TECHNISCHE UNIVERSITÄT MÜNCHEN
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Synthesis and Applications of Bidentate *N*-heterocyclic Mono- and Biscarbene Ligands

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To my family
With deep gratitude and love

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Words are forgotten…..
Memories are remembered……..

Contents

Abbreviations - Spectroscopic

NMR	Nuclear magnetic resonance
δ	NMR chemical shift
J_{YZ}	Coupling constant of Y to Z
V.T.	Variable temperature
s	Singlet
d	Doublet
t	Triplet
q	Quartet
sept	Septet
m	Multiplet
br	Broad
IR	Infrared
$\nu_{(L)}$	IR shift of ligand L
eq	Equatorial
MS	Mass spectrometry
GC	Gas chromatography

Abbreviations - Unit

h	Hour
min	Minute
s	Second
K	Kelvin
°	Degree

RT	Room temperature
ppm	Parts per million
Hz	Hertz
MHz	Megahertz
cm^{-1}	Wavenumber
kJ	Kilojoule
Å	Angstrom
g	Gram
mg	Milligram
mL	Millilitre
μL	Microlitre
mol	Mole
mmol	Millimol

Abbreviations - Chemical

NHC	N-heterocyclic carbene
COD	Cyclo-1,5-octadien
M	Metal
L	Ligand
X	Halide or heteroatom
R	Alkyl or aryl group
Ar	Aryl
Me	Methyl
Et	Ethyl
^{i}Pr	Isopropyl

^{t}Bu	*tert*-Butyl
Bn	Benzyl
Mes	Mesityl (2,4,6-trimethylphenyl)
Ad	Adamantyl
i-	*Ipso*
o-	*Ortho*
m-	*Meta*
p-	*Para*
THF	Tetrahydrofuran
MeOH	Methanol
EtOH	Ethanol
DCM	Dichloromethane
DMSO	Dimethyl sulfoxide
TOF	Turnover frequency

Chapter 1

Introduction

1. Introduction

1.1. The concept of catalysis

The objectives of this chapter are to develop an understanding of catalysts from the history side, reaction mechanisms and catalyst design. The beginning of the thesis starts with one citation: ``*Catalysis is leaving the realm of alchemy and entering the field of science. It is still pretty much of an art to design and optimize new catalysts and to improve upon existing catalysts, but it is no longer a black art*``[1] claimed Edward Hayes of the National Science Foundation (NSF) in a 1983 Science article. The idea of catalysis has been used by humankind for over 2000 years[2], although the science behind the phenomenon was just beginning to be discovered in the 19th century. Even with all the advanced research and development of catalysts, the relationship between catalyst structure and function are complex and must be determined separately on a case by case basis.

Centuries ago, the catalysts were first used, in the making of wine, cheese, and other food and beverages. During that time it was determined that it was always necessary to add small amounts of the previous batch to make the current batch. Many reasons, however, can speed up a chemical reaction. The most providing straight forward one was heating a reaction up to speed up the reaction; however the thermo idea fails in cases where the substance is not stable to high temperature. On other hand, heating makes a process more expensive. A great effort was made to find alternative ways to speed up the reactions. Berzelius was the first to coin the word ``catalyst`` in 1835[3], when he had noticed changes in substances when they were brought in contact with small amounts of certain species called "ferments". The first mention and definition of the term ``catalysis`` came from Berzelius. He used the Greek word “κατάλυσις” (Greek kata = wholly and lein = to loosen).[3] At the beginning of the 20th century, Nobel Laureate Friedrich Wilhelm Ostwald came up with the definition that is in use until today: ``*A catalyst is a substance which increases the rate at*

which a chemical reaction approaches equilibrium without becoming itself permanently involved``[3c].

Accordingly, catalysts are used as substances that increase the rate of the chemical reaction without being consumed during the reaction. Because they are not being consumed, only a small amount of catalyst is needed to speed up the reaction. Each catalyst has its own specific way of functioning in the catalytic reaction. In general, however, they speed up the rate of chemical reaction by lowering the activation energy.

The principle role and functionality of the catalyst present in the reaction is described in figure 1[3d]. For a simple chemical reaction where A + B are transformed to C + D the presence of a catalyst lowers the activation energy of the reaction, resulting in acceleration of the reaction rate[4-6]. In comparison, the activation energy of the reaction without catalyst is relatively high; therefore the reaction rate would be relatively low.

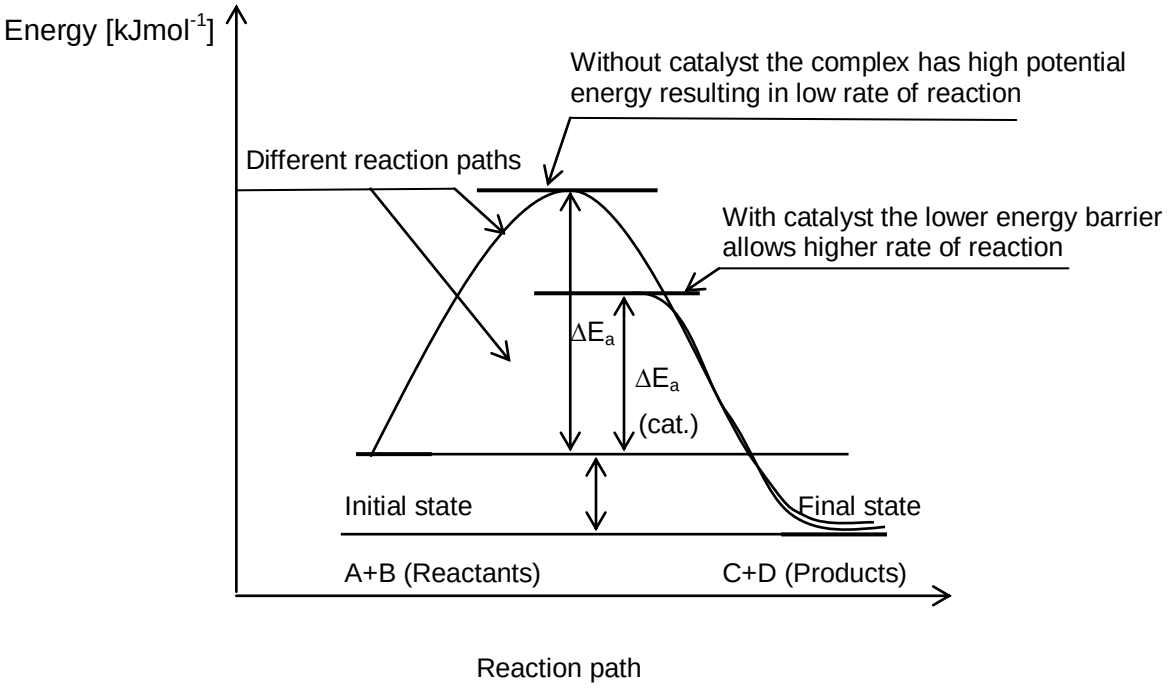


Figure 1: Different reaction paths.

Since the catalyst is chemically unchanged during the reaction, its role is to provide a new, alternative reaction pathway with lower activation energy for the reaction. The catalyst speeds up the reaction; however it never changes the chemical balance or the endpoint of the reaction. A catalyst takes its own part in the reaction, but does not appear in the final products, and should therefore theoretically not be consumed.

The investigation of operating modes of catalysts is immensely important for their use in industrial processes, intensively seeking for new efficient ways for the production of important chemicals. Today, catalysts have come to play a major economic role in the world market[3b]. Their major applications are in petroleum refining and chemical production[3b]. With expansion in the catalysts-based industries in the word, the preparation of new catalysts and studies of their activation processes have obtained much more importance.[3b] This part of thesis finishes with another citation*: ``Catalysis is the key to both life and lifestyle. It is an essential technology for chemical and materials manufacturing, for fuel cells and other energy conversion systems, for combustion devices, and for pollution control systems which greatly impact everyone on our planet*.``[7]

1.1.1. Types of catalysts

Homogeneous and heterogeneous catalysts can be distinguished as follows,

1) Heterogeneous catalysis occurs when the catalyst and the reactants are in different phases. Usually, the catalyst represents a solid phase and the reagents and products either dissolved in a liquid phase or exist as gases, therefore innately separating reagents and catalyst into two different phases[8-10].

2) In homogenous catalysis, the reactants, the catalyst and the products are in the same phase, for the most part dissolved in a liquid phase[10-12]. The advantages of homogeneous catalysts over heterogeneous ones are: (i) generally far more selective for a single product

(ii) generally milder reaction conditions; (iii) high activity and selectivity and (iv) low susceptibility towards catalyst poisoning[13].

Table 1: The comparison between homogeneous and heterogeneous catalysis

	Homogeneous	**Heterogeneous**
Concentration	low	high
Selectivity	high	low
Diffusion problems	practically absent	present (mass-transfer-controlled reaction)
Reaction conditions	mild (50 ^{o}C - 200 ^{o}C)	severe (often > 250 ^{o}C)
Applicability	limited	wide
Activity loss	irreversible reaction with products(cluster formation) poisoning	sintering of the metal crystallites poisoning
Catalyst properties		
Stucture/ stoichiometry	defined	undefined
Modification possibilities	high	low
Thermal stability	low	high
Catalyst separation	sometimes laborious(chemical decomposition, distillation, extraction)	fixed-bed, unnecessary suspension, filtration
Catalyst recycling	possible	unnecessary(fixed-bed) or easy suspension
Cost of catalyst losses	high	low

The middle of last century was important for a dramatic development in the field of organometallic chemistry: to search for efficient catalysts to optimize industrial processes[14]. Industrially important fields of the use of organometallic compounds as homogeneous catalysts include developments in the fields of transition metal catalyzed hydrogenation, coupling reactions, hydrosilylation, hydrocyanation and olefin metathesis.[15-18]

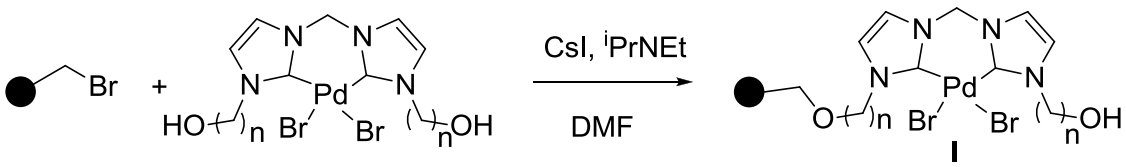
Industry only uses homogeneous catalysts when selectivity is important due to problems associated with separating the products from the catalysts solution. Industry makes extensive use of heterogeneous catalysts due to the ease of separating products from the catalysts, and the usually significantly higher thermal stability of heterogeneous catalyst. Table 1 shows, both types of catalysts have their advantages and disadvantages and are thus useful for different fields of application.[8-12]

Many amazing catalytic discoveries have been reported by researches both in industry and academia. Many research groups around the world have therefore developed a multitude of novel mono- and polydentate phosphorus[19] or nitrogen-containing ligands[20] as well as hybrid P, N-ligands[20] or *N*-heterocyclic carbene ligand[21] that can efficiently be employed as ligands coordinating to transition metals for the preparation of new catalyst complexes.

The most widely used carbenes as ligands for transition metal catalysts are *N*-heterocyclic carbenes. Homogeneous NHCs palladium and rhodium complexes are widely used for a variety of organic transformations. In particular, such compounds have been recognized as powerful catalysts.

As already mentioned previously, the major advantages of heterogeneous catalysts are the simplicity of catalyst separation from reaction media, economic efficiency and little need for ligands. Because of that, heterogeneous catalysts are more desirable for their usage in many industrial processes. However, many heterogeneous catalysts show comparatively low selectivity and low activity. These drawbacks need to be overcome. One method of combining the advantages of both homogeneous and heterogeneous catalysis is to immobilize homogeneous catalysts on a modified support material such as polymers, siliceous materials, zeolites, metalc-organic frame and nanotubes.

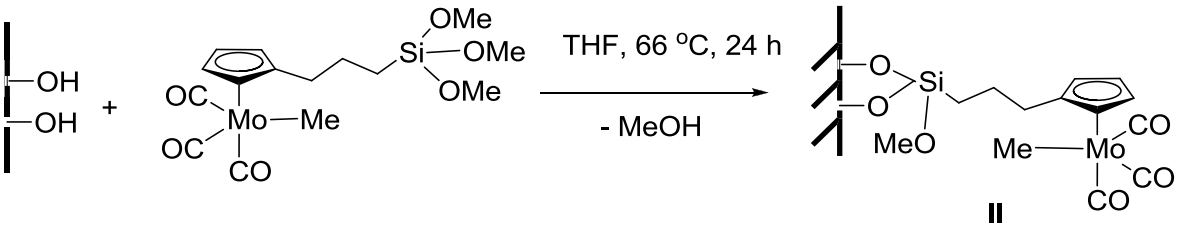
Several research groups, for example, have immobilized NHC-Pd complexes on polystyrene-based supports through several immobilization methods. Scheme 1 depicts a bidentate NHC-Pd complex, immobilized on Wang resin. Such a compound was, for example, successfully applied for the Heck reaction of aryl bromides by Herrmann *el al*.[22].



Scheme 1: Immobilizilation of Bis(NHC)-Palladium-Complex.

Luo's group prepared a polystyrene-based Pd catalyst with another bidentate NHC-Pd complex for the Suzuki reaction. In this case, they anchored a bis-imidazolium precursor, which was synthesized in solution, on a Merrifield resin and then reacted the resin with $Pd(OAc)_2$[23]. Lee´s group has also developed several polymer supports for immobilizing NHC-Pd complexes. These material exhibited excellent catalytic performance in both Suzuki and Heck reactions.[24]

Kühn and his co-workers immobilized molybdenum complexes on a mesopourous solid support, MCM-41 (Scheme 2)[25].



Scheme 2: Molybdenum complex on MCM-41.

Heterogenisation of molybdenum catalysts on inorganic supporting materials, especially on mesoporous sieves[26, 27] is an important research field in our group[25]. The system shows high yields and selectivity in oxidation catalysis with a good recyclability as well.

1.1.2. Factors which influence the Catalytic Ability of a Metal Complex

The features of the metal complexes are defined by the observation of its overall properties, such as, the nature of the metal center, ligands, co-ligands as well as the counter ions. Figure 2[28] shows the general structure of a homogeneous catalyst. The catalytic performance of such a complex strongly depends on the nature of the metal and ligands / co-ligands. Other important conditions for the catalyzed reaction, which affect the catalyst´s performance, are the type of solvent, temperature, pressure and concentration.

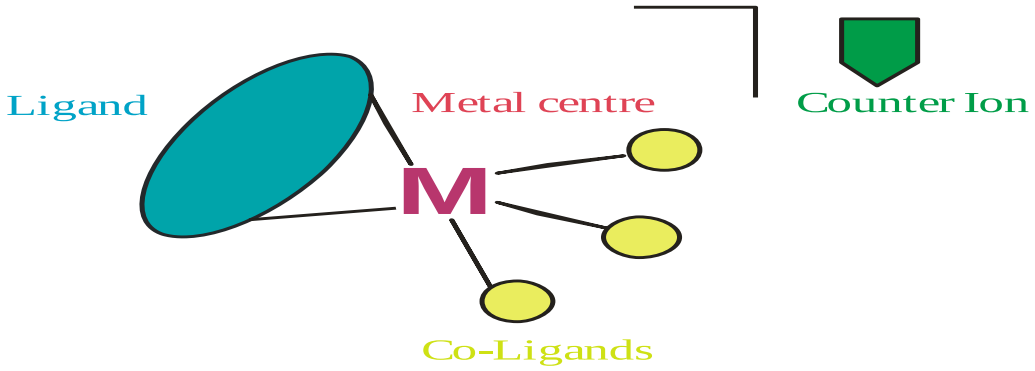


Figure 2: General structure of a homogeneous catalyst.

During the performance of a catalytic cycle, the metal complex undergoes a series of processes: the metal centre can undergo ligand substitution, ligand rearrangements, insertion, oxidative addition and reductive elimination. For a catalyst to be effective, it is essential that the metal centre is able to adopt oxidation states and / or coordination geometries under the reaction conditions. The metal centre is required to be initially coordinatively unsaturated to enable the binding of the substrate molecule[16-18]. A series of rhodium and iridium complexes have been used for a variety of applications quite early in

homogeneous catalysis. Examples include the highly efficient hydrogenation catalysts $[Rh(PPh_3)_3Cl]$ (Wilkinson's catalyst) and $[Ir(P(Cy)_3)(pyridine)(COD)]PF_6$ where Cy = cyclohexyl (Crabtree's catalyst).[29] In addition to rhodium and iridium, palladium complexes can also be utilized for many applications in homogeneous catalysis. Excellent examples are the palladium-catalyzed Suzuki cross-coupling reaction[30,31] and the Buchwald-Hartwig arylamination reaction, etc.[32 33]

The continuous development of novel catalysts containing rhodium, iridium and palladium has nowadays rendered these methodologies a mature synthetic tool and allowed them to find application not only in academia but also in an industrial context.[1]

The overall catalytic activity of the metal complex is usually the result of the interplay between the electronic and steric effects of the ligands, co-ligands and metal. One of the roles of the ligands is to moderate the electron density on a metal centre by either donating or withdrawing electrons from the metal centre. Ligands are often described in terms of their σ-donor or π-acceptor properties. Good σ-donor ligands include phosphines, amines, imines and *N*-heterocyclic carbenes, which generally bind to a metal by donating a lone pair of electrons to the *d* orbital of a metal centre, forming the metal-ligand σ-bond, and therefore increasing the electron density on the metal. On the other hand, good π acceptors decrease electron density on a metal by delocalising the metal's electrons onto the ligands. Carbon monoxide, alkynes/alkenes are the good examples of good π acceptor ligands. It is often desirable to incorporate both σ donor and π acceptor ligands into a metal complex to create electronic balance on the metal centre.[16,17,34] The term ``co - ligand`` is used to refer to a ligand that does not possess the ``essential information``, such as the stereo-directing centre of a chiral ligand, and is in many cases displaced by substrates or products during catalytic cycles. For example, the co-ligand 1,5-cyclooctadiene (COD), which is present in many active hydrogenation catalysts such as Crabtree's catalyst $[Ir(P(Cy)_3)(pyridine)(COD)]PF_6$, is normally hydrogenated and released during the hydrogenation process.[29] The geometry and size of the ligand has an important role in determining the reactivity of the metal complex. The substrate accessibility of the metal centre is strongly affected by steric factors.

Multidentate ligands are frequently used in catalysis as they offer increased stability of the resulting metal complexes due to the chelate effect.[16-18]

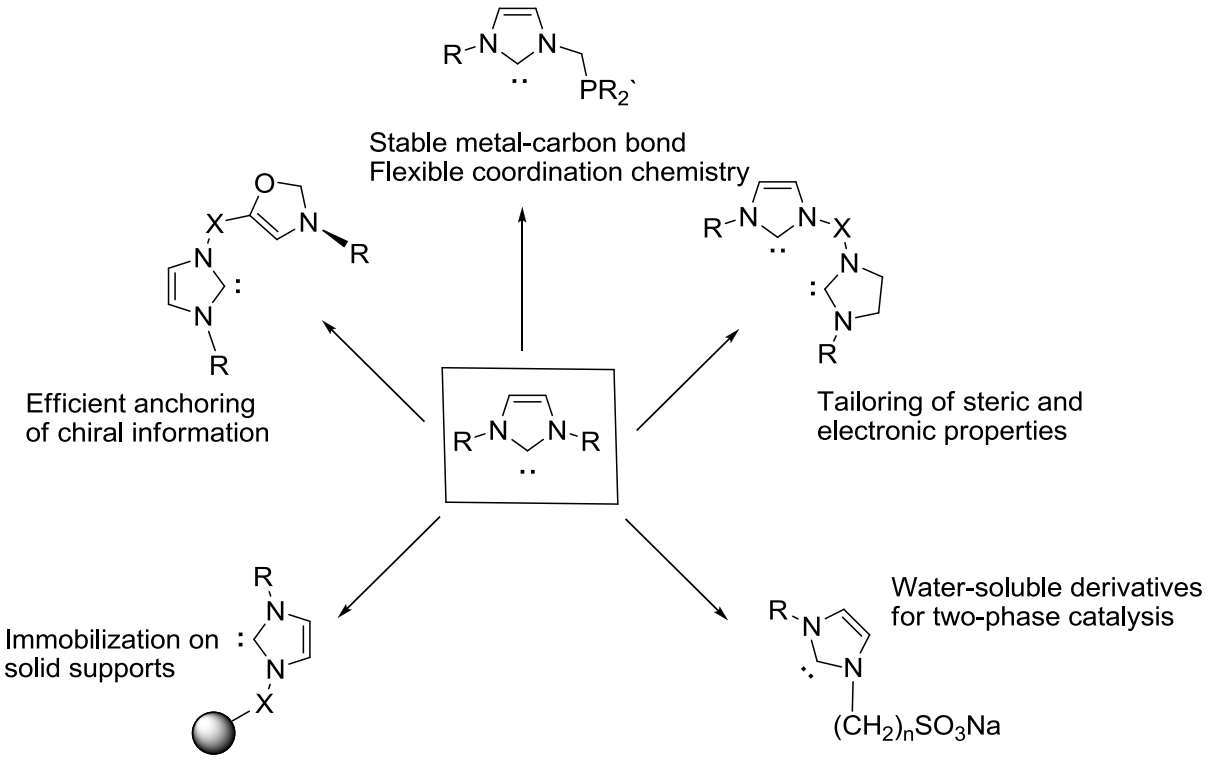
Undoubtedly, phosphine and *N*-hetrocyclic carbene (NHC) ligands are all good σ-donors and weak π–acceptors[16,35-39]. In comparison, phosphine donors generally have higher donating capacity then nitrogen donors.

During a catalytic cycle, the *trans* effects of a ligand can play a significant role. NHC and phosphine ligands both have a similar and strong *trans* effect, both stronger than the *trans* effect of nitrogen donor ligands. Studies have shown that the counter ions of ionic metal complexes can also influence the efficiency of the catalyst[34,35]. Since 30 years, the term ``noncoordinating anion`` is commonly used when a coordinating anion , such as a halide X^-, (X = Cl - I) is replaced by a complex anion, such as BF_4^-, SbF_6^-, ClO_4^-, BPh_4^-, and BARF, *tetrakis*-(3,5-*bis* (trifluoromethyl) phenyl)borate.

1.2. Introduction to N-heterocyclic carbenes

Since the carbenes were introduced by, Doering in 1954, they became universal ligands. Since then, an extensive effort has been made to isolate the free stable carbenes. In the past few years, the chemistry of carbenes has gained importance in catalysis, thereby *N*-hetrocyclic carbene (NHC) have become an important class of compounds in a large variety of research areas[36]. *N*-heterocyclic carbenes have been of interest because of their use as spectator ligands for transition metal complexes.[42] NHCs are relatively easy to synthesize, characterize and coordinate. Their steric and electronic properties make them one of the most interesting class of ligands and organocatalysts. A number of examples show that *N*-hetrocyclic carbene are widely used as a replacement of phosphine ligands[43]. Undoubtedly, the main advantage of NHCs over phosphines is their ability to build complexes with nearly all metals, starting from electron rich transition metals such as Pd (0) and Rh (I)[44], electron poor main group metal cations such as Be^{2+}, and metals in high oxidation states such as Ti (IV), Nb (V) and Rh (VII). Interestingly, the variety of synthetic ways, which are shown on

scheme 3[45], allow convenient access to *N*-heterocyclic carbenes[46,38,47] so, that a large number of substituted, chiral, functionalized,[48] chelating,[49] immobilized,[50] or water soluble,[51] substances[48] are now available for different applications.

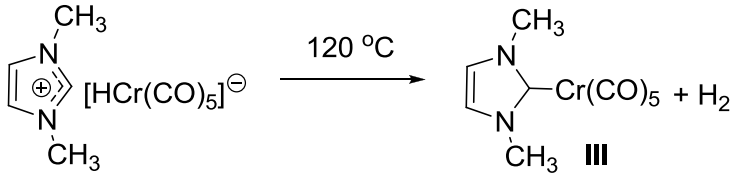


Scheme 3: Versatile *N*-heterocyclic carbenes.

1.2.1. Historical perspective

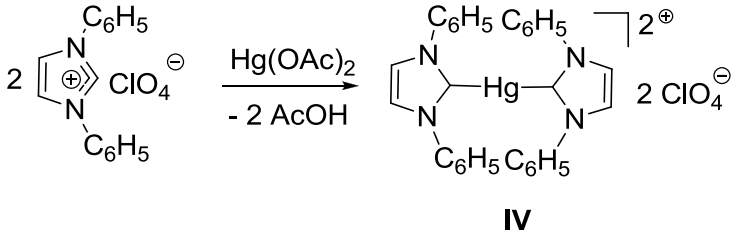
During the last two decades, *N*-heterocyclic ligands have become important in organometallic and inorganic chemistry[52-56]. Hence, they have been studied as antibiotics (with silver)[57] and anticancer drugs (with palladium and gold),[58,59] used as building blocks for supramolecular chemistry[60] and polymers.[61,62] Some NHC precursors are commercially available, essentially because they are easily accessible. The large dissociation energies associated with most NHC-M bonds make these molecules particularly useful as ancillary

ligands in catalysis. Early attempts to trap the free *N*-heterocyclic carbenes (NHCs) led to the first metal complexes of NHCs as reported in 1968[46,63] by Öfele *et al.* and Wanzlick *et al.* Scheme 4 shows Öfele´s NHC synthesis procedure.[46]



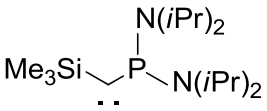
Scheme 4: Öfele´s NHC comlex.

Scheme 5 depicts the synthesis route to the NHC complex reported by Wanzlick *et al*., which was synthesized by the reaction of 1,3 diphenylimidazolium perchlorate with mercury(II) acetate.[63]



Scheme 5: Wanzlick`s NHC complex.

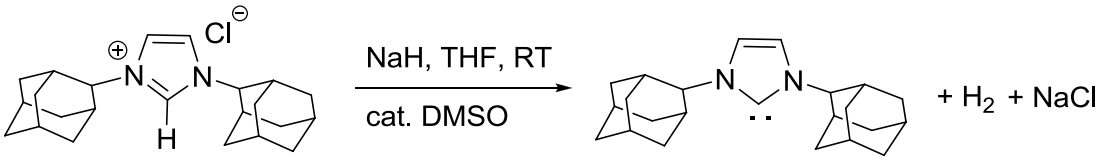
Many efforts had been performed since the first synthesis of an isolable phosphanylsilycarbene was reported in 1988 by Bertrand[57] (Figure 3). These efforts resulted in the rapid development of *N*-heterocyclic carbene (NHCs) complexes and in particular the application of NHCs as ligands.



V

Figure 3: Bertrand's carbene.

The break-through for NHCs was achieved in 1991 by Arduengo *et al,* who were able to isolate a free NHC as illustrated in scheme 6.[65] These NHC carbenes were synthesized by deprotonation of the imidazolium salt with sodium or potassium hydride in the presence of a catalytic amount of dimethylsulfoxide (DMSO). The colorless crystals of **VIb** are stable up to 240 °C without decomposition.



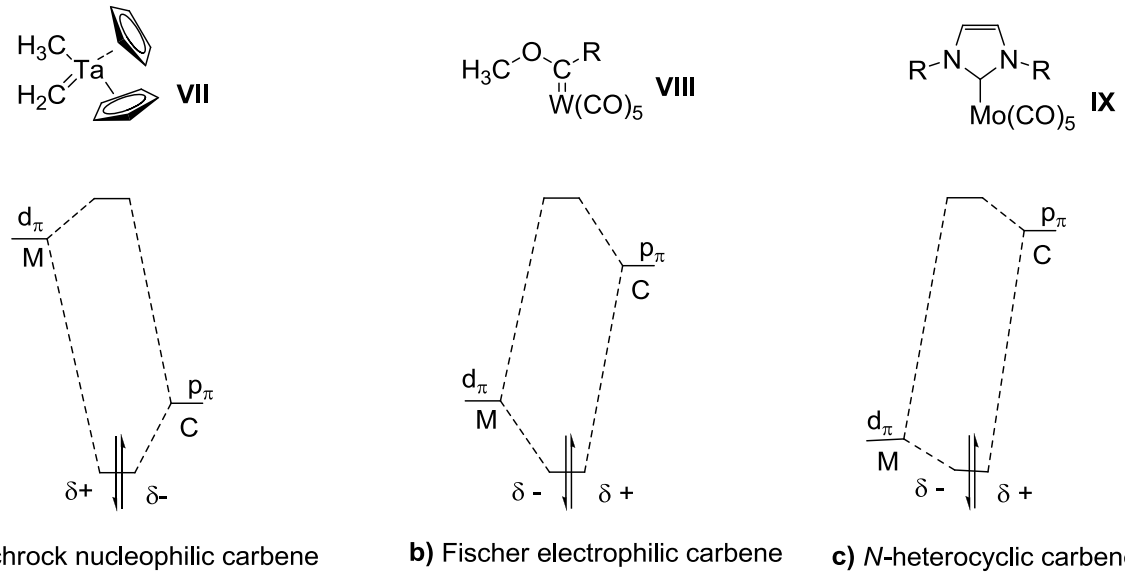
VI$_a$ **VI$_b$**

Scheme 6: Arduengo´s Carbene.

1.2.2. Properties of carbene ligands

The discovery of the compound **VII** (Figure 4a) by Schrock[66] and **VIII** (Figure 4b) by Fischer[67] has established a novel class of compounds. Fischer carbenes have one or two π–donor substituents such as N or O directly attached to the carbene carbon and show a typical behavior of electrophiles ($C^{\delta+}$). Schrock carbene complexes have nucleophilioc properties ($C^{\delta-}$) and stabilize metals in high formal oxidation states with additional donor ligands. The molecular orbital diagram, Figure 4, illustrates the bonding of Schrock, Fischer and *N*-hetrocyclic carbene complexes. The metal-carbene bond in Schrock and Fischer carbene complexes are both described as double bonds and are differing by the polarity of the

electron density[66-68]. This difference arises from the energy difference between the d_π orbital of the metal and the p_π orbital of the carbene.



a) Schrock nucleophilic carbene **b)** Fischer electrophilic carbene **c)** *N*-heterocyclic carbene

Figure 4: Partial molecular diagram of Schrock, Fischer and NHC carbene complex.

Studies have shown that carbenes are neutral species, with six electrons, with two non-bonding electrons in their valence shell [42], and are exist in two different geometries: either linear or bent, depending on the sp or sp^2 hybridization (Figure 5). The linear *sp*-hybridized carbene possess two non-bonding degenerate 2p orbitals at the cabon atom p_x, p_y orbitals. Most carbenes are bent and their frontier orbitals will be systematically called σ and p_π.

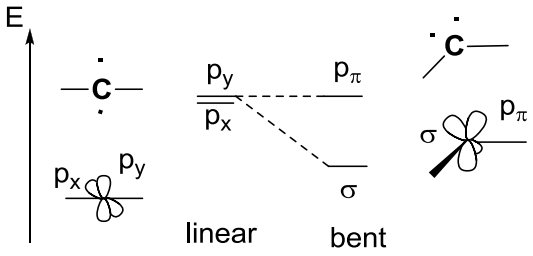


Figure 5: Relationship between the carbene bond angle and the nature of the frontier orbitals.

The non-bonding electrons can either be spin paired (singlet state) or have parallel spins in different orbitals (triplet state). Figure 6 illustrates the possible arrangements of these two electrons in four different possible electronic configurations, however, only the $^3B_1$ **(i)** and $^1A_1$ **(ii)** states.[56a,68-70.]

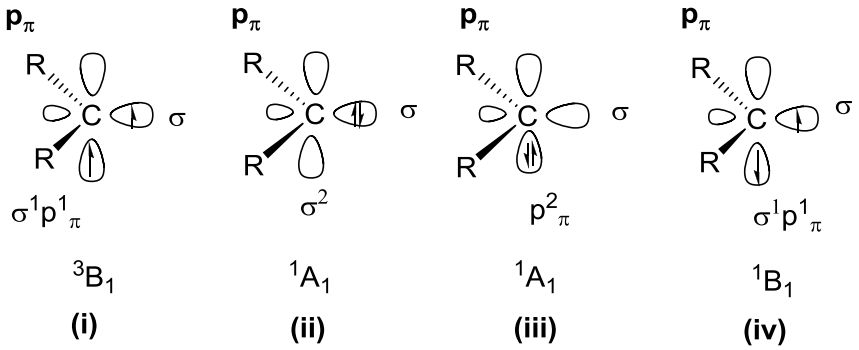


Figure 6: The four different electron configurations possible for a basic six-electron divalent carbene compound.

Four possible electronic configurations (^{3}**B$_1$**, ^{1}**A$_1$**, ^{1}**A$_1$**, ^{1}**B$_1$**): with one electron in both σ and p_π orbital assigning the carbene a triplet state (^{3}**B$_1$**), or with the pair located in either the σ (^{1}**A$_1$**) or the p_π (^{1}**A$_1$**) orbital, resulting in a singlet state. The energy state (^{3}**B$_1$**) has one electron in the σ and one in the pπ, as for (^{1}**B$_1$**) state, but with antiparallel spins.

The reactivity of carbenes depends on their ground state spin multiplicity, a singlet carbene with a free orbital and one filled with a pair of electrons can be seen as amphiphilic, potentially able to be attacked by either a nucleophile or an electrophile.[71-76] The triplet carbenes with a single electron in each orbital are diradicals. Calculations by Hoffmann[77] predicted that the bigger the gap between the σ and p_π orbital is, more likely the carbene will be in singlet state configuration, while a low energy gap will induce a triplet state carbene. Steric and electronic effects play an important role in the understanding of the reactivity of carbenes.

1.2.3. Synthesis of N-heterocyclic carbene

N-hetrocyclic carbenes can be obtained from the corresponding azolium salts imidazolium, imidazolinium, triazolium, pyrazolium, benzimidazolium, thiazolium, and oxazolium salts by deprotonation. The functional groups can be introduced in the imidazole side chain by conventional synthetic methods. Figure 7[78a] shows, the principal classes of NHCs derived from azolium salts.

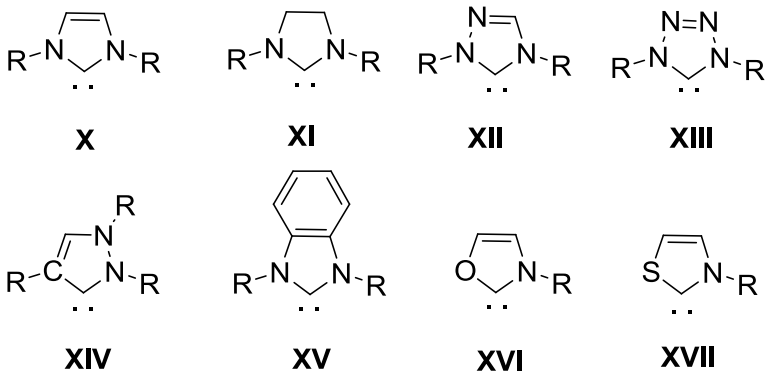
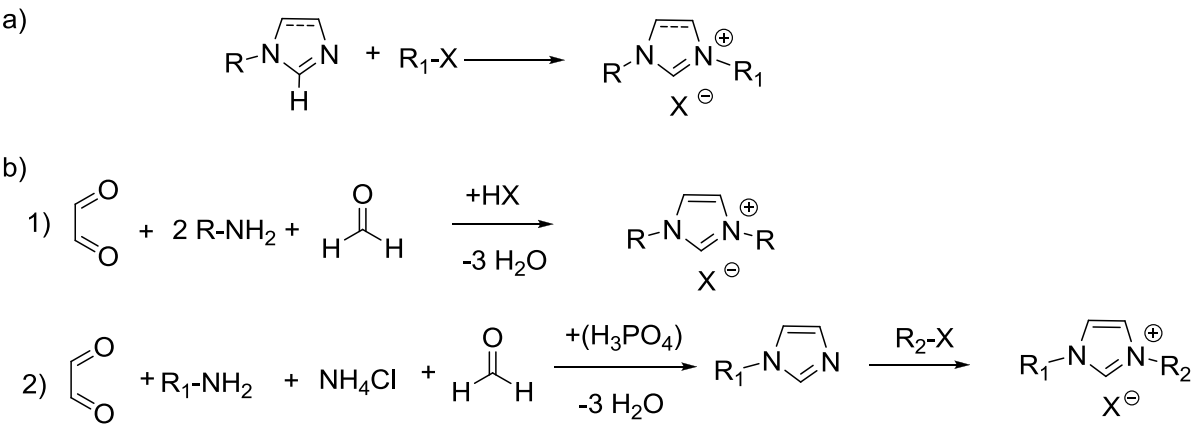
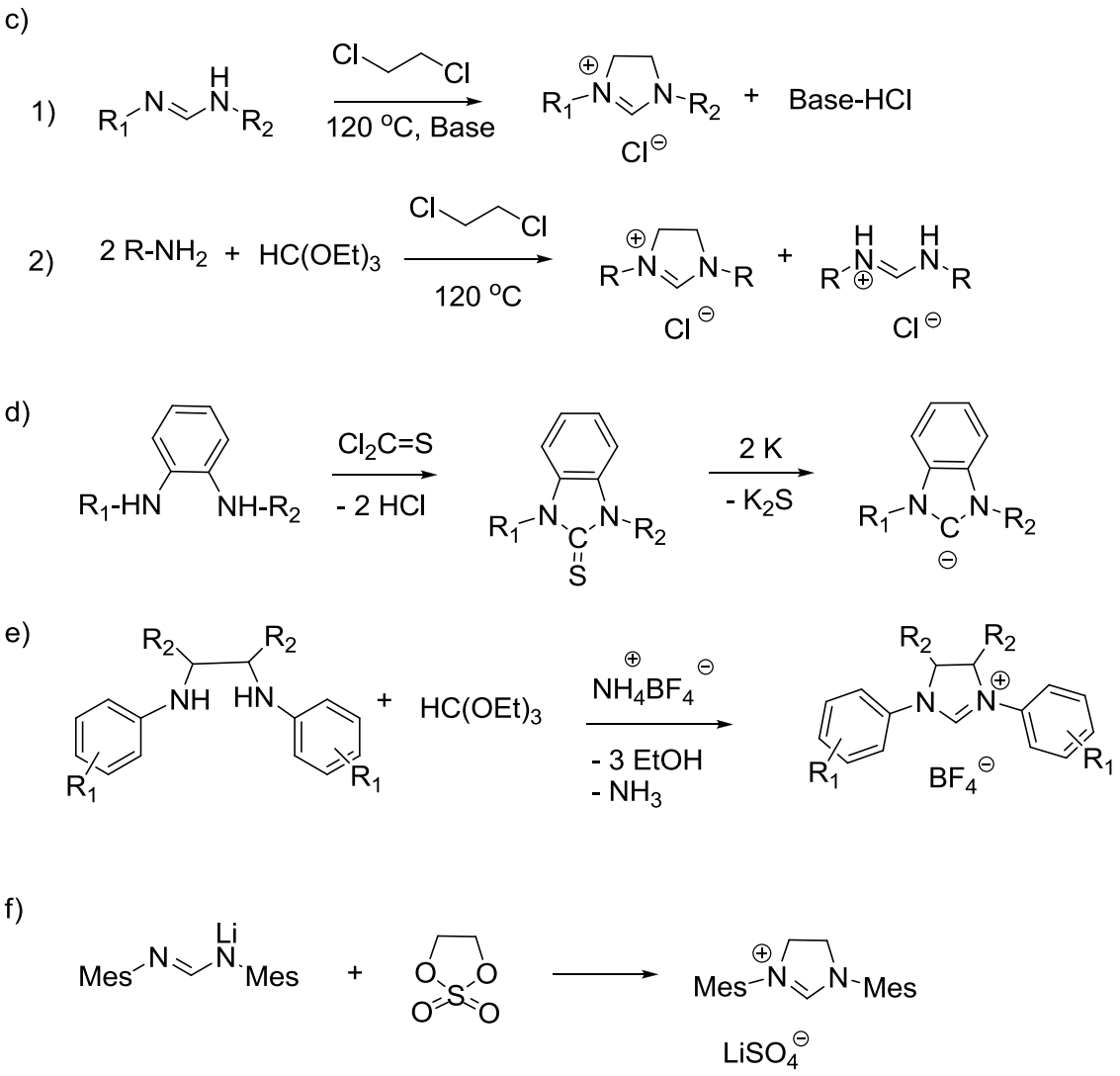


Figure 7: NHCs derived from azolium salts.

