left under irradiation for 5 or 15 min at 120 °C, whereupon the reaction mixture was poured into water (excess) and extracted with dichloromethane (3 x 25 ml). The organic extract was dried with $MgSO_4$ and evaporated *in vacuo*, the crude residue was purified by column chromatography on silica (hexane-DCM 10:1 as the eluent) followed by evaporation of the solvent *in vacuo* to afford the biphenyl product in 60–98% yield (pure by ^1H and ^{13}C NMR). The preparation of the catalyst solutions was as follows: 5 x10^{-3} mmol of the catalyst were dissolved in 10 ml acetone; by subsequent dilutions, solutions containing 5 x 10^{-4} mmol in 10 ml acetone (*i.e.*, with concentrations of 5 x10^{-5} M) was prepared.

References

[1] W. v. E. Doering, A. K. Hoffmann, *J. Am. Chem. Soc.* **1954**, *76*, 6162

[2] H. Tomioka, *Acc. Chem. Res.* **1997**, *30*, 315

[3] H. W. Wanzlick, E. Schikora, *Angew. Chem.* **1960**, *72*, 494

[4] H. J. Schoenherr, H. W. Wanzlick, *Chem. Ber.* **1970**, *103*, 1037

[5] A. Igau, H. Grutzmacher, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **1988**, *110*, 6463

[6] A. J. Arduengo, III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361

[7] (a) A. J. Arduengo, III, J. R. Goerlich, W. J. Marshall, *J. Am. Chem. Soc.* **1995**, *117*, 11027. (b) R. W. Alder, P. R. Allen, M. Murray, A. G. Orpen, *Angew. Chem., Int. Ed.* **1996**, *35*, 1121

[8] E. Despagnet-Ayoub, R. H. Grubbs, *J. Am. Chem. Soc.* **2004**, *126*, 10198

[9] (a) V. Lavallo, J. Mafhouz, Y. Canac, B. Donnadieu, W. W. Schoeller, G. Bertrand, *J. Am. Chem. Soc.* **2004**, *126*, 8670 (b) V. Lavallo, J. Mafhouz, Y. Canac, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Science* **2006**, *312*, 722

[10] (a) M. Denk, R. Lennon, R. Hayashi, R. West, A.V. Belyakov, H.P.Verne, A. Haaland, M. Wagner, N. Metzler, *J. Am. Chem. Soc.* **1994**, *116*, 2691 (b) B. Gehrhus, M. F. Lappert, J. Heinicke, R. Boese, D.Bläser, *J. Chem. Soc. Chem. Commun.* **1995**, 1931 (c) W. A. Herrmann, M. Denk, J. Behm, W. Scherer, F.R. Klingan, H. Bock, B. Solouki, M. Wagner, *Angew. Chem.* **1992**, *104*, 1489; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1485

[11] (a) A. J. Arduengo, III, F. Davidson, H.V. Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall, T. K. Prakasha, *J. Am. Chem. Soc.* **1997**, *119*, 12742 (b) A. J. Arduengo, III, J. R. Goerlich, W. J. Marshall, *Liebigs Ann.,* **1997**, 365

[12] L. Pauling, *J. Chem. Soc., Chem. Commun.* **1980**, 688

[13] R. W. Alder, P. R. Allen, M. Murray, A.G. Orpen, *Angew. Chem., Int. Ed.* **1996**, *35*, 1121

[14] R. W. Alder, M. E. Blake, L. Chaker, J. N. Harvey, F. Paolini, J. Schuetz, *Angew. Chem., Int. Ed.* **2004**, *43*, 5896

[15] D. Bourissou, O. Guerret, F. P. Gabbaie, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39

[16] (a) R. W. Alder, M. E. Blake, J. M. Oliva, *J. Phys. Chem. A* **1999**, *103*, 11200 (b) R. W. Alder, in *Carbene Chemistry*, **2002**, pp. 153

[17] Y.-J. Kim, A. Streitwieser, *J. Am. Chem. Soc.* **2002**, *124*, 5757

[18] W. A. Herrmann, C. Koecher, L. J. Goossen, G. R. J. Artus, *Chem. Eur. J.* **1996**, *2*, 1627

[19] N. Kuhn, T. Kratz, *Synthesis* **1993**, 561

[20] D. Enders, K. Breuer, G. Raabe, J. Runsink, J. H. Teles, J.-P. Melder, K. Ebel, S. Brode, *Angew. Chem., Int. Ed.* **1995**, *34*, 1021

[21] G. W. Nyce, S. Csihony, R. M. Waymouth, J. L. Hedrick, *Chem Eur. J.* **2004**, 10, 4073

[22] W. A. Herrmann, L. J. Goossen, M. Spiegler, *J. Organomett. Chem.* **1997**, *547*, 357

[23] D. S. McGuinness, K. J. Cavell, *Organometallics* **2000**, *19*, 741

[24] a) R. Wang, Z. Zeng, B. Twamley, M. M. Piekarski, J. M. Shreeve, Eur. *J. Org. Chem.* **2007**, 655 b) H. M. Lee, P. L. Chiu, C.-H. Hu, C.-L. Lai, Y.-C. Chou, *J. Organomet. Chem*. **2005**, *690*, 403

[25] a) C. Yang, H. M. Lee, S. P. Nolan, *Org. Lett.* **2001**, *3*, 1511 b) H. M. Lee, P. L. Chiu, J. Y. Zeng, *Inorg. Chim. Acta* **2004**, *357*, 4313

