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Synthesis, Characterization and Catalytic Applications of Water-Soluble Carbene Complexes for the Hydrogenation of Acetophenone

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To my beloved sister, Olivia Hidayat,

I dedicate my work especially to you.

With deep gratitude and love.

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Abbreviations and Acronyms

Å	Angstrom
Ar	Aromatic substituent
CP-MAS	cross pulse magic angle spinning
Cy	Cyclohexyl substituent
δ	Chemical shift
DMSO	Dimethylsulfoxide
eq.	Molar equivalents
FAB-MS	Fast atom bombardment mass spectroscopy
GC	Gas Chromatography
Hz	Hertz
J	Coupling constant
L	Ligand
m	multiplet (NMR)
MS	mass spectroscopy
MHz	Megahertz
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance
Ph	phenyl moiety
ppm	Parts per million
R	alkyl or aryl moiety
RT	Room temperature
s	Singlet (NMR)
t	triplet (NMR)

Table of Contents

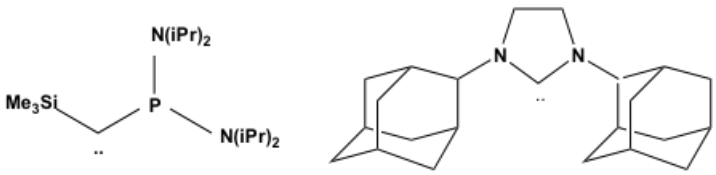
1 Introduction

1.1 *N*-Heterocyclic Carbenes (NHC)

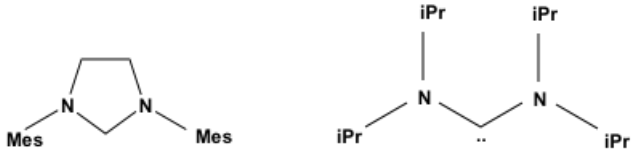
1.1.1 Historical Perspective

Carbenes have been recognized as a unique type of intermediates since the pioneering work of Doering in 1954 [1]. First attempts to stabilize carbenes were made in the 1980s when Tomioka started to study persistent triplet diarylcarbenes [2].

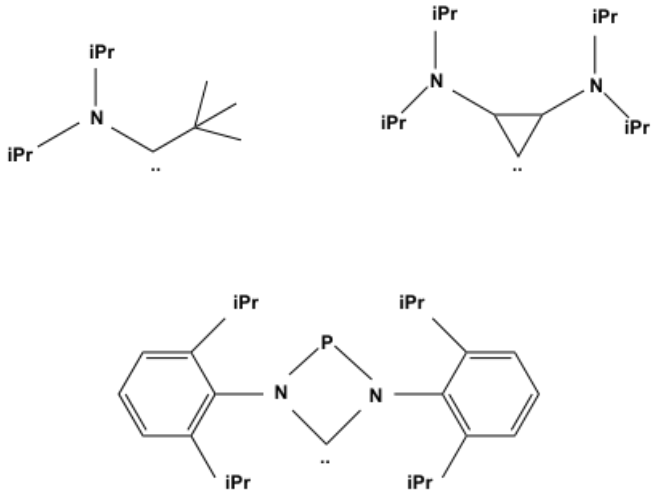
NHCs have been known since the pioneering work of Wanzlick [3 - 4]. Wanzlick, however, could not isolate the free carbene. In the following years stabilization by heteroatoms seemed the most promising way to stabilize carbenes. The first stable isolated carbenes were reported in 1988 by Bertrand [5] and in 1991 by Ardenguo [6]. Phosphinocarbene can even be distilled at 80 – 85 °C / 10^{-2} Torr and NHC is a crystalline solid that melts above 240 – 241 °C without decomposition (Scheme 1.1). Further analogues were synthesized in the next following years (Scheme 1.2). These carbenes represent highly air- and water-sensitive compounds at room temperature.