There are six different routes for the synthesis of unsaturated imidazolium salts shown in Scheme 7a-f[78a]:





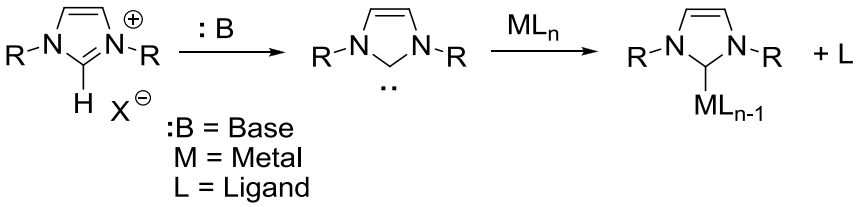
Scheme 7: The synthesis of imidazolium salts.

The first route is the alkylation of substituted imidazoles / imidazolines with alkyl / aryl halides to give the substituted imidazoles (a).[78b, 79.] Symmetrical imidazolium salts can be prepared by reacting primary amines, glyoxal and paraformaldehyde (b_1). Unsymmetrical imidazolium salts are obtained if one equivalent of primary amine and one equivalent NH_4Cl are reacted with glyoxal and paraformaldehyde followed by the quaternization of one nitrogen atom with an alkyl halide (b_2)[64, 66, 80-82]. Another ring closing reaction that leads to imidazolium salt was developed recently and involves the reaction of formamidines with dichloroethane in the presence of a base. In addition to this methodology is also applied for the synthesis of

symmetric imidazolinium chlorides(c).[83] Some azolium salts can be generated by desulfuration of cyclic thiourea derivatives, however under drastic conditions (d).[69] The formation of symmetrical or unsymmetrical imidazolinium salts can be achieved via the ring closure reaction of orthoformate in the presence of ammoniumtetrafluoroborate at 120°C, in acidic conditions (e).[66] An alternative route to imidazolinium salts is addition of *bis*-electrophiles to lithiated formamidines (f).[84]

1.3. Complexation to the metals

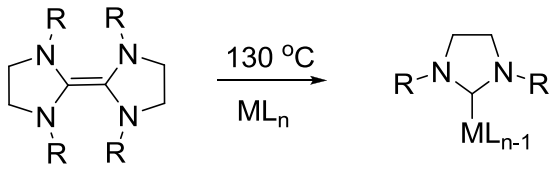
The Scheme 8 depicts the general design for the synthesis of NHC complexes.



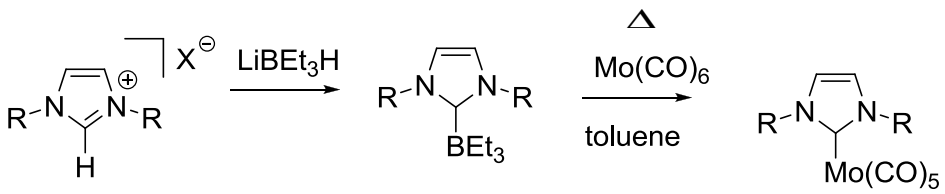
Scheme 8: General routes for the synthesis of NHC complexes.

Some examples for the preparation of NHC-metal complexes are shown in Scheme 9[78a]:

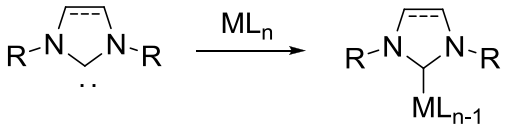
a)

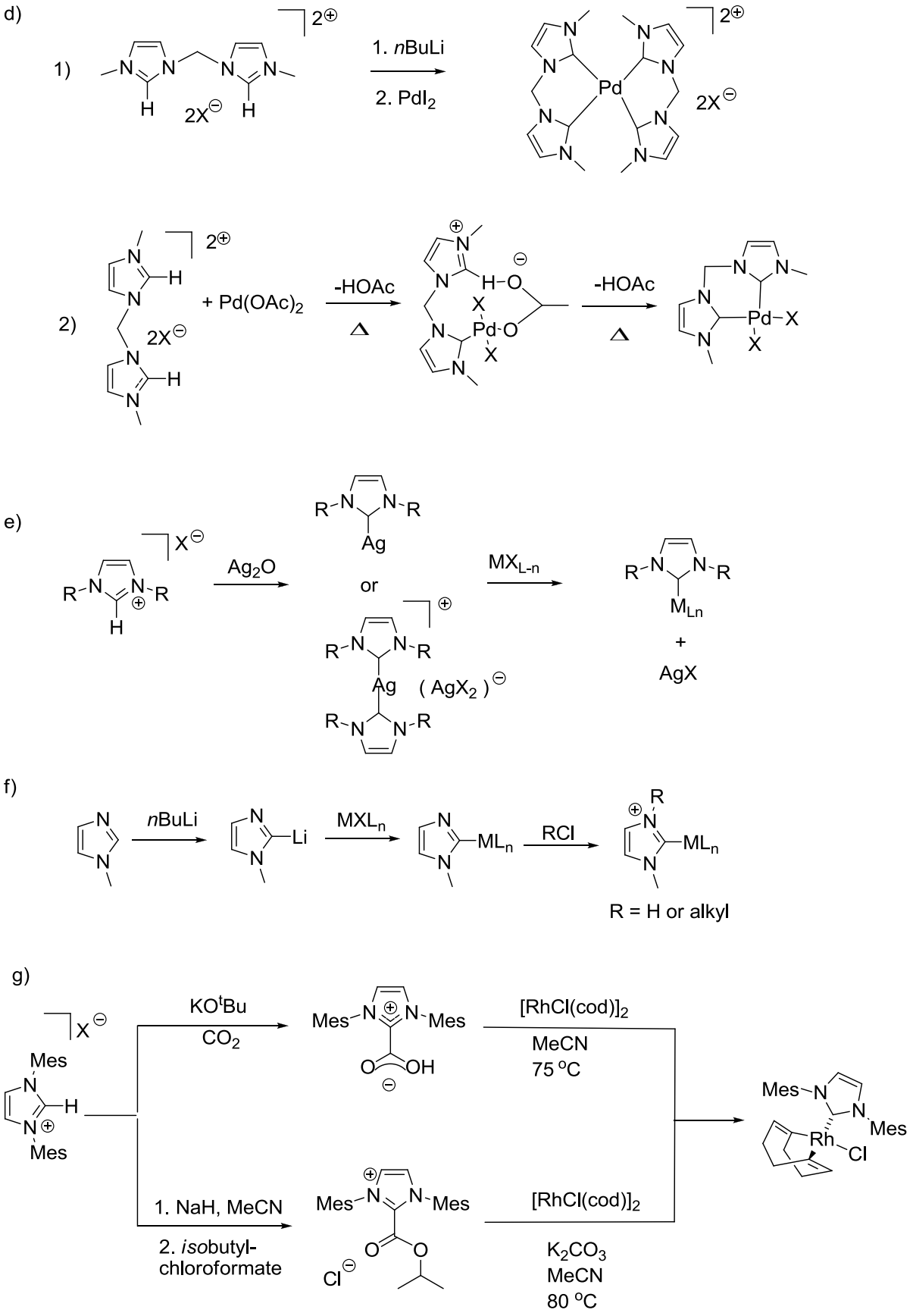


b)



c)





Scheme 9: General routes for the preparation of NHC-metal complexes.

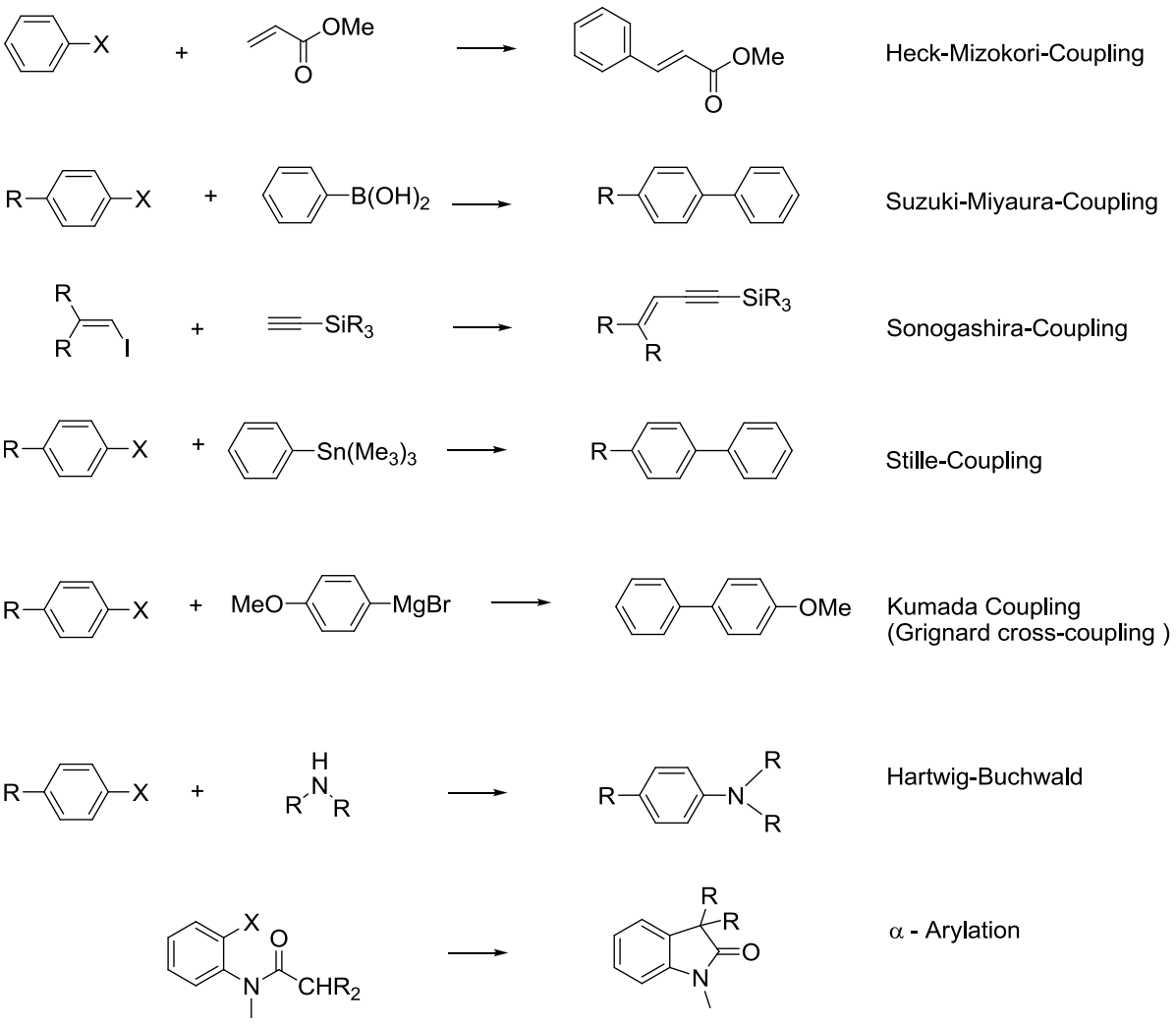
The first route is an insertion of metal into an electron rich C=C bond of an olefin. The thermal cleavage is performend with electron rich alkenes and saturated NHCs are obtained in this way. This method was introduced by Lappert and coworkers (a).[85] An NHC-borane adduct can be used as a versatile stable synthon for the preparation of NHC complexes.[86] Next procedure is similar to that reported by Angelici and co-workers (b). Another procedure starts from isolated free carbenes since these carbenes are sterically as well as electronically stable. The ability of these carbenes to replace labile ligands is a big advantage in coordination chemistry (c). *In situ* deprotonation of azolium salt can be carried out by two ways: (i) either with an external base, mono, bis and tridentate NHC ligands have been prepared in this way, or (ii) deprotonation of metal complex containing basic ligand, with acetate (d). Another convenient method was developed by Lin's group.[87] According to this method, silver-NHC complexes were firstly synthesized and later transmetallated with several other metals. Silver NHC complexes are prepared by the corresponding imidazolium salt with Ag_2O at room temperature. A weak NHC-Ag bond makes this reagent a good transfer agent. Complexes can be substituted by Au, Cu, Ni, Pd, Pt, Rh, Ir or Ru. The driving force for the metal exchange reaction is the lability of the NHC-Ag bond and insolubility of the silver halide (e). The NHC complexes can be achieved by the transmetallation with lithiated heterocycles(f).[88] Another method was reported in 2005 by Crabtree and coworkers. According to this method, the preparation of NHC metal complexes is achieved by a two step reaction. First deprotonation takes place which results in C2-carboxylate or ester intermediates and continues with decarboxylation of the intermediates and coordination with rhodium to form a complex (g).[89]

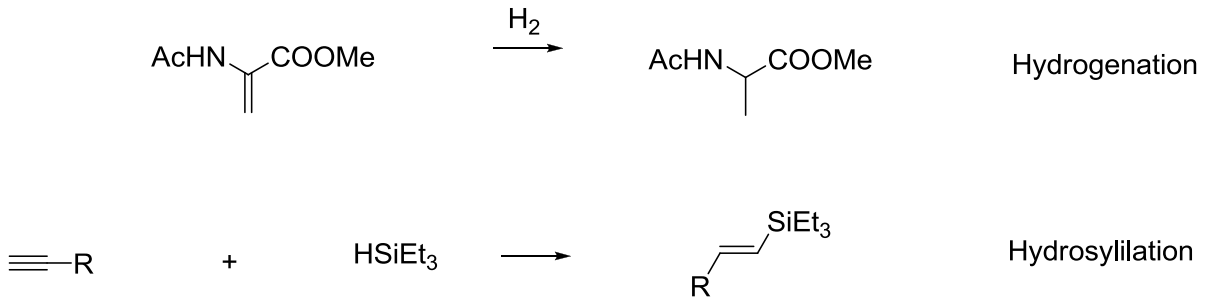
1.4. N-hetrocyclic carbene complexes in catalysis

The main reasons for the success of *N*-heterocyclic carbenes in catalysis are their properties such as the strong σ-donating ability, a strong metal-carbon bond and poor π-accepting

ability leading to the formation of many stable metal complexes used in organometallic chemistry and catalysis.[41, 90, 91]

Scheme 10 summarizes some catalytic reactions involving *N*-heterocyclic carbene catalysts[92c-j, 93] including polymerization (e.g. copolymerization of ethylene and CO)[92b], Heck-, Suzuki[68]-, Sonogashira[93a-d]-, Stille[92f]- and Kumada coupling[56], Hartwig-Buchwald-reactions[92g,h], α-arylation of amides, hydrogenation[68,93a,93i] hydrosilylation,[92k-q,] hydroboration,[92k] hydroformylation,[92r-u] allylic substitution,[92u] methylation, ruthenium catalyzed olefine metathesis, transfer hydrogenation[92a-b] reactions and cross coupling reactions to form C-C or C-N bonds.[36, 92a-b, 93e,l,m, 94.], and many other[92o,p, 93j,k]





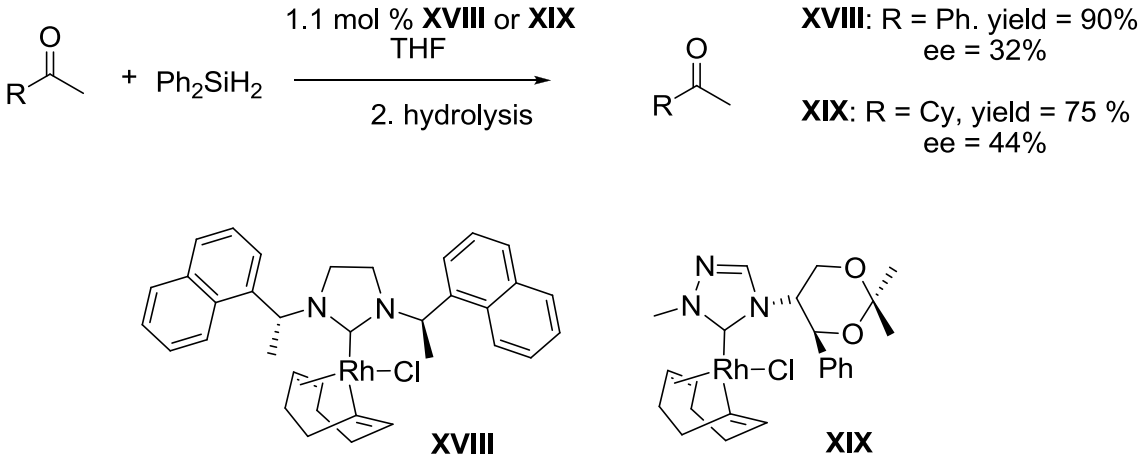
Scheme 10: NCH-M catalyzed reactions.

1.4.1. Applications of NHC-metal Complexes in Hydrosilylation and Transfer hydrogenation reactions

As already mentioned previously, NHCs with their desirable properties as transition metal ligands have often surpassed phosphine based metal catalysis both in activity and scope of the application[92m, 95, 96] Undoubtedly, this is due to their advantages as transition metal ligands such as resistance towards dissociation, easy accessibility and tunability of the molecular architecture. NHC complexes consisting of electron rich metal centers supported by chiral NHC ligands have been applied to hydrosilylation, hydrogenation and a plethora of other chiral transformations[36, 92, 93]

1.4.1.1. Hydrosilylation

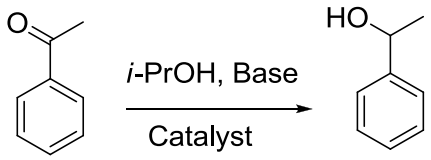
Scheme 11 depicts NHC complexes, which were reported as the first stereo selective hydrosilylation agents of acetophenone and cyclohexylmethyl ketone, respectively, by Herrmann[93j] and Enders[97] *et al.* Enders successfully applied NHC compounds and their derivatives in carbene catalysed asymmetric nucleophilic acylation processes. Ruthenium, rhodium and iridium complexes are usually used as catalyst metals. Based on these reports, the field has largely expanded and now there are many reports on the use of NHCs for asymmetric homogeneous catalysis.[98]



Scheme 11: The first example of asymmetric hydrosilylation.

1.4.1.2. Transfer Hydrogenation

Catalytic transfer hydrogenation of ketones to alcohols with 2-isopropanol is also a well studied area in organic chemistry.[21] This method is successful without the use of hydrogen pressure, which makes it a low-cost process.[99] Transfer hydrogenation (TH) can take place under two major types of mechanisms: a metal-template concerted process [Meenvein-Pondorf-Verley (MPV) reduction] and metal hydride mediated process (hydridic reduction).[99]



Scheme 12: Transfer hydrogenation of acetophenone.

Transfer hydrogenation of ketones to alcohols with 2-propanol is more attractive than the reaction with molecular hydrogen because of favorable properties of the organic hydrogen source.[100] Hard, electronically rich chiral amine complexes of transition metals are among the most widely used catalysts for that process.[99b] Because of this rhodium and iridium

complexes with NHC-ligands were applied for the transfer hydrogenation of acetophenone with 2-propanol and KO^{t}Bu (Scheme 12).

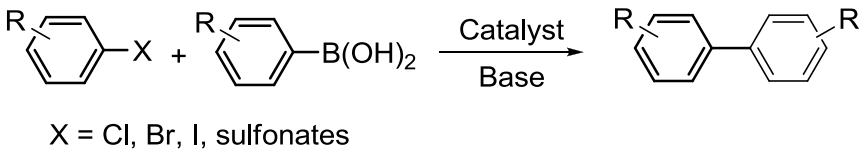
There are many advantages associated with the transfer hydrogenation reaction over the hydrogenation. Undoubtedly, the transfer hydrogenation is cheaper, safer and the yield and enantiomeric excess are comparable to that obtained from gaseous hydrogenation. The low cost and the desirable properties of the applied hydrogen donor as well as the operational simplicity contribute to the advantage. [99b]

1.4.2. Suzuki-Miyaura coupling reaction

During the past 20 years, palladium catalysis has become an extremely active researched field within organometallic chemistry.[94] Palladium catalysts have gained widespread use in industrial and academic synthetic chemistry laboratories as due to their high activity in a C-C and C-heteroatom coupling reactions. The advantages associated with N-heterocyclic carbene complexes are: (i) cheap, (ii) easy to prepare, (iii) non-toxic, (iv) thermally stable and (v) exceptionally stable M-C bonds towards hydrolysis under high temperatures.[101]

The Suzuki-Miyaura cross-*coupling* reaction is the coupling of arylboronic compounds with aryl halides or pseudohalide*s* (Scheme 13). The reaction has emerged as one of the most important carbon-carbon bond formation methods in the synthesis of organic materials, pharmaceutical agents, and natural products.[64] Advantages of using the air and moisture stable aryl boronic acids make this reagent particularly attractive when compared to Stille and Kumada reagents, because they are fairly insensitive to water and oxygen, relatively cheap, display a low toxicity and are thermally stable. The activity of the various phosphine ligands were tested for the palladium catalyzed Suzuki cross-coupling reaction using different aryl halide substrates.[102] [93c]

In recent years, NHCs have been used as ligands for a varity of transition metal-catalysed cross-coupling reactions including the Suzuki reaction.[36]



Scheme 13: General Suzuki coupling reaction.

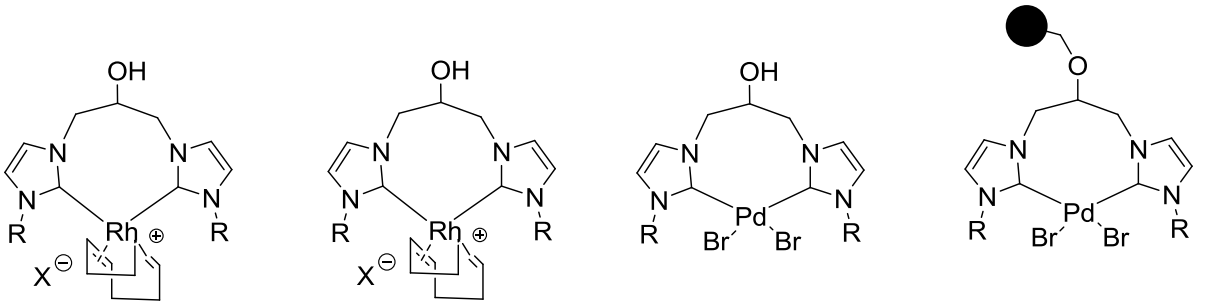
Several Suzuki-Miyaura coupling reactions have been developed with different substrates, which are good examples for coupling reactions catalyzed by M-NHC complexes in organic solution. The best examples obtained by Herrmann *et al*., indicated to have higher activity with bis-NHC Pd(0) for Suzuki cross couplings of both electron-rich and electron-poor aryl chlorides with aryl boronic acids at the room temperature[36].

1.5. Objectives

In the past, transition metal NHC complexes have been applied as homogeneous and heterogeneous catalysts, achieving good to excellent results. *N*-hetrocyclic carbene complexes have been explored by numerous research groups and became an important class of complexes in organometalllic chemistry in the last 20 years. This attention was due to the high thermal, chemical stability and high dissociation energies. Additionally more and more bis(NHC)-complexes with a function group on the bridge found an application.

The success of bis(NHC) rhodium and palladium organometallic complexes synthesized by Strassner, Peris, Crabtree and co-workers, which were found to be highly active catalysts in transfer hydrogenation and Suzuki coupling reactions, respectively, prompted us to synthesize similar bis(NHC) complexes.

The goal was to synthesize new bidentate bis(NHC) ligands containing a functionalized bridging group that could be used as a linker to a solid support. Furthermore the corresponding rhodium and palladium complexes should be prepared and immobilized on a solid support such as polystyrene resin.



1c R = Me
2c R = Et
3c R = ^{i}Pr
4c R = ^{t}Bu
5c^{PF6} R = Bn
6c R = Mes
X = PF_6

5c^{BPh4} R = Bn
X = BPh_4

1e R = Me
5e R = Bn

6f R = Me

Figure 8: Bis(NHC) Rhodium (I) und Palladium (II) complexes.

Finally the catalytic properties of the free and immobilized complexes should be investigated in a comparative study; while the potential of the rhodium complexes was to be evaluated for the hydosilylation and transfer hydrogenation of ketones, the Palladium complexes should be examined as catalysts for Suzuki coupling.

The focus of a second, smaller project was to investigate the potential of hemilabile ligands in the Pd - catalyzed Suzuki coupling. For this purpose a new donor - functionalized NHC ligand should be developed and investigated for the Suzuki coupling of a broad range of arylhalogenides.

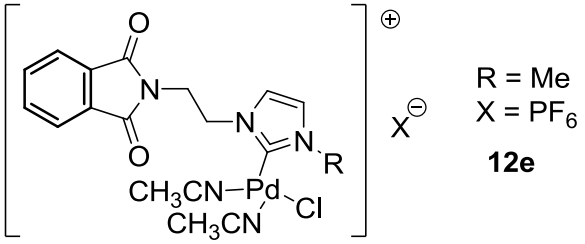


Figure 9: Phthalimido-functionalized N-heterocyclic mono-carbene complex of palladium(II).

Chapter 2

Bridge functionalised bis-*N*-heterocyclic carbene rhodium(I) complexes and their application in catalytic hydrosilylation

This chapter contains the following publication:
Claudia S. Straubinger, Nadežda B. Jokić, Manuel P. Högerl,
Eberhardt Herdtweck, Wolfgang A. Herrmann, and Fritz E. Kühn,
Journal of Organometallic Chemistry, 696, **2011**, 687-692

Symmetrical bridged bis-*N*-heterocyclic carbene rhodium(I) complexes and their catalytic application for transfer hydrogenation reaction

This chapter contains the following publication:
Nadežda B. Jokić., Mei Zhang-Presse, Serena Li Min Goh, Claudia S. Straubinger,
Bettina Bechlars, Wolfgang A. Herrmann, Fritz E. Kühn
Journal of Organometallic Chemistry, 696, **2011**, 3900-3905

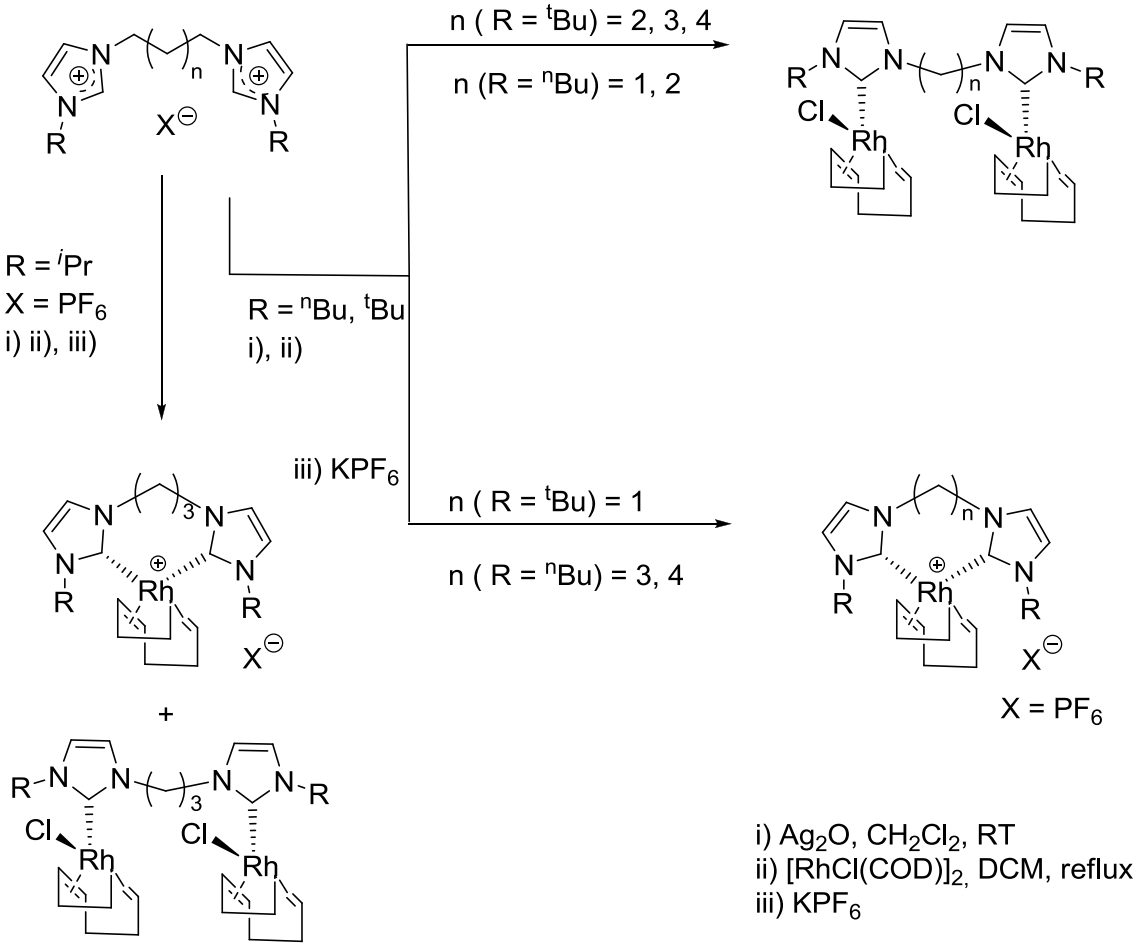
2. Symmetrical bridged bis(*N*-heterocyclic carbene) rhodium(I) complexes and their catalytic applications for hydrosilylation and transfer hydrogenation reactions

In the light of the literature, Rh-complexes play an important role in organometallic chemistry [103-105]. *N*-heterocyclic carbenes as ligands in organometallic complexes act as strong σ-donors and weak π-acceptors. In many cases NHC complexes are air- and moisture stable and show high thermal stability. As it is explained in the introduction section, many Rh-complexes bearing NHC ligands are efficient catalysts for a range of organic transformations such as hydrosilylation and transfer hydrogenation. Rh occupies a particular position in the late transition metal chemistry of NHCs. It belongs, along with Pd and Ni, to the "heavyweight category" in terms of catalytic applications[103]. It is also one of the very first late transition metals to have shown promising potential with NHCs, almost 20 years ago. Many novel [(NHC)Rh] complexes are important not only for their catalytic applications but also for their various kinds of biochemical applications.[106.].

A wide range of bis(NHC)-complexes were studied by Crabtree, Peris and their co-workers. The Rh species of [Rh(III)bis-carbene)$OAcI_2$] was firstly synthesized and subsequently tested as a catalyst by this group.[107] They also have published chelating Rh(I) bis-carbene compounds. The reaction of silver bis-imidazolylidene complexes with $[Rh(COD)Cl]_2$ can either yield dimetallic complexes of Rh(I) with a bridging bis-imidazolylidene, or monometallic Rh(I) complexes with a chelate bis(NHC) ligand, depending on the length of the linker between the azole rings and on the reaction temperature (Scheme 14)[108]. The size of the N-subsituents also contributes to the final structure of the complex.[109]

In recent years the interest in "green" environmentally benign chemistry has been continuously increasing. In this context, the immobilization of NHC-metal complexes on insoluble supports to facilitate their reuse and recycling is emerging as a preferable

alternative for the application of homogeneous catalysis, which usually requires energy intensive processes to separate catalyst from product. In order to achieve immobilisation more easily a functional group is attached to the complexes to allow a connection to the surface. Ligands with tethered hydroxy groups have been successfully utilized for the immobilization of other catalysts before, usually accounting for quite low leaching[24a-c.] This concept was applied to synthesise novel hydroxy-functionalized bridged bis-carbene complexes.

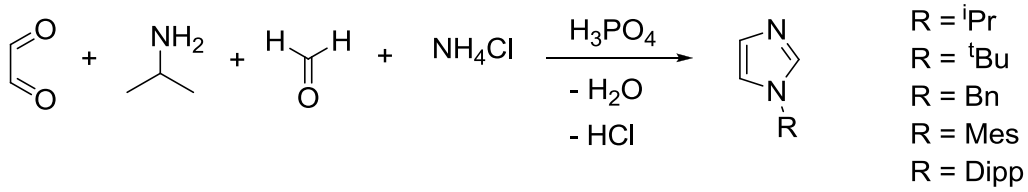


Scheme 14: Synthesis of bis(NHC) Rh(I) complexes.

2.1. Synthesis of bis(N-hetrocyclic carbene) ligands

2.1.1. Synthesis of the functionalized bis-imidazolium dibromide salts

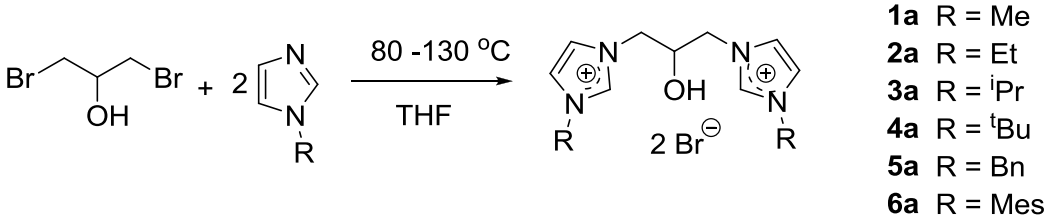
The bridged bis-carbene ligands have often been prepared from *N*-alkyl or aryl imidazolium salts with different dibromoalkanes. The preparation of the imidazolium precursors is usually straightforward from commercially available products. The substituted imidazole precursors are accessible via one-pot synthesis route according to Gridnev and Mihaltseva. (Scheme 15) The products can be purified by extraction, recrystallization or distillation.



Scheme 15: Synthesis of *1*-substituted imidazoles.

A various kinds of modified bridged imidazolium salts were prepared by general synthetic route. Alkyl - and – aryl - bridged bis-imidazolium salts are typically prepared by reacting two equivalents of the corresponding *N*-substituted imidazoles with one equivalent of alkyl- or aryldihalide.[23]

This method was successfully applied to synthesize novel bis-imidazolium compounds with a hydroxyl - functionalized propyl - bridge as shown in Scheme 16.



Scheme 16: Synthesis of hydroxyl - bis(imidazolium) - bromide salts.

1,3-bis (*N*-R-imidazolium) propan-2-ol with R = methyl (Me), ethyl (Et), *iso*propyl (^{i}Pr), *tert*butyl (^{t}Bu), benzyl (Bn), mesityl (Mes) were obtained by the reaction of *N*-substituted imidazole with 1,3-dibromopropan-2-ol in THF at reflux temperature in a pressure tube. The air stable, hygroscopic products were purified by washing with THF and were dried under vacuum. All bromide salts are soluble in polar solvents such as methanol and dimethylsulfoxide. All are air and moisture stable except compound **3a** which is very hygroscopic and should be stored under argon atmosphere.

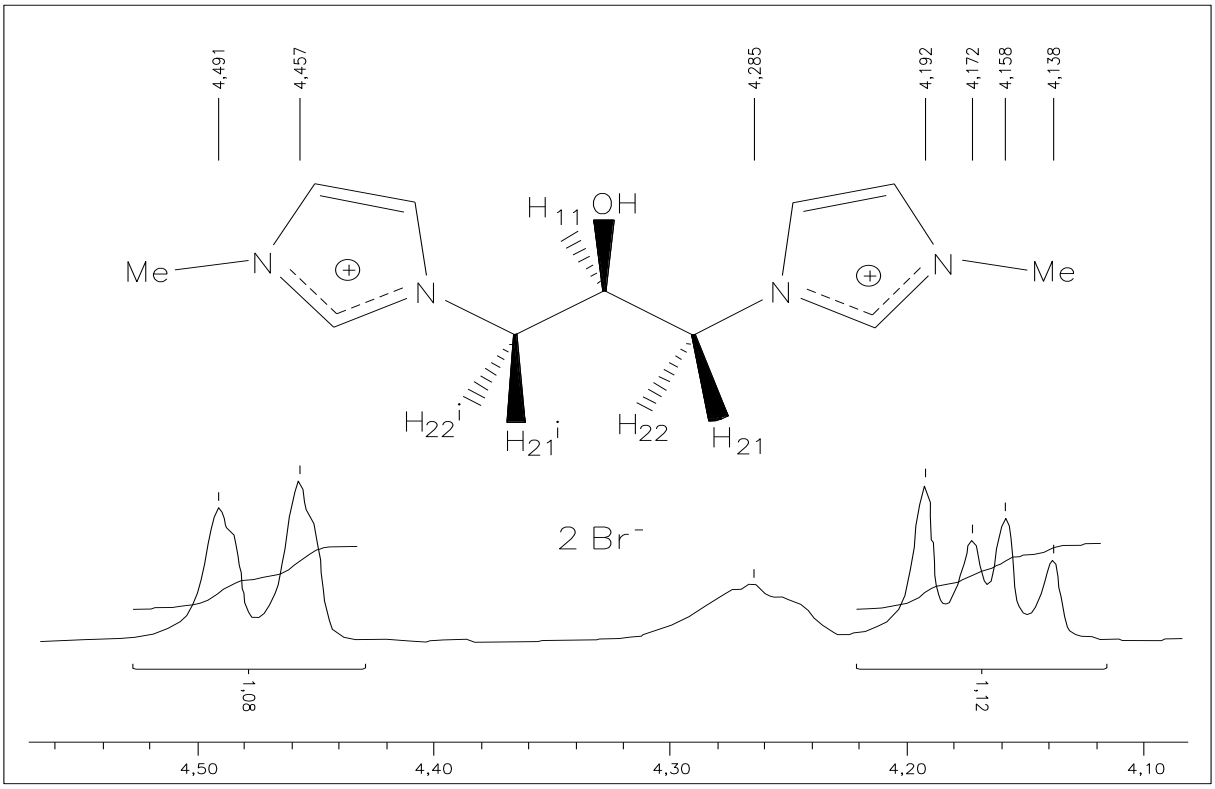


Figure 10: ^{1}H NMR spectrum of ligand **1a**.