[26] (a) V. César, S. Bellemin-Laponnaz, L. H. Gade, *Chem. Soc. Rev.*, **2004**, *33*, 619 (b) M. C. Perry and K. Burgess, *Tetrahedron: Asymmetry,* **2003**, *14*, 951

[27] S.Hauptmann, Organische Chemie, Deutscher Verlag für Grundstoffindustrie, Leipzig, 1985

[28] C. Yang, H. M. Lee, S. P. Nolan, *Org. Lett.*, **2001**, *3*, 1511

[29] M. Frøseth, K. A. Netland, K. W. Törnroos, A. Dhindsa, M. Tilset, *Dalton Trans.*, **2005**, 1664

[30] E. O. Fischer, A. Maasboel, *Angew. Chem.* **1964**, *76*, 645

[31] H. W. Wanzlick, H. J. Schoenherr, *Angew. Chem., Int. Ed.* **1968**, *7*, 141

[32] K. Oefele, *J. Organomet. Chem.* **1968**, *12*, 42

[33] R. R. Schrock, *J. Am. Chem. Soc.* **1974**, *96*, 6796

[34] T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem., Int. Ed.* **1998**, *37*, 2490

[35] C. Koecher, W. A. Herrmann, *J. Organomet. Chem.* **1997**, *532*, 261

[36] (a) W. A. Herrmann, T. Weskamp, V. P. W. Bohm, *Adv. Organomet. Chem.* **2001**, *48*, 1 (b) A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller, R. H. Crabtree, *Organometallics* **2003**, *22*, 1663

[37] T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrmann, *Angew. Chem., Int. Ed.* **1999**, *38*, 2416

[38] J. Huang, E. D. Stevens, S. P. Nolan, J. L. Petersen, *J. Am. Chem. Soc.* **1999**, *121*, 2674

[39] J. Huang, H.-J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 2370

[40] J. Schwarz, V. P. W. Bohm, M. G. Gardiner, M. Grosche, W. A. Herrmann, W. Hieringer, G. Raudaschl-Sieber, *Chem. Eur. J.* **2000**, *6*, 1773

[41] C. Boehme, G. Frenking, *Organometallics* **1998**, *17*, 5801

[42] J. C. Green, R. G. Scurr, P. L. Arnold, F. G. N. Cloke, *Chem. Comm.* **1997**, 1963

[43] R. Schmidt, *Dissertation,* Technische Universität München, **1997**

[44] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313

[45] W. A. Herrmann, M. Elison, J. Fischer, C. Koecher, G. R. J. Artus, *Chem. Eur. J.* **1996**, *2*, 772

[46] T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem., Int. Ed.* **1998**, *37*, 2490

[47] A. C. Hillier, H. M. Lee, E. D. Stevens, S. P. Nolan, *Organometallics* **2001**, *20*, 4246

[48] C. Koecher, W. A. Herrmann, *J. Organomet. Chem.* **1997**, *532*, 261

[49] K. Oefele, W. A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, W. Scherer, J. Mink, *J. Organomet. Chem.* **1993**, *459*, 177

[50] D. Enders, H. Gielen, J. Runsink, K. Breuer, S. Brode, K. Boehn, *Eur. J. Inorg. Chem.* **1998**, 913

[51] A. A. D. Tulloch, A. A. Danopoulos, S. M. Cafferkey, S. Kleinhenz, M. B. Hursthouse, R. P. Tooze, *Chem. Comm.* **2000**, 1247

[52] J. H. Davis, Jr., C. M. Lake, M. A. Bernard, *Inorg. Chem.* **1998**, *37*, 5412

[53] H. M. J. Wang, I. J. B. Lin, *Organometallics* **1998**, *17*, 972

[54] D. S. McGuinness, K.J. Cavell, *Organometallics* **2000**, *19*, 741

[55] A. Fürstner, G. Seidel, D. Kremzow, C. W. Lehmann, *Organometallics* **2003**, *22*, 907

[56] (a) P.J. Fraser, W. R. Roper, F.G. Stone, *J. Chem. Soc., Dalton Trans.,* **1974**, 102
(b) P.J. Fraser, W. R. Roper, F.G. Stone, *J. Chem. Soc., Dalton Trans.,* **1974**, 102
(c) M .F. Lappert, *J. Organomet .Chem.,* **1975**, *100*, 139

[57] A. J. Arduengo III, S. F. Gamper, J.C. Calabrese, F. Davidson, *J. Am. Chem. Soc.* **1994**, *116*, 4391

[58] P. L. Arnold, G. N. Cloke, T. Geldbach, P. B. Hitchcock, *Organometallics* **1999**, *1*, 3228

[59] (a) W. P. Fehlhammer, G. Beck, *J. Organomet. Chem.* **1989**, *369*, 105 (b) K. Bartel, W. P. Fehlhammer, *Angew. Chem., Int. Ed.* **1974**, *13*, 599

[60] (a) D. Rieger, S. D. Lotz, U. Kernbach, S. Schröder C. Andre, W. P. Fehlhammer, *Inorg. Chim. Acta.* **1994**, *222*, 275 (b) S. D. Lotz, D. Rieger, U. Kernbach, J. Bertran Nadal, C. André, W. P. Fehlhammer, *J. Organomet. Chem.* **1995**, *491*, 135

[61] (a) K. Öfele, C. G. Kreiter, *Chem. Ber.* **1972**, *105*, 529 (b) K. Öfele, M. Herberhold, *Z. Naturforsch. B* **1973**, *B 28*, 306