Scheme 1.1 the first stable isolated carbene



Scheme 1.2 Novel Stable NHCs (to be continued)



Scheme 1.2 Novel Stable NHCs

1.1.2 General Characteristics [7]

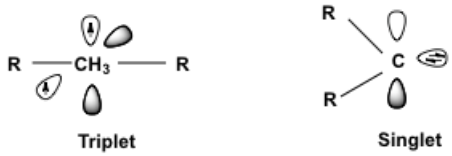
Carbenes are neutral compounds. They contain divalent carbon with only six electrons in their valence shell. The geometry at the carbene atom can be linear or bent. The linear geometry is based on an sp-hybridized carbene carbon atom that has two energetically degenerated p orbitals (p_x, p_y). Most carbenes contain an sp^2-hybridized carbon atom and the geometry at the carbene atom is not linear. The energy of one p orbital, conventionally called p_π, practically does not change upon transition from the sp- to the sp^2-hybridization state. The newly formed sp^2-hybrid orbital, called as σ orbital, exhibits partial s character and is thereby energetically stabilized relative to the original p orbital.

The non-bonding orbitals can be occupied in two ways. In triplet carbene, the two nonbonding electrons at the sp^2-hybridized carbene carbon atom can occupy the two empty orbitals with a parallel spin orientation. On the other hand, two electrons occupy the σ orbital with an antiparallel spin orientation leading to the singlet carbene ground state.

The multiplicity of the ground state influences the properties and the reactivity of a carbene [8]. Singlet carbenes have a filled σ and an empty p_π orbital and therefore show an ambiphilic

behavior. Triplet carbenes can be considered as diradicals of their two unpaired electrons. The singlet ground state is observed if there is a large energy difference between the σ and p_π orbitals. Energy difference of 2 eV is required for the stabilization of the singlet carbene based on Quantum chemical calculations [9]. And for the triplet ground state, an energy difference for stabilization is less than 1.5 eV.

Steric and electronic effects of the substituents at the carbene carbon atom control the multiplicity of the ground state. Substituents with σ-electron donating properties decrease the energy gap between the σ and the p_x orbital and thus stabilize the triplet ground state. The singlet ground state is stabilized by σ-electron withdrawing, generally more electronegative substituents [10 - 13]. Negative inductive effect causes a lowering of the relative energy of the p_π orbital remains essentially unchanged.

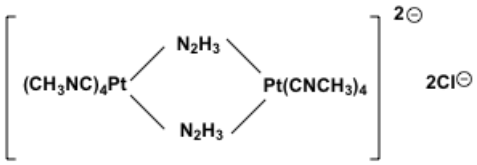


Scheme 1.3 Triplet and singlet carbenes

1.2 *N*-Heterocyclic Carbene Metal Complexes

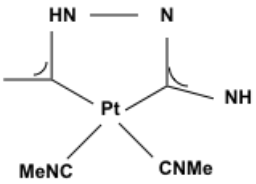
1.2.1 Historical Perspective

The first complex with a heteroatom-stabilized carbene ligand was prepared in 1925 by Tschugaeff (Chugaev) [14]. He reported that treatment of tetrakis(methyl isocyanide) platinum (II) with hydrazine produced a red, crystalline complex, with formal composition ''$[Pt_2(N_2H_3)_2(CNMe)_8]Cl_2$'' which was formulated on the basis of analytical and conductivity data as seen in Scheme 1.4.



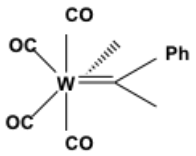
Scheme 1.4 Tschugajeff's Complex

Only 45 years later this complex was shown by means of x-ray difraction by Enemark et al to be heteroatom stabilized carbene complex (Scheme 1.5) [15]. Such structure was not even conceivable in the times of Tschugajeff.