The ^{1}H NMR spectrum of ligand **1a** in DMSO-d_6 exhibits distinct resonances at 9.22 ppm for the NC*H*N proton. As shown in Figure 10, two different coupling constants were determined for the bridge protons: 8Hz for the ^{2}J-coupling of the protons H 22 and H 21. 13.6 Hz for the ^{3}J-coupling between the proton H22 and H11. This is consistent with the crystal structure of **1a** (Figure 11). The crystals suitable for X-ray analysis were obtained by slow diffusion of

THF into a saturated methanol solution of **1a**. The torsion angle between H11−C1−C2−H22 is -66° and between H11−C1−C2−H21 is 176° (Figure 10). According to the Karplus-Curve, the coupling of vicinal protons reaches a minimum when the angle between them is 90°. This is in accordance with the NMR date.

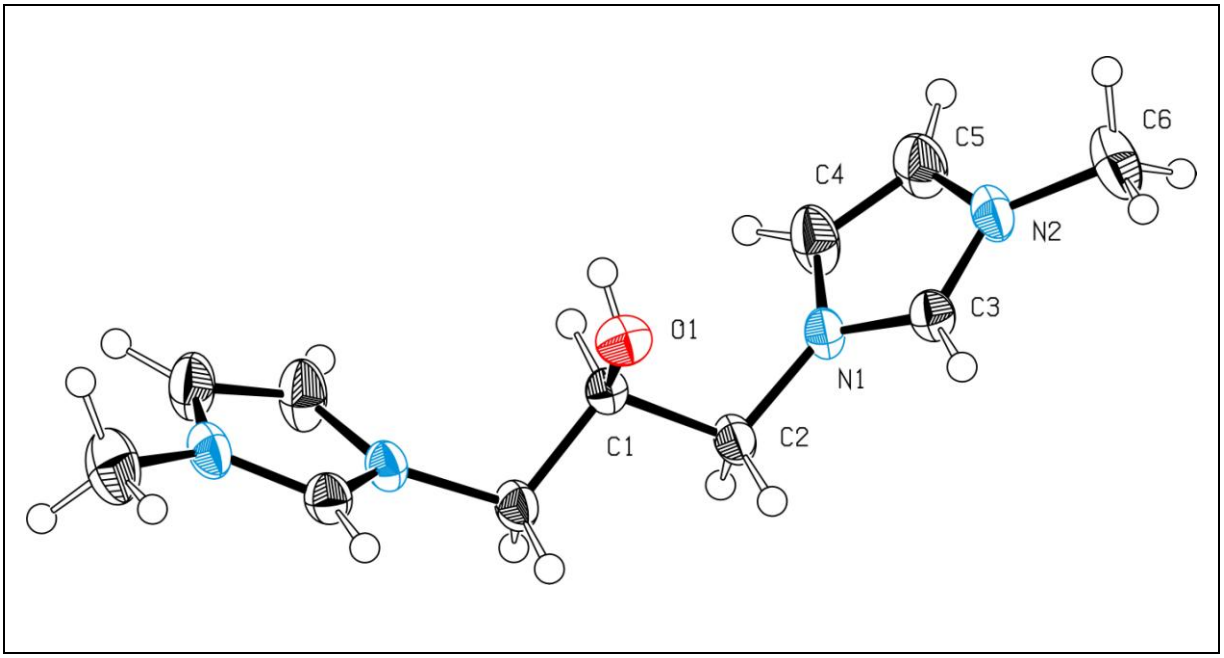
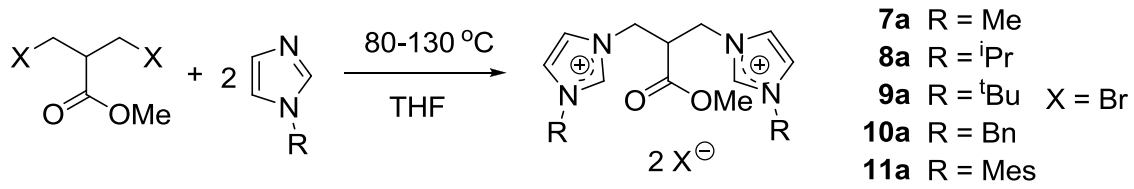


Figure 11: ORTEP style representation of the di-cation of the solid state of **1a**·CH_3OH as determined by single-crystal X-ray crystallography. Thermal ellipsoids are given at a 50% probability level. Solvent molecules and counter ions are omitted for clarity. Selected bond lengths Å and angles: C1-C2 1.521(3), C1-C2^{I} 1.521 (3), N1-C2 1.466(3), N1-C3 1.323(3), N1-C4 1.375(3), N2-C3 1.334(3), N2-C5 1.372(3), N2−C6 1.467(3), C4−C5 1.346(4), O1−C1 1.411(4), O1−C1−C2 109.8(2), C2−C1−C2^{i} 107.0(2), N1−C2−C1 111.0(2), C2−N1−C3 124.9(2), C2−N1−C4 126.1(2), C3−N1−C4 108.9(2), N1−C3−N2 108.3(2), C3−N2−C5 108.6(2), C3−N2−C6 125.3(2), C5−N2−C6 126.1(2), N1−C4−C5 107.0(2), N2−C5−C4 107.2(2). ^{i}symmetry operation for equivalent atoms (x, ½-y, z).

The formation of compounds **1a-6a** was verified by the appearance of the NC*H*N peak at around 9 ppm in the ^{1}H-NMR spectra and 137 ppm in the ^{13}C-NMR spectra, which are in the typical range for the for the NC*H*N proton and the N*C*HN carbon atom, respectively, of imidazolium salts.

Methoxycarbonyl-functionalized Bis(imidazolium)-dibromide (R = Me, ^{i}Pr, ^{t}Bu, Bn, Mes) were achieved by the treatment of *N*-substituted imidazoles with Methyl 3-bromo-2-(bromomethyl)propionate in THF at reflux temperature in a pressure tube (Scheme 17).



Scheme 17: Synthesis of Methoxycarbonyl-Bis(imidazolium)-bromide salts.

The next two Tables (2 and 3) summarize an overview (temperature, reactions time, and yield) of the prepared bridged bis-(imidazolium)-dibromide salts.

Table 2: Bis(imidazolium)-dibromid with hydroxyl-functionalized bridge

Compound	Substituent	Temperature [°C]	Reactions Time [day]	Yield [%]
1a	Me	80	3	82
2a	Et	80	3	82
3a	^{i}Pr	130	5	79
4a	^{t}Bu	130	5	70
5a	Bn	110	4	96
6a	Mes	130	7	65

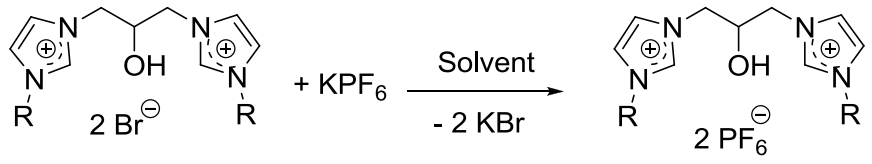
Table 3: Bis(imidazolium)-dibromid salt with methoxy carbonyl-functionalized bridge

Compound	Substituent	Temperature [°C]	Reactions Time [day]	Yield [%]
7a	Me	80	3	95
8a	^{i}Pr	80	3	93
9a	^{t}Bu	80	3	95
10a	Bn	100	5	88
11a	Mes	120	7	31

2.1.2. The anion exchange reactions

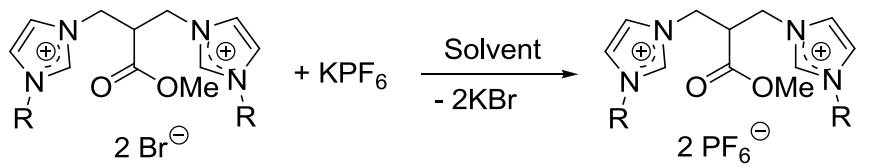
For the synthesis of rhodium(I) bis-carbene complexes, it is necessary to exchange the anion of the bromide salts with various available substituted imidazoles as bromides are strongly coordinating anions. As reported by R. H. Crabtree, the counter anions strongly influence the structure of the resulting Rh(I) bis-carbene complexes.[110] It is noted that using bromide salts enhance the formation of binuclear Rh(I)-NHC complexes. However, by using salts having weakly coordinating anions such as hexafluorophosphate, tetraphylborat, led to the formation of chelating bis-carbene complexes.

The anion exchange from the bromide salts (**1a-9a**) to the corresponding hexafluorophosphate salts (**1b-9b**) was carried out by mixing an aqueous solution of the bromide salt with a saturated aqueous solution of KPF_6 (Scheme 18 and 19).



1b R = Me
2b R = Et
3b R = ^{i}Pr
4b R = ^{t}Bu
5b R = Bn
6b R = Mes
Solvent = H_2O

Scheme 18: Anion exchange reaction; **1a**-**6a** to **1b**-**6b**, Br^- / PF_6^-.

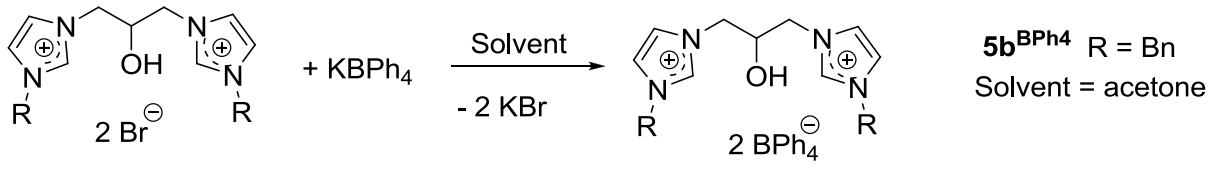


7b R = Me
8b R = ^{i}Pr
9b R = ^{t}Bu
Solvent = H_2O

Scheme 19: Anion exchange reaction; **7a**-**9a** to **7b**-**9b**, Br^- / PF_6^-.

The PF_6^- salts precipitate from the solution instantly. The formation of **1b**-**9b** was verified by FAB mass spectrometry, elemental analysis and the septet signal around -140 ppm in the ^{31}P-NMR spectra.

The exchange of the bromide anions (**5a**) with tetraphenylborate anions was obtained by the reaction of the bromide salts with $KBPh_4$ in acetone (Scheme 20) yielding compound (**5b^{BPh4}**.) The formation of compound (**5b^{BPh4}**) was verified by FAB-MS, elemental analysis and NMR spectroscopy.



Scheme 20: Anion exchange reaction Br^-/BPh_4^-.

The tables (4 and 5) illustrate the overview (yield) of the prepared PF_6^- / BPh_4^- salts.

Table 4: Bis(imidazolium) - hexafluorophosphate / tetraphenylborate with hydroxyl-functionalized bridge

Compound	Substituent	Yield [%]
1b	Me	51
2b	Et	50
3b	^{i}Pr	59
4b	^{t}Bu	60
5b^{PF6}	Bn	72
5b^{BPh4}	Bn	48
6b	Mes	39

Table 5: Bis(imidazolium)- hexafluorophosphate salt with methoxy carbonyl-functionalized bridge

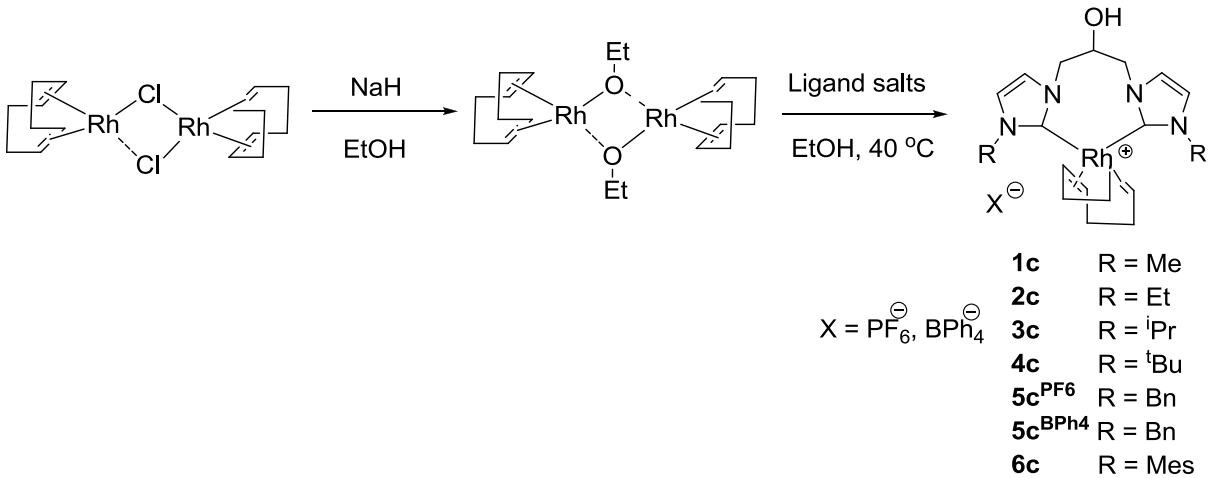
Compound	Substituent	Yield [%]
7b	Me	41
8b	^{i}Pr	89
9b	^{t}Bu	50

2.2. Symmetrical bridged bis(N-heterocyclic carbene) rhodium(I) complexes

2.2.1. Synthesis of hydroxy-functionalized rhodium(I)-carbene complexes

This work describes the synthesis of the series of bis-carbene rhodium (I) complexes containing bis-carbenes with a hydroxy functionalized alkyl bridge, which represent adequate solid precursors to be linked to a support, such as Wang-resin, or inorganic materials, such as MCM-41 for using in heterogeneous catalysis.

The rhodium(I) complexes **1c-6c** were prepared by the treatment of $[Rh(COD)Cl]_2$ with two equivalents of the corresponding PF_6^- imidazolium salts **1b-6b** (Scheme 21) at room temperature under argon atmosphere.



Scheme 21: Synthesis of rhodium(I) bis(NHC) complexes.

The *in-situ* synthesis of $[Rh(COD)(OEt)]_2$ in the presence of NaH in ethanol, which is followed by a colour change from orange to bright yellow. Then the bis-imidazolium hexafluorophosphate salt is added to the suspension and stirred over night. The yellow precipitate is filtered off, re-crystallized with DCM / Pentane.

The Rh-bis(NHC) complexes **1c-6c** were obtained as yellow crystals which are air- and moisture-stable and soluble in organic polar solvents like, DCM, THF, acetone and 1,2-dichloroethane. The synthesis of the complexes **5c**^{BPh_4} is carried out in the same way starting from tetraphenylborate salt.

The formation of the carbene complexes **1c-6c** was confirmed by NMR spectroscopy. The Rh-bounded carbon atom is shifted from 137 ppm to ~180 ppm and the signal of the C4 and C5 protons of the imidazole from 9 ppm to ~7 ppm after complexation.

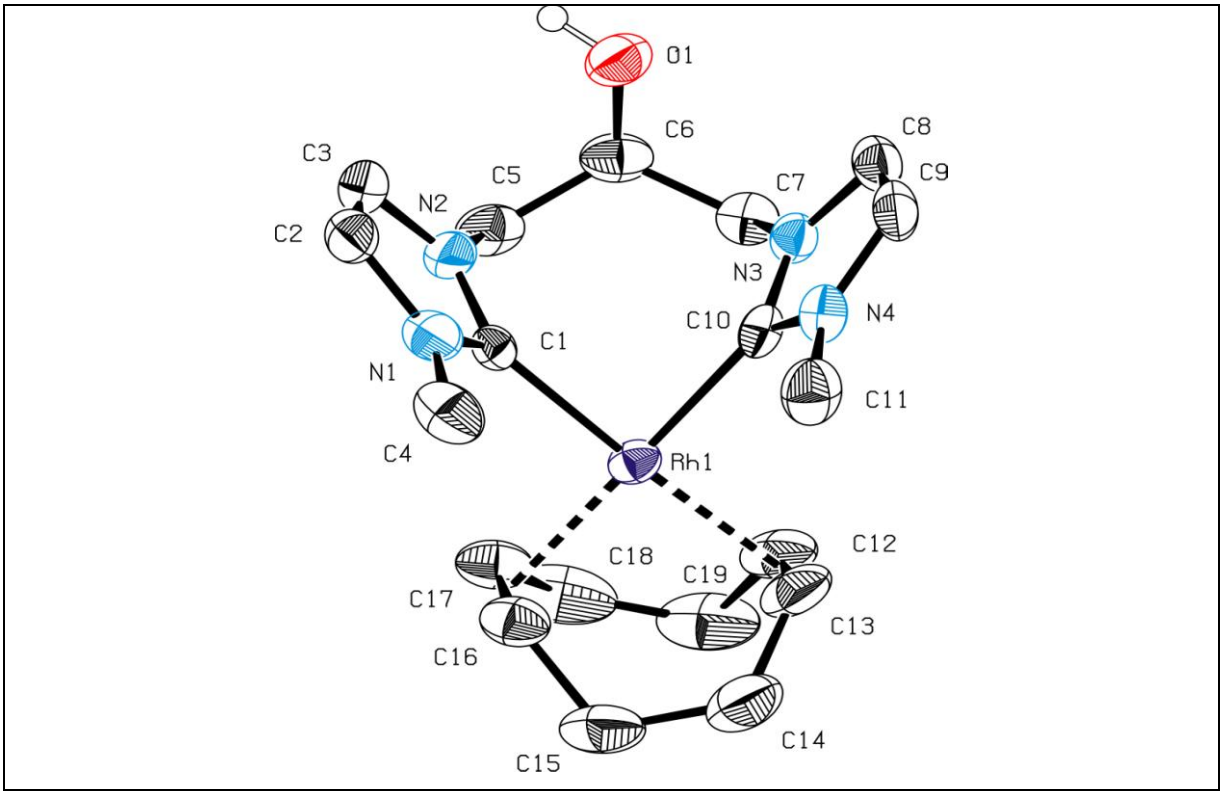


Figure 12: ORTEP style plot of the cationic part of compound **1c** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. The PF_6 anion and hydrogen atoms are omitted for clarity except the hydroxyl hydrogen atom. Selected bond lengths (Å) and bond

angles (°): Rh−C1 2.030(5), Rh−C10 2.042(6), Rh−Cg1 2.100, Rh−Cg2 2.082, C6−O1 1.418(7), C1−Rh−C10 83.6(2), C1−Rh−Cg1 176.9, C1−Rh−Cg2 96.0, C10−Rh−Cg1 93.4, C10−Rh−Cg2 178.8, Cg1−Rh−Cg2 87.0, N1−C1−N2 104.2(4), C5−C6−O1 111.1(4), C7−C6−O1 107.7(4), C5−C6−C7 118.4(5).

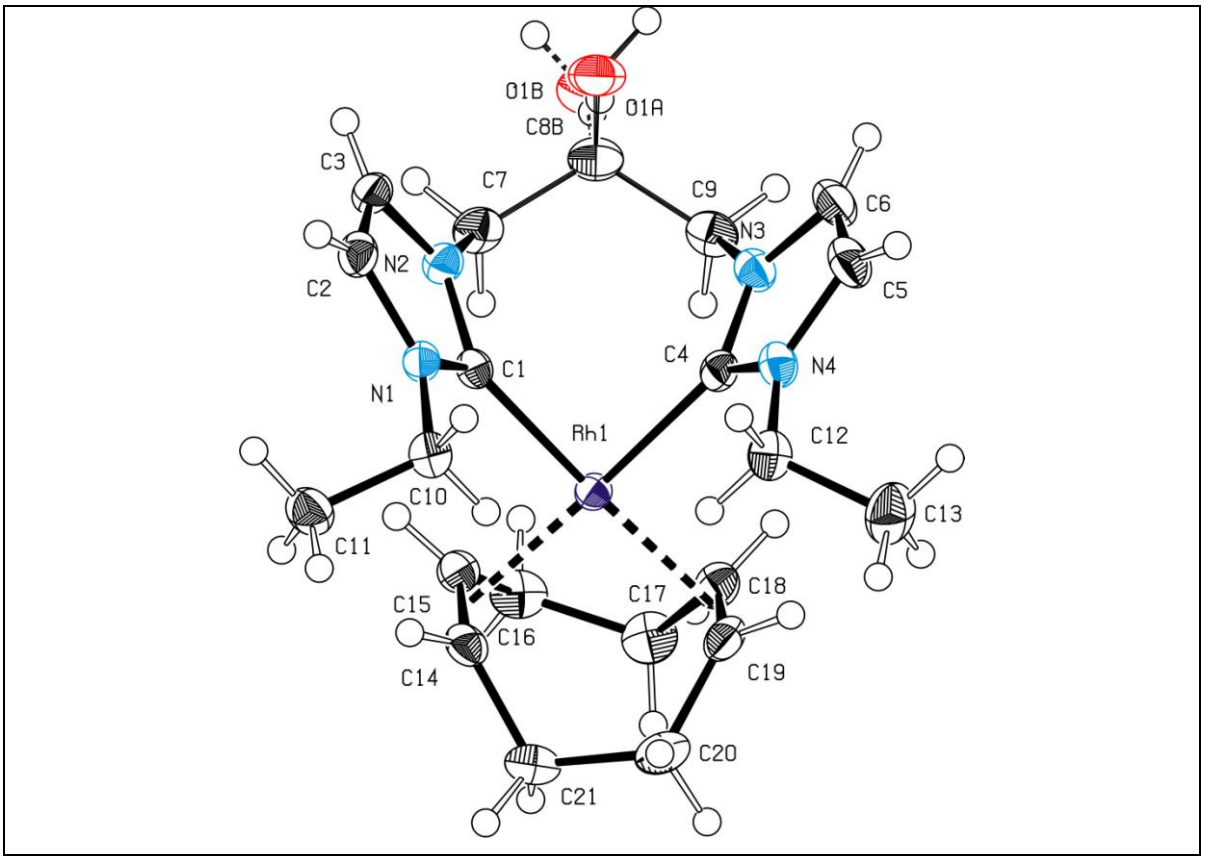


Figure 13: ORTEP style plot of the cationic part of compound **2c** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (°): Rh1 C4 2.033(3), Rh1 C1 2.037(3), Rh1 C19 2.192(3), Rh1 C15 2.195(3), Rh1 C18 2.197(3), Rh1 C14 2.197(3), N1 C1 1.352(3), N3 C4 1.363(3), N4 C4 1.355(3), C8A O1A 1.428(4), C4 Rh1 C1 83.82(10), C4 Rh1 C19 93.07(10), C4 Rh1 C15 157.09(11), C1 Rh1 C15 92.69(10), C4 Rh1 C18 94.26(10), C18 Rh1 C14 88.20(11), N1 C1 N2 104.1(2), O1A C8A C7 106.6(2), O1A C8A C9 110.5(3), C7 C8A C9 115.9(2).

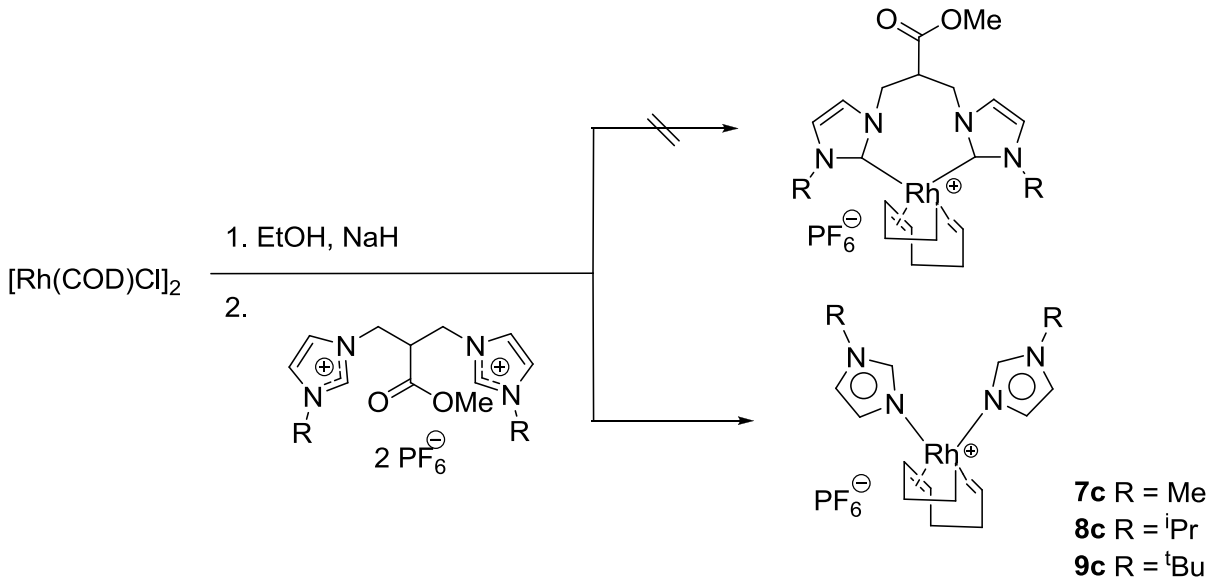
The structures of **1c** and **2c** were determined by single X-ray crystallography (Figure 12 and Figure 13). As for the related bis-carbene complexes, a boat conformation could be established[23] with a non-coordinating hydroxy group pointing away from the metal center.

The single crystals of **1c** and **2c** were obtained by vapor diffusion of diethyl ether into a concentrated solution of **1c** and **2c** in DCM. Figure 12 and 13 show the crystal structure of

the complexes **1c** and **2c**.and confirm square-planar geometry. Rh-$C_{carbene}$ bond lengths for **1c** (2.030(5) Å) and **2c** (2.033(3) Å) are in very good agreement with similar Rh-bis(NHC) complexes. The selected bond lengths and angles are summarized Tables 18-21 (Appendix).

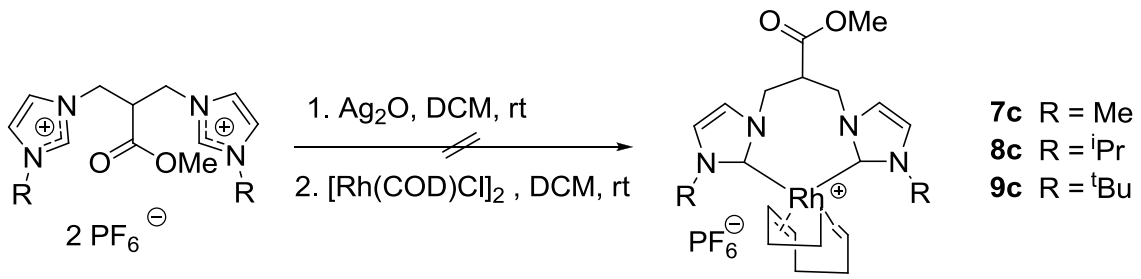
2.2.2. Synthesis of ester functionalized Rhodium(I)-carbene complexes

The corresponding bis-imidazolium salt was reacted with $Rh[(COD)Cl]_2$ in the same way as the hydroxy - functionalized carbene-complexes. Evidence for the formation of the ester-functionalized biscarbene Rh(I) complexes was detected in the NMR spectrum together with the large amounts of impurities.



Scheme 22: Reaction of the ester functionalized salts with $[Rh(COD)Cl]_2$.

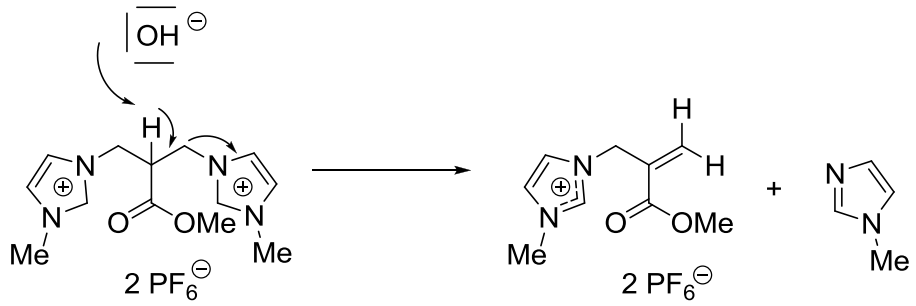
Scheme 22 illustrates the preparation procedure of the ester - functionalized complexes **7c**-**9c**. However the attempt to synthesize or isolate the desired complexes failed and only resulted in by-product *Bis(3-substituted-1H-imidazole)-(η^4-1,5-cyclooctadienyl)rhodium(I)-hexafluorophosphat* (**7c^{bp}**). The silver route also led to the formation of *Bis(3- substituted-1H-imidazole)-(η^4-1,5-cyclooctadienyl)rhodium(I)-hexafluorophosphat* without the desired products (Scheme 23). As illustrated in the scheme 22, the byproduct could be formed by deprotonation of the acidic proton adjacent to the ester - functionality.



Scheme 23: Reaction of the ester functionalized salts with $[Rh(COD)Cl]_2$.

The formation of by-product was confirmed by NMR spectroscopy. The lack of the Rh-bounded carbon atom seen at ~180 ppm and the bridged C = O seen at ~170 ppm led the complexation might occur as shown in Scheme 22 which was proved after the single crystal picture depicted in Figure 14. The single crystal of the by-product **7c^{bp}** was obtained by vapor diffusion of diethyl ether into a concentrated solution of **7c^{bp}** in DCM. (Figure 14) and confirms square-planer geometry. Rh - $C_{carbene}$ bond lengths for **7c^{bp}** (2.094(2) Å) and (2.121(2) Å) are in consistence with similar Rh-NHC complexes[111].

Scheme 24 indicates the proposed mechanism in where imidazolium salt and N-Metylimidazol have allocated which might be explained by the Hoffmann-Elimination[112] of amines decomposition.



Scheme 24: The possible mechanism for the decomposition of **7c**.

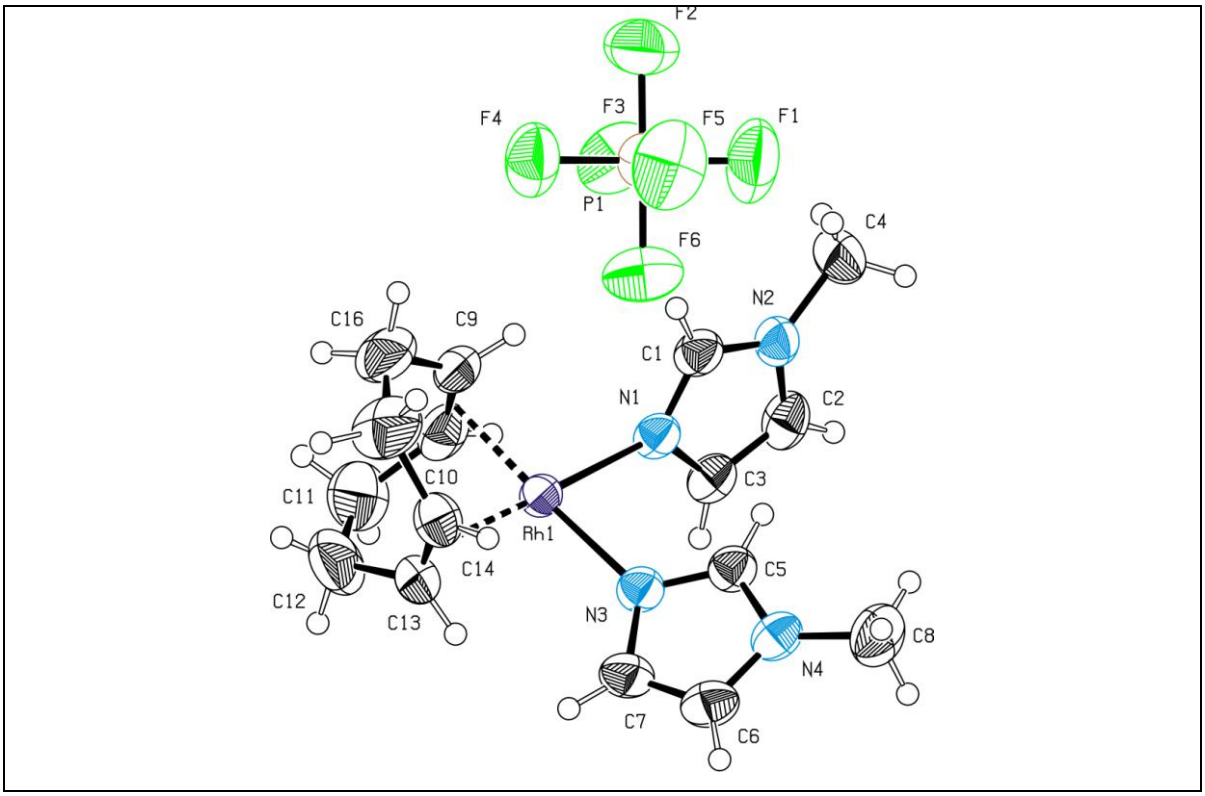


Figure 14: ORTEP style plot of the cationic part of compound **7c**[x] in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and bond angles (°): Rh1-N1 2.094(2), Rh1-N3 2.121(2), Rh1-C9 2.131(3), Rh1-C10 2.128(3), Rh1-C13 2.135(3), Rh1-C14 2.131(3), N1-Rh1-N3 87.54(9), N1-Rh1-C9 91.40(11), N1-Rh1-C10 90.46(11), N1-Rh1-c13 161.75(13), N1-Rh1-C14 160.38(12), N3-Rh1-C9 158.45(12), N3-Rh1-C10 163.44(12). N3-Rh1-C13 95.30(10), N3-Rh1-C14 91.51(11), C9-Rh1-C10 37.99(15), C9-Rh1-C13 92.41(13), C9- Rh1-C14 82.36(13), C10-Rh1-C13 81.69(13),C10-Rh1-C14 95.79(13), C13-Rh1-C14 37.80 (13).

2.2.3. Catalytic activity of bis(N-hetrocyclic carbene) rhodium(I) complexes

The synthesized Rh(I) complexes were tested as homogeneous catalysts for the hydrosilylation reaction of acetophenone with diphenylsilane and transfer hydrogenation of acetophenone with various bases. A detailed description of the catalytic reaction will be given in the Experimental Section.

2.2.3.1. *The application of bis(N-hetrocyclic carbene) rhodium (I) complexes in catalytic hydrosilylation*

The hydrosilylation reactions require the addition of an organic or inorganic silicone-hydride to a double or triple bond. This is one of the most popular methods to introduce a silicone atom into an organic molecule.[113] Hydrosilylation is also an important reaction for the preparation of various intermediates in organic synthesis and is generally catalyzed by rhodium, ruthenium, or platinum complexes. Since the first study reported by L. H. Sommer in 1947 about hydrosilylation.[114] it plays an important role in the silicium chemistry.

According to the literature, hydrosilylation is one of the most preferred catalytic reactions and generally ketone, imines, alkyne and alkenes are chosen as a substrate. However, transformations of ketone and alkyne substrates are the most popular. Similar to transfer hydrogenation reactions, both monodentate and multidentate NHC ligands are most successful in Rh(I)-catalyzed hydrosilylation applications[115]. A number of [bis-(NHC)Rh] complexes were found to be effective for hydrosilylation reaction of ketones.[115-117]

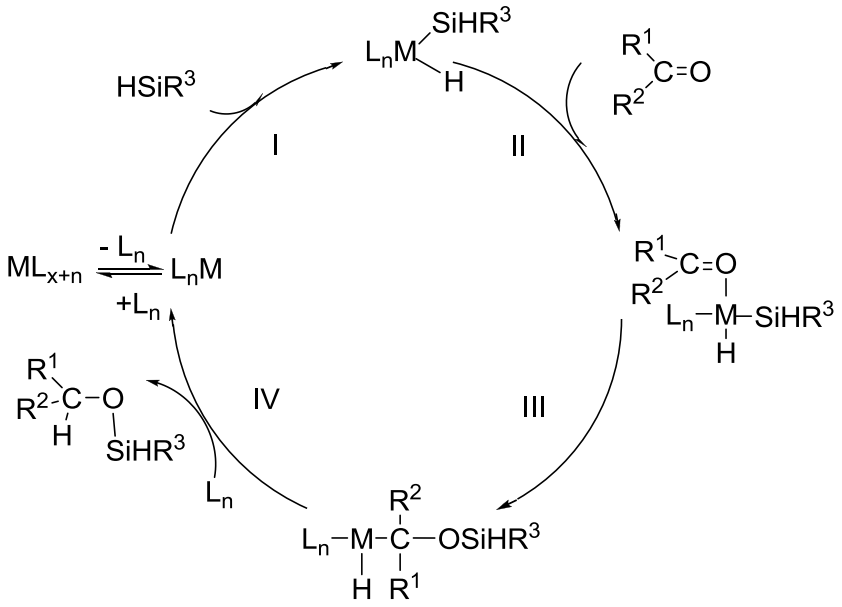
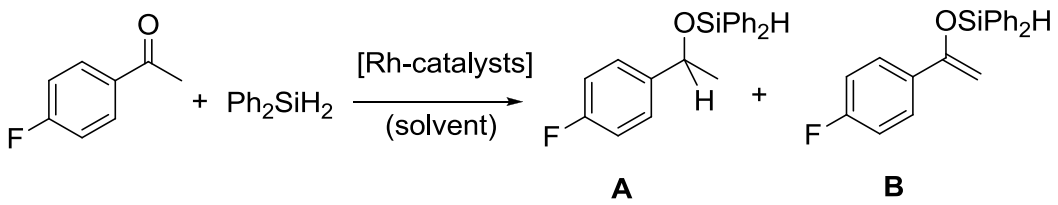


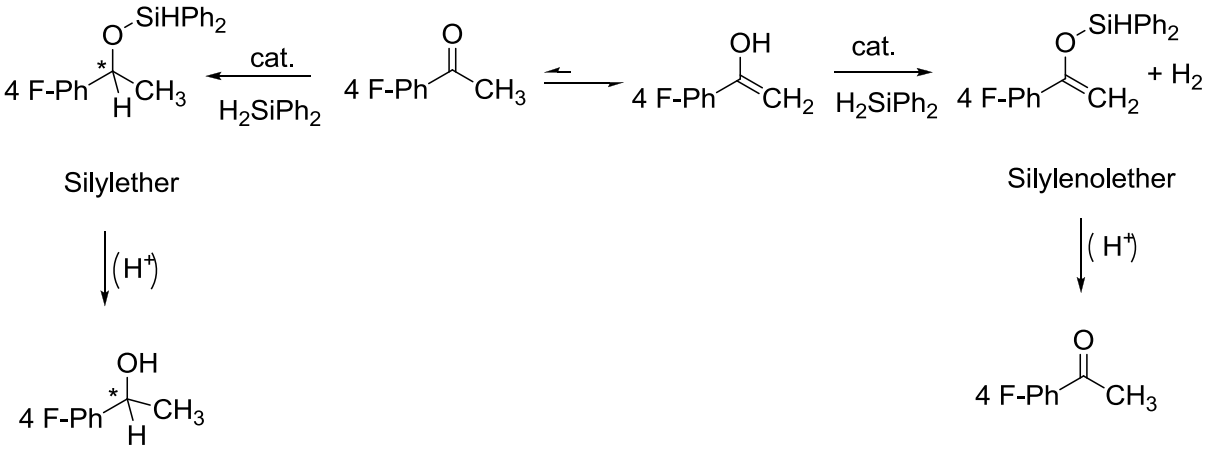
Figure 15: General mechanism of the hydrosilylation reaction.