[62] (a) R. E. Douthwaite, M. L. H. Green, P. J. Silcock, P.T. Gomes, *J. Chem. Soc., Dalton Trans.* **2002**, 1386 (b) D. J. Nielsen, K. J. Cavell, B. W. Skelton, A. H. White, *Inorg. Chim. Acta* **2002**, *327*, 116 (c) D. S. McGuinness, W. Mueller, P. Wasserscheid, K. J. Cavell, B. W. Skelton, A. H. White, U. Englert, *Organometallics* **2002**, 21, 175

[63] J. K. Huang, H. J. Schanz, E. D. Stevens, S.P. Nolan, *Organometallics* **1999**, *18*, 2370

[64] (a) S. -J. Li, J. -H. Zhong, Y. G. Wang, *Tetrahedron: Asymmetry.,* **2006**, 17, 1650 (b) D. Martin, S. Kehrli, M. D'Augustin, H. Clavier, M. Mauduit, A. Alexakis, *J. Am. Chem. Soc.* **2006**, *128*, 8416 (c) M. He, J. R. Struble, J. W. Bode, *J. Am. Chem. Soc.* **2006**, *128*, 8418 (d) C. Marshall, M. F. Ward, W. T. A. Harrison, *J. Organomet. Chem.* **2005**, *690*, 3970 (e) Y. Suzuki, K. Muramatsu, M. Sato, *Chem. Comm*. **2004**, *23*, 2770

[65] (a) J. Zhong, J.- H, Xie, A.-E. Wang, W. Zhang, Q.-L. Zhou, *Synlett* **2006**, *8*, 1193 (b) W. –F. Li, H. -M. Sun, Z. –G. Wang, M. –Z. Chen, Q. Shen, Y. Zhang, *J. Organomet. Chem*. **2005**, *690*, 6227 (c) H. Jacobsen, *J. Organometal. Chem.* **2005**, *690*, 6068 (d) J. –M. Becht, E. Bappert, G. Helmchen, *Adv. Synth. & Cat.* **2005**, *374*, 1495

[66] (a) E. Peris, R. H. Crabtree, *Coord. Chem. Rev.* **2004**, *248*, 2239 (b) H. M. L. Davies, A. M. Walji, *Org. Lett.* **2003**, 5, 479 (c) A. Fürstner, L. Ackermann, K. Beck, H. Hori, D. Koch, K. Langemann, M. Liebl, C. Six, W. Leitner, *J. Am.*

Chem. Soc. **2001**, *123*, 9000 (d) D. Enders, H. Gielen, K. Breuer, *Molec. Online* **1998**, *2*, 105

[67] (a) H. Werner, *Organometallics* **2005**, *24*, 1036 (b) C. Ciardi, G. Reeginato, L. Gonsalvi, I. de Rios, A. Romerosi, M. Peruzzini, *Organometallics* **2004**, *23*, 2020 (c) T. L. Amyes, S. T. Diver, J. P. Richard, R. F. M. Rivas, K. Toth, *J. Am. Chem. Soc*. **2004**, *126*, 4366 (d) M. Saoud, A. Romerosa, M. Peruzzini *Organometallics* **2000**, *19*, 4005

[68] T. J. Seiders, D. W. Ward, R. H. Grubbs, *Org. Lett.* **2001**, *3*, 3225

[69] D. Enders, H. Gielen, K. Breuer, *Tetrahedron: Asymmetry* **1997**, *8*, 3571

[70] (a) W. A. Herrmann, M. Elison, J. Fischer, C. Koecher, G. R. J. Artus, *Angew. Chem.* **1995**, *107*, 2602; (b) W. A. Herrmann, L. J. Goossen, C. Koecher, G. R. J. Artus, *Angew. Chem., Int. Ed.* **1997**, *35*, 2805.

[71] V. Cesar, S. Bellemin-Laponnaz, L. H. Gade, *Chem. Soc. Rev.* **2004**, *33*, 619

[72] L. H. Gade, V. Cesar, S. Bellemin-Laponnaz, *Angew. Chem., Int. Ed.* **2004**, *43*, 1014

[73] W.-L. Duan, M. Shi, G.-B. Rong, *Chem. Comm.* **2003**, 2916

[74] A. H. Hoveyda, D. G. Gillingham, J. J. Van Veldhuizen, O. Kataoka, S. B. Garber, J. S. Kingsbury, J. P. A. Harrity, *Org. Biomol. Chem.* **2004**, *2*, 8

[75] S. Lee, J. F. Hartwig, *J. Org. Chem.* **2001**, *66*, 3402

[76] L. G. Bonnet, R. E. Douthwaite, B. M. Kariuki, *Organometallics* **2003**, *22*, 4187

[77] F. Glorius, G. Altenhoff, R. Goddard, C. Lehmann, *Chem. Comm.* **2002**, 2704

[78] H. Seo, B. Y. Kim, J. H. Lee, H.-J. Park, S. U. Son, Y. K. Chung, *Organometallics* **2003**, *22*, 4783

[79] F. Guillen, C. L. Winn, A. Alexakis, *Tetrahedron: Asymmetry* **2001**, *12*, 2083

[80] A. Alexakis, C. L. Winn, F. Guillen, J. Pytkowicz, S. Roland, P. Mangeney, *Adv. Synth. Catal.* **2003**, *345*, 345

[81] J. Pytkowicz, S. Roland, P. Mangeney, *Tetrahedron: Asymmetry* **2001**, *12*, 2087

[82] L. Fadini, A. Togni, *Chem. Comm.* **2003**, 30

[83] D.P. Allen, C.M. Crudden, L.A. Calhoun, R. Wang, A. Decken, *J. Organomet. Chem.* **2005**, *690*, 5736