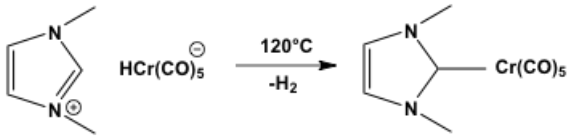


Scheme 1.5

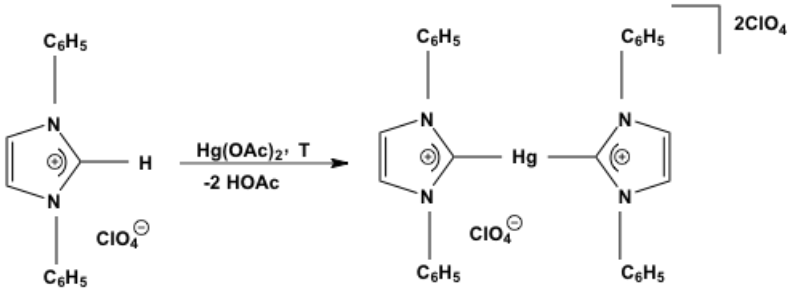
So it lasted till 1964, when carbenes were really introduced to inorganic Chemistry by Fischer and Massböl who reported that reaction of phenyl lithium with $W(CO)_6$, followed by addition of acid and then diazomethane, gave complex as shown on Scheme 1.6 [16]. A few years later Ofele's and Wanzlick's first syntheses of NHC metal complexes on Scheme 1.7 and Scheme 1.8 respectively, extended the Fischer type carbene family [17 - 18]. Wanzlick treated an imidazolium salt with mercury(II) acetate [18], and Öfele simply heated dimethylimidazolium hydridpentacarbonylchromate(II) [17]. In both cases, a ligand of the metal salt used acted as a base for the deprotonation of the imidazolium salt to the imidazolin-2-ylidine, which was then stabilized by coordination to the metal centre. In 1974, Schrock developed a new type of carbene, so-called Schrock carbene, Scheme 1.9, with a totally different reactivity [19].



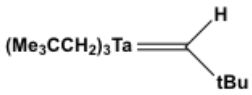
Scheme 1.6 Fischer's complex



Scheme 1.7 Wanzlick's complex



Scheme 1.8 Öfele's complex



Scheme 1.9 Schrock's complex

1.2.2 Complexation to the Metals

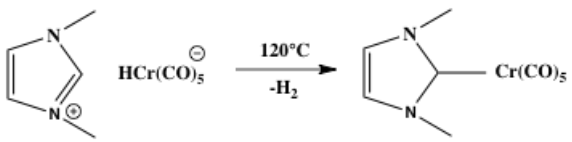
Several synthetic methodologies have been most commonly applied in the literature for the preparation of NHC metal complexes [7, 20]:

1. in situ deprotonation of the imidazolium salts by basic metalates or basic counterions

2. proton abstraction with bases prior to metalation
3. use of an external base in one pot reaction with the metal precursor
4. transmetalation via silver complexes
5. oxidative addition of 2-chloro-1,3-disubstitueted imidazolinium salts to appropriate metal complexes
6. metal atom cocondensation
7. synthesis of carbene in the coordination sphere of metal

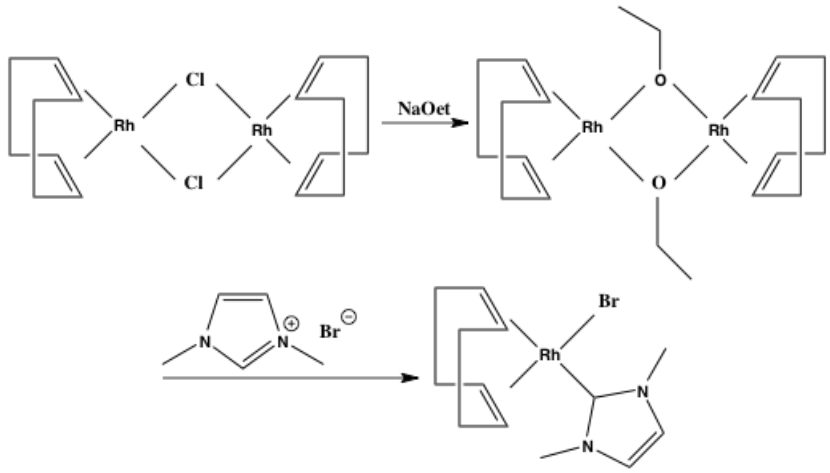
NHCs are very strong σ donors and show dissociation energies higher than phosphines for a large range of metals. If their free form can be isolated, their complexation is achieved in high yield.

Wanzlick and Öfele showed that NHC complexes could be obtained by in situ deprotonation of azolium salts in the presence of a suitable metal complex, without isolation of the free carbene ligand. Wanzlick and Schönherr treated an imidazolium salt with mercury (II) acetate and generated the carbene complex and acetic acid [18], while Metal-NHC complex (Scheme 1.10) was formed by Öfele by simply heating dimethylimidazolium hydridopentacarbonylchromate(-II) resulting in formation of the carbene complex and molecular hydrogen [17]. The basic metalate ion $[HCr(CO)_5]^-$ serves as base and ligand acceptor at the same time. The drawback of this method is the limited availability of the metal precursors.