Figure 15 shows the general mechanism of the hydrosilylation reaction[113,114]. The catalysis starts with the oxidative addition from silane to the metal center (1), followed by the coordination of the carbonyl group (2) and its insertion into the metal-silicon bond (3), and terminates with the reductive elimination of the product and the regeneration of the catalytically active intermediate (4)[118].

In the hydrosilylation of ketones or aldehydes, one of the Si-H bonds of diphenylsilane is added to carbonyl bonds to give silyl ether (Scheme 25, **A**).[99a-b] As a by-product silylenol ether (Scheme 25, **B**)[99a-b] is formed which is converted to the starting material after hydrolysis reaction. Schemes 25 and 26 describe the catalytic hydrosilylation of 4-fluoro acetophenone with diphenylsilane in the presence of Rh(I) complexes (**1c**, **3c**,**5c**^{PF6},**5c**^{BPh4}).



Scheme 25: Hydrosilylation of 4-Floroacetophenone with Diphenylsilane.



Scheme 26: Hydrosilylation of 4-Floroacetophenone with Diphenylsilane.

The substrate, acetophenone, was replaced by 4-fluoroacetophenone in order to conveniently monitor the reaction progress *in-situ* by ^{19}F NMR instead of ^{1}H NMR spectroscopy to avoid .the overlapping of the integrals that is observed in ^{1}H NMR spectra.

The newly synthesised rhodium complexes (**1c**, **3c**, **5c^{PF6}**, **5c^{BPh4}**) were tested in hydrosilylation of acetophenone with diphenylsilane yielding silylether **A** and silylenolether **B**[116]. The results are summarized in Table 6. For a better comparison of the relative catalyst activities, the time-conversion curves are shown in Figure 16.

Table 6: Results for the hydrosilylation of 4-fluoro-acetophenone

Entry	[Rh]	[R]	X	T[^{o}C]	Solvent	Time [h]	Conv. [%]	A [%]	B [%]	TOF [h^{-1}]
1	**1c**	Me	PF_6	25	DCM	15	73	51	49	15
2	**1c**	Me	PF_6	60	DCE	4	100	63	37	30
3	**3c**	^{i}Pr	PF_6	25	DCM	2	100	66	34	70
4	**3c**	^{i}Pr	PF_6	25	THF	4	100	40	60	55
5	**5c^{PF6}**	Bn	PF_6	25	DCM	24	81	64	36	5
6	**5c^{BPh4}**	Bn	BPh_4	25	DCM	50min	100	72	28	70

Reaction conditions: 2 mol % catalyst, 0.504 mmol of 4-fluoro-acetophenone, 0.756 mmol of diphenylsilane, 0.3 ml dichloromethane (entry 2: 1,2-dichloroethane DCE). Conversions were determined by ^{19}F-NMR spectroscopy. No spectroscopic evidence was found for defluorination, nor the formation of other products than A and B. TOFs have been calculated at the maximal slope of the time conversion curve.

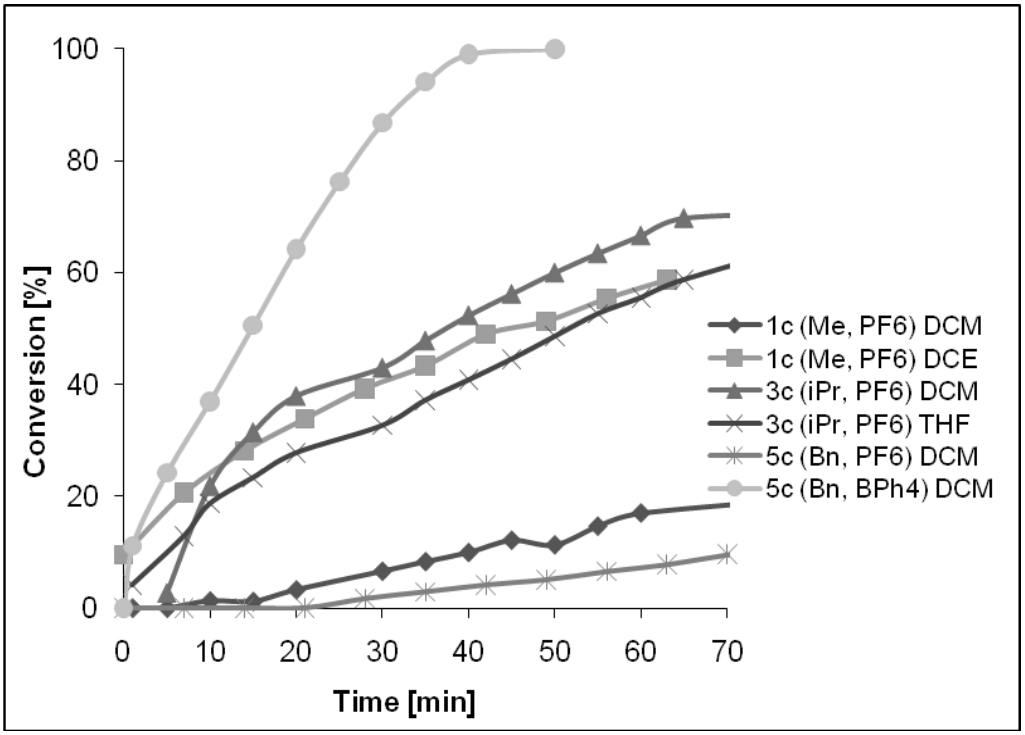


Figure 16: Time-conversion-curves of the hydrosilylation reaction.

It was found that the selectivity increased with the streric demand of the *N*-substituents. The catalyst **1c** with a methyl substituent led to a conversion of 73%, while **3c** and **5c**^{PF6} with ^{i}Pr and Bn substituents resulted in a conversion of 100%. The highest turnover frequency (TOF) was achieved with **3c** (70 h^{-1}). In the case of **1c,** it was observed that increasing the temperature from 25 °C to 60 °C doubles the value of TOF from 15 h^{-1} to 30 h^{-1} and complete conversion is achieved after 4 h reaction time (entry 2). It should be noted that the selectivity and the TOF also depends on the solvent that is used (entry 3 also entry 4, Table 6). Interestingly, the conditions seems to significantly affect the catalytic activity changing the anion from **5c**^{PF6} with a PF_6^- anion, to **5c**^{BPh4} with a BPh_4^- increased the TOF from 5 to 70 h^{-1} (entry 5 also 6, Table 6).

Considering these results, it found that besides the reaction temperature and the solvent, both the wingtip groups and the anion play an important role in this reaction. The observed TOF values are within the range of previously published catalysts for hydrosilylation reactions of acetophenone[117]. All complexes show high activities under mild conditions.

2.2.3.2. *The application of bis(N-hetrocyclic carbene) rhodium(I) complexes in catalytic transfer hydrogenation*

Experimental and theoretical studies indicate that homogeneously catalyzed transfer hydrogenation became a powerful tool in synthetic chemistry and a wide range of unsaturated substrates can be employed in this reaction[119-122]. It was shown that asymmetric versions of this reaction could be powerful methods for the enantioselective reduction of ketones.[99a-b,119-122]

Early transition metals and lanthanoids[123,124] as well as late transition metals, mostly ruthenium,[124-129] iridium[130,131] and rhodium.[132-134] have been used and are highly active in a large number of interesting transfer hydrogenation. The most popular catalytic systems; are reported by Mathey and coworker, the ruthenium (II) arene complexes and rhodium (III) (cyclopentadienyl) complexes in combination with 2-isopropanol or formic acid / triethylamine mixtures, which resulted with very high TONs and TOFs.[135] Impressive activities (> 1×10^6 h^{-1}) and selectivities have been obtained for these complexes. Le Floch et al. reported a TOF of 1.2×10^6 h^{-1} for acetophenone and 1.33×10^6 h^{-1} for cyclohexanone at 90 °C and substrate to catalyst ratio (S:C) of 20×10^6 with a cationic 1-(2-methylpyridine)-phosphole cymene ruthenium complex in isopropanol.[125] Impressive activities have been reported also by Baratta et al., TOF = 1.5×10^6 h^{-1} (cyclohexanone or acetophenone) at S:C of 0.1×10^5 with a ruthenium complex in 2-isopropanol.[128]

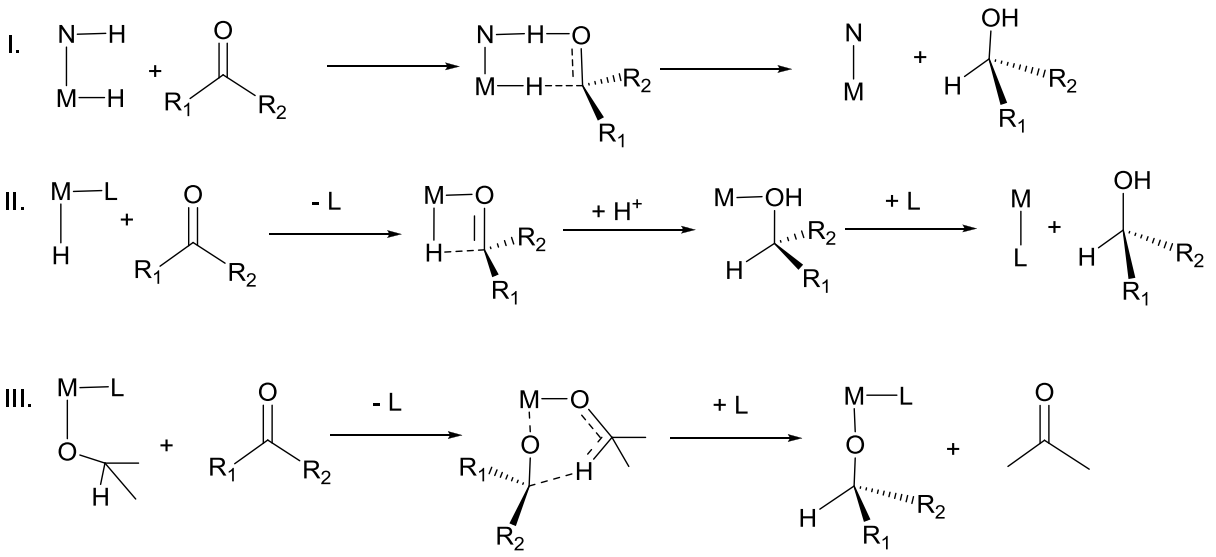
A considerable number of monodentate NHC complexes, is known to be highly active for transfer hydrogenation and only a few highly active catalysts bearing chelating bis-carbene ligands were reported to date.[92d,135, 136]

As stated before, Crabtree, Albrecht and co-workers were the first who synthesize bis-carbene iridium and rhodium complexes, such as $[M(III)(biscarbene)(OAc)]I_2$[80b,92f,99a-b] with observed TOF up to 50000 [h^{-1}].

Table 7: Characteristics of Transfer Hydrogenation

Stereoselectivity	Aromatic: 95-98%
Substrate concentration	Up to 1M
Reactivity	Slower then Hydrogenation
Solvent	Organics; H_2O is possible
Large scale synthesis	Small-medium scale
Turn over Number (TON)	Up to 10^4
Catalyst loading	10^{-2} mol%
Hydrogen source	*i*-PrOH or formic acid
External base	*i*-PrOH: 10^{-1} eq. of *i*-PROK

A classical method for the reduction of double bonds is the use of molecular hydrogen as reductant in the presence of heterogeneous[137] or homogeneous[138,139] catalysts. Since hydrogen is one of the cleanest reductant and also highly flammable. The use of hydrogen in transfer hydrogenation reaction was eliminated due to the risks associated. As an alternative, the reaction is often carried out refluxing in 2-isopropanol (80 °C) as hydrogen source.[140-142] Only few catalysts showing high reactivity at room temperature are currently known.[134, 143.]



Scheme 27: Mechanism for transfer hydrogenation.

Three reaction mechanisms for the transition metal catalyzed transfer hydrogenation reaction were previously proposed.[121,144-146] These mechanisms differ in the way the hydrogen is transferred to the ketone, as shown in Scheme 27.

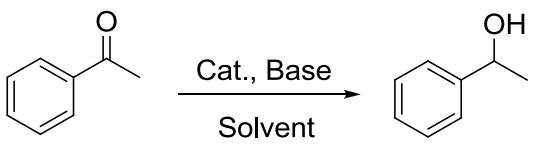
In the first mechanism a concerted transfer of a proton from the amine ligand and hydride from the metal to the ketone occurs. This is often termed the metal-ligand bifunctional or Noyori mechanism and is very important for late transition metal complexes with amine ligands. In this case the ketone does not coordinate to the metal; the reaction happens in the outer sphere of the catalyst.[147]

The second mechanism involves the insertion of the ketone in the M-H bond of the metal hydride complex. This hydridic mechanism is observed in transition metal catalysts lacking suitable amine functions.

The third mechanism operates via direct transfer of the α-hydrogen of the metal alcoholate complex to the ketone. This is known as Meenwein-Pondorf-Verley mechanism and is most often proposed for catalysts based on main group elements, early transition metals and lanthanoids.

2.2.3.2.1. Catalytic activity of bis(N-hetrocyclic carbene) Rh(I) complexes in the transfer hydrogenation

The bis(NHC)-rhodium(I) complexes **1c-5c^{PF6}** were examined as catalysts for the transfer hydrogenation of acetophenone to 1-phenylethanol using 2-propanol or methanol as hydrogen donor in the presence of suitable bases namely KOH, *i*PrONa, and K_2CO_3 (Scheme 28).



Scheme 28: Transfer Hydrogenation of acetophenone.

No conversion was observed in methanol. In the absence of a catalyst, no significant amount of 1-phenylethanol is formed. However, the conversion was occurred in 2-propanol and in the present of suitable bases having different hardness like KOH, *i*PrONa and K_2CO_3, with a ratio of substrate : cat. : base = 100 : 1 (or 0.5) : 10. The results of the examined catalysts are summarized in Tables 8 - 10. The time conversion curves are depicted in Figure 17 (Base: KOH) and Figure 18 (Base: *i*PrONa). The highest catalytic activity was observed with bis-carbene rhodium(I) complex **3c**.

Türkmen and co-workers observed that the conversion was strongly dependent on the base strength, stronger the bases higher the yields. Additionally with the bases having different strengths requires longer reaction times.[145a,b]

Crabtree and co-worker published that potassium carbonate can be used for transfer hydrogenation of acetophenone using Rh(III) and Ir(III) complexes, but the reaction occurs faster with potassium hydroxide.

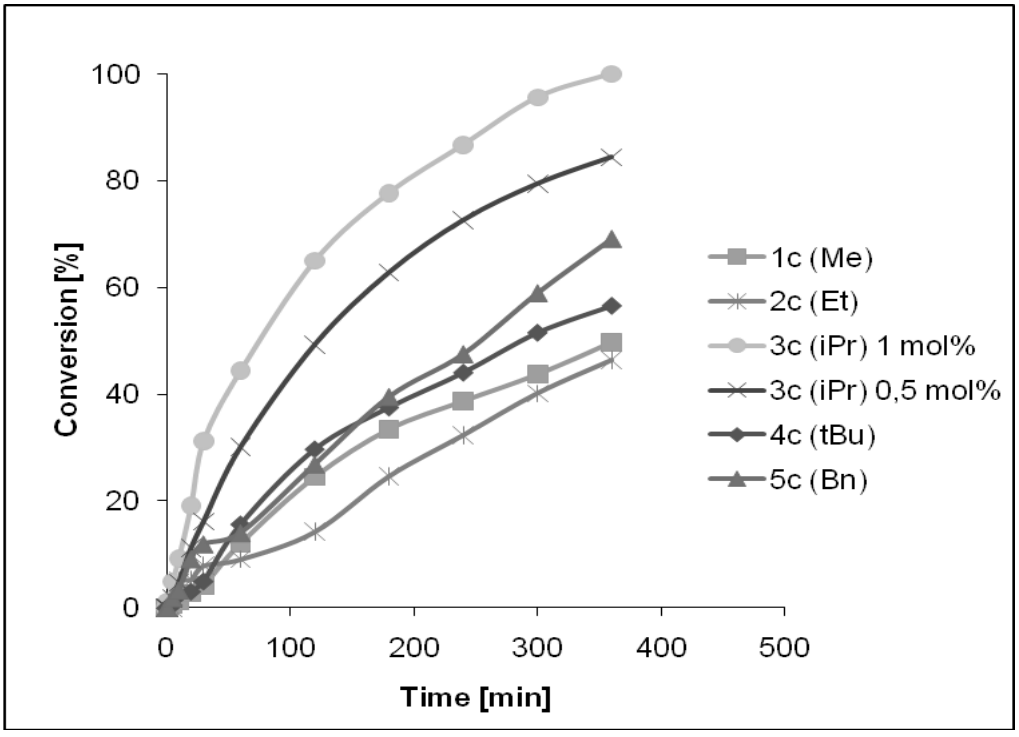


Figure 17: Time-conversion curves of the transfer hydrogenation with KOH as base and compounds **1c**-**5c** as catalysts.

Table 8: Results for the transfer hydrogenation with KOH as base

Entry	[Rh]	[R]	Time	Conv.[%]	TOF [h-1]
1	**1c**	Me	24	94	20
2	**2c**	Et	24	86	15
3	**3c**	^{i}Pr	24	95	80
4	**3c**	^{i}Pr	6	100	70
5	**4c**	^{t}Bu	24	92	20
6	**5c^{PF6}**	Bn	24	96	35

Reaction conditions: S / C / B = 100: 1 :10 with 1 mmol of acetophenone and 0.01 mmol of KOH in 10 mL of *i*PrOH at 80°; yields determined by GC. Reaction conditions of **3c**: S / C / B = 100: 0.5 :10.

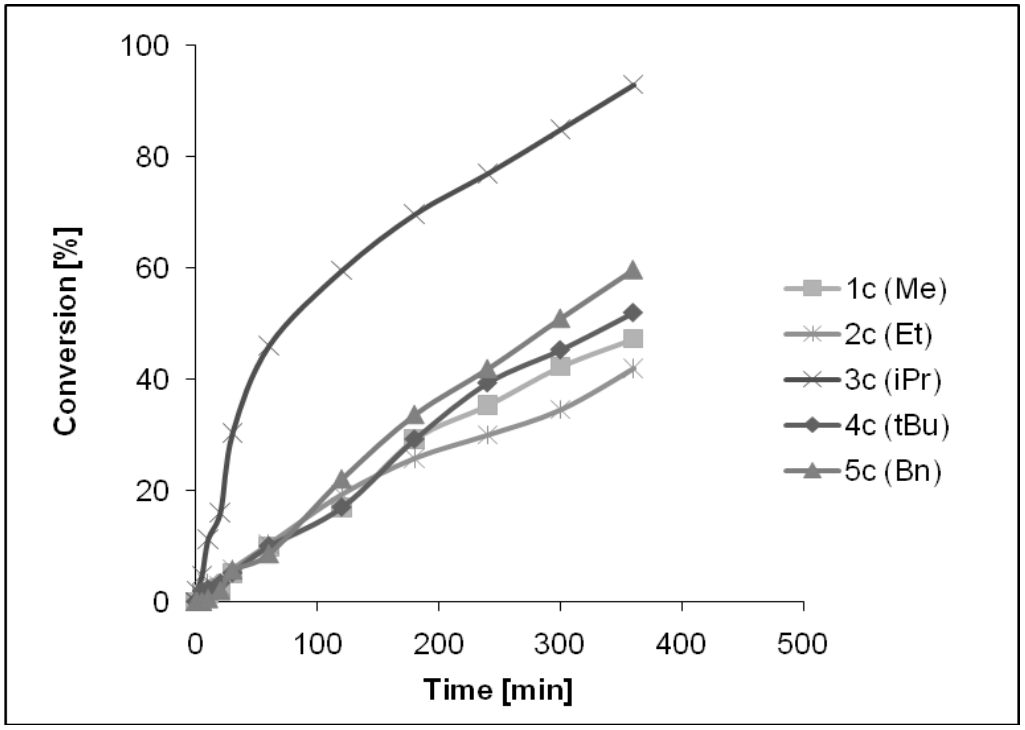


Figure 18: Time-conversion curves of the transfer hydrogenation with *i*PrONa as base and compounds **1c** - **5c** as catalysts.

Table 9: Results for the transfer hydrogenation with *i*PrONa as base

Entry	[Rh]	[R]	Time [h]	Conv.[%]	TOF[h^{-1}]
1	**1c**	Me	24	87	35
2	**1c**	Et	24	76	25
3	**3c**	^{i}Pr	7	100	120
4	**4c**	^{t}Bu	24	88	40
5	**5c^{PF6}**	Bn	24	95	35

Reaction conditions: S / C / B = 100: 1:10 with 1 mmol of acetophenone and 0.01 mmol of KOH in 10 mL of *i*PrOH at 80°; yields determined by GC.

However, even after the long reaction time (24 h), catalysts **1c** and **2c** did not reach to 100% conversion with KOH and *i*PrONa (entry 1 and 2, Table 8 and 9), led to the conversions of 94% (87%) and 86% (76%). The conversion resulted in 92% (88%) with catalyst **4c** and 96% (95%) regarding the catalyst **5c**.

The most active catalyst, **3c** was tested at lower concentration and in different bases, namely KOH, *i*PrONa, and K_2CO_3. As shown in Figure 19, full conversion after 6h and the highest TOF was obtained for KOH with 70 h^{-1}. Similarly good results were observed for *i*PrONa with 120 h^{-1} and 100 % conversion after 7h, with K_2CO_3 incomplete conversion occurs even after 24h and a very low TOF of 8.47 h^{-1} (Table 10).

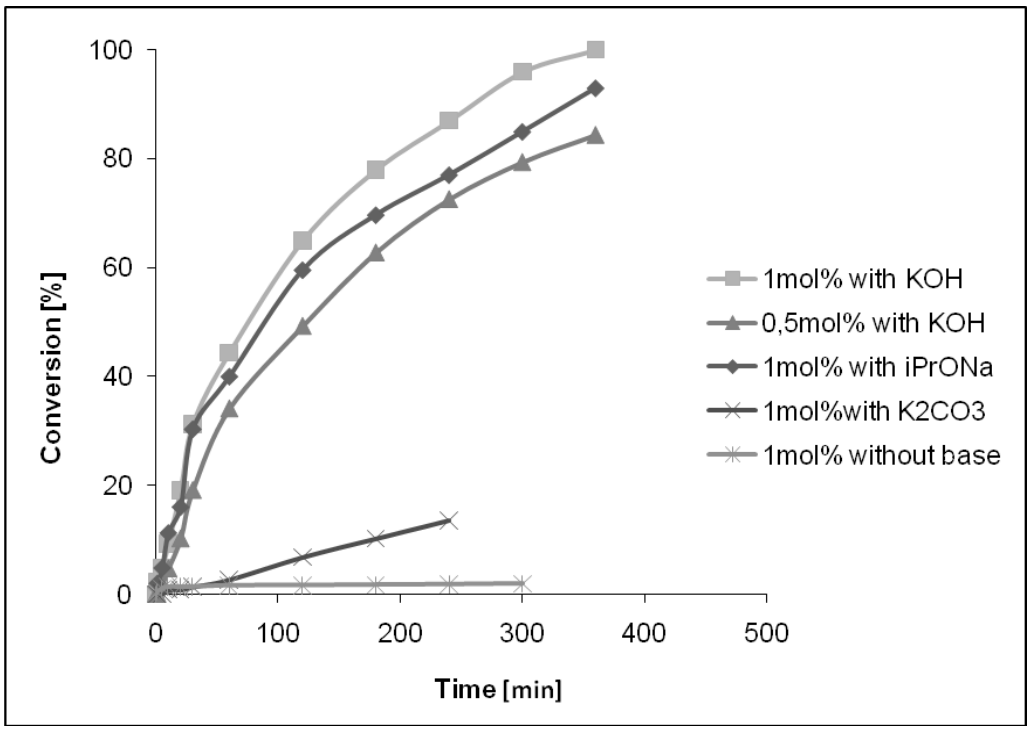


Figure 19: Time-conversion curves of **3c** (1 mol %) as catalyst applying different basses in transfer hydrogenation.

Table 10: The comparison complex **3c** with different base

Entry	Base	Time[h]	Conv.[%]	TOF [h^{-1}]
1	KOH	6	100	70
2	*i*PrONa	7	100	120
3	K_2CO_3	24	53	8.5
4	no Base	24	4.6	-

Reaction conditions of **3c** : S / C / B = 100: 1 :10 with 1 mmol of acetophenone and 0.01 mmol of base in 10 mL of *i*PrOH at 80°; yields determined by GC.

The results show that the catalytic activity is influenced by the steric bulk of the wingtip substituents of the NHC-ligand and also by the applied base. Nolan and coworkers investigated the reaction of a series of NHC ligands to establish their electronic and steric properties. They explained the steric influence of the carbene ligands by the hypothesis of the buried volume[145c-g]. During the catalytic cycle the *N*-substitutents provide steric shielding of the metal center and therefore enhance the stability of the active catalytic species[145c-g]. Alternatively, a very bulky *N*-substituent may increase the lability of the NHC donor, thus leading to more reactive metal center[145c-g].

Catalyst **1c**, **2c**, **4c** and **5c** display a turn over frequency between 25 and 40 with *i*PrONa and of 15-35 with KOH, **3c** is 2-4 times more active. The ethyl and benzyl wingtip can be rotated about the N-C bond, facing away from the metal, to minimize the steric interaction with the metal center and therefore resembling a CH_2-H group (**1a**). Complex **4c** is very bulky and both the COD and ^{t}Bu substituents are distorted, as reported previously[145h]. Compound **3c** has an intermediate steric size, being the only compound with two (alkyl) substituents an the wingtip CHR_2 -group.

2.3. Conclusion

The synthesis and structural characterization of Rh(I) complexes is reported. The synthesized novel complexes were tested as a homogeneous catalyst both in hydrosilylation and transfer hydrogenation reactions. As already mentioned, different parameters for hydrosylilation reaction such as the wingtip groups, different anions, solvent and temperature and for transfer hydrogenation like wingtip groups, bases with different strength play an important role in catalytic performance.

The best catalysts among the examined ones are, *[3,3´-(2-Hydroxypropan-1,3-diyl)bis(1-benzyl-1H-imidazolium-2,2´-diyliden)]-(η^4-1,5-cyclooctadienyl)rhodium(I)-tetraphenylborat* (**5c**^{BPh4}) for hydrosilylation reaction and *[3,3´-(2-Hydroxypropan-1,3-diyl)bis(1-isopropyl-1H-imidazolium-2,2´-diyliden)]-(η^4-1,5cyclooctadienyl) rhodium(I)-hexafluorophosphat;* (**3c**) for transfer hydrogenation reaction.

Despite good results obtained for Rh (I) complexes in homogeneous catalysis, increasing attention is being drawn to studying and developing heterogeneous catalysts since these can be easily separated from the reaction mixture and recycled, which is of significant industrial interest. Transfer hydrogenation is preferred for large-scale industrial use in the hope of developing a greener process by reducing waste production and energy and lowering toxicity.[133]

The rhodium (I) complexes was anchored through the NHC ligand onto insoluble poly(styrene)-based Wang resin and showed catalytic activity in hydrosilylation reactions reported by Kühn et al.[148] which can be a candidate for transfer hydrogenation reaction.

Chapter 3

Symmetrically Bis-(NHC) palladium (II) complexes: Synthesis, structure, and application in catalysis

This chapter contains the following publication:

Nadežda B. Jokić, Claudia S. Straubinger, Serena Li Min Goh ,
Eberhardt Herdtweck, Wolfgang A. Herrmann and Fritz E. Kühn;
Inorganica Chemica Acta 363, **2010**, 4181-4188

3. Symmetrically Bis-(NHC) palladium (II) complexes: Synthesis, structure, and application in catalysis

3.1. Synthesis of bis(NHC)-Ag(I) and bis(NHC)-Pd(II) complexes

Since the discovery of *N*-heterocyclic carbenes (NHCs),[46a,63,65,149] many transition metal compounds, as well as, main group metal complexes bearing NHC-ligands have been prepared and successfully applied in a number of catalytic processes.[1,150] Among them cross-coupling chemistry[151] is one of the most explored fields.

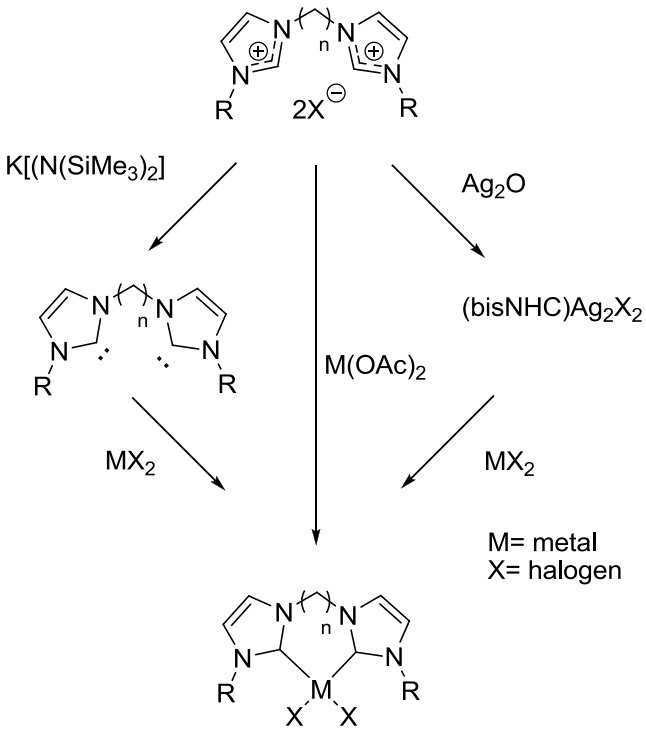
Given the successful use of chelating phosphane ligands in transition-metal catalyzed homogeneous catalysis, several studies into the properties of chelating N-heterocyclic carbenes have been explored. Since then many complexes bearing chelating NHCs have been reported as homogeneous catalysts. The strong σ-donating and little or no π−backbonding ability of the carbene ligands leads to increased electron density at the metal centers for which NHC can generally be seen as alternatives to the widely used phosphine ligands[152]. One of the major advantages for the use of Pd complexes is the stability of metal-carbene bonds in the biscarbene in contrast to conventional phosphine and amine ligands, which tend to leaching or decompose at high temperatures or when exposed to air and moisture. Chelating biscarbene palladium complexes are easy to handle, relatively nontoxic and mostly insensitive to oxygen, or acid, extremely stabile in the presence of heat and moisture leading to remarkable catalytic properties.[150-152]

The use of a bis-NHC Pd(0) catalyst by *Hermann*[152] et al. was shown to be very efficient for room temperature C-C cross coupling of both electron-rich and electron-poor aryl chlorides with phenyl boronic acid. The results obtained in toluene, with K_2CO_3 as a base, show that aryl bromides can be coupled with phenylboronic acid resulting in good to excellent yields using only 0.5mol% of catalyst loading.[153]

Many previously reported reasons have opened a special interest in the immobilization of palladium complexes on inorganic or organic materials e.g. resins, clay, and silicon.[22,23,43c,68,154,156] NHC ligands are known to bind stronger to both Pd^0 and Pd^{II} centers than phosphine ligands, therefore they appear to be highly suitable for the attachment of the catalyst to solid supports[157]. The polymer-supported NHC-Pd catalysts developed by Lee and coworkers require heating and usually more active substrates such as aryliodides[24a-c]. In recent years, research groups focused on a green chemistry approach for cross-coupling reactions by using recyclable catalysts,[106] solid-phase Suzuki coupling and "green solvents" for a broad range of biaryl products along with simple protocols.[107,108]

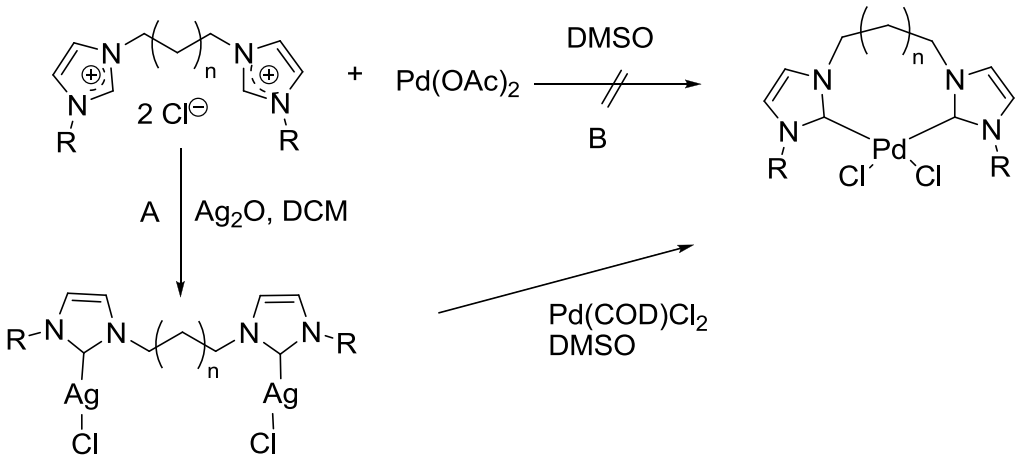
3.1.1. Synthesis of hydroxy-functionalized palladium(II)-carbene complexes

In literature, there are basically three synthetic routes, to synthesize bis(NHC) complexes of palladium (II). The Scheme 29 depicts these routes: the free carbene route, the metal acetate route and the silver transmetallation route.



Scheme 29: General synthetic routes into bis(NHC) complexes.

Strassner and coworkers[158a] published a number of palladium(II) complexes with chelating methyl bridged bis(NHC) ligands, which were synthesized via de-protonation of their imidazolium precursors with $Pd(OAc)_2$. The synthesis was failed, however, in preparing derivatives with alkyl bridges longer than two carbon atoms with this direct protonation method. Hahn *et.al*., have described the synthesis of the palladium complexes with bis(NHC) ligands, bridged by a propylene group, however, without a hydroxyl-functionalized group attached to the bridging moiety (Scheme 30). [158b, c]

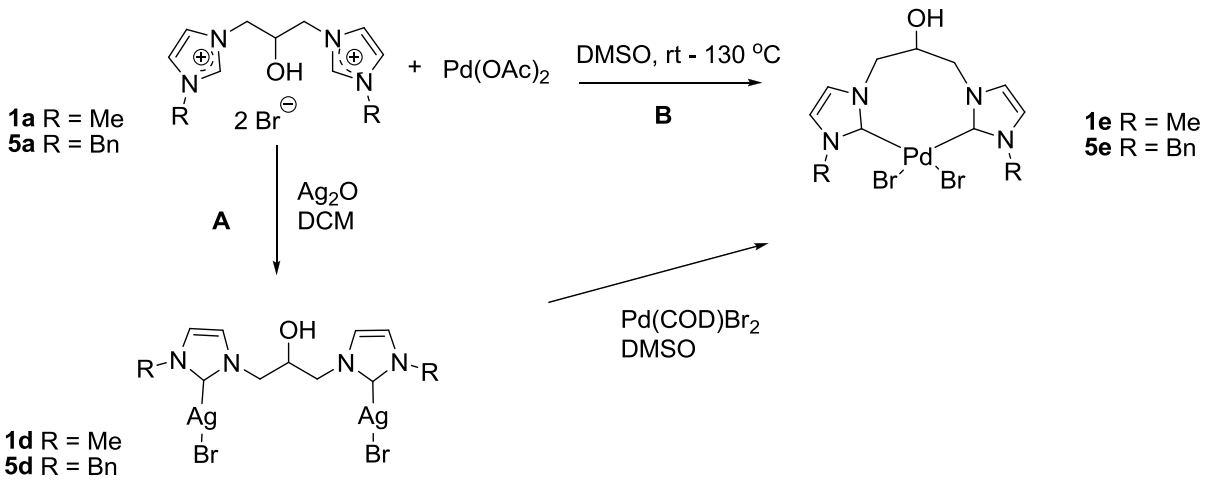


Scheme 30: Synthesis of palladium (II) Bis-imidazol-2-ylidene complexes via the ``silver route`` A and ``acetate route`` B.

The great advantages of bis(NHC) complexes, prompted us to develop the synthesis of hydroxyl-functionalized bis(NHC) complexes. As shown in scheme 31, the Pd (II) complexes were successfully prepared by reacting the corresponding bis-imidazolium salts with $Pd(OAc)_2$, or alternatively via the silver route. Herein, both strategies were successfully applied to prepare the chelate complexes, [Pd (**1a**)Br_2] (**1e**) and [Pd(**5a**)Br_2] (**5e**) by method B led to higher yields in comparison with method A [A: (60% for **1e**, 59 % for **5e**); B: (70 % for **1e**, 76 % for **5e**)][159]

The purity of **1d**, **5d**, **1e** and **5e** was confirmed by elemental analysis. All complexes prepared here are both air- and moisture stable. An evidence for the formation of the

carbene complexes was the absence of any signal in the 8-10 ppm region, indicating the successful deprotonation of the carbonic protons in **1e** and **5e** and by the absence of the carben peak at around ^{13}C~160 ppm.



Scheme 31: Synthesis of palladium (II) Bis-imidazol-2-ylidene complexes via the ``silver route`` A and ``acetate-route`` B.

The complexes **1e** and **5e** are only soluble in highly polar organic solvents such as DMSO, DMF, acetonitrile, nitromethane and methanol, and are found to be insoluble in diethyl ether, dichloromethane, THF and hydrocarbons. They are air and moisture stable and can only decompose at temperatures higher than 215 °C.

Crystals of X-ray quality were obtained for **1e** by vapor diffusion of diethyl ether into a concentrated solution of **1e** in DMF. The molecular structure of **1e** is shown in Figure 20 and confirms square-plane geometry. The bond lengths M-Br (2.5042(4) and 2.4975(3)) and M-C (1.976(2) Å and 1.974(2) Å) are within the typical range for these bond types[160]. Other selected bond lengths and angles are summarized in Tables 24-25 (Appendix).