[84] J. W. Spengers, J. Wassenaar, , D.N. Clement, R. J. Cavell, C. J. Elsevier, *Angew. Chem., Int. Ed.* **2005**, *44*, 2026

[85] U. L. Dharmasena, H. M. Foucaul, E.N. dos Santos, D. E. Fogg, S. P. Nolan,

Organometalliscs, **2005**, *24*, 1056

[86] D. Enders, K. Breuer, J. Runsink, J. H. Teles, *Helvetica Chim. Acta.* **1996**, *79*, 1899

[87] R. L. Knight, F. J. Leeper, *J. Chem. Soc., Perkin Trans.* **1998**, 1891

[88] D. Enders, H. Gielen, K. Breuer, *Tetrahedron: Asymmetry* **1997**, *8*, 3571

[89] D. Enders, K. Breuer, J. H. Teles, *Helvetica Chim. Acta.* **1996**, *79*, 1217

[90] M. S. Kerr, J. R. de Alaniz, T. Rovis *J. Am. Chem. Soc.* **2002**, *124*, 10298

[91] H. Seo, K. Breuer, B.Y. Kim, J. H. Lee, H. J. Park, S. U. Son, Y. K. Chung *Organometallics* **2003**, *22*, 4783

[92] S. Saba, A. M. Brescia, M. K. Kaloustain, *Tetrahedron Lett.* **1991**, *32*, 5031

[93] P.K. Fraser, S. Woodward, *Tetrahedron Lett.* **2001**, *42*, 2747

[94] A. Alexakis, C. Benhaim, S. Rosset, *J. Am. Chem. Soc*. **2002**, *124*, 5262

[95] B. L. Feringa, *Acc. Chem. Res.* **2000**, *33*, 346

[96] A. Alexakis, C.L.Winn, F. Guillen, J. Pytkowicz, S. Roland, P. Mangeney, *Adv. Synth. Catal.* **2003**, *3*, 345

[97] (a) W.A. Herrmann, C. Brossmer, K. Öfele, C.-P. Reisinger, T. Priermeier, M. Beller, H. Fischer, *Angew. Chem.* **1995**, *107,* 1989; *Angew. Chem., Int. Ed. Engl.* **1995**, *34,* 1844; (b) W.A. Herrmann, C. Brossmer, C.-P. Reisinger, T.H. Riermeier, K. Öfele, M. Beller, *Chem. Eur. J.* **1997***, 3,* 1357; (c) W.A. Herrmann, V.P.W. Böhm, *J. Organomet. Chem.* **1999**, *572,* 141; (d) V.P.W. Böhm, W.A. Herrmann, *Chem. Eur. J.* **2000**, *6*, 1017; (e) M. Beller, H. Fischer, W.A. Herrmann, K. Öfele, C. Brossmer, *Angew. Chem.* **1995**, *107,* 1992; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1848.

[98] M. Ohff, A. Ohff, M.E. van der Boom, D. Milstein, *J. Am. Chem. Soc.* **1997**, *119*, 11687.

[99] B.L. Shaw, S.D. Perera, E.A. Staley, *Chem. Commun.* **1998**, 1361.

[100] G.D. Frey, C.-P. Reisinger, E. Herdtweck, W.A. Herrmann, J. *Organomet. Chem.* **2005**, *690,* 3193.

[101] (a) K. Öfele, W.A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, W. Scherer, J. Mink, *J. Organomet. Chem.* **1993**, *459,* 177; (b) W.A. Herrmann, K. Öfele, M. Elison, F.E. Kühn, P.W. Roesky, *J. Organomet. Chem.* **1994**, *480,* C7.

[102] (a) T. Weskamp, F.J. Kohl, W. Hieringer, D. Gleich, W.A. Herrmann, *Angew. Chem.* **1999**, *111,* 2573; *Angew. Chem., Int. Ed.*, **1999**, *38,* 2416; (b) W.A.

Herrmann, T. Weskamp, V.P.W. Böhm, *Adv. Organomet. Chem.* **2001**, *48* 1; (c) W.A. Herrmann, *Angew. Chem.* **2002**, *14,* 1343; *Angew. Chem., Int. Ed.* **2002**, *41,* 1290; (d) M. Bortenschlanger, J. Schütz, D. von Preysing, O. Nuyken, W.A. Herrmann, R. Weberskirch, *J. Organomet. Chem.* **2005**, *690,* 6233.

[103] (a) E. Peris, R.H. Crabtree, *Coord. Chem. Rev.* **2004**, *248,* 2239; (b) C.M. Crudden, D.P. Allen, *Coord. Chem. Rev.* **2004**, *248,* 2247; (c) I. Dragutan, V. Dragutan, L. Delaude, A. Demonceau, *Arkivoc* **2005**, *10,* 206; (d) J.C. Garrison, W.J. Youngs, *Chem. Rev.* **2005**, *105,* 3978.

[104] A.M. Magill, K.J. Cavell, B.F. Yales, *J. Am. Chem. Soc.* **2004**, *126,* 8717.

[105] (a) J. Schwarz, V.P.W. Böhm, M.G. Gardiner, M. Grosche, W.A. Herrmann, W. Hieringer, G. Raudaschl-Sieber, *Chem. Eur. J.* **2000**, *6,* 1773; (b) L. Xu, W. Chen, J. Xiao, *Organometallics.* **2000**, *19,* 1123; (c) T. Weskamp, V.P.W. Böhm, W.A. Herrmann, *J. Organomet. Chem.* **1999***, 585,* 348; (d) M.L. Trudell, C. Zhang, *Tetrahedron Lett.* **2000**, *41,* 59.