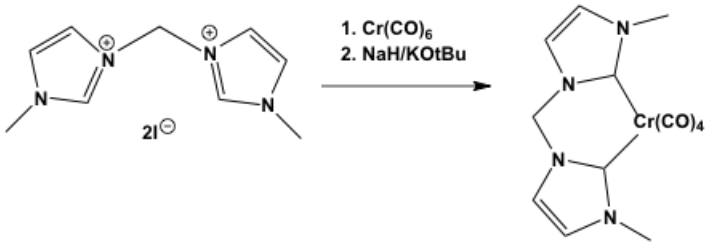
Scheme 1.10 Öfele's in situ deprotonation by a basic metalate ion

Basic counter-ions of the metal precursors can also act as deprotonating agents. For example, a convenient method to synthesize NHC-Pd(II) complexes is by mixing $Pd(OAc)_2$ with the corresponding imidazolium salt. In a similar way, μ-alkoxo complexes of [μ^4-cod) rhodium (I) and iridium (I), formed in situ by adding μ-chloro bridged analogues to a solution of sodium alkoxide in the corresponding alcohol, will deprotonate imidazolium salt and deliver the corresponding NHC complex, as seen on Scheme 1.11 [21].



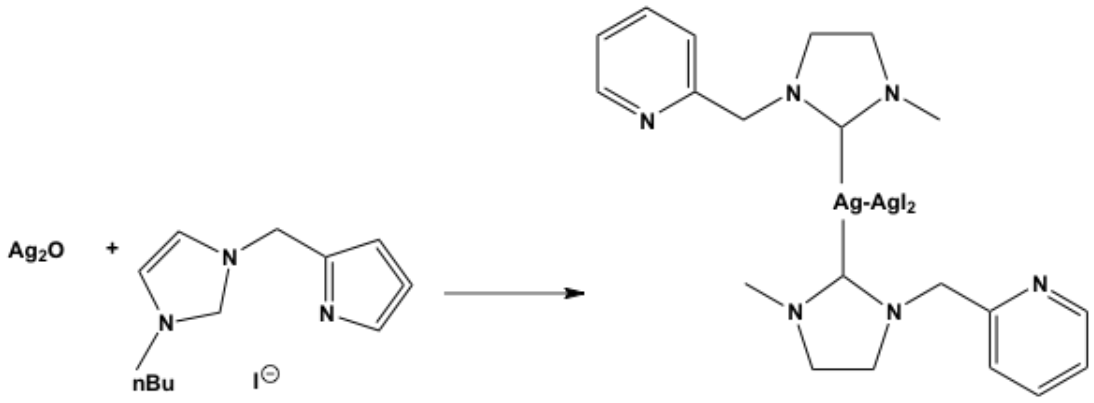
Scheme 1.11 Synthesis of NHC – complexes by deprotonation with basic counter – ions of metal precursors

The use of an external base to generate NHCs in the presence of metal precursors is also an efficient method, (Scheme 1.12). Potassium tert-butoxylate and sodium hydride in THF at room temperature can be used to coordinate NHCs to $Cr(CO)_6$ and to $W(CO)_6$ in situ [22]. A large variety of bases ranging from triethylamine [23], lithium diisopropylamide [24], NaOAc, NaH, KO*t*Bu, or MHMDS (M = Li, Na, K) to phosphane bases [25] has been successfully used over the past years.