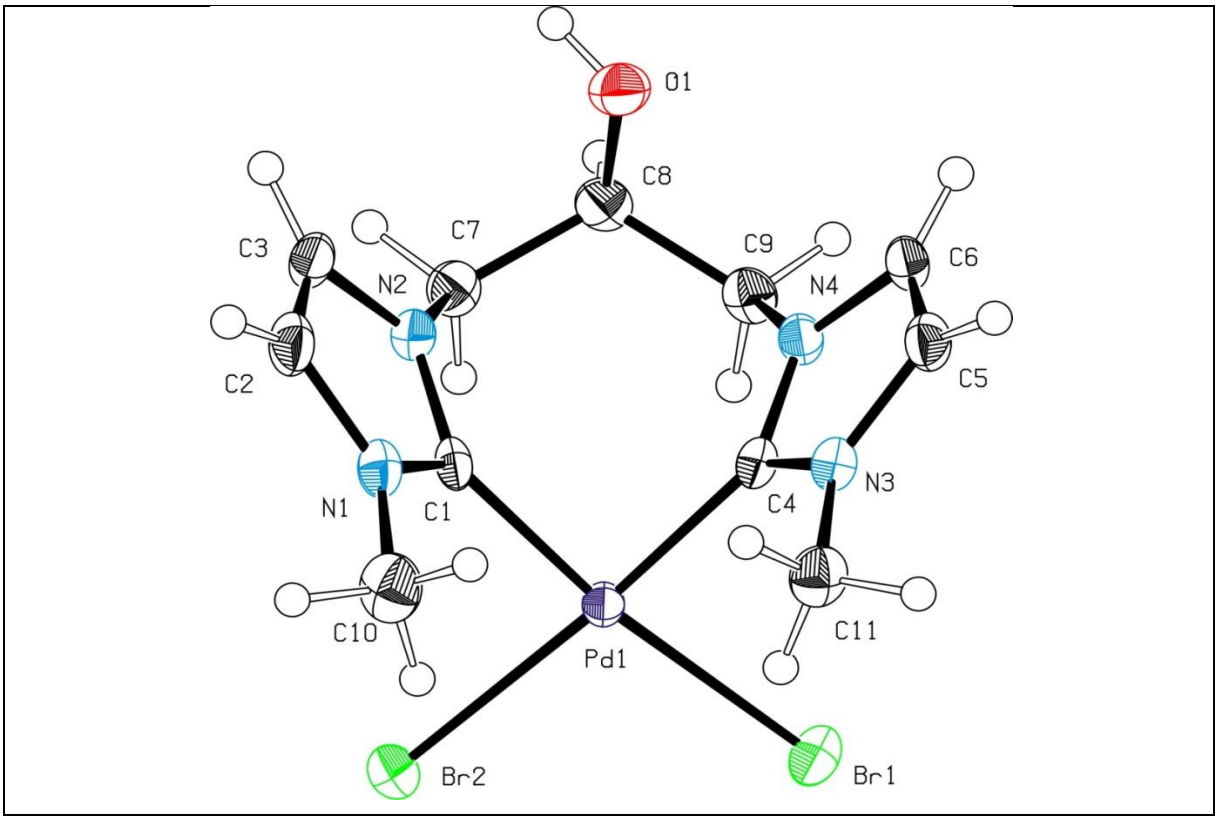
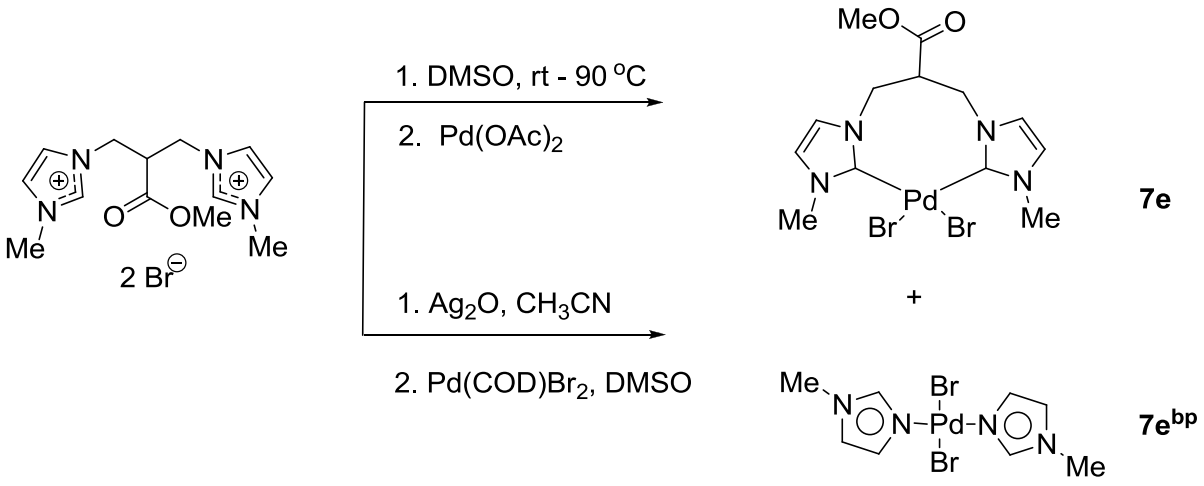


Figure 20: ORTEP style representation of the molecular structure of complex **6a**·2(C_3H_7NO) as determined by single-crystal X-ray crystallography. Thermal ellipsoids are given at a 50% probability level. Solvent molecules are omitted for clarity. Selected bond lengths and : Pd1−Br 2.5042(4), Pd1−Br2 2.4975(3), Pd1−C1 1.976(2), Pd1−C4 1.974(2), N1−C1 1.346(3), N2−C1 1.353(3), N3−C4 1.348(3), O1−C8 1.420(3), Br1−Pd1−Br2 95.39(1), Br1−Pd1−C1 95.39(1), Br1−Pd1−C1 172.73(6), Br1−Pd1−C4 89.15(6), Br2−Pd1−C1 91.23(7), Br2−Pd1−C4 175.43(6), C1−Pd1−C4 84.26(9), N1−C1−N2 105.7(2), N3−C4−N4 105.6(2), O1−C8−C7 112.5(2), O1−C8−C9 107.7(2), C7−C8−C9 116.1(2).

3.1.2. Synthesis of ester functionalized palladium(II)-carbene complexes

An attempt to synthesize the analogues ester-functionalized bis carbene Pd (II) complexes by reacting the corresponding bis-imidazolium salt with $Pd(OAc)_2$, was failed. The mixture of the complex and the by-product together was monitored by NMR spectroscopy. Several signals, however, appeared, that could not be attributed to the expected complex, 3,3'-(2-Methoxycarbonylpropan-1,3-diyl)bis(1-methyl-1H-imidazolium-2,2`diyliden))palladium(II)-dibromide,(**7e**), but instead indicate the formation of the by-product trans[Pd-bis(N-methylimidazol)]dibromide, (**7e**^{bp}), shown in scheme 32. On the other hand the silver route

did not lead to the only desired product both the expected product 3,3'-(2-Methoxycarbonyl-propan-1,3-diyl)bis(1-methyl-1H-imidazolium-2,2`-diyliden))palladium(II)-dibromide complex and the by-product trans[Pd-bis(N-methylimidazol)]dibromide was formed (Scheme 32). This same manner was already been discussed in the Rh section (Chapter 2; 2.2.3). As stated above the product formation failed however implications were seen in ^{1}H NMR spectroscopy along with by-product. In the case of NC*H*N proton peak seen in ~ 9 ppm for the free ligand disappeared which proved the complex formation and proton signal in 8.16 showed the by-product formation, the NC*H* proton signals of the imidazolium salt for the by-product shifted from ~ 8 ppm to ~ 7 ppm and did not have any significant shifting for the complex, however appearance of the OCH_3 at 3.70 ppm represented the formation of the expected product.

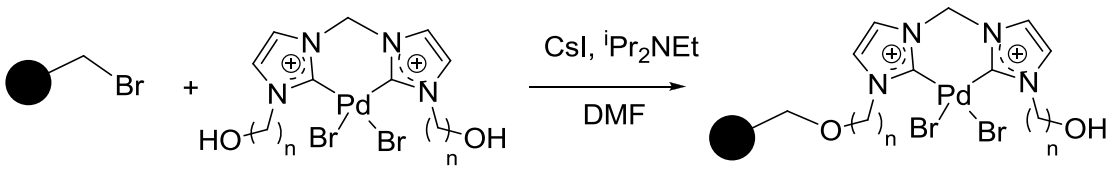


Scheme 32: Synthesis of complex **7e** along with its by-product **7e^{bp}**.

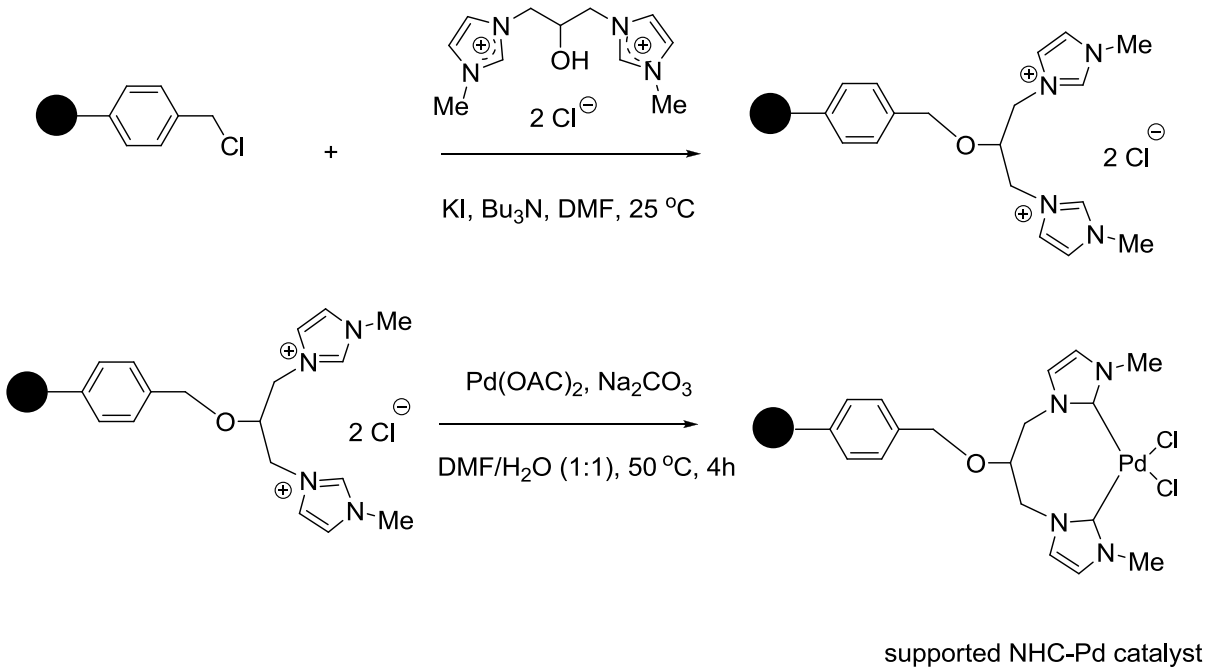
*3.2. Immobilization of **6e** on 4-(bromomethyl) phenoxymethyl polystyrene*

The first report on a polymer supported chelated Pd bis(NHC)-complex was published by Herrmann *et al.* in 2000[22]. This complex was anchored through the NHC ligand onto an insoluble poly (styrene)-based Wang resin. The catalytic activity of this system examined for the Heck-reaction.

Schwarz and coworkers have reported the synthesis and the catalytic activity of heterogeneous Pd catalysts[22] for the Heck reaction. They immobilized a palladium bis-NHC complex to a polystyrene Wang resin via a hydroxyl-containing *N*-substituent, which reacted with the brominated resin to form an ether bridge (Scheme 33).



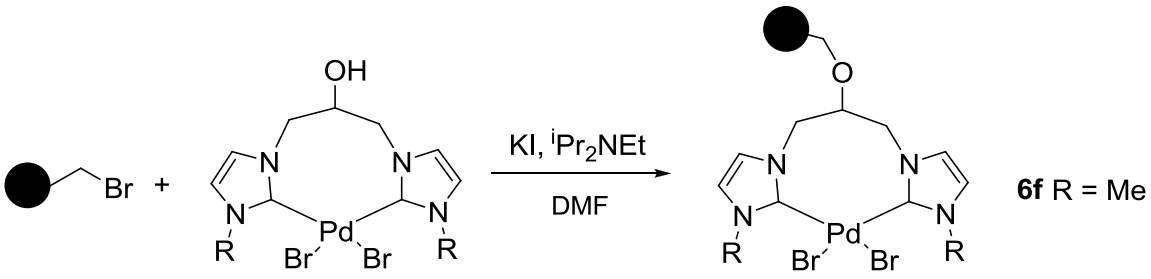
Scheme 33: Immobilization of the palladium catalyst by J. Schwarz *et al*.



Scheme 34: Immobilization of the palladium catalyst by T. Kang et.al.

Another way to immobilize Pd-complexes was developed by T. Kang *et.al*.[23] In this work the bisimidazolium salt was first attached to the Merrifield resin via an ether linkage (Scheme 34) and the deprotonated by $Pd(OAc)_2$ to form the immobilized Pd complex.

Based on the studies reported by Schwarz and T Kang, the compound **1e** was immobilized with a brominated polystyrene resin and have used for Suzuki reaction. The complex **1e** was immobilized on a functionalized polystyrene resin (50-100 mesh size, 1.97 mmol Br/g) as shown in Scheme 35. The reaction was carried out in DMF in the presence of $^{i}Pr_2NEt$ as a proton acceptor and with catalytic amounts of KI at RT, following the procedure reported by Luo *et al*.[23] with modification.[159] The loading of the imidazolium groups was determined by means of the nitrogen and palladium content obtained from elemental analysis (Calc (%) of 1.1 Pd, N 0.56, found Pd 1.0, N 0.49) and characterized by FTIR spectroscopy (IR(KBr): γ= 1648 (m, C=O), 1383 (m, CH_3)).

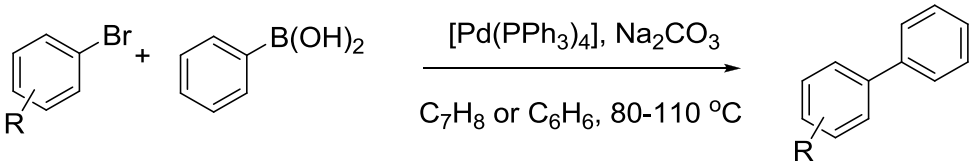


Scheme 35: Synthesis of the polystyrene - supported NHC-Pd complex **6f.**

3.3. Catalytic activity of bis-N-hetrocyclic carbene palladium(II) complexes

3.3.1. Theoretical background of the Suzuki-Miyaura cross-coupling reaction

In 1981, Suzuki and co-workers reported the coupling of aryl iodides or bromides with phenylboronic acid in toluene or benzene in the presence of catalytic $Pd(PPh_3)_4$ and a stoichiometric amount of sodium carbonate (Scheme 36). Since then, many novel and varied complexes have been tested in Suziki-Miyaura coupling reaction.[161,162]



Scheme 36: Suzuki-Miyaura cross-coupling reaction.

The Suzuki-Miyaura cross-coupling is one of the most common and important organic synthetic applications of C-C bond forming reactions for about 30 years[161]. The Suzuki-Miyaura coupling is applied extensively to synthesize pharmaceuticals[163], bio-organic substances[164], high-tech products[165], agricultural chemicals[166] and more.[167] In recent years, research groups focused on a green chemistry approach for cross-coupling reactions by using recyclable catalysts[168], solid-phase Suzuki coupling and "green solvents" for a broad range of biaryl products along with simple protocols.[169,170]

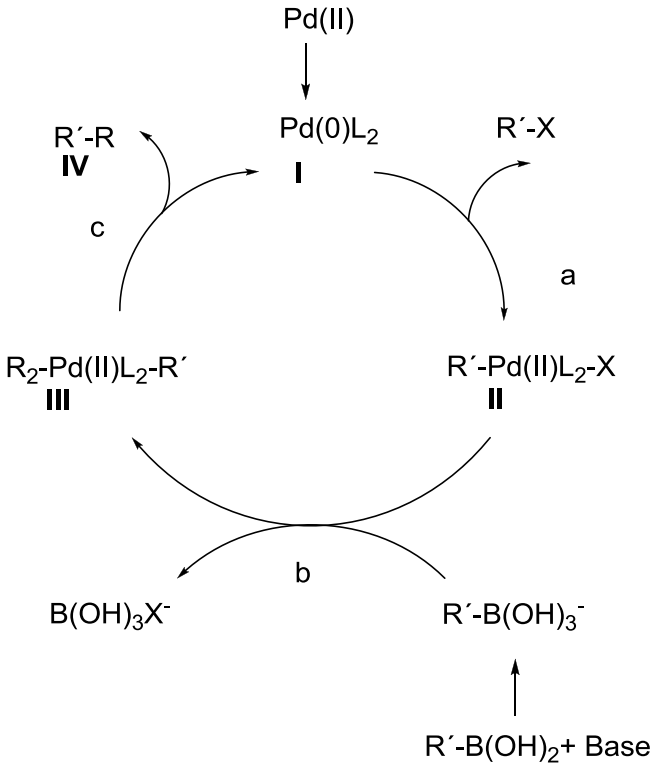
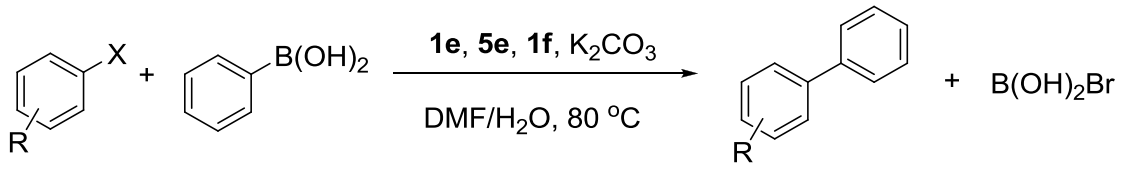


Figure 21: Mechanism of the Suzuki -Miyaura coupling reaction.

Figure 21 depicts the mechanism of the Suzuki-Miyaura reaction, which contains three steps. First, the oxidative addition of the vinylic or aromatic halide to a Pd(0) complex (**I**) generates the Pd(II) intermediate (**II**).[161c] Then, the boronic acid is activated, usually with a base such as potassium ethoxide and potassium hydroxide. The base converts the borne [R´B(OH)$_2$] into more reactive boronate [R´B(OH)$_3$]. Activation of the boron atom enhances the polarization of the organic ligand R´ and facilitates the transmetallation step to form R´-Pd(II)L$_2$ -R (**III**)(b). In the last step reductive elimination leads to the formation of the C-C coupling product **IV** and the reformation of the active species Pd(0) L$_2$(**I**) (c).

3.3.2. Catalytic activity of Bis(NHC) Pd(II) complexes

Through the synthesized palladium bis(NHC) complexes, **1e**, **5e** and **1f** found to be active for the Suzuki - Miyaura coupling reaction. The catalytic properties of **1e**, **5e** and **1f** were evaluated for the cross coupling reaction of aryl bromides with aryl boronic acids (Scheme 37).

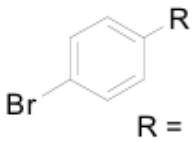


Scheme 37: Suzuki-Miyaura cross-coupling.

Both activated; non-activated and de-activated substrates were used for the sake of comparison. The reaction was carried out either at room temperature or at 80 °C. At room temperature non-coupling products were observed. The results of the reaction at 80 °C are given in Table 11. As expected, the reaction of phenylboronic acid with *p*-bromoacetophenone to yield 4-acetobiphenyl was achieved with 66 % yield (Table 11, entry 3). A turnover frequency of ca. 500 h^{-1} and a conversion of about 60 % after 24 h was

observed for both complexes **1e** and **5e** (Table 11, entry 3 and 6). For the coupling of phenylboronic acid with bromobenzene yielding biphenyl as the product (Table 11, entry 1 and 4) the yield is about 40 % and the TOFs is ca. 400 h^{-1}. With 4-bromoanisole as substrate, yielding 4-methoxybiphenyl as product (Table 11, entry 2 and 5), the obtained product yield is only 15 %, the turnover frequencies were calculated to be around 150 h^{-1}. According to these results it seems that the substituents at the nitrogen atoms of the imidazole rings do not significantly affect the catalytic activity of the complex in the Suzuki coupling. For a better comparison of the activity, the time-curves of catalyst **1e** are given in figure 22.

Table 11: Suzuki-Miyaura cross-coupling of bulky aryl halides and aryl boronic acids, and complexes **1e** and **5e**

Entry	[Pd]	Solvent		Time [h]	Yield [%]	TOF[h^{-1}]
1	**1e**	DMF/H_2O	H	24	38	460
2	**1e**	DMF/H_2O	OCH_3	24	15	160
3	**1e**	DMF/H_2O	$C(O)CH_3$	24	66	530
4	**5e**	DMF/H_2O	H	24	35	400
5	**5e**	DMF/H_2O	OCH_3	24	18	150
6	**5e**	DMF/H_2O	$C(O)CH_3$	24	60	480

Reaction conditions: Catalyst concentration (0.2 mol %), 1.00 mmol arylbromide, 1.2 mmol phenylboronic acid, 1.5 mmol K_2CO_3, T = 353K. Yields were calculated via GC-FID with diethylenglycol di-n-butyl-ether as internal standard. TOFs have been calculated from the conversion after 10min.

The immobilized complex **1f** was tested in heterogeneous Suzuki-Miyaura coupling reaction, in order to compare its activity with the homogeneous complex **1e**. The reaction conditions were the same as used in the homogeneous reaction. The results are summarized in table in 12.

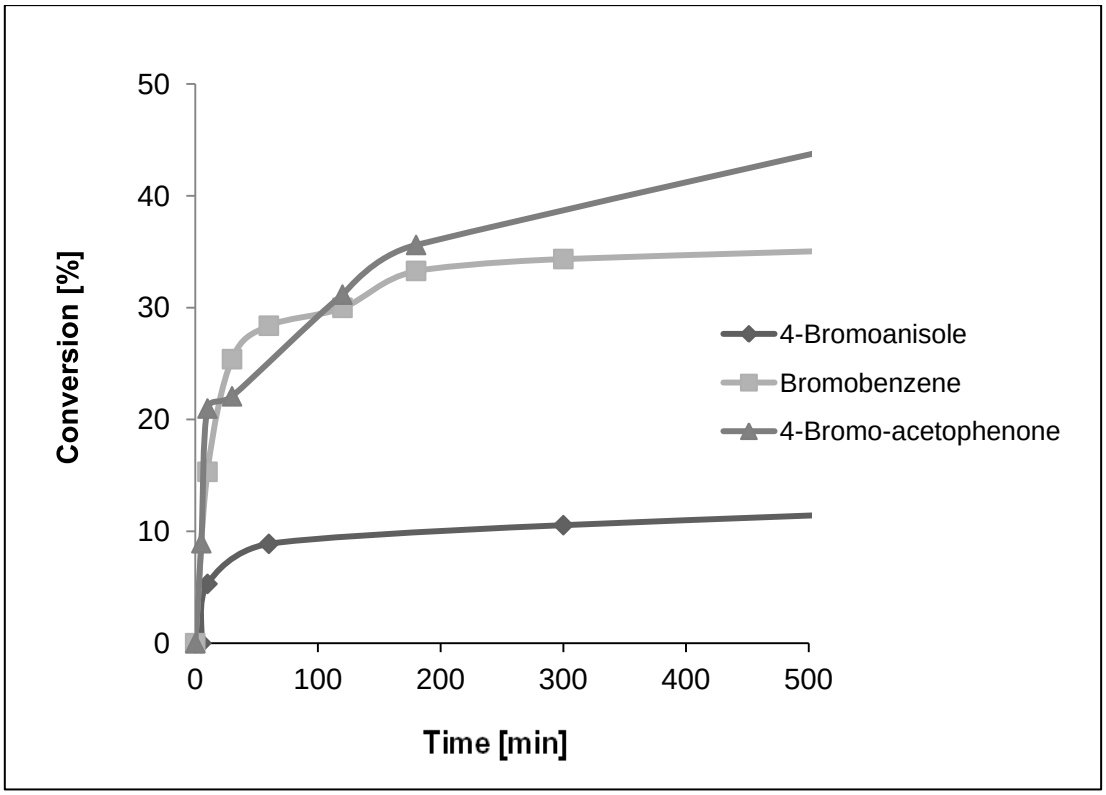
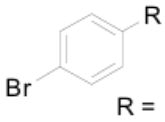


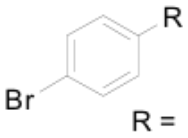
Figure 22: Time - conversion curve of compound **1e** in Suzuki-Miyaura reaction

Table 12: Suzuki-Miyaura reaction with heterogeneous complex **1f**

Entry	[Pd]	Solvent	 R =	Time [h]	Yield[%]
1	**1f**	DMF/H_2O	H	24	33
2	**1f**	DMF/H_2O	OCH_3	24	10
3	**1f**	DMF/H_2O	$C(O)CH_3$	24	58

Reaction conditions: Catalyst concentration (2 mol %), 1.00 mmol arylbromide, 1.2 mmol phenylboronic acid, 1.5 mmol K_2CO_3, T = 353K. Yields were calculated via GC-FID with diethylenglycol di-n-butyl-ether as internal standard. TOFs have been calculated from the conversion after 10min.

Table 13: Comparison of the results in homogeneous and heterogeneous catalysis

[Pd]		time [h]	yield[%]
1d	H	24	38
1d	OCH_3	24	15
1d	$C(O)CH_3$	24	66
1e	H	24	33
1e	OCH_3	24	10
1e	$C(O)CH_3$	24	58

The reaction of bromobenzene with phenyl boronic acid yielded 33 % biphenyl as product within 24h. The highest yield of 58% was observed using the activated 4-bromoacetophenone as substrate. As shown in Table 13, the results obtained with the immobilized (heterogeneous) catalyst are quite similar to these in the homogeneous reaction. Accordingly, immobilization does not significantly reduce the catalytic activity of the complexes. Examination of the liquid phase of the catalytic reactions showed, that catalyst **1f** remains immobilized during the course of the reaction. This is in accordance with the catalytic results reported by Luo *et al*.[23,156] who emphasized the low leaching tendency of such catalyst systems.

3.4. Conclusion

New hydroxyl-functionalized bisimidazolium precursors were prepared and employed for the synthesis of Palladium bis(NHC) complexes as well as their immobilized derivatives. The obtained compounds were applied as catalyst for both homogeneous and heterogeneous Suzuki-Miyaura reaction of different arylbromiodes with phenylboronic acid. The reaction was carried out at 80 ^{o}C in air. For both reactions similar results were obtained, showing that immobilization does not significantly reduce the catalytic activity.

Chapter 4

A novel phthalimido-functionalized N-heterocyclic mono-carbene complex of palladium(II) as catalyst for Suzuki coupling reactions in water and air

This chapter contains the following unpublication:

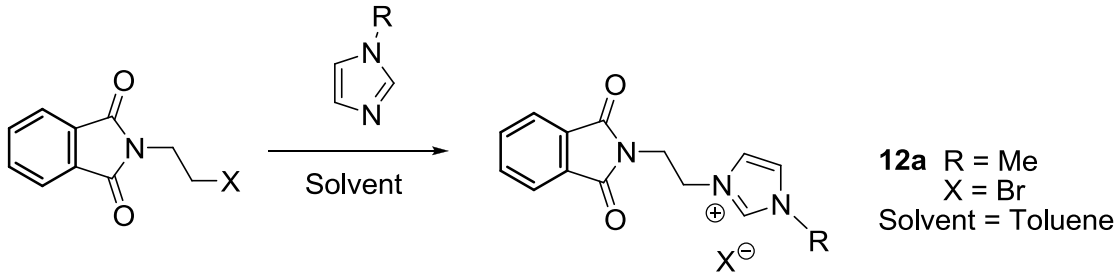
Serena Li Min Goh, Manuel P. Högerl, Alexandrina D. Tanase, Nadežda B. Jokić, Bettina Bechlars, Walter Baratta, Fritz E. Kühn

4. A novel phthalimido-functionalized N-heterocyclic mono-carbene complex of palladium(II) as catalyst for Suzuki coupling reactions in water and air

In the past, only a few cationic Pd(II) complexes with one NHC ligand successfully were applied as catalysts for Suzuki coupling with yields up to good to excellent yield.[161,771-173] Most of them, either contain a chelating NHC ligand with a P-, N- or S- donor functionality,[174-177] or a monodendate NHC ligand along with additional ligands such as phosphanes and allyl.[177,178] So far none of these catalysts were examined in terms of reusability by performing consecutive runs in aqueous solution. Therefore the cationic complex *cis*-[(Me-NHCphthaloyl)(CH_3CN)$_2$ClPd](PF_6), was synthesized and its catalytic activity was investigated. It contains a NHC ligand with phtaloyl moiety and is soluble in polar and aqueous solvents. Promising results were obtained, the catalyst proved to be highly active in aqueous dimethylformamide (H_2O : DMF = 4 : 1) medium and remains active after several reaction cycles.

4.1. Synthesis of phthalimido-functionalized imidazolium salts **12a**

Based on a previous by published procedure the imidazolium salt **12a** functionalized with the phthalamido group were obtained by quaternization of alkyl- or aryl-imidazoles with *N*-(2-bromoethyl)- phthalimide.[179,180] (Scheme 38).

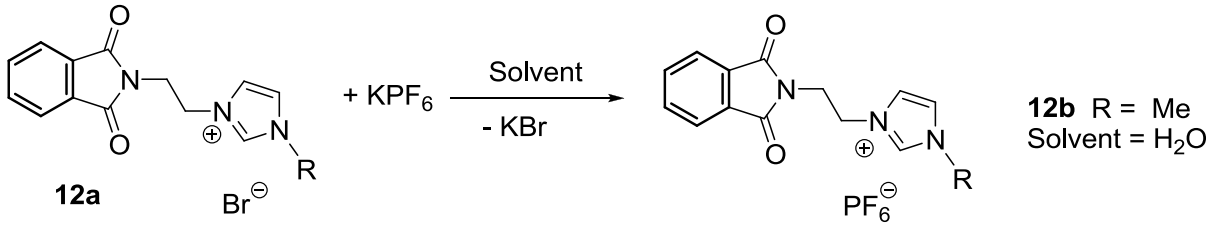


Scheme 38: Synthesis of phthalimido-functionalized imidazolium salt **12a**

The hybrid salt **12a** is an air stable powder and was characterized by elemental analysis, high-resolution mass spectrometry (FAB), and ^{1}H and $^{13}C\{1H\}$ NMR spectroscopy. The ^{1}H NMR spectrum of **12a** shows resonance signal at δ = 9.11 ppm, which is characteristic for the NC*H*N imidazolium proton.

4.1.1. The anion exchange reaction of the ligand **12a**

The anion exchange from the bromide salt **12a** to the corresponding hexafluorophosphate salt **12b** was carried out by mixing an aqueous solution of **12a** with a saturated aqueous solution of KPF_6 at 60 ^{o}C, which led to the precipitation of **12b** (Scheme 39). **12b** was characterized by FAB mass spectrometry, elemental analysis and ^{1}H and ^{31}P-NMR spectroscopy.

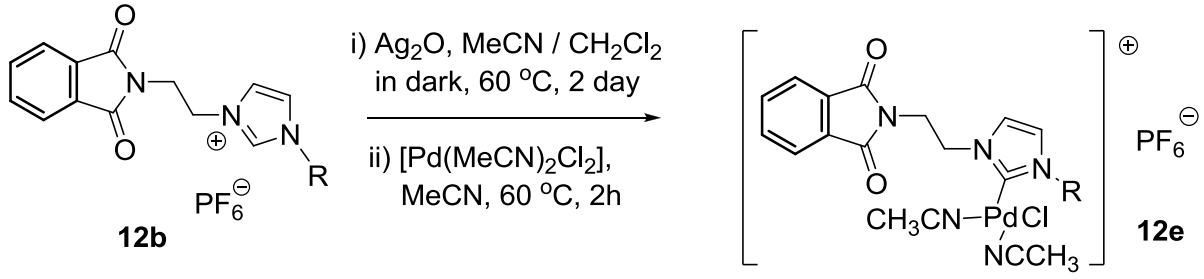


Scheme 39: Anion exchange reaction Br^{-}/ PF_6^{-} to form **12b**

4.2. Synthesis of phthalimido - functionalized N-heterocyclic mono - carbene complex of palladium(II) ***12e***

Imidazolium salts are frequently used as precursors for metal *N*-heterocyclic carbene complex. Stirring a mixture of the water-soluble imidazolium salt **12b** and Ag_2O in acetonitrile / dichloromethane led to gave a clear solution of the silver carbene complex **12d** (Scheme 40), which could be isolated with yields ranging between 43-67%[172]. In the second step, the NHC ligand was transferred to Pd complex by reacting **12d** with $[Pd(MeCN_2)Cl_2]$ in

acetonitrile, which led to the formation of the complex *cis*-[(Me-NHCphthaloyl)(CH_3CN)$_2$ ClPd](PF_6) (**12e**), which contains an NHC ligand with a phtaloyl moiety and displays a good solubility in polar and aqueous solvents.



Scheme 40: Synthesis of complex **12e**

As a solid, **12e** is stable towards air and moisture for several weeks without decomposition. ^{1}H, ^{13}C{^{1}H}, and ^{31}P NMR spectroscopy and X-ray crystallography were used to determine the structure of the complex **12e**, and its composition was confirmed by mass spectrometry (ion peak for [Me-NHCphthaloylClPd]$^{+}$ at *m*/*z* = 398 (10%)) and elemental analysis.

The ^{1}H NMR spectra of **12e** in d_6-DMSO and also in d_3-MeCN show four resonance signals with multiplet structures, which were assigned to two sets of chemically and magnetically inequivalent protons H_a/H_a' and H_b/H_b' of the ethylene bridge. This clearly indicates a restricted rotation of the tethered phtalimido moiety with respect to the palladium center.

The carbene carbon atom gives rise to an uncommonly high upfield shifted signal in the ^{13}C{^{1}H} NMR spectrum at 143 ppm. The carbene carbon signals of most monocationic NHC palladium complexes appear in the range of 160 to 190 ppm.[173,181] Only a series of dicationic phosphine-functionalized NHC palladium complexes with similar carbon shifts of 142 to 149 ppm were reported before.[177] Cationic bis(NHC) - palladium complexes also display similar carbene carbon shifts around 143-157 ppm.[176, 182]

Yellow crystals suitable for X-ray crystallography were grown by slow diffusion of diethylether into a concentrated acetonitrile solution of compound **12e** at room temperature. As shown in Figure 23, the monodendate phthalimido-functionalized NHC ligand, two acetonitrile molecules and one chloro ligand occupy the coordination sites of a square planar geometry.

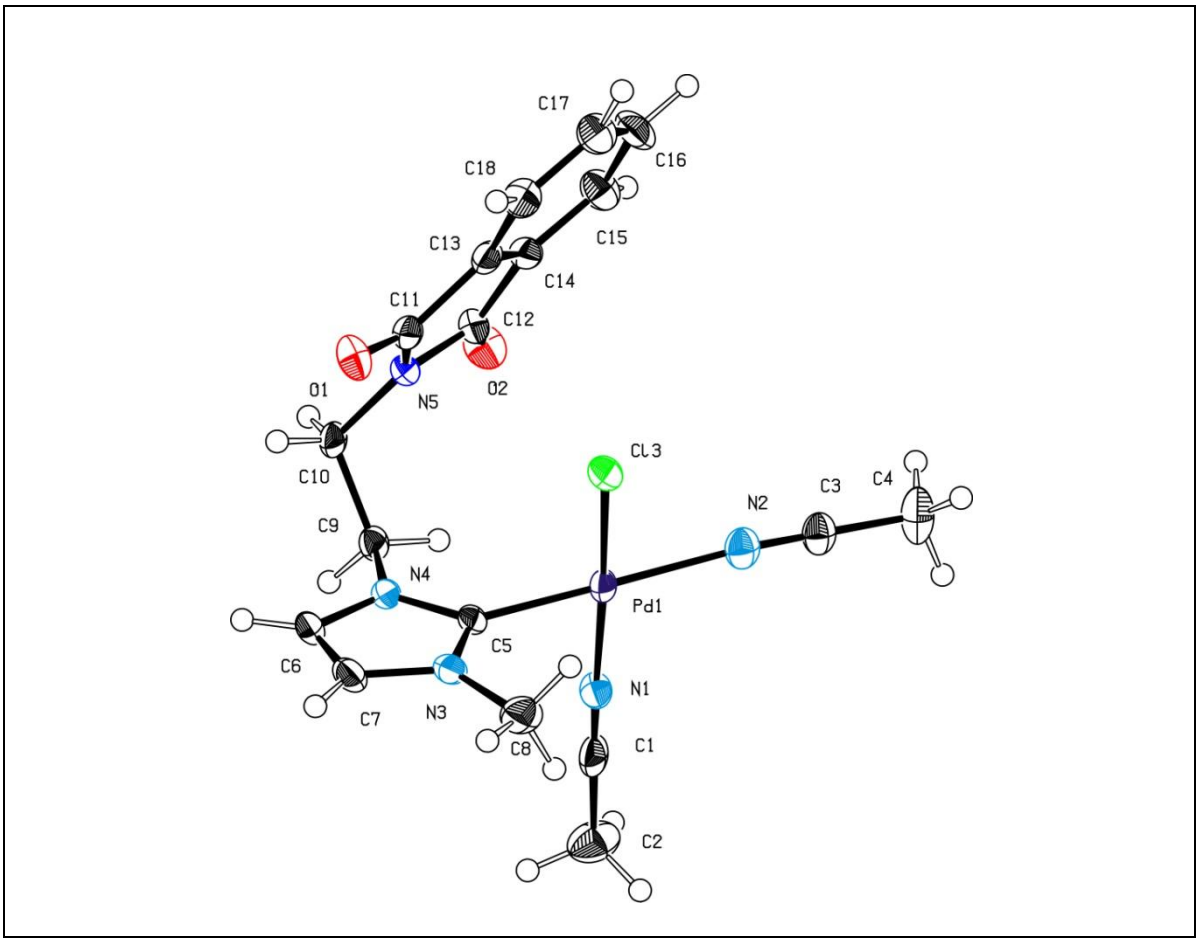


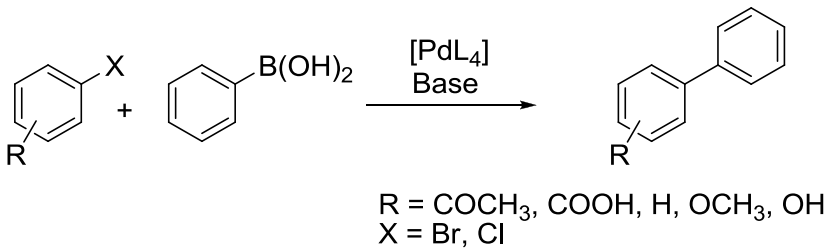
Figure 23: Solid state structure of the cationic complex in **12e**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level.

Selected bond lengths (Å) and angles (°): Pd1-C5 1.965(2), Pd1-N1 2.018(2), Pd1-N2 2.096(2), Pd1-Cl1 2.284(1), C5-Pd1-N1 90.65(7), C5-Pd1-N2 178.5(1), N1-Pd1-N2 89.2(1), C5-Pd1-Cl1 88.1(1), N1- Pd1-Cl1 178.4(1), N2-Pd1-Cl1 92.1(1).