[106] S.R. Stauffer, S. Lee, J.P. Stambuli, S. I. Hauck and J. F. Hartwig, *Org. Lett.* **2000,** *2,* 1423.

[107] C.-P. Reisinger, Ph.D. Thesis, Technische Universität München **1997** ISBN 3-933083-00-1.

[108] G.D. Frey, J. Schütz, E. Herdtweck, W.A. Herrmann, *Organometallics* **2005**, *24,* 4416.

[109] G.D. Frey, Phosphapalladacyclen mit *N*-heterocyclischen Carbenen: Katalysatoren für die *Heck*-Olefinierung, 1st ed., Verlag Dr. Hut, München, **2005**.

[110] D.A. Albisson, R.B. Bedford, S.E. Lawrence, P.N. Scully, *Chem.Commun.* **1998**, 2095.

[111] G.D. Frey, Ph.D. Thesis, Technische Universität München, **2005**, ISBN 3-89963-186-2.

[112] R.B. Bedford, M. Betham, M.E. Blake, R.M. Frost, P.N. Horton, M.B. Hursthouse, R.-M. López-Nicolás, *Dalton Trans.* **2005**, *16,* 2774.

[113] G.D. Frey, J. Schütz, W.A. Herrmann, *J. Organomet.Chem.* **2006**, *691,* 2403.

[114] M. Mühlhofer, T. Strassner, E. Herdtweck, W.A. Herrmann, *J. Organomet. Chem.* **2002**, *660,* 121.

[115] R.B. Bedford, M. Betham, S.J.Coles, P.H. Horton, M. López- Sáez, *Polyhedron* **2006**, *25,* 1003.

[116] W.A. Herrmann, V.P.W. Böhm, C.-P. Reisinger, *J. Organomet. Chem.* **1999**, *576,* 23.

[117] A.J. Arduengo III, H. Bock, H. Chen, M. Denk, D.A. Dixon, J.C. Green, W.A. Herrmann, N.L. Jones, M. Wagner, R. West, *J. Am. Chem. Soc.* **1994**, *116*, 6641.

[118] (a) Data Collection Software for NONIUS κ–CCD devices, Delft, The Netherlands, **2001**; (b) Z. Otwinowski, W. Minor, *Methods in Enzymology* **1997**, *276,* 307ff; (c) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, SIR92, *J. Appl. Crystallogr.* **1994**, *27,* 435; (d) A.J.C. Wilson (Ed.), *International Tables for Crystallography*, Vol. C, Tables 6.1.1.4, 4.2.6.8, and 4.2.4.2, Kluwer Academic Publishers, Dordrecht, The Netherlands, **1992**; (e) G.M. Sheldrick, *SHELXL-97*, Universität Göttingen, Göttingen, Germany, **1998**; (f) A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, **2001**; (g) L.J. Farrugia, WINGX, Version 1.70.01 January 2005, *J. Appl. Crystallogr.* **1999**, *32*, 837; (h) K. Brandenburg, DIAMOND, Version 3.1d, Crystal Impact GbR, Bonn, Germany, **2006**.

[119] Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41,* 1290

[120] (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Stanforth, S. P. *Tetrahedron* **1998**, *54*, 263; (c) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147.

[121] Beller, M.; Fischer, H.; Herrmann, W. A.; Öfele, K.; Brossmer, C. *Angew. Chem., Int. Ed.* **1995**, *34*, 1848

[122] (a) Bedford, R. B.; Draper, S. M.; Scully P. N.; Welch, S. L. *New J. Chem.* **2000**, *24*, 745. (b) Albisson, D. A.; Bedford, R. B.; Lawrence, S. E.; Scully, P. N. *Chem. Commun.* **1998**, 2095. (c) Bedford, R. B.; Welch, S. L. *Chem. Commun.* **2001**, 129.

[123] A. D. Tanase, G. D. Frey a, E. Herdtweck , S. D. Hoffmann , W. A. Herrmann *J. Organomet. Chem.* **2007**, *692*, 3316.

[124] P. K. Byers, A. J. Canty, *Organometallics*, **1990**, *9***,** 210.

[125] D. S. McGuinness, K. J. Cavell, *Organometallics*, **2000**, *19***,** 741.

[126] E. Mas-Marzá, M. Poyatos, M. Sanau, E. Peris, *Organometallics,* **2004**, *23,* 323.

[127] A. D. D. Tulloch, A. A. Danopoulos, S. Winston, S. Kleinhenz, G. Eastham, *J. Chem. Soc., Dalton Trans.,* **2000**, 4499.

[128] M. C. Navarro- Ranninger, *Acta Cryst*., **1983**, *C39*, 186.

[129] A. A. D. Tulloch, A. A. Danopoulos, R. P. Tooze, S. M. Cafferkey, M. B. Hursthouse, *Chem. Comm.* **2000**, *1248*.

[130] C. J. Mathews, P. J. Smith, T. Welton, *J. Mol. Cat., A*, **2003**, *206*, 77.

[131] J. Lasri, M.N.Kopylovich, M.F.C. Guedes da Silva, M. A. Janu´ario Charmier and A. J. L. Pombeiro, *Chem.–Eur. J.*, **2008**, *14*, 9312.