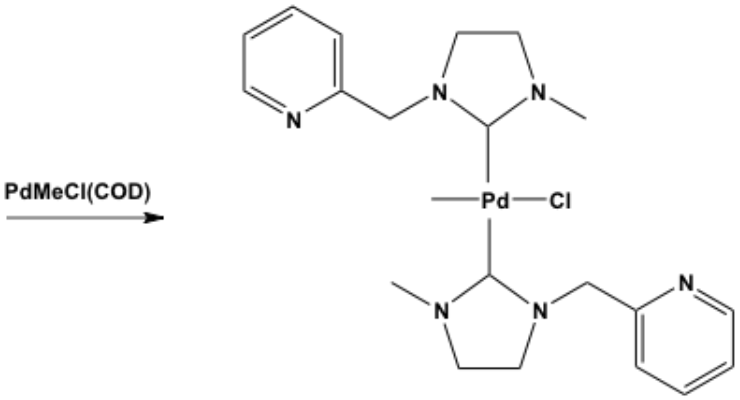


Scheme 1.12 Synthesis of NHC – complexes by deprotonation with basic counter – ions of metal precursors

A method for preparing NHC metal complexes via corresponding silver carbene complexes has been developed by Wang [26]. Silver NHC complexes are readily prepared upon mixing the corresponding imidazolium with Ag_2O in CH_2Cl_2 at room temperature. Subsequent reaction with chloro – metal precursors give the desired NHC metal complex that can be easily separated from AgX, the latter being insoluble in THF (see Scheme 1.13) [27]. The advantage of this method is the tolerance for sensitive *N*-substituents, which can be destroyed by conventional deprotonation of imidazolium salt with strong bases.

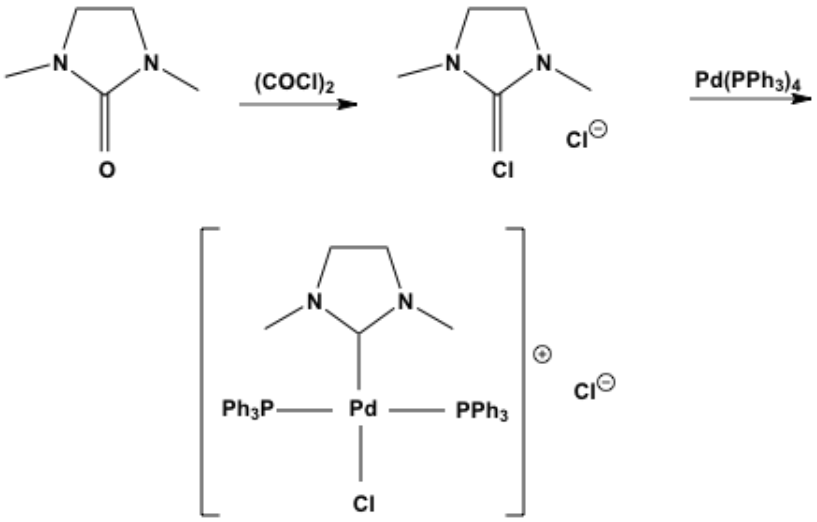


Scheme 1.13 Preparation of metal complexes by transmetalation via silver (I) complexes (to be continued)



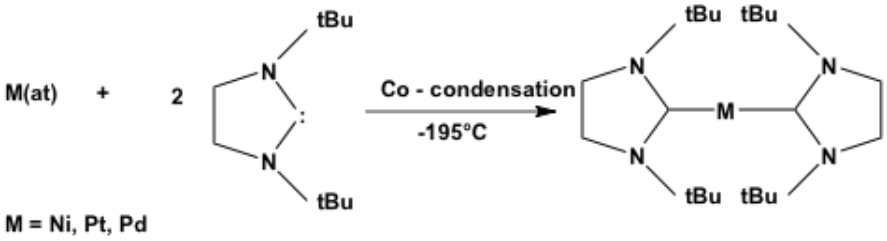
Scheme 1.13 Preparation of metal complexes by transmetalation via silver (I) complexes

Oxidative addition of a low-valent metal to 2-chloro-1,3-disubstituted imidazolinium salts was recently used by Fürstner et al. for the synthesis of a large number of carbene complexes, Scheme 1.14 [28]. Stone et al. who has showed that oxidative addition of metals to 2-chlorothiazolium or 2-chloro-1-metylpyridniumsalts affords the corresponding carbene complexes in excellent yields [29 - 31], discovered this method. This novel method allows substantial structural variations, since the required 2-chloro-1,3-disubstituted imidazolinium salts can be easily prepared from cyclic ureas or thioureas on treatment with, for example, oxalyl chloride.