The complex was tested for its catalytic properties in the Suzuki cross-coupling reaction with various substrates. The catalyst proved to be highly active in aqueous dimethylformamide (H_2O : DMF = 4:1) and remains active after several reaction cycles.

4.3. Catalytic activity of phthalimido-functionalized N-heterocyclic mono-carbene complex of palladium(II)

As already mentioned previously, the Suzuki-Miyaura cross-coupling reaction of aryl bromides with arylboronic acids catalyzed by Pd-NHC complexes is extensive by documented. To evaluate the activity of **12e**, it was tested performance as a catalyst in the Suzuki-Miyaura cross-coupling reaction for various substrates. The reaction of the coupling of 4-bromoacetophenone to 4-acetylbiphenyl shown in scheme 41, was carried out in DMF at 80 °C in the presence of **12e**. The conversion of the reaction versus time is shown in figure 24.



Scheme 41: Suzuki-Miyaura cross-coupling.[a,b,c].

Interestingly, no induction period was observed, even though palladium has the oxidation state of +2, suggesting that the Pd(II) complex is either reduced to the active Pd(0) species rapidly or **12e** operates through a Pd(II)/Pd(IV) catalytic cycle as proposed by Herrmann *et al*.[183]

In order to evaluate the influence of different solvents, 4-bromoacetophenone was used as a substrate and the reactions were conducted on air. Traditionally, solvents like THF, dioxane and toluene are typical employed for the Suzuki-Miyaura cross-coupling reactions. Instead dimethylformamide (DMF), acetonitrile MeCN, toluene, and water were used for this study.

Figure 25 demonstrates that the con conversion rate increases in the following order: dimethylformamide (DMF) < acetonitrile (MeCN) < toluene < acetonitrile-water (1:1).

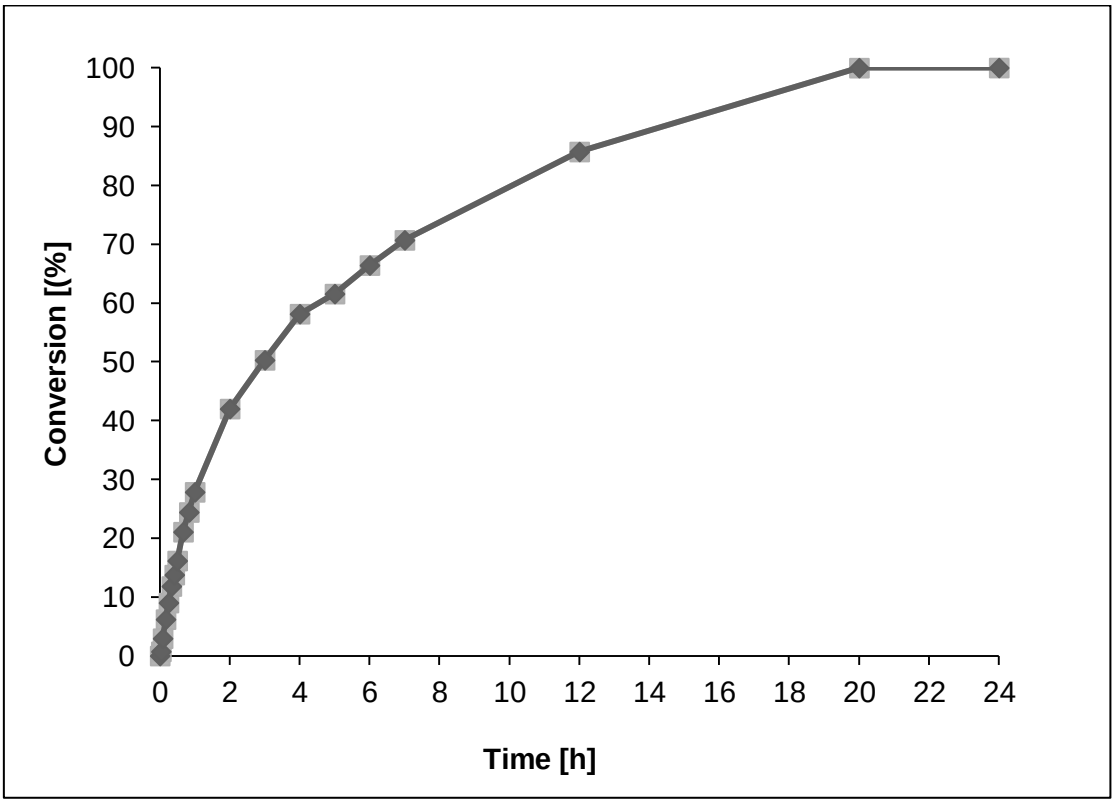


Figure 24: Solvent effects in the Suzuki coupling reaction using complex **12e** as catalyst.

[a] Reaction conditions: 1 mmol of 4-bromoacetophenone and 1.2 mmol of phenylboronic acid in 4 ml DMF; 1 ml of complex **12e** in DMF (0.1 mol%); 2 equivalents of K_2CO_3; 80 °C

[b] Conversion was determined for two separate runs, average values are used.

[c] Conversions were determined by GC.

With the addition of water, the reaction rate reaches a conversion of more than 90% in 5 hours and approaches (almost) completion within 24 hours (98%).[184,185] This observation prompted us to test mixtures of solvent and water: H_2O:DMF (1:1), H_2O:DMF (4:1) and pure H_2O. At higher water concentrations, however, product precipitation did not allow a kinetic evaluation. Instead the amount of precipitated product was used to judge the reaction progress.[169]

For a catalyst concentration of 0.01 mol% the highest conversion (71%) was achieved after 15 minutes in a 4:1 mixture of water and DMF. In pure water, only 39% of the substrate was converted at the same reaction conditions. This was attributed to the low solubility of the hydrophobic substrates in water. Therefore, further experiments were carried out in a 4:1 mixture of H_2O and DMF, when 1.0 mol% of **12e** was used.

To evaluate the catalysts versatility, the Suzuki-Miyaura coupling reaction, involving a range of aryl halides and phenylboronic acid was carried out. As shown in table 14, excellent results were achieved within 24 hours for the coupling of 4-bromoacetophenone, 4-bromobenzoic acid, 4-bromoanisole, 4-bromophenol and 4-bromobenzene with phenylboronic acid at 80 °C.

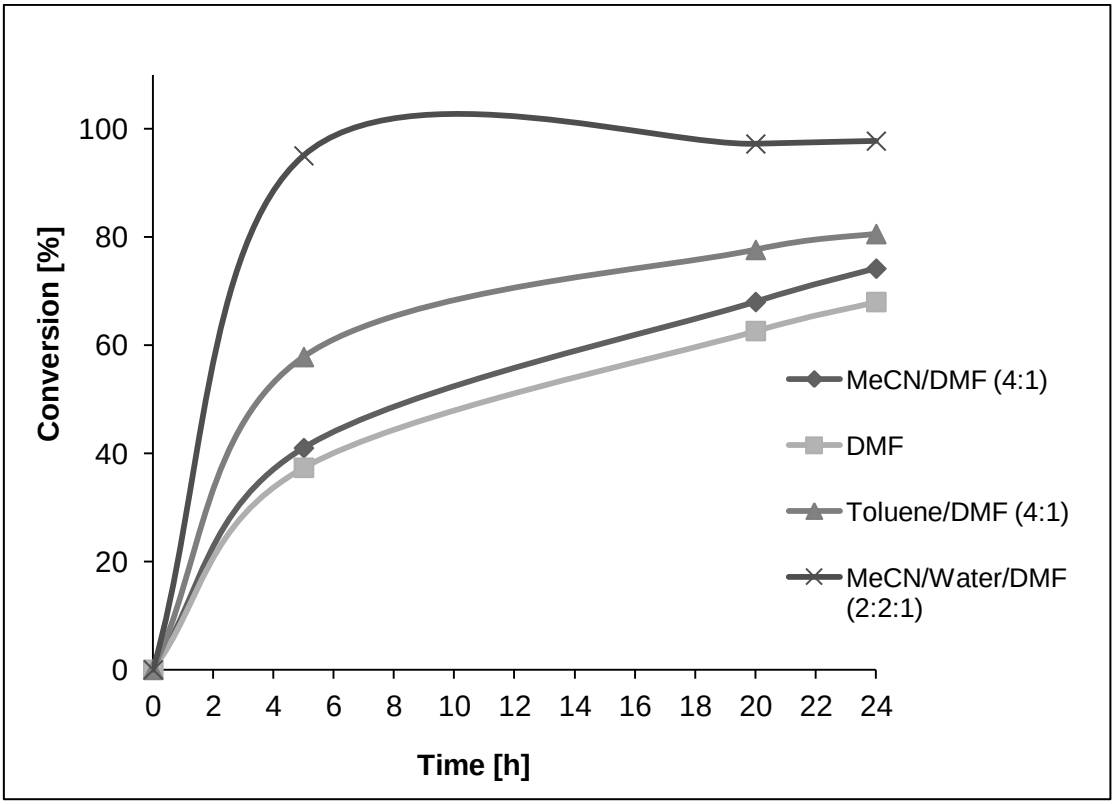
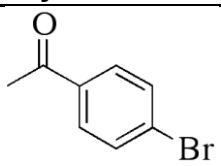
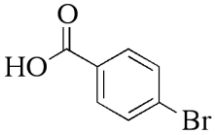
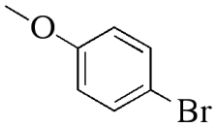
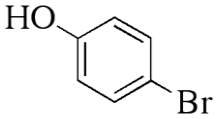
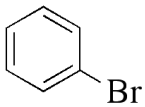
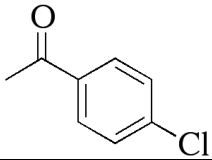


Figure 25: Conversion of 4-bromoacetophenone over time in DMF.

[a] Reaction conditions: 1 mmol of 4-bromoacetophenone; 1.2 mmol of phenylboronic acid; 4 ml of solvent; 2 equivalents of K_2CO_3; 80 °C; 1 ml of catalyst **12e** (1.0 mol%) in DMF. Conversions were determined by GC.

In the case of 4-bromobenzoic acid, homo-coupling of the phenylboronic acid resulted in the formation of biphenyl as a side product. The coupling of 4-chloroacetophenone with phenylboronic acid only proceeded to 26% conversion in the presence of 1.0 mol% of **12e** and the formation of biphenyl and dehalogenation of the substrate were observed.

Table 14: Influence of catalyst loading on the different substrates in Suzuki-Miyaura cross-coupling reactions.[a]

Entry	Aryl halide RX	Cat mol [%]	Conv. [%][b]
1		1.0	>99
2		0.1	>99[c]
3			97[d]
4		0.01	>99[c]
5			71[d]
6		0.001	14
7		1.0	>99
8		0.1	>99
9		1.0	91
10		0.1	70
11		1.0	>99
12		0.1	>99
13		1.0	82
14		0.1	50
15		1.0	26
16		0.1	0

[a] Reaction conditions: 1 mmol of aryl halide; 1.2 mmol of phenylboronic acid; 4 ml of water; 2 equivalents of K_2CO_3; 80 °C ; 1 ml of complex **12e** in DMF in varying concentration; 24 hours. Reaction times are not optimized.

[b] Conversions were determined by GC.

[c] Reaction time after 60 minutes and 24 hours.

[d] Reaction time after 15 minutes.

To evaluate the influence of catalyst loading for each substrate, the catalyst concentration was reduced. When the catalyst concentration of **12e** was lowered to 0.1 mol%, while all other reaction conditions were retained, the conversion of deactivated 4-bromoanisole and non-activated 4-bromobenzene decreased by approximately 20 - 30%, the activated aryl bromides and the deactivated 4-bromophenol, however, were still converted quantitatively. No conversion was observed for 4-chloroacetophenone at lower catalyst concentration. Quantitative conversion was still achieved in case of 4-bromoacetophenone when the catalyst loading was further reduced to 0.01 mol%, only at a catalyst loading of 0.001mol% the conversion significantly decreased (14% after 24 hours).

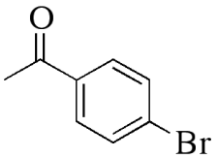
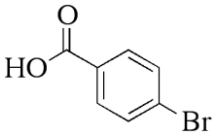
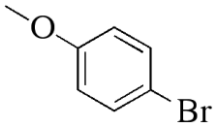
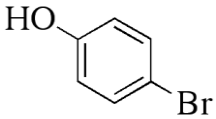
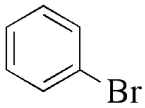
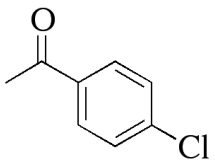
To determine the time that is actually required to fully convert 4-bromoacetophenone, samples were taken at shorter reaction time intervals. At a catalyst loading of 0.1 mol%, 97% and full conversion was reached after 15 and 60 minutes, respectively. With 0.01 mol% catalyst, only 71% of the substrate was converted after 15 minutes. With the assumption no induction period exists and that the time-conversion curve is linear for the first 15 min, a TOF of 28400 h^{-1} was determined.

With respect to conversion, the obtained results are comparable to other NHCs ligated catalysts with different side-functionalities.[184,186] The reaction times, however, are significantly shorter than for other NHC Pd complexes, which required 6 to 24 h for the full conversion of similar substrate.[185,187]

To further optimize the reaction conditions, at different temperatures were applied (table 15). The reduction of the reaction temperature from 80 °C to 50 °C and 30 °C at a catalyst loading

of 0.1mol% led to a significant decrease of the conversion of 4-bromoacetophenone after 15 minutes from 97% to 72% and 40%, respectively.

Table 15: Suzuki-Miyaura cross-coupling reactions at different temperature.[a]

Entry	Aryl halide RX	Temp [°C]	Conv. [%][b]
1		30	40[c]
2		50	72[c]
3		80	97[c]
4		80	>99
5		100	>99
6		80	70
7		100	95
8		80	>99
9		100	>99
10		80	50
11		100	77
12		80	26[d]
13		100	59[d]

[a] Reaction conditions: 1 mmol of aryl halide; 1.2 mmol of phenylboronic acid; 4 ml of water; 2 equivalents of K_2CO_3; 1 ml of complex **12e** in DMF (0.1 mol%); 24 hours. Reaction times are not optimized.

[b] Conversions were determined by GC.

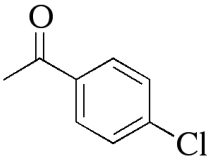
[c] Reaction time after 15 minutes.

[d] 1.0 mol% catalyst loading of complex **12e**.

As expected, a higher reaction temperature (100 °C) led to an increased conversion of all substrates. Even for 4-chloroacetophenone, a significant conversion of 59% was observed at

100 °C. In order to further increase the conversion of this substrate, additives were applied to the reaction mixture (Table 16).[188, 189]

Table 16: Addition of additives for the Suzuki-Miyaura cross-coupling reactions of 4-chloroacetophenone.[a]

Entry	Aryl halide RX	Additives	Conv. [%][b]
1		-	59
2		nBu$_3$P (0.04 eqv)	73
3		TBAB (2.0 eqv)	19
4		TBAB (0.5 eqv)	43

[a] Reaction conditions: 1 mmol of aryl halide; 1.2 mmol of phenylboronic acid; 4 ml of water; 2 equivalents of K_2CO_3; 100 °C; 1 ml of complex **12e** in DMF (1.0 mol%); 24 hours. Reaction times are not optimized.

[b] Conversions were determined by GC.

The best result for 4-chloroacetophenone (73% conversion) is reached when small amounts of *n*-tributylphosphine (nBu$_3$P) (0.04 equivalents) are added to the reaction mixture containing 1.0 mol% of **12e** at 100 °C. Yet, when 2.0 equivalents of tetra-*n*-butylammonium bromide (TBAB) are added as additive and stabilizer of the possible catalytically active palladium nanocluster,[188,190] the conversion decreases is significantly from 59% to 19%, which is unexpected. TBAB actually hinders the cross-coupling process. This could be attributed to the influence of the excessive bromide anions from TBAB, which could play a role in the mechanism of the catalytic cycle as suggested by Amatore and Jutand.[191]

To determine whether **12e** is still active after converting the first batch of 4-bromoacetophenone, a second fresh batch of 4-bromoacetophenone was added to the reaction mixture after one hour. As shown in figure 26, the catalytic activity slightly decreased to 85% conversion after a second run. Consecutive six additions of the bromoacetophenone resulted in 61% total yield. The decrease in conversion could be due to the lipophilic biaryl

product, which precipitates during the catalytic reaction, leading to a decreased homogeneity of the reaction mixture.

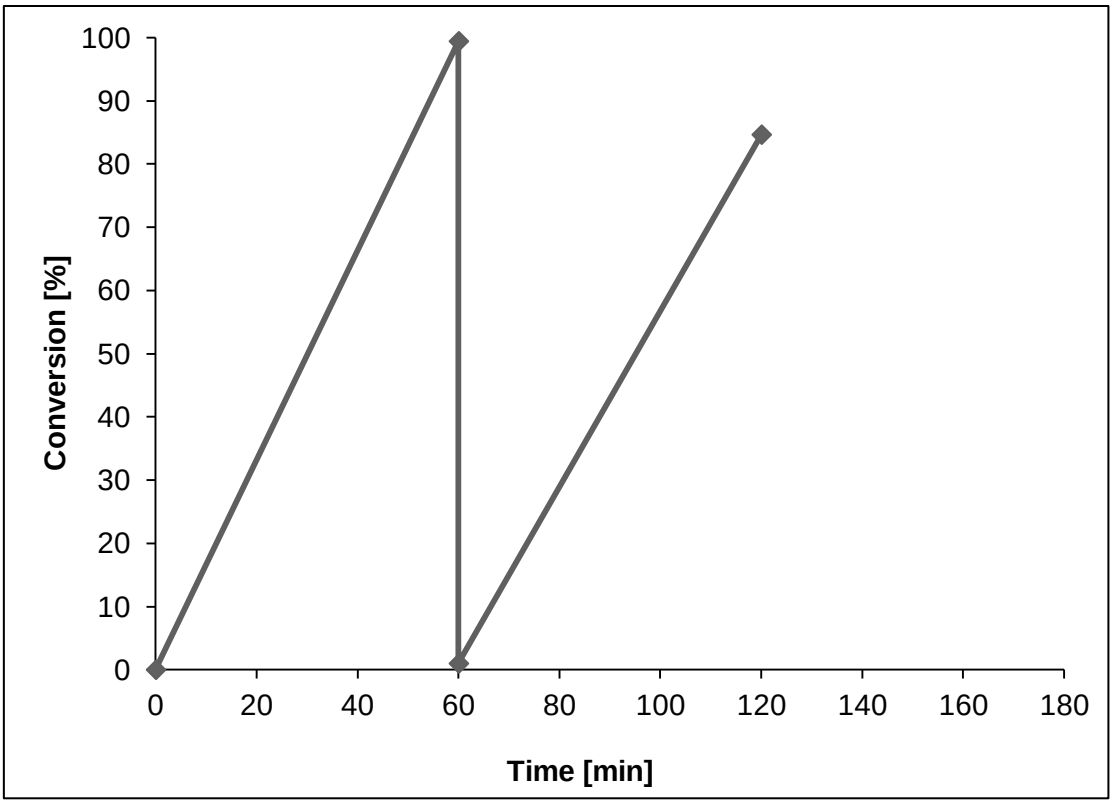


Figure 26: Conversion of 4-bromoacetophenone over time. Study of the catalytic reaction of the complex **12e** after 2 reaction cycles.

[a] Reaction conditions: 1 mmol of of 4-bromoacetophenone; 1.2 mmol of phenylboronic acid; 4 ml of water; 2 equivalents of K_2CO_3; 0.1 mol% of complex **12e** in 1 ml DMF.

[b] Conversions were determined by GC.

4.4. Conclusion

A novel monocationic Pd(II) complex, containing a phthalimido-functionalized NHC ligand, was synthesized and fully characterized. Since not many of the known mono-cationic NHC-Pd complexes were tested in Suzuki-Miyaura cross-coupling reaction, the catalytic performance of **12e** was evaluated in different reaction conditions for various substrates,

including aryl chloride. The synthesized catalysts are air-stable and showing good catalytic activity for the Suzuki-Miyaura cross-coupling of biaryls in an aqueous DMF solution (H_2O:DMF (4:1)).

Additionally reduction of the Pd(II) complex to the corresponding active Pd(0) species proceeds the either rather fast (< 2 min) or not at all in DMF, since no induction period is observed. **12e** is active for repeated runs, rendering it as a potential recyclable catalyst. At a catalyst loading of only 0.01 mol%, 4-bromoacetophenone is fully converted with a TOF of at least 28 400 h^{-1} at 80 °C, thus making **12e** the most active NHC Pd(II) reported to date in Suzuki-Miyaura cross-coupling reactions.

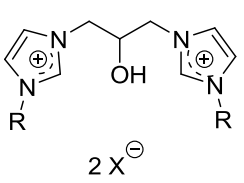
Chapter 5

Summary

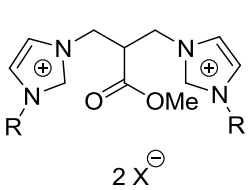
5. Summary

As mentioned in the introduction section, NHCs have been established as a major ligand-class in organometallic chemistry in recent years. One of the major advantages of NHC ligands is to provide extra stability to metal complexes.

The objectives of this work, which have been mentioned already previously (introduction 1.5) focused on two different projects. In the first project, the preparation of rhodium (Chapter 2) and palladium (Chapter 3) bis(NHC) complexes and the examination of their catalytic properties in hydrosilylation (Chapter 2), transfer hydrogenation (Chapter 2) and Suzuki coupling (Chapter 3) was in the focus. The bis(NHC) complexes were found to have excellent air and thermal stabilities even at elevated temperatures. The first challenge was the synthesis of new bis imidazolium salts as ligand precursors with a functional group attached to the bridging moiety that could serve as a linker to a solid support.



1a,b R = Me X = Br, PF_6
2a,b R = Et X = Br, PF_6
3a,b R = ^{i}Pr X = Br, PF_6,
4a,b R = ^{t}Bu X = Br, PF_6
5a,b R = Bn X = Br, PF_6 , BPh_4
6a,b R = Mes X = Br, PF_6

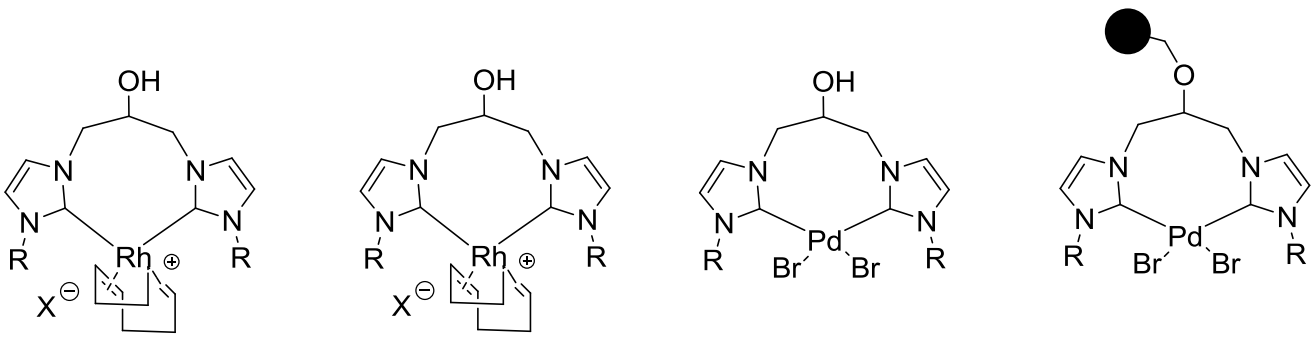


7a,b R = Me X = Br, PF_6
8a,b R = ^{i}Pr X = Br, PF_6
9a,b R = ^{t}Bu X = Br, PF_6
10a R = Bn X = Br
11a R = Mes X = Br

Figure 27: Bis(NHC) Ligands.

As discussed in chapter 2 a series of hydroxyl - methoxy carbonyl functional bis-imidazolium salts was prepared and characterized. Only the hydroxyl-functionalized bis-imidazolium salts could be successfully applied for the synthesis of the corresponding rhodium (Chapter 2) and palladium (Chapter 3) complexes. In general, all compounds are easily accessible, air stable and can be obtained in good yields [yield (bis-imidazolium salts) = 65 – 96 %; yield (bis(NHC)-rhodium and bis(NHC)-palladium complexes) = 55 – 82 %].

The rhodium (I) complexes were tested in homogeneous hydrosilylation reaction of acetophenone with diphenylsilane and in the transfer hydrogenation of acetophenone and show good activities. The choice of the *N*-substituent, the anion, the solvent and the base are important parameters influencing the catalytic reaction. The best result was obtained with the Bn-substituted bis NHC and the BPh_4^- -anion in the hydrosilylation of 4-frouro-acetophenone (100% conversion is reached within 50 min) and the best result for transfer hydrogenation of acetophenone was obtained with the ^{i}Pr-substituted bis NHCs and PF_6^- anion in the presence of the strong base KOH and 2-isopropanol as hydrogen donor (100 % conversion is reached within 360 min).



1c R = Me
2c R = Et
3c R = ^{i}Pr
4c R = ^{t}Bu
5c^{PF6} R = Bn
6c R = Mes
X = PF_6

5c^{BPh4} R = Bn
X = BPh_4

1e R = Me
5e R = Bn

6f R = Me

Figure 28: Summary of this thesis synthesized Rh(I) and Pd(II) biscarbene complexes.

The free and immobilized Pd-complexes were applied as catalyst for both homogeneous and heterogeneous Suzuki-Miyaura reactions of different arylbromiodes with phenylboronic acid. In both reactions similar results were obtained, indicating that immobilization does not significantly reduce the catalytic activity.

In the second project was to investigate the catalytic potential of a palladium (II) complex with a donor-functionalized NHC ligand for Suzuki coupling reaction. Hence, a novel monocationic Pd (II) complex, containing a phthalimido - functionalized NHC ligand has been synthesized and fully characterized.

The catalyst is air-stable and of good activity for the Suzuki-Miyaura cross-coupling of biaryls in an aqueous DMF solution (H_2O:DMF (4:1)). Interestingly the reduction of the Pd(II) complex to the corresponding active Pd(0) species proceeds either rather fast (< 2 min) or not at all in DMF, since no induction period is observed. **12e** is active in several consecutive runs, rendering it as a potential recyclable catalyst with a TOF of 28 400 h^{-1} for the conversion of 4-bromoacetophenone at a catalyst loading of only 0,01mol% at 80 ^{o}C the most active NHC Pd(II) reported to date.

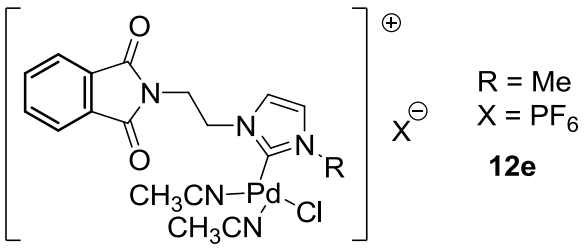


Figure 29: Phthalimido-functionalized *N*-heterocyclic mono-carbene complex of palladium(II).

Chapter 6

Experimental Section

6. Experimental Section

6.1. Methods and Handling of Chemicals

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

Solvents were dried by standard procedures (THF, *n*-hexane, toluene and over Na/benzophenone; CH_2Cl_2 over CaH_2, Methanol and Ethanol were dried over Mg and I_2), distilled under nitrogen, and kept over 4 Å respectively 3 Å molecular sieves. The solvents were also dried with an alumina based solvent purification system. Solvents used in reactions where carbocyclic or free carbene generation was expected were distilled just before use. Solvents used in catalytic testing were distilled 24 hours before use. All other materials used were obtained from commercial resources (Sigma-Aldrich, Fluka, Acros Organics, Lancaster and Merk) and used as delivered unless otherwise noted.

6.2. Techniques Used for Characterization

6.2.1. Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) spectra were recorded on Jeol-JNM-GX-270, Jeol-JNM-GX-400 and Bruker AMX-400 MHz spectrometers operating on following frequencies (Table 17). When needed, the signals were assigned by 2D NMR experiments (APT, DEPT, COSY, HMQC, HMBC and NOESY).

Table 17: 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.

6.2.2. Infrared spectroscopy

Infrared spectra were recorded on a JASKO FT/IR-4000 spectrometer; bands were reported in wave numbers (cm^{-1}). Samples of isolated air and water stable compounds were measured as KBr pellets or made up in a solvent and a dilute solution was evaporated on a thin film of Teflon. IR spectra of these compounds as well as more sensitive compounds were also run in solution using a KBr plate solution cell in various solvents.

6.2.3. Mass spectroscopy

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

6.2.4. Melting points

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

6.2.5. Elemental analysis

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

6.2.6. Gas chromatography

A Varian CP-3800 gas chromatograph coupled with a mass spectrometer (electron impact source, 70 eV), GC/MS, was used for identification of organic products as well as inorganic decomposition products.

A VF-5mf (length 30m, inner diameter 0.25 mm, film thickness 0.25 µm) column was used to facilitate separation, helium was employed as the carrier gas, and injection port temperature split injector flow, and temperature ramp were varied to optimize peak separation with a minimum run time. Resulting mass spectra were matched to the information contained in the

instrument spectral library to elucidate molecules present in the reaction mixture. AGC/MS/MS was carried out under similar conditions on a Varian CP-3800 1200L quadrupole MS/MS in parent-daughter mode to further identify organic molecules.

6.2.7. Gas Chromatography Flame Ionization Detection

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

6.2.8. X-ray analysis

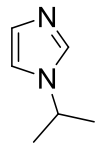
X-ray analyses were carried out by Dr. E. Herdtweck and Dr. B. Bechlars in the Anorganisch-chemische Institut at the Technischen Universitaet München. The single-crystal X-ray diffraction experiment was performed using a Bruker APEX2 diffractometer equipped with a Mo-anode (Mo-K α radiation: λ = 7.1073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

6.3. Synthesis of mono alkyl /aryl imidazolium salts

6.3.1. Mono substituted imidazolium salts 1-Alkylimidazoles

A 100 mL flask equipped with mechanical stirrer, dropping funnel and reflux condenser was loaded with glyoxal (0.1 mol, of 40% aqueous solution), formaldehyde (0.1 mol, of 37% aqueous solution) and alkylammonium salt (0.1 mol), which had been obtained by acidification of the appropriate alkyl amine solution in 20 mL of water with phosphoric acid 85% until the pH 2. The reaction mixture was warmed to 90 - 95 °C and a saturated aqueous solution of 0.1 mol ammonium chloride was added to the stirred reaction mixture over a period of 60 - 75 min. After an additional 10 min of stirring at 95 °C, the crimson reaction mixture was chilled, solid KOH was added and the mixture was extracted with ethyl acetate three times. The combined extract was evaporated and distilled under vacuum.

6.3.1.1. N-Isopropylimidazole



^{1}H-NMR (400 MHz, 298 K, d-$CDCl_3$): δ = 7.30 (1H, s, NC*H*N), 6.81 (1H, s, NC*H*), 6.74 (1H, s, NC*H*), 4.16-4.48 (1H, sept, C*H*), 1.24 (6H, d, CH_3), ppm.

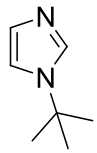
^{13}C{^{1}H}-NMR(100 MHz, 298 K, d-$CDCl_3$): δ = 135.9 (N*C*HN), 129.9 (N*C*H), 117.3 (N*C*H), 49.8 (*C*-H), 24.4 (NCH_3) ppm.

Elem. Anal. Calc. for $C_6H_{10}N_2$

Calc.:	C	65.42	H	9.15	N	25.43
Found:	C	65.40	H	9.13	N	25.40

Yield: 20 %.

6.3.1.2. N-Tert-butylimidazole



^{1}H-NMR (400 MHz, 298 K, d-$CDCl_3$): δ = 7.57 (1H, s, NC*H*N), 7.02 (1H, d, NC*H*), 7.00 (1H, d, NC*H*), 1.53 (9H, s, CH_3) ppm.

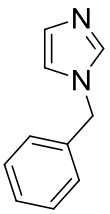
^{13}C{^{1}H}-NMR(100 MHz, 298 K, d_1-$CDCl_3$): δ = 134.0 (N*C*HN), 128.8 (N*C*H), 116.0 (N*C*H), 54.4 (*C*-H), 30.3 (N*C*H_3) ppm.

Elem. Anal. Calc. for $C_7H_{12}N_2$

Calc.:	C	67.70	H	9.74	N	22.56
Found:	C	67.67	H	9.72	N	22.56

Yield: 28 %.

6.3.1.3. N-Benzylimidazole



^{1}H-NMR (400 MHz, 298 K, d-$CDCl_3$): δ = 7.57 (1H, s, NC*H*N), 7.33 (3H, dd, H_{Ar}), 7.14 (2H, d, H_{Ar}), 7.08 (1H,s, NC*H*), 6.89 (1H,s, NHC), 5.10 (2H, s, NCH_2) ppm.

^{13}C{^{1}H}-NMR(100 MHz, 298 K, d-$CDCl_3$): δ = 137.4 (N*C*HN), 136.2 (C_{Ar}), 129.8 (N*C*H), 129.0 (C_{Ar}), 128.2(C_{Ar}), 119.3(N*C*H), 50.7 (N*C*H_2) ppm.

Elem. Anal. Calc for $C_{10}H_{10}N_2$

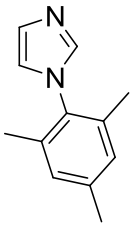
Calc.:	C	75.92	H	6.37	N	17.71
Found:	C	75.90	H	6.36	N	17.70

Yield: 31 %.

6.3.2. Mono substituted imidazolium salts 1-Arylimidazoles

Substituted aniline (0.1 mol) in MeOH (50 mL) was treated with 30% aq glyoxal (0.1 mol) for 16 h at rt. A yellowish mixture was formed. NH_4Cl (0.2 mol) was followed by 37% aq formaldehyde (0.2 mol). The mixture was diluted with MeOH (400 mL) and the resulting mixture was refluxed for 1h. H_3PO_4 (85%) was added over a period of 10 min. The resulting mixture was then stirred at reflux for a further 4-8 h. The reaction was monitored by TLC. After removal of the solvent the dark residue was poured onto ice (300 g) and neutralized with aq. 40% KOH solution until pH 9. The resulting mixture was extracted with Et_2O (5x150mL). The organic phases were combined and washed with H_2O brine and dried (Na_2SO_4). The solvent was removed and the residue was chromatographied on silica gel (petroleum ether-EtOAc) to afford for pure products. All compounds were characterized by ^{1}H NHR, ^{13}C NMR, MS and EA data

6.3.2.1. N-mesitylimidazole



^{1}H-NMR (**400 MHz, $CDCl_3$):** δ = 7.43 (1 H, s, 2H, NC*H*N), 7.23 (1H, s, 4H, N*H*C), 6.97 (2H, s, H_{Ar}), 6.89 (1H, s, NC*H*), 2.34 (3H, s , $CH_{3,para}$), 1.99 (6H, s ,$CH_{3,ortho}$)

^{13}C{1H}-NMR (100 MHz, $CDCl_3$): δ = 138.8 (C_{Ar}, *p*-C), 137,5 (C2, C_{Ar}), 135,5 (NCHN, *o*-C), 133,5 (C_{Ar}, NC(Mes)), 129 (C4, C_{Ar}), 128.0 (C5, NH*C*), 120.1 (C5, NH*C*), 21.0 (*p*-$CCH_{3,para}$), 17.3 (o-$CCH_{3,para}$) ppm.

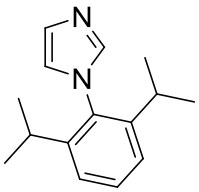
MS (EI), *m/z* (%): 186 (41) $[M]^+$, 158 (70) $[M-(2xCH_3)]^+$, 144 (100) $[M-(3xCH^3)]+$.

Elem. Anal. Calc. for $C_{12}H_{14}N_2$

Calc.:	C	77.38	H	7.58	N	15.04
Found:	C	77.37	H	7.58	N	15.04

Yield: 20 %

6.3.2.2. 1-(2,6-diisopropylphenyl)imidazole



^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.23, 7.43 (2x1H, bs, C*H*$_{(imidazole)}$) 6.97 (2H, s, *m*-C*H*(Ph)), 6.89 (1H, bs, C*H*$_{(imidazole)}$), 2.34 (2H, sept, C*H*), 1.25 (s, C*H*$_3$) ppm.

^{13}C{1H}-NMR (100.53 MHz, $CDCl_3$) δ= 138.8, 137.4, 135.4, 133.4, 129.5, 128.9, 120 (3x *C*H$_{(imidazole)}$, *ipso*-, *C*(Ph)), 21.0(*C*H), 11.3(*C*H$_3$) ppm.

MS (EI), *m/z* (%): 228 (M^+, 50%)

Elem. Anal. Calc. for $C_{15}H_{20}N_2$

Calc.:	C	78.90	H	8.83	N	12.27
Found:	C	78.89	H	8.82	N	12.26

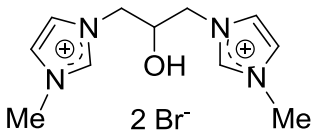
Yield: 51 %.

6.4. Synthesis of bridge Bis(imidazolium)-salts

*6.4.1. General synthesis for 1,1'-substituted 3,3'-alkyl bridged bis-imidazolium salts (**1a-11a**)*

To a solution of 2.5 equivalent of the corresponding *N*-imidazole in 5 mL THF in an ACE pressure tube was added 1 equivalent of the bis-bromo-alkyl compound. The solution is heated at 110 ^{o}C for 72 h. The solution is filtered off and the precipitate is washed with 2 x 5 ml THF and dried under vacuum to yield a white powder.

*6.4.1.1. 1,1'-(2-Hydroxy-1,3-propandiyl)bis[3-methyl-1H-imidazolium]dibromide **1a***



^{1}H-NMR(400 MHz, 298 K, d_6-DMSO): δ = 9.22 (2H, s, NC*H*N), 7.81 (2H, d, NC*H*), 7.76 (2H, d, NC*H*), 5.92 (1H, s, O*H*), 4.48 (2H, d, NCH_2), 4.25 (1H, m, C*H*), 4.17 (2H, dd, CH_2), 3.87 (6H, s, NCH_3) ppm.

^{13}C{^{1}H}-NMR(100 MHz, 298 K, d_6-DMSO): δ = 137.1 (N*C*HN), 123.4 (N*C*H), 122.9 (N*C*H), 67.6 (*C*-H), 51.7 (NCH_2), 35.8 (NCH_3) ppm.

MS (FAB): m/z (%): 303 (50, [M-Br]), 221 (72, [M-Br-Br]).