[132] (a) L. Ray, M. N. Shaikh and P. Ghosh, *Organometallics*, **2007**, *26*, 958; (b) L. Braun, P. Liptau, G. Kehr, J. Ugolotti, R. Frohlich and G. Erker, *Dalton Trans.*, **2007**, 1409; (c) H. Hagiwara, K. H. Ko, T. Hoshi and T. Suzuki, *Chem. Commun.*, **2007**, 2838; (*d*) Q. Luo, S. Eibauer and O. Reiser, *J. Mol. Catal. A*, **2007**, *268,* 65; (*e*) J. K. Eberhardt, R. Fröhlichand E.-U. Würthwein, *J. Org. Chem.*, **2003**, *68*, 6690.

[133] R. Griesser, H. Sigel , *Org. Biomol. Chem.*, **2003**, *1*, 1819.

[134] He, W.; Hanney, B.; Myers, M. R.; Condon, S.; Becker, M. R.; Spada, A. P.; Burns, C.; Brown, K.; Colussi, D.; Chu, V. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 919.

[135] Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972.

[136] Fuwei Li, Shiqiang Bai, T. S. Andy Hor *Organometallics* **2008**, *27*, 672.

[137] (a) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Organometallics* **2002**, *21*, 5204. (b) Loch, J. A.; Albrecht, M.; Peris, E.; Mata, J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 700. (c) Poyatos, M.; Maisse-François, A.; Bellemin Laponnaz, S.; Gade, L. H. *Organometallics* **2006**, *25*, 2634.

[138] Chernyshova, E. S.; Goddard, R.; Pörschke, K.-R. *Organometallics* **2007**, *26*, 3236.

[139] Filipuzzi, S.; Pregosin, P. S.; Albinati, A.; Rizzato, S. *Organometallics* **2008**, *27*, 437.

[140] (a) Vriez, K. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; pp 441-483. (b) Breutel, C.; Pregosin, P. S.; Salzmann, R.; Togni, A. *J. Am. Chem. Soc.* **1994**, *116*, 4067. (c) Pregosin, P. S.; Salzmann, R. *Coord. Chem. Rev.* **1996**, *155*, 35. (d) Kumar, P. G. A.; Dotta, P.; Hermatschweiler, R.; Pregosin, P. S.; Albinati, A.; Rizzato, S. *Organometallics* **2005**, *24*, 1306. (e) Faller, J. W.; Sarantopoulos, N. *Organometallics* **2004**, *23*, 2008.

[142] Gogoll, A.; Ornebro, J.; Grennberg, H.; Bäckvall, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 3631.

[143] (a) Marion, N.; Navarro, O.; Mei, J.; Stevens, E. D.; Scott, N. M.; Nolan, S. P. *J. Am. Chem. Soc.* **2006**, *128*, 4101. (b) Xu, L.; Shi, Y. *J. Org. Chem.* **2008**, *73*, 749. (c) Roland, S.; Audouin, M.; Mangeney, P. *Organometallics* **2004**, *23*, 3075.

[144] Hong Mei Peng, Guoyong Song, Yongxin Li, Xingwei Li *Inorg. Chem.* **2004**, *23*, 3075.

[145] (a) Harjani, J. R.; Friščić, T.; MacGillivray, L. R.; Singer, R. D. *Inorg. Chem.,* **2006**, *45*, 10025. (b) Harjani, J. R.; Friščić, T.; MacGillivray, L. R.; Singer, R. D. *Dalton Trans.*, **2008**, 4595.

[146] (a) Garrison, J. C.; Youngs, W. J. *Chem. Rev.* **2005**, *105*, 3978. (b) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663. (c) Simons, R. S.; Custer, P.; Tessier, C. A.; Youngs, W. J. *Organometallics* **2003**, *22*, 1979. (d) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972.

[147] (a) Huynh, H. V.; Yeo, C. H.; Tan G. K. *Chem. Comm.* **2006**, 3833. (b) Tulloch, A. A. D.; Danopoulos, A. A.; Tooze, R. P.; Cafferkey, S. M.; Kleinhenz, S.; Hursthouse, M. B. *Chem. Commun.* **2000**, 1247. (d) Tulloch, A. A. D.; Winston, S.; Danopoulos, A. A.; Eastham, G.; Hursthouse, M. B. *Dalton Trans.* **2003**, 699. (e) Tsoureas, N.; Danopoulos, A. A.; Tulloch, A. A. D.; Light, M. E. *Organometallics* **2003**, *22*, 4750.

[148] McGuinness, D. S.; Green, M. J.; Cavell, K. J.; Skelton, B.W.; White, A. H. *J. Organomet. Chem.*, **1998**, *565*, 165. Magill, A.M., McGuinness, D.S., Cavell, K.J., Britovsek,G. J. P., Gibson, V.C., A. White, J. P., Williams, D. J., White, A.H., Skelton, B.W. *J. Organomet. Chem.* **2001**, *617- 618,* 546.

[149] (a) Gründemann, S.; Albrecht, M.; Loch, J. A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2001**, *20*, 5485-5488. (b) Herrmann, W. A.; Böhm, V. P. W.; Gstöttmayr, C. W. K.; Grosche, M.; Reisinger, C.-P.; Weskamp, T. *J. Organomet. Chem*. **2001**, *617-618*, 616-628. (c) Herrmann, W. A.; Schwarz, J.; Gardiner, M. G.; Spiegler, M. *J. Organomet. Chem*. **1999**, *575*, 80-86. (d) Gardiner, M. G.; Herrmann, W. A.; Reisinger, C.-P.; Schwarz, J.; Spiegler, M.

J. Organomet. Chem. **1999**, *572*, 239. (e) Perry, M.C., Cui, X., Burgess, K. *Tetrahedron: Asymmetry* **2002**, *13,* 1969.