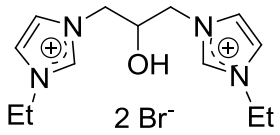
Elem. Anal. Calc. for $C_{11}H_{18}Br_2N_4O$:

Calc.:	C	34.58	H	4.75	N	14.66
Found:	C	34.39	H	4.83	N	14.58

Reaction time: 3 d

Yield: 82 %;

*6.4.1.2. 1,1`-(2-Hydroxy-1,3-propandiyl)bis[3-ethyl-1H-imidazolium] dibromide **2a***



^{1}H NMR (400 MHz, 298 K, d_6-DMSO): δ = 9.32 (2H, s, NC*H*N), 7.85 (2H, d, NC*H*), 7.81 (2H, d, NC*H*), 5.88 (1H, s, OH), 4.47 (2H, d, NCH_2), 4.28 (1H, m, CH), 4.17 (6H, dd, CH_3), 1.36 (4H, s, NCH_2) ppm.

^{13}C{1H} NMR(100 MHz, 298 K, d_6-DMSO): δ = 137.69 (NCHN), 124.35 (NCH), 123.25 (NCH), 68.94 (C–H), 53.17 (NCH_2) 40.92 (NC_2H_5) ppm.

MS (FAB): m/z (%): 328.12 (50, [M–Br]), 221 (72, [M–Br–Br]).

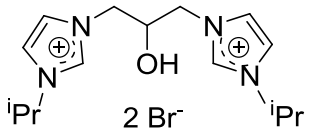
Elem. Anal. Calc. for $C_{13}H_{22}Br_2N_4O$:

Calc.:	C	38.07	H	5.41	N	13.66
Found:	C	37.98	H	5.33	N	13.63

Reaction time: 3 d

Yield: 81%.

*6.4.1.3. 1,1'-(2-Hydroxy-1,3-propanediyl)bis[3-isopropyl-1H-imidazolium]dibromide **3a***



^{1}H-NMR(400 MHz, 298 K, d_6-DMSO): δ = 9.28 (2H, s, NC*H*N), 7.94 (2H, d, NC*H*), 7.78 (2H, d, NC*H*), 5.95 (1H, d, O*H*), 4.67 (2H, sept, CH_{iPr}), 4.40 (2H, d, CH_2), 4.25 (1H, m, C*H*), 4.12 (2H, dd, CH_2), 1.46 (12H, d, CH_3) ppm.

^{13}C{^{1}H}-NMR(100 MHz, 298 K, d_6-DMSO): δ = 135.4 (NCHN), 123.1 (NCH), 120.3 (NCH), 67.5 (*C*-H), 52.2 (CH_{iPr}), 51.9 (NCH_2) 22.2 (CH_3) ppm.

MS (FAB): m/z (%): 356.9 (40, [M-Br]), 277.0 (34, [M-Br-Br]).

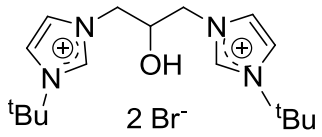
Elem. Anal. Calc for $C_{15}H_{26}Br_2N_4O$:

Calc.:	C	41.11	H	5.98	N	12.79
Found:	C	40.64	H	6.09	N	12.65

Reaction time: 5 d

Yield: 76 %.

*6.4.1.4. 1,1`-(2-Hydroxy-1,3-propandiyl)bis[3-tertbutyl-1H-imidazolium]dibromide **4a***



^{1}H NMR (400 MHz, 298 K, d_6-DMSO): δ = 9.45 (2H, s, NC*H*N), 8.06 (2H, d, NC*H*), 7.88 (2H, d, NC*H*), 5.88 (1H, s, OH), 4.43 (2H, d, NCH_2), 4.33 (1H, m, C*H*), 4.11 (2H, dd, CH_2), 1.59 (18H, s, CH_3) ppm.

^{13}C{^{1}H} NMR(100 MHz, 298 K, d_6-DMSO): δ = 135.0 (N*C*HN), 123.3 (N*C*H), 120.0 (N*C*H), 67,6 (*C*-H), 59,5 (C_{tert}), 51,9 (NCH_2), 29,0 (CH_3) ppm.

MS (FAB): m/z (%): 385.1 (50, [M–Br]), 178.0 (34, [M-Br-Br]).

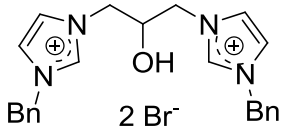
Elem. Anal. Calc. for $C_{17}H_{30}Br_2N_4O$:

Calc.:	C	43.79	H	6.49	N	12.02
Found:	C	43.56	H	6.33	N	11.98

Reaction time: 5 d

Yield: 70%.

*6.4.1.5. 1,1'-(2-Hydroxy-1,3-propandiyl)bis[3-benzyl-1H-imidazolium]dibromide **5a***



^{1}H-NMR(400 MHz, 298 K, d_6-DMSO): δ = 9.39 (2H, s, NC*H*N), 7.86 (4H, s, NC*H*), 7.44 (10H, m, H_{Ar}), 5.99 (1H, s, O*H*), 5.49 (4H, s, CH_2-Ar), 4.50 (2H, d, NCH_2), 4.25 (1H, m, C*H*), 4.17 (2H, dd, CH_2) ppm.

^{13}C{^{1}H}-NMR(100 MHz, 298 K, d_6-DMSO): δ = 136.7 (N*C*HN), 134.7 (C_{Ar}), 128.8 (C_{Ar}), 128.6 (C_{Ar}), 123.2 (N*C*H), 122.3 (N*C*H), 67.4 (*C*-H), 51.9 (Ar-N*C*H_2) 51.7 (N*C*H_2) ppm.

MS (FAB): m/z (%): 455 (33, [M-Br]), 373 (26, [M-Br-Br]), 215 (100).

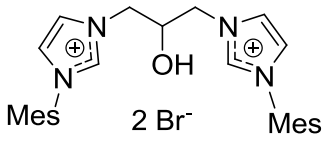
Elem. Anal. Calc. for $C_{23}H_{26}Br_2N_4O$:

Calc.:	C	51.70	H	4.98	N	10.49
Found:	C	51.71	H	5.07	N	10.46

Reaction time: 4 d

Yield: 96 %.

*6.4.1.6. 1,1'-(2-Hydroxy-1,3-propandiyl)bis[3-mesityl-1H-imidazolium]dibromide **6a***



^{1}H-NMR(400 MHz, 298 K, d_6-DMSO): δ = 9.55 (2H, s, NC*H*N), 8.16 (2H, s, NC*H*), 7.97 (2H, s, NC*H*), 7.14 (4H, s, H_{Ar}), 6.13 (1H, s, OH), 4.65 (2H, d, NCH_2), 4.61 (1H, m, C*H*), 4.30 (2H, dd, CH_2), 2.33 (6H, s, CH_3-para), 2.05 (12H, s, CH_3-ortho) ppm.

$^{13}C\{^{1}H\}$-NMR(100 MHz, 298 K, d_6-DMSO): δ = 140.1 (C_{Ar}),137.9 (N*C*HN), 134.3 (C_{Ar}), 131.0 (C_{Ar}), 129.1 (C_{Ar}), 123.8 (N*C*H), 123.6 (N*C*H), 67.4 (*C*-H), 52.4 (NCH_2), 20.5 (CH_3-para), 16.9(CH_3-ortho) ppm.

MS (FAB): m/z (%): 511 (11, [M-Br]), 429 (12, [M-Br-Br]), 243 (100).

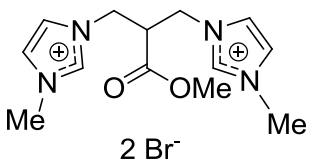
Elem. Anal. Calc. for $C_{27}H_{34}Br_2N_4O$:

Calc.:	C	54.93	H	5.74	N	9.49
Found:	C	53.87	H	5.71	N	9.39

Reaction time: 7 d

Yield: 65 %.

6.4.1.7. 1,1'-(2-Methoxycarbonyl-1,3-propandiyl)bis[3-methyl-1H- imidazolium]dibromide ***7a***



^{1}H-NMR(400 MHz, 298 K, d_6-DMSO): δ = 9.39 (2H, s, NC*H*N), 7.90 (2H, d, NC*H*), 7.78 (2H, d, NC*H*), 4.59 (4H, d, NCH_2), 3.89 (6H, s, NCH_3+1H, CH), 3.62 (3H, s, OCH_3) ppm.

$^{13}C\{^{1}H\}$-NMR(100 MHz, 298 K, d_6-DMSO): δ = 169.8 (*C*=O),137.3 (N*C*HN), 123.5 (N*C*H), 122.6 (N*C*H), 52.6 (OCH_3),47.0 (NCH_2), 45.3 (*C*-H), 35.8 (NCH_3) ppm.

MS (FAB): m/z (%): 345 (22, [M-Br]).

Elem. Anal. Calc. for $C_{13}H_{20}Br_2N_4O_2$:

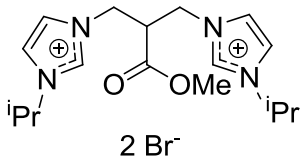
Calc.:	C	36.81	H	4.75	N	13.21
Found:	C	36.86	H	4.69	N	13.47

Reaction time: 3 d

Yield: 95 %.

6.4.1.8. 1,1'-(2-Methoxycarbonyl-1,3-propandiyl)bis[3-isopropyl-1H-imidazolium]dibromide

8a



^{1}H-NMR(400 MHz, 298 K, d_6-DMSO): δ = 9.54 (2H, s, NC*H*N), 7.96 (2H, d, NC*H*), 7.92 (2H, d, NC*H*), 4.67 (2H, sept., CH_{iPr}), 4.57 (4H, d, NCH_2), 3.97 (1H, t, C*H*), 3.60 (3H, s, OCH_3), 1.47 (12H, s, CH_3) ppm.

^{13}C{^{1}H}-NMR(100 MHz, 298 K, d_6-DMSO): δ = 169.9 (*C*=O),135.8 (N*C*HN), 122.9 (N*C*H), 120.6 (N*C*H), 52.6 (O*C*H$_{iPr}$), 47.3 (N*C*H$_2$), 45.2 (*C*-H), 22.2 (NCH$_3$) ppm.

MS (FAB): m/z (%): 399 (22, [M-Br]).

Elem. Anal. Calc. for $C_{17}H_{28}Br_2N_4O_2$:

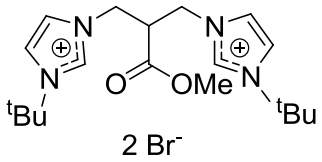
Calc.:	C	42.52	H	5.88	N	11.67
Found:	C	42.40	H	5.81	N	11.58

Reaction time: 3 d

Yield: 93 %.

6.4.1.9. 1,1'-(2-Methoxycarbonyl-1,3-propandiyl)bis[3-tertbutyl-1H-imidazolium]dibromide

9a



^{1}H-NMR(400 MHz, 298 K, d_6-DMSO): δ = 9.61 (2H, s, NC*H*N), 8.05 (2H, d, NC*H*), 7.94 (2H, d, NC*H*), 4.57 (4H, d, NCH_2), 4.09 (1H, t, NC*H*), 3.60 (3H, s, OCH_3), 1.60 (18H, s, CH_3) ppm.

$^{13}C\{^{1}H\}$-NMR(100 MHz, 298 K, d_6-DMSO): δ = 169.9 (*C*=O),135.5 (N*C*HN), 123.0 (N*C*H), 120.2 (N*C*H), 59.7 (C_{tert}), 52.5 (O*C*H_3), 47.3 (N*C*H_2), 45.1(C-H), 28.9 (CH_3) ppm.

MS (FAB): m/z (%): 427 (32, [M-Br]).

Elem. Anal. Calc. for $C_{19}H_{32}Br_2N_4O_2$:

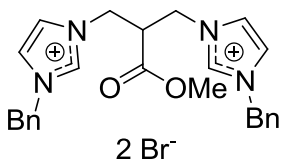
Calc.:	C	44.90	H	6.35	N	11.02
Found:	C	44.40	H	6.67	N	10.90

Reaction time: 3 d

Yield: 95 %.

6.4.1.10. 1,1'-(2-Methoxycarbonyl-1,3-propandiyl)bis[3-benzyl-1H-imidazolium]dibromide

10a



^{1}H-NMR(400 MHz, 298 K, d_6-DMSO): δ = 9.53 (2H, s, NC*H*N), 7.92 (2H, d, NC*H*), 7.86 (2H, d, NC*H*), 7.43 (10H, m, H_{Ar}), 5.49 (4H, s, CH_2Ph), 4.60 (4H, d, NCH_2), 3.88 (1H, m, C*H*), 3.49 (3H, s, OCH_3) ppm.

$^{13}C\{^{1}H\}$-NMR(100 MHz, 298 K, d_6-DMSO): δ = 169.8 (*C*=O),137.0 (N*C*HN), 134.6 (C_{Ar}),128.9 (C_{Ar}), 128.2 (C_{Ar}), 123.1 (N*C*H), 122.5 (N*C*H), 52.4 (Ph-N*C*H_2), 51.9 (N*C*H_2), 47.3 (*C*-H), 45.3 (*C*-H) ppm.

MS (FAB): m/z (%): 494.5 (19, [M-Br]), 257 (100, [M-2xBr,-Bn-Im]).

Elem. Anal. Calc. for $C_{25}H_{28}Br_2N_4O_2$:

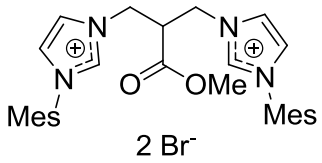
Calc.:	C	52.10	H	4.90	N	9.72
Found:	C	51.59	H	4.91	N	9.56

Reaction time: 5 d

Yield: 89 %.

6.4.1.11. 1,1'-(2-Methoxycarbonyl-1,3-propandiyl)bis[3-mesityl-1H-imidazolium]dibromid

11a



^{1}H-NMR(400 MHz, 298 K, d_6-DMSO): δ = 9.54 (2H, s, NC*H*N), 7.93 (2H, d, NC*H*), 7.87 (2H, d, NC*H*), 7.13 (4H, m, H_{Ar}), 5.15 (4H, d, NCH_2), 4.63 (1H, t, C*H*), 3.59 (3H, s, OCH_3), 2.32 (6H, s, CH_3-*para*), 2.02 (12H, s, CH_3-ortho) ppm.

^{13}C{^{1}H}-NMR(100 MHz, 298 K, d_6-DMSO): δ = 169.8 (*C*=O), 140.1 (C_{Ar}), 137.7 (NCHN), 134.3 (C_{Ar}), 131.0 (C_{Ar}), 129.1 (C_{Ar}), 123.8 (NCH), 123.4 (NCH), 66.9 (*C*-H), 49.9 (OCH_3), 52.4 (NCH_2), 20.4 (CH_3-para),16.7 (CH_3-ortho) ppm.

MS (FAB): m/z (%): 471 (3, [M-2xBr]).

Elem. Anal. Calc. for $C_{29}H_{36}Br_2N_4O$:

Calc.:	C	55.07	H	5.74	N	8.86
Found:	C	55.25	H	6.09	N	8.10

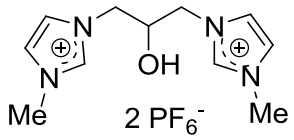
Reaction time: 7 d

Yield: 39 %.

6.4.2. General procedure for the PF_6^- Salts (**1b-9b**)

The corresponding bromine salts **1a-9a** were dissolved in a minimum amount of water and added to a saturated solution of KPF_6 in water. The precipitated imidazolium hexafluorophosphate salts are filtered off, washed with water and diethylether and dried under vacuum yielding the imidazolium salts **1b-9b**.

6.4.2.1. 1,1'-(2-Hydroxy-1,3-propanediyl)bis[3-methyl-1H-imidazolium] di(hexafluorophosphate) ***1b***



^{1}H-NMR(400 MHz, 298 K, d_6-Aceton): δ = 9.00 (2H, s, NC*H*N), 7.72 (4H, d, NC*H*), 5.50 (1H, d, O*H*), 4.71 (2H, d, NCH_2), 4.56 (1H, m, C*H*), 4.42 (2H, dd, CH_2), 4.07 (6H, s, NCH_3) ppm.

^{13}C{^{1}H}-NMR(100 MHz, 298 K, d_6-Aceton): δ = 138.0 (N*C*HN), 124.6 (N*C*H), 124.0 (N*C*H), 69.2 (*C*-H), 53.1 (NCH_2), 36.5 (NCH_3) ppm.

^{31}P{^{1}H}-NMR(161 MHz, 298 K, d_6-Aceton): δ = -130.5 - -158.0 ppm.

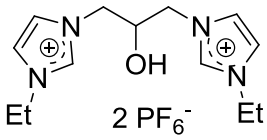
MS (FAB): m/z (%): 367 (75, [M-PF_6]), 221 (100, [M-2xPF_6]).

Elem. Anal. Calc for $C_{11}H_{18}F_{12}N_4OP_2$*2KBr:

Calc.:	C	17.61	H	2.42	N	7.47
Found:	C	17.84	H	2.42	N	7.33

Yield: 51 %.

6.4.2.2. 1,1`-(2-Hydroxy-1,3-propanediyl)bis[3-ethyl-1H-imidazolium] di(hexafluorophosphate) ***2b***



^{1}H-NMR(400 MHz, 298 K, d_6-Aceton): δ = 9.03 (2H, s, NC*H*N), 7.19 (4H, d, NC*H*), 5.50 (1H, d, OH), 4.69 (2H, d,NCH_2), 4.57 (1H,m, C*H*), 4.42 (2H, dd, CH_2), 4.07 (6H, s, NCH_3), 1,53 (4H,s,NCH_2) ppm.

^{13}C {1H}-NMR (100MHz, 298 K, d_6-Aceton): δ = 136.39 (N*C*HN), 123.42 (N*C*H), 122.24 (N*C*H), 68.41(*C*-H), 52.42 (N*C*H2) 45.01 (N*C*H_3), 28.96(N*C*H_2) ppm.

^{31}P{1H}-NMR(161 MHz, 298 K, d_6- Aceton): δ =-130.8 to -158.0 ppm.

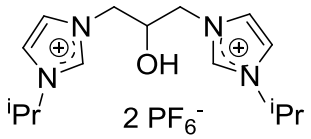
MS (FAB):m/z (%): 395.1 (75, [M-PF_6]), 225 (100, [M-2xPF_6]).

Anal. Calc for $C_{13}H_2F_{12}N_4OP_2$:

Calc.:	C	28.90	H	4.10	N	10.37
Found:	C	28.14	H	4.02	N	10.28

Yield: 71%.

6.4.2.3. 1,1'-(2-Hydroxy-1,3-propanediyl)bis[3-isopropyl-1H-imidazolium] di(hexafluorophosphate) ***3b***



^{1}H-NMR(400 MHz, 298 K, d_6-Aceton): δ = 9.21 (2H, s, NC*H*N), 7.89 (2H, d, NC*H*), 7.77 (2H, d, NC*H*), 5.91 (1H, s, O*H*), 4.67 (2H, sept, CH_{iPr}), 4.48 (2H, d, NCH_2), 4.26 (1H, m, C*H*), 4.17 (2H, dd, CH_2), 1.48 (12H, s, NCH_3) ppm.

^{31}P{^{1}H}-NMR(161 MHz, 298 K, d_6-Aceton): δ = -131.0 - -157.0 ppm.

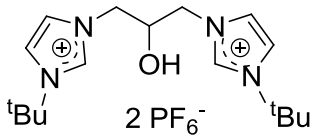
MS (FAB):m/z (%): 423,1 (75, [M-PF_6]), 221 (100, [M-PF_6-PF_6])

Elem. Anal. Calc for $C_{15}H_{26}F_{12}N_4OP_2$*1/2 KBr:

Calc.:	C	28.70	H	4.17	N	8.92.
Found:	C	28.79	H	4.32	N	8.93

Yield: 59 %.

6.4.2.4. 1,1'-(2-Hydroxy-1,3-propanediyl)bis[3-tertbuthyl-1H-imidazolium] di(hexafluorophosphate) ***4b***



^{1}H-NMR(400 MHz, 298 K, d_6-Aceton): δ = 9.05 (2H, s, NC*H*N), 7.96 (2H, d, NC*H*), 7.75 (2H, d, NC*H*), 5.32 (1H, s, O*H*), 4.67 (2H, d, NCH_2), 4.54 (1H, m, C*H*), 4.37 (2H, dd, CH_2), 1.37 (18H, s, NCH_3) ppm.

^{31}P{^{1}H}-NMR(161 MHz, 298 K, d_6-Aceton): δ = -131.5 - -157.5 ppm.

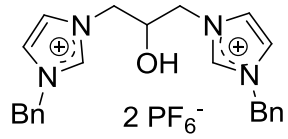
MS(FAB): m/z (%): 367,31 (50, [M–PF_6]), 221 (100, [M–PF_6–PF_6]).

Elem. Anal. Calc for $C_{17}H_{30}F_{12}N_4OP_2$*1/2 KBr:

Calc.:	C	31.13	H	4.61	N	8.54.
Found:	C	29.98	H	4.58	N	8.47

Yield: 60 %.

6.4.2.5. 1,1'-(2-Hydroxy-1,3-propanediyl)bis[3-benzyl-1H-imidazolium] di(hexafluorophosphate) ***5b^{PF6}***



^{1}H-NMR(400 MHz, 298 K, d_6-Aceton): δ = 9.17 (2H, s, NC*H*N), 7.75 (2H, d, NC*H*), 7.48 (2H, d, NC*H*), 7.43 (10H, m, H_{Ar}), 5.58 (5H s, br, 1H-OH + 4H-CH_2-Ph), 4.69 (2H, d, NCH_2), 4.53 (1H, m, C*H*), 4.41 (2H, dd, CH_2) ppm.

^{31}P{^{1}H}-NMR(161 MHz, 298 K, d_6-Aceton): δ = -130.0 - -158.0 ppm.

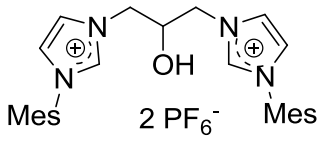
MS (FAB): m/z (%): 518.5 (100, [M-PF_6]), 373 (72, [M-PF_6-PF_6])

Elem. Anal. Calc for $C_{23}H_{26}F_{12}N_4OP_2$:

Calc.:	C	41.58	H	3.94	N	8.43
Found:	C	41.52	H	3.85	N	8.49

Yield: 75 %

6.4.2.6. 1,1'-(2-Hydroxy-1,3-propandiyl)bis[3-mesityl-1H-imidazolium] di(hexafluorophosphate) ***6b***



^{1}H-NMR(400 MHz, 298 K, d_6-Aceton): δ = 9.31 (2H, s, NC*H*N), 8.08 (2H, s, NC*H*), 7.88 (2H, s, NC*H*), 7.13 (4H, s, H_{Ar}), 5.83 (1H, s, OH), 4.93 (2H, d, NCH_2), 4.84 (1H, m, C*H*), 4.64 (2H, dd, CH_2), 2.35 (6H, s, CH_3-para), 2.09 (12H, s, CH_3-ortho) ppm.

^{13}C{^{1}H}-NMR(100 MHz, 298 K, d_6-Aceton): δ = 142.0 (C_{Ar}), 136.8 (N*C*HN), 135.6 (C_{Ar}), 130.5 (C_{Ar}), 130.4 (C_{Ar}), 125.2 (N*C*H),125.0 (N*C*H), 64.8 (*C*-H), 53.9 (NCH_2), 21.0 (CH_3-para), 17.3 (CH_3-ortho) ppm.

^{31}P{^{1}H}-NMR(161 MHz, 298 K, d_6-Aceton): δ = -132.9 - -159.2 ppm.

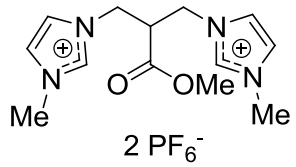
MS (FAB): m/z (%): 575 (30, [M-PF_6]), 429 (23, [M-PF_6-PF_6]).

Elem. Anal. Calc. for $C_{27}H_{34}F_{12}N_4OP_2$:

Calc.:	C	45.01	H	4.76	N	7.78
Found:	C	44.54	H	4.77	N	7.62

Yield: 39 %.

6.4.2.7. 1,1'-(2-Methoxycarbonyl-1,3-propandiyl)bis[3-methyl-1H-imidazolium] di(hexafluorophosphate) ***7b***



^{1}H-NMR(400 MHz, 298 K, d_6-Aceton): δ = 9.00 (2H, s, NC*H*N), 7.73 (2H, d, NC*H*), 7.69 (2H, d, NC*H*), 4.79 (4H, d, NCH_2), 4.03 (6H, s, NCH_3), 3.89 (tt, 1H, C*H*), 3.69 (3H, s, OCH_3) ppm.

^{13}C{^{1}H}-NMR(100 MHz, 298 K, d_6-Aceton): δ = 170.8 (*C*=O),138.4 (N*C*HN), 125.1 (N*C*H), 123.9 (N*C*H), 53.3 (OCH_3), 48.8 (*C*-H), 47.1 (NCH_2), 36.8 (NCH_3) ppm.

^{31}P{^{1}H}-NMR(161 MHz, 298 K, d_6-Aceton): δ = -132.9 - -159.1 ppm.

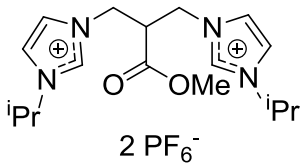
MS (FAB): m/z (%): 412.27 (22, [M-PF_6]).

Elem. Anal. Calc. for $C_{13}H_{20}F_{12}N_4O_2P_2$ * 1/2KBr:

Calc.:	C	25.44	H	3.28	N	9.13
Found:	C	24.15	H	2.89	N	9.43

Yield: 41 %.

6.4.2.8. 1,1'-(2-Methoxycarbonyl-1,3-propandiyl)bis[3-isopropyl-1H-imidazolium] di(hexafluorophosphate) ***8b***



^{1}H-NMR(400 MHz, 298 K, d_6-Aceton): δ = 9.10 (2H, s, NC*H*N), 7.87 (2H, d, NC*H*), 7.77 (2H, d, NC*H*), 4.80 (m, 6H, (4H, NCH_2 + 2H, CH_{iPr}), 3.92 (sept., 1H, C*H*), 3.86 (3H, s, OCH_3) ppm.

$^{13}C\{^{1}H\}$-NMR(100 MHz, 298 K, d_6-Aceton): δ = 170.9 (*C*=O),137.3 (N*C*HN), 123.6 (N*C*H), 122.6 (N*C*H), 54.4 (*C*-H), 53.3 (O*C*H_3), 49.0 (N*C*H_2), 47.0 (C-H), 22.7(*C*H_3) ppm.

$^{31}P\{^{1}H\}$-NMR(161 MHz, 298 K, d_6-Aceton): δ = -130.4 - -156.7 ppm.

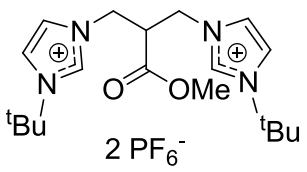
MS (FAB): m/z (%): 465 (66, [M-PF_6]).

Elem. Anal. Calc. for $C_{17}H_{28}F_{12}N_4O_2P_2$:

Calc.:	C	33.45	H	4.62	N	9.18
Found:	C	32.88	H	4.72	N	9.03

Yield: 81 %.

6.4.2.9. 1,1'-(2-Methoxycarbonyl-1,3-propandiyl)bis[3-tertbutyl-1H-imidazolium] di(hexafluorophosphate) ***9b***



^{1}H-NMR(400 MHz, 298 K, d_6-Aceton): δ = 9.15 (2H, s, NC*H*N), 7.99 (2H, d, NC*H*), 7.80 (2H, d, NC*H*), 4.27 (4H, d, NC*H*$_2$), 3.94 (1H, t, C*H*), 3.68 (3H, s, OC*H*$_3$), 1.73 (18H, s, C*H*$_3$) ppm.

$^{13}C\{^{1}H\}$-NMR(100 MHz, 298 K, d_6-Aceton): δ = 170.9 (*C*=O), 136.1 (N*C*HN), 124.3 (N*C*H), 121.5 (N*C*H), 61.4 (*C*-H), 53.3 (O*C*H_3), 49.1 (*C*$_{tert}$), 47.30 (N*C*H_2), 26.9 (*C*H_3) ppm.

MS (FAB): m/z (%): 493 (100, [M-PF_6]).

Elem. Anal. Calc. for $C_{19}H_{32}F_{12}N_4O_2P_2$:

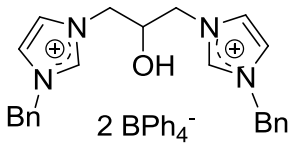
Calc.:	C	35.75	H	5.05	N	8.78
Found:	C	35.92	H	5.21	N	9.43

Yield: 50 %.

6.4.3. Synthesis procedure for the BPh_4^- Salt

The corresponding bromine salt **5a^{BPh4}** was suspended in acetone and a saturated solution of $KBPh_4$ in acetone was added. After a few minutes a precipitate yields in the corresponding tetraphenylborate salt. The solid was filtered off and washed with water, diethylether and pentane and dried under vacuum to yield the imidazolium salt **5b^{BPh4}** in 72 %.

*6.4.3.1. 1,1'-(2-Hydroxy-1,3-propanediyl)bis[3-benzyl-1H-imidazolium] di(hexafluorophosphate) **5b^{BPh4}***



^{1}H-NMR(400 MHz, 298 K, d_6-Aceton): δ = 8.77 (2H, s, NC*H*N), 7.57 (4H, s, NC*H*), 7.40 (20H, d, H_{Ar}), 6.89 (20H, m, H_{Ar}), 6.75 (10H, m, H_{Ar}), 5.39 (4H, s, NCH_2-Ph), 4.42 (2H+1H, m, NCH_2 + C*H*), 4.20 (dd, 2H, NCH_2) ppm.

MS (FAB): m/z (%): 693 (15, [M-BPh_4]), 373 (60, [M-2x BPh_4]).

Elem. Anal. Calc for $C_{23}H_{26}F_{12}N_4OP_2$:

Calc.	C	79.52	H	6.20	N	5.22.
Found:	C	79.62	H	6.13	N	4.98

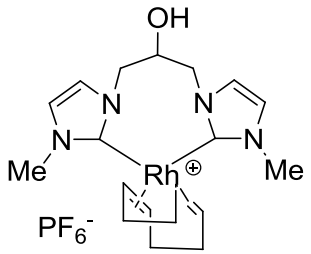
Yield: 72 %;

6.5. Bis-N-heterocyclic carbene complexes of Rhodium(I)

6.5.1. General procedure for the chelating bis(NHC)-Rh(I) complexes

NaH and $[Rh(COD)Cl]_2$ were each dissolved in ethanol and the solutions were combined and stirred for 30 minutes at room temperature. To the resulting suspension the corresponding hexafluorophosphate salts **1b-9b** respectively tetraphenylborate salt (complex **5b^{BPh4}**) were added and stirred for 16 h. After reaction, ethanol was removed under vacuum and the complexes were extracted with dichloromethane. Recrystallisation from a saturated DCM-solution with diethylether yields in the rhodium complexes **1c-9c** as yellow solids. Crystals suitable for X-ray diffraction studies of complexes **1c** and **2c** could be obtained by slowly diffusion of pentane into a dichloromethane solution of complex (**1c** and **2c**).

6.5.1.1. *[3,3´-(2-Hydroxypropan-1,3-diyl)bis(1-methyl-1H-imidazolium-2,2´-diyliden)]-(η^4-1,5-cyclooctadienyl)rhodium(I)-hexafluorophosphate* **1c**



^{1}H-NMR(400 MHz, 298 K, d_2-DCM): δ = 6.97 (2H, d, NC*H*), 6.77 (2H, d, NC*H*), 4.97 (2H, d, NCH_2), 4.54 (4H, m, CH_2-COD), 4.44 (1H, m, C*H*), 4.30 (2H, dd, NCH_2), 3.89 (6H, s, NCH_3), 2.45 (4H, m, CH_2-COD), 2.25 (4H, m, CH_2-COD) ppm.

^{13}C{^{1}H}-NMR(100 MHz, 298 K, d_2-DCM): δ = 183.2 ($C_{Carbene}$), 125.5 (N*C*H), 121.6 (N*C*H), 90.3 (COD), 67.0 (*C*-H), 55.9 (NCH_2), 35.1 (NCH_3), 30.9 (COD) ppm.

^{31}P{^{1}H}-NMR(161 MHz, 298 K, d_2-DCM): δ = -130.5 - -158.0 ppm.

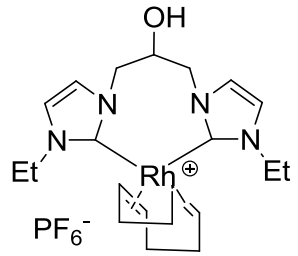
MS (FAB): m/z (%): 431 (100, [M-PF_6]), 323 (70, [M-PF_6-COD]).

Anal. Calc for $C_{19}H_{28}F_6N_4OPRh$:

Calc.:	C	39.60	H	4.90	N	9.72
Found:	C	39.18	H	4.70	N	9.30.

Yield: 69%

6.5.1.2. [3,3´-(2-Hydroxypropan-1,3-diyl)bis(1-ethyl-1H-imidazolium-2,2´-diyliden)]-(η^4-1,5-cyclooctadienyl)rhodium(I)-hexafluorophosphate **2c**



^{1}H-NMR(400 MHz, 298 K, d_2-DCM): δ = 6.97 (2H, d, NC*H*), 6.77 (2H, d, NC*H*), 4.97 (2H, d, NCH_2), 4.54 (4H, m, CH_2-COD), 4.44 (1H, m, C*H*), 4.30 (2H, dd, NCH_2), 3.89 (6H, s, NCH_3), 2.45 (4H, m, CH_2-COD), 2.25 (4H, m, CH_2-COD) ppm.

^{13}C{1H}-NMR(100 MHz, 298 K, d_2-DCM): δ = 183.39 ($C_{Carbene}$), 125.92 (N*C*H), 118.94 (N*C*H), 90.32 (COD), 67.0 (C-H), 55.99 (N*C*H_2), 35.1 (N*C*H_3), 30.88 (COD), 16,37(CH_2) ppm.

^{31}P{1H}-NMR(161 MHz, 298 K, d_2-DCM): δ = -130,8 to -158,0 ppm.

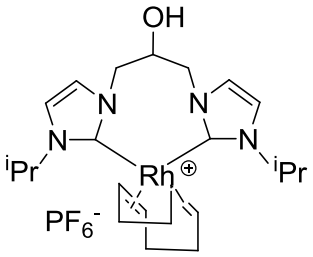
MS (FAB):m/z (%): 604,38 (100 M[PF_6]) 458,9 (70, [M-PF_6]), 323 (70 [M-PF_6-COD]).

Elem. Anal. Calc for $C_{21}H_{32}F_6N_4OPRh$:

Calc.:	C	41.73	H	5.34	N	9.27
Found:	C	41.08	H	4.70	N	9.21.

Yield: 62 %.

6.5.1.3. [3,3´-(2-Hydroxypropan-1,3-diyl)bis(1-isopropyl-1H-imidazolium-2,2´-diyliden)]-(η^4-1,5 cyclooctadienyl)rhodium(I)-hexafluorophosphate **3c**



^{1}H-NMR(400 MHz, 298 K, d_2-DCM): δ = 7.29 (2H, d, NC*H*), 6.75 (2H, d, NC*H*), 5.11 (2H, d, NCH_2 + 1H C*H*), 4.84 (2H, sept., CH_{iPr}), 4.55 (4H, m, CH_2-COD), 4.13 (2H, dd, NCH_2), 2.38 (4H, m, CH_2-COD), 2.21 (4H, m, CH_2-COD), 1.37 (12H, d, CH_3) ppm.

^{13}C{^{1}H}-NMR(100 MHz, 298 K, d_2-DCM): δ = 179.7 ($C_{Carbene}$), 125.4 (N*C*H), 115.8 (N*C*H), 90.1 (COD), 65.0 (*C*-H), 59.6 (*C*-H), 52.4 (NCH_2), 30.9 (COD), 23.8 (CH_3) ppm.

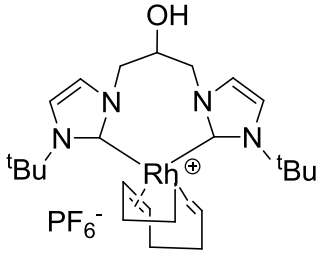
MS (FAB): m/z (%): 487 (100, [M-PF_6]), 379 (100, [M-PF_6-COD]).

Elem. Anal. Calc for $C_{23}H_{36}F_6N_4OPRh$:

Calc.:	C	43.68	H	5.74	N	8.86.
Found:	C	43.12	H	6.12	N	8.79.

Yield: 49%.

6.5.1.4. [3,3´-(2-Hydroxypropan-1,3-diyl)bis(1-tert-butyl-1H-imidazolium-2,2´-diyliden)]-(η^4-1,5-cyclooctadienyl)rhodium(I)-hexafluorophosphate **4c**



^{1}H-NMR(400 MHz, 298 K, d_2-DCM): δ = 7,37 (2H, d, NC*H*), 7.00 (2H, d, NC*H*), 5.55 (1H, br, C-OH), 4.50 (4H, m, CH_2-COD), 4.32 (3H, m, CH+NCH_2), 4.11 (2H, dd, NCH_2), 2.35 (4H, m, CH_2- COD), 2.21 (4H, m, CH_2-COD), 1.64 (18H, s, CH_3) ppm.

^{13}C{1H}-NMR (100 MHz, 298 K, d_2-DCM): δ = 185.8 ($C_{Carbene}$), 124.3 (N*C*H), 120.0 (N*C*H), 88.3 (COD), 70.6 (C-H), 62,0 (*C*-H), 61,2 (NCH_2), 29.7 (COD), 14,3 (CH_3) ppm.

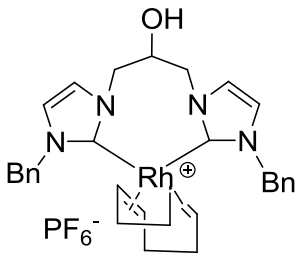
MS (FAB): m/z (%): 660,48 (70, [M-PF_6]), 280 (100, [M-PF_6 - COD]).

Elem. Anal. Calc for $C_{25}H_{40}F_6N_4OPRh$:

Calc.:	C	45.46	H	6.10	N	8.48
Found:	C	45.12	H	6.02	N	8.17..

Yield: 45%.

6.5.1.5. [3,3´-(2-Hydroxypropan-1,3-diyl)bis(1-benzyl-1H-imidazolium-2,2´-diyliden)]-(η^4-1,5-cyclooctadienyl)rhodium(I)-hexafluorophosphate **5c^{PF6}**



^{1}H-NMR(400 MHz, 298 K, d_2-DCM): δ = 7.35 (6H, m, H_{Ar}), 7.11 (2H, d, NC*H*), 6,83 (4H, m, H_{Ar}), 6.64 (4H, d, NC*H*), 5.64 (2H, d, Ph-NCH_2), 5.12 (2H, d, Ph-NCH_2), 4.86 (1H, m, C*H*), 4.64 (4H, m, CH_2-COD + NCH_2), 4.48 (4H, m, CH_2-COD + NCH_2), 2.47 (4H, m, CH_2-COD), 2.25 (4H, m, CH_2-COD ppm).

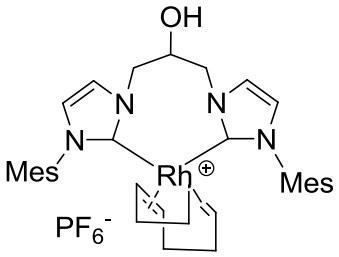
MS (FAB): m/z (%): 582 (100, [M-PF_6]), 474 (81, [M-PF_6-COD]).

Elem. Anal. Calc for $C_{31}H_{36}F_6N_4OPRh$:

Calc.:	C	51.11	H	4.91	N	7.46.
Found:	C	50.27	H 4.98; N 7.69%.			

Yield: 49%.

6.5.1.6. [3,3´-(2-Hydroxypropan-1,3-diyl)bis(1-mesityl-1H-imidazolium-2,2´-diyliden)]-(η⁴-1,5-cyclooctadienyl)rhodium(I)-hexafluorophosphate **6c**



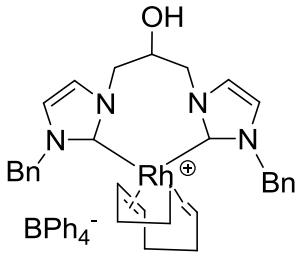
^{1}H-NMR(400 MHz, 298 K, d_2-DCM): δ = 7.77 (2H, d, NC*H*), 7.17 (4H, s, H_{Ar}), 6,99 (2H, d, NC*H*), 4.37 (4H, m, CH_2-*COD*), 3.99 (2H, d, NCH_2), 3.65 (1H, m, C*H*), 3.42 (2H, dd, NCH_2), 2.35 (4H, m, CH_2-COD), 2.17 (4H, m, CH_2-COD), 2.06 (6H, s, CH_3), 1.85 (12H, s, CH_3) ppm.

^{13}C{1H}-NMR (100 MHz, 298 K, d_2-DCM): δ=180.6 ($C_{Carbene}$), 140.3 (C_{Ar}), 134.7 (C_{Ar}), 133.8 (C_{Ar}), 129.0 (C_{Ar}), 126.2 (N*C*H), 124.7 (N*C*H), 91.0 (COD), 66.0 (C-H), 49.5 (N*C*H_2), 30.4 (COD), 21.9 (*C*H_3), 18.1 (CH_3) ppm.

MS (FAB): m/z (%): 582 (100, [M-PF_6]), 474 (81, [M-PF_6-COD]).

Yield: 31%.

6.5.1.7. [3,3´-(2-Hydroxypropan-1,3-diyl)bis(1-benzyl-1H-imidazolium-2,2´-diyliden)]-(η⁴-1,5-cyclooctadienyl)rhodium(I)-tetraphenylborate **5c^{BPh4}**



^{1}H-NMR(400 MHz, 298 K, d_6-Aceton): δ = 7.37 (20H, m, H_{Ar}), 7.04 (2H, s, NC*H*), 7.05 (10H, m, H_{Ar}), 7.04 (2H, s, NC*H*), 5.58 (4H, s, NCH_2-Ph), 4.77 (2H+1H, m, NCH_2 + C*H*), 4.57 (4H, m, CH_2-COD), 4.35 (dd, 2H, NCH_2), 2.44 (4H, m, CH_2-COD), 2.24 (4H, m, CH_2-COD).

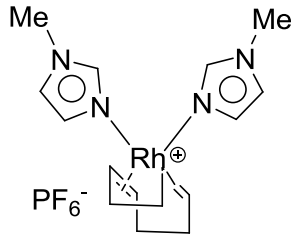
MS (FAB): m/z (%): 583 (100, [M-BPh_4]), 475 (90, [M-BPh_4-COD]).

Elem. Anal. Calc for $C_{55}H_{56}BN_4ORh$*1/2 DCM:

Calc.:	C	70.52	H	6.08	N	5.93
Found:	C	69.94	H	6.39	N	5.15

Yield: 33 %.

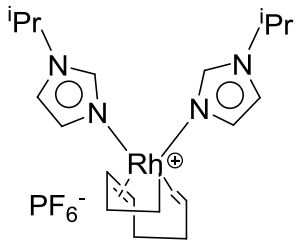
*6.5.1.8. Bis(3-methyl-1H-imidazole)-(η^4-1,5-cyclooctadienyl)rhodium(I)-hexafluorophosphate **7c^{bp}***



^{1}H-NMR(400 MHz, 298 K, d_6-Aceton): δ = 7.30 (2H, s, NC*H*N), 6.94 (2H, s, NC*H*), 6.75 (2H, d, NC*H*), 4.09 (4H, m, CH_2-COD), 3.73 (6H, s, NCH_2), 2.52 (4H, m, CH_2-COD), 1.95 (4H, m, CH_2-COD).

^{13}C{^{1}H}-NMR(100 MHz, 298 K, d_2-DCM): δ = 138.7 (N*C*HN), 128.1 (N*C*H), 122.2 (N*C*H), 82.8 (COD), 34.7 (NCH_3), 31.0 (COD) ppm.

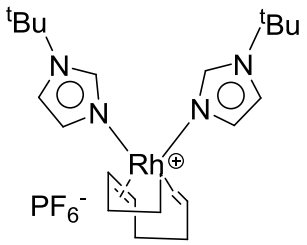
*6.5.1.9. Bis(3-isopropyl-1H-imidazole)-(η^4-1,5-cyclooctadienyl)rhodium(I) hexafluorophosphate **8c^{bp}***



^{1}H-NMR(400 MHz, 298 K, d_2-DCM): δ = 7.36 (2H, s, NC*H*N), 7.02 (2H, d, NC*H*), 6.75 (2H, d, NC*H*), 4.33 (2H, sept., C*H*), 4.11 (4H, m, CH_2-COD), 2.52 (4H, m, CH_2-COD), 1.94 (4H, m, CH_2-COD), 1.40 (12H, d, CH_3) ppm.

^{13}C{^{1}H}-NMR(100 MHz, 298 K, d_2-DCM): δ = 138.7 NC*H*N, 128.1 (NC*H*), 122.2 (NC*H*), 82.8 (COD), 34.7 (NCH_3), 30.9 (COD) ppm.

6.5.1.10. Bis(3-tert-butyl-1H-imidazole)-(η^4-1,5-cyclooctadienyl)rhodium(I)-hexafluorophosphate ***9c^{bp}***



^{1}H-NMR(400 MHz, 298 K, d_2-DCM): δ = 7.38 (2H, d, NC*H*N), 7.11 (2H, d, NC*H*), 6.78 (2H, d, NC*H*), 4.17 (4H, m, CH_2-COD), 2.56 (4H, m, CH_2-COD), 1.96 (4H, m, CH_2- COD), 1.51 (18H, s, CH_3) ppm.

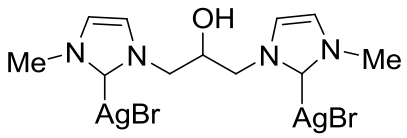
^{13}C{1H}-NMR (100 MHz, 298 K, d_2-DCM): δ = 138.4 (NCHN), 129.0 (NCH), 128.2 (NCH), 82.8 (COD), 47.3 (C_{tert}), 31.0 (COD), 14.2 (CH_3) ppm.

6.6. Bis-N-heterocyclic carbene complexes of Silver(I)

*6.6.1. General procedure for the synthesis of Bis(NHC)-carbene Silver(I) complexes **1d, 5d** and **6d***

One equivalent of the bis-imidazolium salts **1a**, **5a** and **6a** or, resp. and Ag_2O are stirred in 20 mL DCM for 18 h at room temperature under exclusion of light until a white solid precipitates. The solution is filtered off, and the solid residue is dried under vacuum.

*6.6.1.1. 1,1'-methyl-3,3'-(2-hydroxypropylen)diimidazolin-2,2'-diyliden-di-silber(I)-dibromide **1d***



^{1}H-NMR(400 MHz, 298 K, d_6-DMSO): δ = 7.43 (4H, d, NC*H*), 5.74 (1H, s, br, O*H*), 4.32 (1H, m, NC*H*), 4.20 (2H, dd, NCH_2), 4.05 (2H, dd, NCH_2), 3.76 (6H, s, NCH_3) ppm.

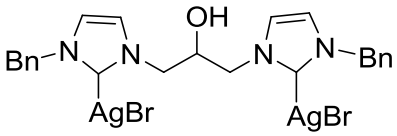
^{13}C{^{1}H}-NMR (100 MHz, 298 K, d_6-DMSO): δ = 180.6 ($C_{Carbene}$), 123.0 (NC*H*), 122.6 (NC*H*), 69.4 (*C*H), 53.6 (N*C*H_2), 38.2 (N*C*H_3) ppm.

Elem. Anal. Calc. for $C_{11}H_{16}Ag_2Br_2N_4O$:

Calc.:	C	22.17	H	2.71	N	9.40
Found:	C	22.22	H	2.61	N	9.61

Yield: 79 %.

6.6.1.2. 1,1'-benzyl-3,3'-(2-hydroxypropylen)diimidazolin-2,2'-diyliden-di-silber(I)-dibromid ***5d***



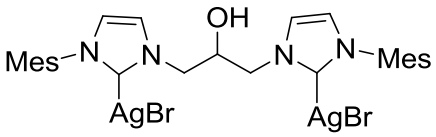
^{1}H-NMR(400 MHz, 298 K, d_6-DMSO): δ = δ = 7.46 (4H, d, NC*H*), 7.26 (10H, m, H_{Ar}), 5.70(1H, s, br, O*H*), 5.29 (4H, s, CH_2-Ph), 4.38 (2H, d, NCH_2), 4.24 (1H, m, C*H*) , 4.06 (2H, dd, NCH_2) ppm.

Elem. Anal. Calc. for $C_{23}H_{26}Ag_2Br_2N_4O$:

Calc.:	C	36.87	H	3.49	N	7.47
Found:	C	36.85	H	3.50	N	7.49

Yield: 59 %.

6.6.1.3. 1,1'-mesityl-3,3'-(2-hydroxypropylen)diimidazolin-2,2'-diyliden-di-silber(I)-dibromid ***6d***



^{1}H-NMR(400 MHz, 298 K, d_6-DMSO): δ = 7.62 (2H, s, NC*H*), 7.42 (2H, s, N*H*C), 6.96 (4H, s, H_{Ar}), 5.91 (1H, s, br, O*H*), 4.42 (2H, d, NCH_2), 4.14 (2H, dd, NCH_2), 2.37 (6H, s, CH_3-para), 1.73 (12H, s, CH_3-ortho) ppm.

Elem. Anal. Calc. for $C_{27}H_{32}Ag_2Br_2N_4O$:

Calc.:	C	40.33	H	4.01	N	6.97

Found: C 39.86 H 3.79 N 6.79

Yield: 39 %.

6.7. Bis-N-heterocyclic carbene complexes of Palladium(II)

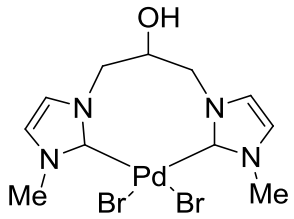
*6.7.1. Syntheses of bis(NHC) carbene Palladium(II) complexes **1e** and **5e** via the silver route*

In 15 mL of DMSO 1.0 mmol of **1d** and **5d** with 1 mmol of 1,5-cyclooctadienepalladium-(II) dichloride are stirred under exclusion of light for 12 h. The precipitated Ag(I)Cl is filtered off, and the solvent of the resulting solution is removed under vacuum until a white residue appears. This residue is washed with 3 mL of acetonitrile, and then the product is extracted with 2 x 15 mL of water. The water is removed under vacuum, and the solid residue is washed with 10 mL of THF and dried.

*6.7.2. Synthesis of bis(NHC) carbene-Pd(II) complexes **1e** and **5e** via acetate route*

$Pd(OAc)_2$ (0.22 mmol) and (0.22 mmol) of ligand **1a** respectively **5a** are dissolved in 10 mL DMSO and heated for 2 h to 60 °C, 2 h to 40 °C, 3h to 80 °C and 2 h from 100 °C to 130 °C. During the reaction the solution turns from dark red to yellow. Then diethyl ether was added until a white precipitate was obtained which was filtered off and dried under vacuum to yield a white powder in 70 % yield. Crystals suitable for X-ray diffraction were grown by slow diffusion of ether into a concentrated solution of **1e** in DMF.

6.7.2.1. (3,3'-(2-Hydroxypropan-1,3-diyl)bis(1-methyl-1H-imidazolium-2,2'-diyliden))palladium(II)-dibromide **1e**



^{1}H -NMR(400 MHz, 298 K, d_6-DMSO): δ = 7.20 (2H, s, NC*H*), 7.11 (2H, s, NC*H*), 5.48 (1H, s, O*H*), 4.94 (2H, d, NCH_2), 4.25 (3H, m, NCH_2 + C*H*), 3.91 (6H, s, NCH_3) ppm.

^{13}C{^{1}H}-NMR(100 MHz, 298 K, d_6-DMSO): δ = 125.3 (N*C*H), 122.1 (N*C*H), 64.5 (*C*H), 54.9 (N*C*H_2), 37.5 (N*C*H_3) ppm.

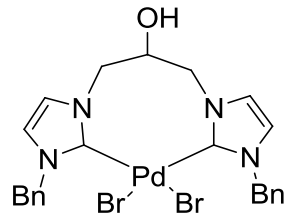
MS (FAB): m/z (%): 406 (55, [M-Br]), 324.5 (80, [M-2xBr]).

Elem. Anal. Calc. for $C_{11}H_{16}Br_2N_4OPd$*1.33 DMSO:

Calc:	C	27.79	H	4.10	N	9.49
Found:	C	27.67	H	3.93	N	9.92

Yield: 70 %.

6.7.2.2. (3,3'-(2-Hydroxypropan-1,3-diyl)bis(1-benzyl-1H-imidazolium-2,2'-diyliden))palladium(II)-dibromide **5e**



^{1}H -NMR(400 MHz, 298 K, d_6-DMSO): δ = 7.28-7.19 (6H, m, H_{Ar}), 7.07-7.04 (4H, d, NC*H*), 6.77 (4H, d, H_{Ar}), 5.91 (1H, d, O*H*), 5.39 (4H, d, NCH_2-Ph), 4.66 (2H, d, NCH_2), 4.06 (1H, m, C*H*), 3.68 (2H, dd, NCH_2) ppm.

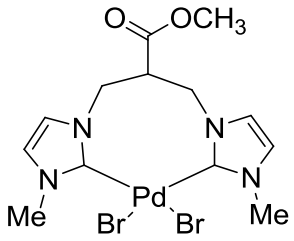
$^{13}C\{^{1}H\}$-NMR(100 MHz, 298 K, d_6-DMSO): δ = 167.3 (C_{Carben}), 135.8 (C_{Ar}), 128.4 (C_{Ar}), 127.8 (C_{Ar}), 126.3 (NCH), 126.0 (NCH), 121.5 (C_{Ar}), 63.8 (C-H), 54.9 (NCH_2), 53.7 (NCH_2) ppm.

Elem. Anal. Calc. for $C_{23}H_{24}Br_2N_4OPd$:

Calc.:	C	43.25	H	3.79	N	8.77
Found:	C	42.78	H	4.51	N	8.16

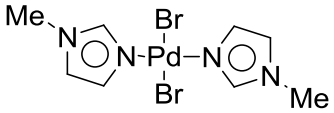
Yield: 76 %.

*6.7.2.3. 3,3´-(2-Methoxypropan-1,3-diyl)bis(1-methyl-1H-imidazolium-2,2´-diyliden))palladium(II)-dibromide **7e***



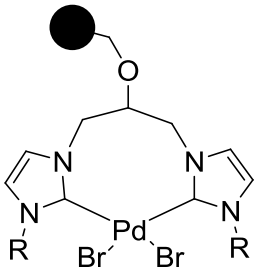
^{1}H -NMR(400 MHz, 298 K, d_6-DMSO): δ = 7.87 (2H, s, NCH), 7.74 (2H, s, NCH), 6.04 (1H, s, C-H), 4.48 (4H, d, NCH_2), 4.97 (6H, s, NCH_3), 3.70 (3H, s, OCH_3) ppm.

*6.7.2.4. Trans-[Pd-bis(N-methylimidazol)dichloride **7e^{bp}***



^{1}H -NMR(400 MHz, 298 K, d_6-DMSO): δ = 8.16 (2H, s, NCHN), 7.34 (2H, s, NCH), 7.13 (2H, s, NCH), 3.90 (3H, s, NCH_3) ppm.

*6.7.2.5. Immobilisation of **6e** on 4-(bromomethyl)phenoxymethyl polystyrene leading to the immobilized compound **6f***



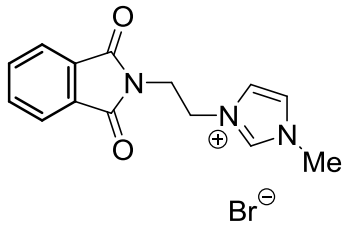
A solution of **6e** (0.19 mmol), 4-bromomethyl)phenoxymethyl polystyrene (c = (Br) = 1.97 mmol g^{-1}), di-iso-propylethylamine (0.57 mmol) and KI (0.06 mmol) in dry DMF (5 mL) was stirred for 72 h at room temperature. The pale yellow solid was collected and washed with N,N-dimethyl acetamide (DMAc 3 x 10 mL) and MeOH (3 x 10mL).

Elemental analysis: Calc. (%) for loading of 1.1 palladium N 0.56, found Pd 1.0, N 0.49.

IR(KBr): γ = 1635 (m, C=O), 1464(m,CH_3)

6.8. Phthalimido-functionalized N-heterocyclic mono-carbene Pd(II) complex

*6.8.1. 1-(2'-phthalamidoethyl)-3-methylimidazolium bromide **12a***



N-(2-bromoethyl)-phthalimide (1.05 g, 3.93 mmol) and 1-methylimidazole (0.32 g, 3.93 mmol) were sealed in a ACE pressure tube in toluene and stirred at 120 °C for 1 day. After allowing the reaction mixture to cool to the room temperature it was filtered and the colorless solid was washed with diethyl ether and dried under vacuum to afford a white solid.

^{1}H NMR (400 MHz, d_6-DMSO): δ = 9.11 (1H, s, NC*H*N), 7.84 (4H, s, C*H* $_{Phth}$), 7.78 (1H, m, C*H*), 7.63 (1H, m, C*H*), 4.43-4.40 (2H, t, $^{3}J_{HH}$ = 6.0 Hz, N-CH_2), 4.01-3.98 (2H, t, $^{3}J_{HH}$ = 6.0 Hz, CH_2-NIm), 3.79 (3H, s, NCH_3) ppm.

^{13}C{1H} 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 (s, *C*5) , 123.37, 122.61 (s, *C*4), 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]).

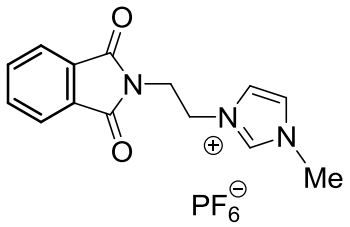
Elem. Anal. Calc. for $C_{14}H_{16}BrN_3O_2$:

Calc.:	C	47.47	H	4.55	N	11.86
Found:	C	47.29	H	4.44	N	11.61

Yield: 84 %.

*6.8.2. 1-(2'-phthalamidoethyl)-3-methylimidazolium hexafluorophosphate **12b***

1-(2'-phthalamidoethyl)-3-methylimidazolium bromide (1.0 g, 2.97 mmol) were dissolved in a round bottom flask in 20 ml of water at 60 °C, followed by the addition KPF_6 (0.802 g, 3.56 mmol) in 10 mL of water. The reaction mixture was heated at 60 °C and immediate white precipitation occurred. The reaction was further stirred for 15 minutes and then for an hour at room temperature. The white precipitate was filtered and washed with water two times before drying under vacuum to obtain white flakes.



^{1}H NMR (400 MHz, d_6-DMSO): δ = 9.16 (1H, s, NC*H*N), 7.88-7.84 (5H, m, C*H* $_{Phth+Im}$), 7.66 (1H, s, CH_{Im}), 4.44-4.42 (2H, t, $^{3}J_{HH}$ = 4.0 Hz, PhtN-CH_2), 4.02-4.00 (2H, t, $^{3}J_{HH}$ = 4.0 Hz, CH_2-NIm), 3.82 (3H, s, ImNCH_3) ppm.

^{13}C{1H} NMR (100 MHz, d_6-DMSO): δ = 167.67 (s, N*C*O), 137.15 (s,*C*2), 134.54 (s, N*C*N), 131.54, 123.59 (s, *C*5) , 123.37, 122.61 (s, *C*4), 47.86 (s, N-*C*H_2), 38.52 (s, *C*H_2-NIm), 35.77 (s, N*C*H_3) ppm.

^{31}P{1H} NMR (161 MHz, DMSO-d_6): δ = 131.03-157.38 (sept, PF_6) ppm.

MS (FAB) *m/z* (%): 256 (100, [M - PF_6]).

Elem. Anal. Calc. for $C_{14}H_{14}F_6N_3O_2P$

Calc.:	C	41.91	H	3.52	F	28.41	N	10.47
Found:	C	42.29	H	3.44	F	28.23	N	10.45

Yield: 66 %.

*6.8.3. Synthesis of Acetonitrile(1-(2'-phthalamidoethyl)-3-methylimidazolin-2-ylidene) silver(I) hexafluorophosphate **12d***

1-(2'-phthalamidoethyl)-3-methylimidazolium hexafluorophosphate (0.200 g, 0.5 mmol) was dissolved in 20 mL of a 1:1 mixture of CH_3CN:CH_2Cl_2 in a Schlenk tube. Ag_2O (0.058 g, 0.25 mmol) was added and the reaction mixture was stirred at 60 °C in the dark for 2 day. The reaction mixture was then filtered through a plug of celite and concentrated to about 5 mL. Et_2O was added to precipitate the Ag complex as a white solid. The white solid was filtered and washed twice with Et_2O before drying under vacuum to obtain a white powder that is sensitive to light.

^{1}H NMR (400 MHz, *d6*-DMSO): δ = 7.79 - 7.55 (4H, m, CH_{Phth}), 7.38 (2H, s, CH_{Im}), 4.30-4.27 (2H, t, PhtN-CH_2), 3.93-3.90 (2H, t, CH_2-NIm), 3.56 (3H, s, ImNCH_3), 2.07 (1H, s, CH_3CN) ppm.

^{31}P NMR (162 MHz, d_6-DMSO): δ = - 131.02 to -157.36 ppm.

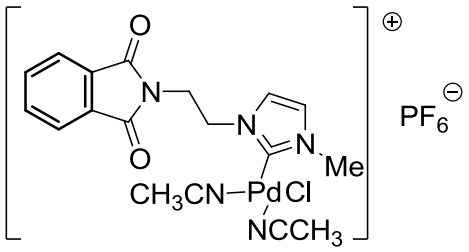
MS (FAB): m/z (%): 619 (40) [M-NHC-CH_3CN-PF_6], 362 (45) [M-CH_3CN-PF_6], 256 (100) [NHC].

Elem. Anal. Calc. for $C_{16}H_{18}Ag_2F_6N_4O_2P$

Calc.:	C	34.87	H	3.29	N	10.17
Found:	C	35.91	H	2.86	N	9.65

Yield: 65 %.

6.8.4. Synthesis of cis-Diacetonitrile(chloro)(1-(2'-phthalamidoethyl)-3-methyl imidazolin-2-ylidene)palladium(II) hexafluorophosphate, **12e**



Acetonitrile (1-(2'-phthalamidoethyl)-3- methylimidazolin-2-ylidene) silver (I) hexafluorophosphate (**12d**, 0.100 g, 0.2 mmol) and $Pd(CH_3CN)_2Cl_2$ (0.047 g, 0.2 mmol) were each dissolved in 10 ml of CH_3CN. The palladium solution was added to the silver complex via cannula. White precipitate was observed immediately with stirring. The reaction mixture was further stirred at 60 °C for another 2 hours before cooling to room temperature. The solution was filtered and the solvent was evaporated off, leaving a light yellow powder. The powder was recrystallized by slowdiffusion of Et_2O into a concentrated CH_3CN solution to give yellow crystals.

^{1}H-NMR (400 MHz, d_6-DMSO): δ = 7.81 (4H, m, C*H* Phth), 7.74 (1H, s, C*H* Im), 7.54 (1H, s, C*H* Im), 4.88-4.84 (1H, m, PhtN-CH_2), 4.54-4.50 (1H, m, PhtN-CH_2), 4.29-4.25 (1H, m, ImN-CH_2), 4.02-3.99 (1H, m, ImN-CH_2), 3.91 (3H, s, ImN-CH_3) ppm.

^{13}C-NMR(100 MHz, d_6-DMSO): δ = 167.93 (s, N*C*O), 142.77 (N*C*N)), 134.18, 132.00, 125.30 (s, *C*5), 123.63 (s, *C*4), 122.96, 118.03 (s, CHs*C*N), 48.07 (s, PhtN-*C*H2), 38.60 (s, *C*H_2-NIm), 37.34 (s, N*C*H_3) 1.13 (s, *C*HsCN) ppm.

^{31}P-NMR (162 MHz, d_6-DMSO): δ = -131.01 to -157.36 ppm (septet, *P*F6) ppm.

MS (FAB): *m/z* (%): 398 (10) $[M - 2CH_3CN - PF_6]^+$, 256 (78) $[NHC]^+$. 67%.

Elem. Anal. Calc. for $C_{18}H_{19}ClF_6N_5O_2PPd$:

Calc:	C	34.63	H	3.07	N	11.22
Found:	C	34.51	H	2.98	N	10.52

Yield: 75 %.

6.9. Catalysis

6.9.1. General procedure for the Hydrosilation of 4-fluoro-acetophenone

4-fluoro-acetophenone (0.504 mmol) and the rhodium complexes (**1c**, **3c**, **5c**^{PF6} respectively **5c**^{BPh4}, 0.02 mmol) in 0.3 mL solvent (DCM, THF or DCE) were stirred for 10 min. Diphenylsilane (0.765 mmol) was added and the mixture solution was kept in a thermostatic bath at 60^{o} C and the progress of the reactions was monitored by ^{19}F-NMR spectroscopy.

6.9.2. General procedure for the transfer Hydrogenation

The reduction of acetophenone taken as a model ketone, was carried out in 2-propanol respectively methanol by using rhodium complexes **1c-5c**^{PF6} with different base, with ratio of substrate : cat : base = 100 : 1 (0.5) : 10. The catalytic experiments were carried out using 1 mmol of acetophenone, 0.01 mmol of rhodium complex **1c**-**5c**^{PF6}, 0.1 mmol of base, 10 mL of 2-propanol respectively methanol and vatratrole (250 µL) as an internal GC standard.
The mixture was heated to 80 °C for 30 min. Aliquots (0.4 mL) were taken at fixed time, diluted in ether (0.6 mL) and filtered through a short path column of SiO_2, which was washed with 0.5 mL ether again. The product ratio was determined by GC analysis.

*6.9.3. General procedure for the Suzuki-Miyaura coupling reaction for **1e**, **5e** and **1f***

Catalytic reactions were carried out by employing standard conditions with aryl halide (1.00 mmol), phenylboronic acid (1.50 mmol) and base K_2CO_3 (2.00 mmol), 114 mL diethylene glycol di-n-butyl ether as internal standard and 5 mL degassed solvent. After thermo stating for 10 min at the reaction temperature (80 °C), the catalyst solution was added. To end the

reaction, the mixture was cooled to room temperature and the water phase was extracted three times with 2 mL of diethyl ether.

*6.9.4. General procedure for the Suzuki-Miyaura coupling reaction for **12d***

Catalytic test reactions were performed on a Raldeys® catalysis carousel. A carousel tube was charged with a mixture of aryl halides (ArX, X = Br or Cl) (1 mmol), phenylboronic acid (1.2 mmol) and K_2CO_3 (2 mmol). 4 ml of water were added to the tube and the reaction mixture was heated to the required temperature for 15 min. The precatalyst **12d** was dissolved in dimethylformamide to the appropriate mol% concentration 1 mL of the catalyst solution was then added to the reaction mixture and stirred for the desired reaction time. After which, 1M hydrochloric acid was added and the aqueous phase was extracted with ethyl acetate (5 mL). 0.1 mL of the organic phase was diluted with 1.9 mL of ethyl acetate and then filtered through a $NaSO_4$ filled glass pipette; the sample was analyzed by gas chromatography.

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Appendix

Table 18: Crystallographic Data for compound **1c**

Sum formula	$C_{19}H_{28}F_6N_4OPRh$
Fw	576.33
Color / habit	Yellow / fragment
Crystal dimensions (mm^3)	$0.20 \times 0.25 \times 0.46$
Crystal system	Monoclinic
Space Group	$P2_1/c$ (no. 14)
a (Å)	14.2479(6)
b (Å)	12.6485(5)
c (Å)	13.6367(6)
β (°)	114.119(2)
V ($Å^3$)	2242.99(17)
Z	4
T (K)	123
D_{calcd} (g cm^{-3})	1.707
μ (mm^{-1})	0.902
F(000)	1168
θ Range (°)	1.57 – 25.31
Index ranges (h, k, l)	-16/+17, ±15, ±16
No. of rflns. collected	60597
No. of indep. rflns. / R_{int}	4083 / 0.021
No. of obsd. rflns. ($I>2\sigma(I)$)	3957
No. of data/restraints/params	4083 / 0 / 291
R_1/wR_2 ($I>2\sigma(I)$)[a]	0.0488 / 0.1141
R_1/wR_2 (all data)[a]	0.0504 / 0.1154
GOF (on F^2)[a]	1.160
Largest diff. peak and hole (e $Å^{-3}$)	+1.06 / -0.86

[a] $R_1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]\}^{1/2}$;
$GOF = \{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$

Table 19: Selected bond distances (Å) and Angles (deg) for compound **1c**

Bond distance (Å**)**	
Rh−C1	2.030(5)
Rh−C10	2.042(6)
Rh−Cg1	2.100
Rh−Cg2	2.082
C6−O1	1.418(7)
Bond angle (deg)	
C1−Rh−C10	83.6(2)
C1−Rh−Cg1	176.9
C1−Rh−Cg2	96.0
C10−Rh−Cg1	93.4
C10−Rh−Cg2	178.8
Cg1−Rh−Cg2	87.0
N1−C1−N2	104.2(4)
C5−C6−O1	111.1(4)
C7−C6−O1	107.7(4)
C5−C6−C7	118.4(5)
N3−C10−N4	104.9(5)

[a)] Cg is defined as the midpoint of the double bonds Cg1: C12=C13, and C16=C17, resp.

Table 20: Crystallographic data and structure refinement **2c**

Sum formula	C_{21} H_{32} F_6 N_4 O P Rh
Fw	604.39
Color//habit	Yellow /fragment
Crystal dimensions (mm^3)	0.25 x 0.13 x 0.13
Crystal system	Triclinic
Space Group	P-1(No. 2)
a (Å)	9.8096(4)
b (Å)	10.2582(4)
c (Å)	13.4056(8)
ß (^{o})	103.976(2)
V (Å ^{3})	1215.5(1)
Z	2
T (K)	173(2)
D_{calcd} (g cm^{-3})	1.651
µ (mm^{-1})	0.836
F(000)	616
Θ Range (^{o})	1.7-26.1
Index ranges (h,k,l)	-12/+12;-12/+12 ; -16/+16
No. of rflns.collected	22293
No. of indep.rflns. /R_{int}	4667/0.028
No .of odsd. rflns. (I>2σ(I))	4423
No. of date/restraints/params	4667 /0 / 456
R_1/wR_2 (I > 2σ (I))[a]	0.0291 / 0.0663
R_1/wR_2 (all data)[a]	0.0311 / 0.0672
GOF (on F^2)[a]	1.045
Largest diff. peak and hole (e $Å^{-3}$)	1.070 / -0.905

[a] $R1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $GOF = \{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$

Table 21: Selected bond lengths (Å) and bond angles (°) for complex **2c**

Rh1 C4	2.033(3)	C4 Rh1 C1	83.82(10)
Rh1 C1	2.037(3)	C4 Rh1 C19	93.07(10)
Rh1 C19	2.192(3)	C4 Rh1 C15	157.09(11)
Rh1 C15	2.195(3)	C1 Rh1 C15	92.69(10)
Rh1 C18	2.197(3)	C4 Rh1 C18	94.26(10)
Rh1 C14	2.197(3)	C18 Rh1 C14	88.20(11)
N1 C1	1.352(3)	N1 C1 N2	104.1(2)
N2 C1	1.367(3)	O1A C8A C7	106.6(2)
N3 C4	1.363(3)	O1A C8A C9	110.5(3)
N4 C4	1.355(3)	C7 C8A C9	115.9(2)
C8A O1A	1.428(4)		

Table 22: Selected bond lengths (Å) and bond angles (°) for complex **1a**·CH_3OH

C1−C2	1.521(3)	O1−C1−C2	109.8(2)
C1−C2^{i}	1.521(3)	C2−C1−C2^{i}	107.0(2)
N1−C2	1.466(3)	N1−C2−C1	111.0(2)
N1−C3	1.323(3)	C2−N1−C3	124.9(2)
N1−C4	1.375(3)	C2−N1−C4	126.1(2)
N2−C3	1.334(3)	C3−N1−C4	108.9(2)
N2−C5	1.372(3)	N1−C3−N2	108.3(2)
N2−C6	1.467(3)	C3−N2−C5	108.6(2)
C4−C5	1.346(4)	C3−N2−C6	125.3(2)
O1−C1	1.411(4)	C5−N2−C6	126.1(2)
		N1−C4−C5	107.0(2)
		N2−C5−C4	107.2(2)

^{i} symmetry operation for equivalent atoms (x, ½-y, z)

Table 23: Selected bond lengths (Å) and bond angles (°) for complex **1a**·CH_3OH

C1−C2	1.521(3)	O1−C1−C2	109.8(2)
C1−C2[i]	1.521(3)	C2−C1−C2[i]	107.0(2)
N1−C2	1.466(3)	N1−C2−C1	111.0(2)
N1−C3	1.323(3)	C2−N1−C3	124.9(2)
N1−C4	1.375(3)	C2−N1−C4	126.1(2)
N2−C3	1.334(3)	C3−N1−C4	108.9(2)
N2−C5	1.372(3)	N1−C3−N2	108.3(2)
N2−C6	1.467(3)	C3−N2−C5	108.6(2)
C4−C5	1.346(4)	C3−N2−C6	125.3(2)
O1−C1	1.411(4)	C5−N2−C6	126.1(2)
		N1−C4−C5	107.0(2)
		N2−C5−C4	107.2(2)

[i] symmetry operation for equivalent atoms (x, ½-y, z)

Table 24: Crystallographic data for complex **1a**·CH_3OH and complex **1e**·$2(C_3H_7NO)$

Sum formula	$C_{11}H_{18}Br_2N_4O$, CH_3OH	$C_{11}H_{16}Br_2N_4OPd$, $2(C_3H_7NO)$
Formula weight	414.14	632.67
Color/habit	pale yellow / block	colorless / fragment
Crystal dimensions (mm^3)	$0.56 \times 0.56 \times 0.56$	$0.36 \times 0.51 \times 0.51$
Crystal system	monoclinic	triclinic
Space group	$P2_1/m$(no. 11)	$P\bar{1}$ (no. 2)
a (Å)	4.9378(3)	9.4660(4)
b (Å)	15.0212(7)	11.9219(6)
c (Å)	11.6184(7)	12.0247(6)
α (°)	90	67.709(2)
ß(°)	90.166(5)	71.725(2)
γ (°)	90	89.736(2)
V ($Å^3$)	861.75(8)	1182.14(10)
Z	2	2
T (K)	153	173
D_{calc} (g cm^{-3})	1.596	1.777
μ (mm^{-1})	4.710	4.194
F(000)	416	628
θ Range (°)	4.94 – 25.29	1.86 – 25.33
Index ranges (h, k, l)	±5, ±18, ±13	±11, ±14, ±14
Number of reflections collected	16370	47547
Number of independent reflections/R_{int}	1608/0.073	4236/0.055
Number of observed reflections ($I>2\sigma(I)$)	1381	4155
Number of data/restraints/parameters	1608/0/109	4236/0/270
$R1$/$wR2$ ($I>2\sigma(I)$)[a]	0.0229 / 0.0511	0.0206 / 0.0528
$R1$/$wR2$ (all data)[a]	0.0313 / 0.0529	0.0210 / 0.0530
Godness-of-fit (on F^2)[a]	1.012	1.042
Largest diff peak and hole (e $Å^{-3}$)	+0.31 / -0.40	+0.57 / -0.54

[a] $R1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $GOF = \{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$

Table 25: Selected bond lengths (Å) and bond angles (°) for complex **1e**·2(C_3H_7NO)

Pd1−Br1	2.5042(4)	Br1−Pd1−Br2	95.39(1)
Pd1−Br2	2.4975(3)	Br1−Pd1−C1	172.73(6)
Pd1−C1	1.976(2)	Br1−Pd1−C4	89.15(6)
Pd1−C4	1.974(2)	Br2−Pd1−C1	91.23(7)
N1−C1	1.346(3)	Br2−Pd1−C4	175.43(6)
N2−C1	1.353(3)	C1−Pd1−C4	84.26(9)
N3−C4	1.348(3)	N1−C1−N2	105.7(2)
N4−C4	1.351(3)	N3−C4−N4	105.6(2)
O1−C8	1.420(3)	O1−C8−C7	112.5(2)
		O1−C8−C9	107.7(2)
		C7−C8−C9	116.1(2)

Table 26: Crystallographic details of **12d** MeCN

Sum formula	$C_{18}H_{19}ClF_6N_5O_2PPd$-$C_2H_3N$
M_r (g/mol)	665.26
Crystal description	yellow fragment
Crystal dimensions (mm^3)	0.27 x 0.24 x 0.13
Temperature (K)	173(2)
crystal system, space group	triclinic, *P1* (No.: 2)
a (Å)	9.0321(5)
b (Å)	9.3818(5)
c (Å)	15.6702(9)
a(°)	88.090(2)
b (°)	83.804(2)
g(°)	88.582(2)
V ($Å^3$)	1319.1(1)
Z	2
*d*calc (g/cm3)	1.675
F_{000}	664
m (mm^{-1})	0.938
Index ranges (±h, ±k, ± l)	13/-12, 13/-13, 23/-23
θranges (°)	1.31-33.03
Collected reflections	45584
Unique reflections [all data]	8233
*R*int/*R* σ	0.0411/0.0315
Unique reflections [I_0>2 σ (I_0)]	7255
Data/Restraints/Parameter	7255/0/375
GoF (on F^2)	1.109
R_1/wR_2 [I_0>2 σ (I_0)]	0.0328/0.0832
R_1/wR_2 [all data]	0.0399/0.0874
Max./Min. residual electron density	0.864/-1.215

[a] $R1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $GOF = \{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$

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