[150] Pytkowicz, J.; Roland, S.; Mangeney, P.; Meyer, G.; Jutand, A. *J. Organomet. Chem.* **2003**, *678*, 166.

[151] (a) Bildstein, B.; Malaun, M.; Kopacka, H.; Ongania, K. H.; Wurst, K. *J. Organomet. Chem.* **1998**, *552*, 45. (b) Xu, L.; Chen, W.; Bickley, J. F.; Steiner, A.; Xiao, J. *J. Organomet. Chem.* **2000**, *598*, 409. (c) Glas, H.; Herdtweck, E.; Spiegler, M.; Pleier, A. K.; Thiel, W. R. *J. Organomet. Chem.* **2001**, *626*, 100. (d) Glorius, F.; Altenhoff, G.; Goddard, R.; Lehmann, C. *Chem. Commun.* **2002**, *22*, 2704. (e) Pytkowicz, J.; Roland, S.; Mangeney, P.; Meyer, G.; Jutand, A. *J. Organomet. Chem.* **2003**, *678*, 166.

[152] Chianese, A. R.; Kovacevic, A.; Zeglis, B. M.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2004**, *23*, 2461.

[153] Peng, H. M.; Song, G.; Li, Y.; Li X. *Inorg.Chem.* **2008**, *47*, 8041.

[154] Ghosh P., Shaikh, M. M., Lipika, K. *Organometallics* **2007**, *26*, 958.

[155] (a) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Organometallics* **2002**, *21*, 5204. (b) Loch, J. A.; Albrecht, M.; Peris, E.; Mata, J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 700. (c) Poyatos, M.; Maisse-François, A.; Bellemin-Laponnaz, S.; Gade, L. H. *Organometallics* **2006**, *25*, 2634.

X-ray single crystal diffraction data

Crystallographic Data for **1a·(CH_2Cl_2)**

	1a·(CH_2Cl_2)
Formula	$C_{89}H_{132}Cl_2O_{10}P_2Pd_2$
Fw	1707.63
Color / habit	Colorless / fragment
Crystal dimensions (mm^3)	0.28 × 0.33 × 0.46
Crystal system	Triclinic
Space Group	$P\bar{1}$ (no. 2)
a (Å)	15.3542(1)
b (Å)	16.8517(1)
c (Å)	18.4679(2)
a (°)	91.4991(3)
β (°)	95.5910(3)
g (°)	92.0949(3)
V ($Å^3$)	4750.43(7)
Z	2
T (K)	173
D_{calcd} (g cm^{-3})	1.194
μ (mm^{-1})	0.519
F(000)	1804
θ Range (°)	1.21 – 25.36
Index ranges (*h*, *k*, *l*)	±18, ±20, ±22
No. of rflns. collected	74051
No. of indep. rflns. / R_{int}	17380 / 0.036
No. of obsd. rflns. [$I>2\sigma(I)$]	14563
No. of data/restraints/params	17380 / 0 / 984
R_1/wR_2 [$I>2\sigma(I)$][a]	0.0307 / 0.0728
R_1/wR_2 (all data)[a]	0.0409/ 0.0763
GOF (on F^2)[a]	1.032
Largest diff. peak and hole (e $Å^{-3}$)	+0.65 / -0.48

[a] $R_1 = S(||F_o|-|F_c||)/S|F_o|$; $wR_2 = \{S[w(F_o^2-F_c^2)^2]/S[w(F_o^2)^2]\}^{1/2}$; $GOF = \{S[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$

Crystallographic Data for **5b·3(CH_2Cl_2)**

	5b·3(CH_2Cl_2)
Formula	$C_{97}H_{146}Cl_8N_4O_6P_2Pd_2$
Fw	2022.56
Color / habit	Colorless / fragment
Crystal dimensions (mm^3)	0.23 × 0.28 × 0.48
Crystal system	Triclinic
Space Group	$P\bar{1}$ (no. 2)
a (Å)	11.1224(1)
b (Å)	20.7167(2)
c (Å)	24.1982(2)
a (°)	100.1638(4)
β (°)	103.0992(4)
g (°)	94.0864(3)
V ($Å^3$)	5309.31(8)
Z	2
T (K)	173
D_{calcd} (g cm^{-3})	1.265
μ (mm^{-1})	0.619
F(000)	2124
θ Range (°)	1.46 – 25.36
Index ranges (*h*, *k*, *l*)	±13, ±24, ±29
No. of rflns. collected	55808
No. of indep. rflns. / R_{int}	18623 / 0.032
No. of obsd. rflns. [$I>2\sigma(I)$]	15639
No. of data/restraints/params	18623 / 0 / 1151
R_1/wR_2 [$I>2\sigma(I)$][a]	0.0339 / 0.0795
R_1/wR_2 (all data)[a]	0.0447/ 0.0847
GOF (on F^2)[a]	1.030
Largest diff. peak and hole (e $Å^{-3}$)	+0.68 / -0.88

[a] $R_1 = S(||F_o|-|F_c||)/S|F_o|$; $wR_2 = \{S[w(F_o^2-F_c^2)^2]/S[w(F_o^2)^2]\}^{1/2}$; $GOF = \{S[w(F_o^2 F_c^2)^2]/(n-p)\}^{1/2}$

Crystallographic Data for **11**.

	11
Formula	$C_{20}H_{31}O_2PPd$
Fw	440.84
Color / habit	Colorless / plate
Crystal dimensions (mm^3)	0.10 × 0.23 × 0.30
Crystal system	Orthorhombic
Space Group	*Pbca* (no. 61)
a (Å)	8.4230(3)
b (Å)	15.8029(6)
c (Å)	31.2520(15)
a (°)	90
β (°)	90
g (°)	90
V ($Å^3$)	4159.9(3)
Z	8
T (K)	173
D_{calcd} (g cm^{-3})	1.408
μ (mm^{-1})	0.978
F(000)	1824
θ Range (°)	1.30 – 23.25
Index ranges (*h*, *k*, *l*)	±9, ±17, ±34
No. of rflns. collected	13426
No. of indep. rflns. / R_{int}	2868 / 0.075
No. of obsd. rflns. [$I>2\sigma(I)$]	1937
No. of data/restraints/params	2868 / 0 / 225
R_1/wR_2 [$I>2\sigma(I)$][a]	0.0453 / 0.0800
R_1/wR_2 (all data)[a]	0.0882 / 0.0924
GOF (on F^2)[a]	1.025
Largest diff. peak and hole (e $Å^{-3}$)	+0.60 / -0.68

[a] $R_1 = S(||F_o|-|F_c||)/S|F_o|$; $wR_2 = \{S[w(F_o^2-F_c^2)^2]/S[w(F_o^2)^2]\}^{1/2}$; $GOF = \{S[w(F_o^2 F_c^2)^2]/(n-p)\}^{1/2}$

Publications:

- *"Preparation of NHC-substituted phosphitepalladacycles"*.
  A. D. Tanase, G. D. Frey, E. Herdtweck, S. D. Hoffmann and W. A. Herrmann. *J. Organomet. Chem.,* **2007**, *692 (16)*, 3316-3327.

- "*A Palladium(II) Complex Containing Imidazole Moieties. Synthesis and Structural Examination*".
  A. D. Tanase, E. Herdtweck, W. A. Herrmann, F. E. Kühn. *Heterocycles*, **2007**, *73*, 651-659.

- *"Phthalimido-Functionalized N-Heterocyclic Carbene Complexes of Palladium(II): Halide Scrambling via Silver Transmetalation***".**
  A. D. Tanase, E. Herdtweck, W. A. Herrmann, F. E. Kühn *Dalton Trans.* **2009***,* submitted.

- *"Synthesis, Structures and Solution Dynamics of Palladium and Rhodium Complexes with Benzenimidazole-Functionalized N-Heterocyclic Carbene*".
  A. D. Tanase, W. A. Herrmann, E. Herdtweck, F. E. Kühn, *Eur. J. Inorg. Chem.* **2009***,* in preparation.

- *"Synthesis and characterization of novel rhodium and ruthenium complexes with non-chelating heterocyclic phthalimidocarbene ligands"*.
  A. D. Tanase, W. A. Herrmann and F. E. Kühn *J. Organomet. Chem.* **2009***,* in preparation.

Posters:

- *„NHC-substituted phosphitepalladacycles: Synthesis, structure, and catalysis"*.
  A.D. Tanase, W. A. Herrmann, 1st NANOCAT forum, Tutzing, 5 -7 June **2008**.

- *"New O and N-Functionalized N-heterocyclic Carbene Complexes of Palladium(II): Synthesis, Characterization and Their Properties in Suzuki-Miyaura Catalysis"*.

A. D. Tanase, W. A. Herrmann, F. E. Kühn, *The XXIIIth International Conference on Organometallic Chemistry* (ICOMC), Rennes, 13 -18 July **2008**, 798.

Lebenslauf

Name:	Alexandrina Doina Rusu (geb. Tanase)
Geburtsdatum:	27.07.1977
Geburtsort:	Bistrita, Rumänien
Staatsangehörigkeit:	rumänisch
Familienstand:	heiratet
Eltern:	Alexandru Tanase und Elena Doina Tanase (geb. Sidor)

Schulbildung:

1984 – 1988	Grundschule (1-4) Bistrita, Rumänien
1988 – 1992	Gymnasium (5-8) Bistrita, Rumänien
1992 – 1996	Lyzeum (9-12) “Andrei Muresan”, Bistrita, Rumänien

Studium:

1998 – 2002	Chemie-Studium an der Babes-Bolyai University, Cluj-Napoca, Rumänien, Faculty of Chemistry & Chemical Engineering, BSc, bei Prof. Dr. Ing. Adrian Nicoara Thema: “Investigation of some adsorbed redox couples”
2002 – 2003	Chemie-Studium an der Babes-Bolyai University, Cluj-Napoca, Rumänien, Faculty of Chemistry & Chemical Engineering, MSc (englisch), bei Prof. Dr. Cristian Silvestru Thema: “Organozinc(II) and -Cadmium(II) Halides”
03/2004 – 09/2004	ERASMUS studenten an der Universität Bremen, Bremen, Deutschland, Institut für Anorganische und Physikalische Chemie, bei Prof. Dr. H.J. Breunig Thema: Research on the synthesis and characterization of new organoantimony (III) compunds
2006 – 2009	International Doctorate Program NANOCAT (Nanodesign of High Performance Catalysts), Elite Netzwerk Bayern
2008 – 2009	International Graduate School of Science and Engineering (IGSEE) an der Technische Universität München

Promotion:

01/2006 – 06/2009	Dissertation am Lehrstuhl für Anorganische Chemie, Technische Universität München, bei Prof. Dr. Wolfgang A. Herrmann Thema: “Synthesis and Catalytic Applications of Carbene-Functionalized Hybrid Catalysts”

Garching, den Signature