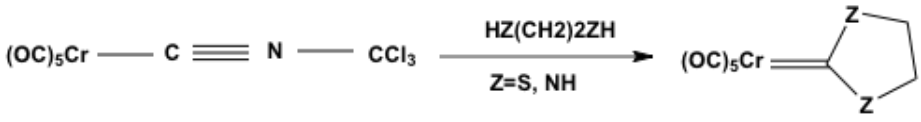
Scheme 1.14 Synthesis of NHC – complexes by oxidative addition

First stable 14-electron carbene complexes with two-fold coordinated Ni(0) and Pt(0) were synthesized by DuPont in 1994 directly by reaction of isolated carbene with metal precursor in solution [32]. However, Pd(0) complexes were not accessible by this method. In 1999, it was possible to synthesize low-coordinated homoleptic carbene complex. Group of elements by cocondensation of carbene with metal vapor. The advantage of this method is the absence of competing ligands from starting materals or solvents (Scheme 1.15) [33].



Scheme 1.15 Synthesis of NHC – complexes by metal atom cocondensation

The other synthetic strategy for the formation of metal carbene complexes is nucleophilic addition to the metal-coordinated isocyanide ligands. These additions can be carried either inter or intramolecular and represent very broadly applicable method for the generation of carbene complexes. It was reported by Fehlhammer and coworkers that $(CO)_5CrCNCCl_3$ reacted with dithiols and diamines to yield the heterocyclic electron-rich carbene complexes (Scheme 1.16) [34 - 37].



Scheme 1.16 Synthesis of carbene complexes within the coordination of metal

The further development of this methodology is synthesis of *N*-heterocyclic carbenes by Ugi-anologous metalorganic 4CC-reaction (four component condensation reaction) of metal coordinated hydroisocyanic acid.

1.2.3 Advantages of *N*-Heterocyclic Carbenes over Phosphines

The advantages are (i) NHCs are considered as stabilizing ligands for transition metal complexes; thus they might improve the stability of the catalyst in water; (ii) phosphines are easily oxidized and often generate undesirable by-products or residues - most likely avoidable with carbene ligands; and (iii) NHCs are known to be less toxic than phosphines [38 - 41] (iv) since metal-carbon in NHC-complexes are much stronger than phosphor - metal bond in phosphine complexes, the problem of the weak ligand-metal bond is avoided. Furthermore *N*-heterocyclic carbenes cannot dissociate from the metal and so no large excess of the ligand is required [42 - 43]. (v) Because of their pronounced σ-donor ability *N*-heterocyclic carbenes can coordinate to the metals which are not able of π-back donation, since *N*-heterocyclic carbenes, with their lone-pair delocalization on nitrogen atoms, no need any backbonding to the metal [44 - 45].

1.3 Objective of the Work

The goal of this dissertation is to explore synthetic strategies and catalytic applications of new water-soluble *N*-heterocyclic carbene ligands. In the first part of the thesis, some new water-soluble complexes containing Ir, Rh, Ru and an NHC ligand have been synthesized using sulfonate moieties as polar substituents.

Synthesis of water-soluble complexes using hydroxy functional group and rhodium as metal precursor is represented in the second part of the thesis.

To synthesis other catalyst library, in the third chapter, the synthesis was broadened on the variation of the substitutent R on sulfonate and hydroxy functional group. It is acknowledged that the variation of substituent R will change the electronic properties and the strength of ligand's σ-donor.

2 Green Chemistry

There is a growing need for more environmentally acceptable processes in the chemical industry. This trend towards what has become acknowledged as ‘Green Chemistry’ [46 - 55] or ‘Sustainable Technology’ necessitates a paradigm shift from traditional concepts of process efficiency, that focus on chemical yield, to one that assigns economic value to eliminating waste at source and avoiding the use of toxic and/or hazardous substances. Anastas [48] of the US Environmental Protection Agency (EPA) coined the term ‘Green Chemistry’. A definition of green chemistry can be formulated as follows [56]: Green Chemistry efficiently utilizes (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and / or hazardous reagents and solvents in the manufacture and application of the chemical products. The guiding principle in green chemistry is the design of environmentally benign products and processes (benign by design) [49]. This concept is embodied in the 12 Principles of Green Chemistry [46, 49], which can be paraphrased as:

1. Waste prevention instead of remediation
2. Atom efficiency
3. Less hazardous / toxic chemicals
4. Safer products by design
5. Innocuous solvents and auxiliaries
6. Energy efficient by design
7. Preferably renewable raw materials
8. Shorter syntheses (avoid derivatization)
9. Catalytic rather than stoichiometric reagents
10. Design products for degradation
11. Analytical methodologies for pollution prevention
12. Inherently safer processes

2.1 Green Chemistry Metrics

E factor was invented by Roger Sheldon. It is defined as the mass ratio of waste to desired product. It takes the chemical yield into account and includes reagents, solvent losses, all process aids and, in principle, even fuel (although this is often difficult to quantify). There is one exception: water is generally not included in the E factor. For example, when considering an aqueous waste stream only the inorganic salts and organic compounds contained in the water are counted; the water is excluded. Otherwise, this would lead to exceptionally high E factors, which are not useful for comparing processes [53]. A higher E factors means more waste and, consequently, greater negative environmental impact. The ideal E factor is zero [56].

Atom efficiency, calculated by dividing the molecular weight of the desired product by the sum of the molecular weights of all substances produced in the stoichiometric equation.

Hudlicky and coworkers have also proposed other metrics, effective mass yield (EMY), for measuring the environmental acceptability of processes. EMY is defined as the percentage of product of all the materials used in its preparation [57].

Constable and coworkers of GlaxoSmithKline [58] proposed the use of mass intensity (MI), defined as the total mass used in a process divided by the mass of product, i.e. MI = E factor +1 and the odeal MI is 1 compared with zero for the E factor. These authors also suggest the use of mass productivity, which is the reciprocal of the MI and, hence, is effectively the same as EMY.

2.2 The Role of Catalysis in Green Chemistry

As green chemistry subject has developed, it has become increasingly clear that catalysis is

one of the central tools for the greening of chemistry. Catalysis not only can improve the selectivity of a reaction but also, by doing so, it can decrease or even remove the need for downstream processing, thereby reducing the material and energy associated with purification. This is particularly important because the solvent requirements for purification processes are often much greater than the usage of solvent in the original reaction. The best solvent is no solvent and if a solvent is needed then water is preferred [59].

2.3. Water-soluble Catalysts

2.3.1 General Principles

Development of catalysts applicable in aqueous systems is very important for a sustainable, environmentally friendly green chemistry. As solvent, water bears a number of attractive physicochemical properties in comparison to traditional organic solvents, which are in many cases flammable, explosive, toxic or carcinogenic. Water is in particular one of the least expensive and most easily accessible solvents [60]. Organometallic catalysis in aqueous media has attracted interest since the 1970s, with pioneering work being carried out for example by Joo, Sasson, and Sinou. A great number of aqueous phase catalytic reactions have been documented since then [60 - 63]. Sometimes reaction rates even increase when water replaces organic solvents, particularly in Diels Alder and some coupling reactions.

Some of the known properties of water are listed below [61]:

(1) Polar and easy to separate from apolar solvents or products; polarity may influence (improve) reactivity

(2) Widely available in suitable quality

(3) Formation of a hexagonal two-dimensional surface structure and a tetrahedron three-dimensional molecular network, which influence the mutual (in) solubility significantly; chaotropic compounds lower the order by H-bond breaking

(6) High hildebrand parameter, as unit of solubility of non-electrolytes in organic solvents

(7) A density of 1 g/cm^3 provides a sufficient difference

(8) Very high dielectric constant

(9) High Thermal conductivity, high specific heat capacity, and high evaporation Enthalphy

(10) Low refractive index

(11) High solubility for many gases, especially CO_2

(12) Formation of hydrates and solvates

(13) Highly dispersible and high tendency toward micelle formation, stabilization by additives

(14) Amphoteric behavior in the Brønsted sense

(15) Advantageous influence on chemical reactivity

(16) Water does not ignite, does not burn, is odorless and colorless, and it is important prequisities for the solvent of choice in catalytic process

The main advantages of using water as the solvent are following:

(1) as the most abundant liquid that occurs on earth, water is very cheap and more importantly it is not toxic. Therefore, it can be used in large amounts without any associated hazards;

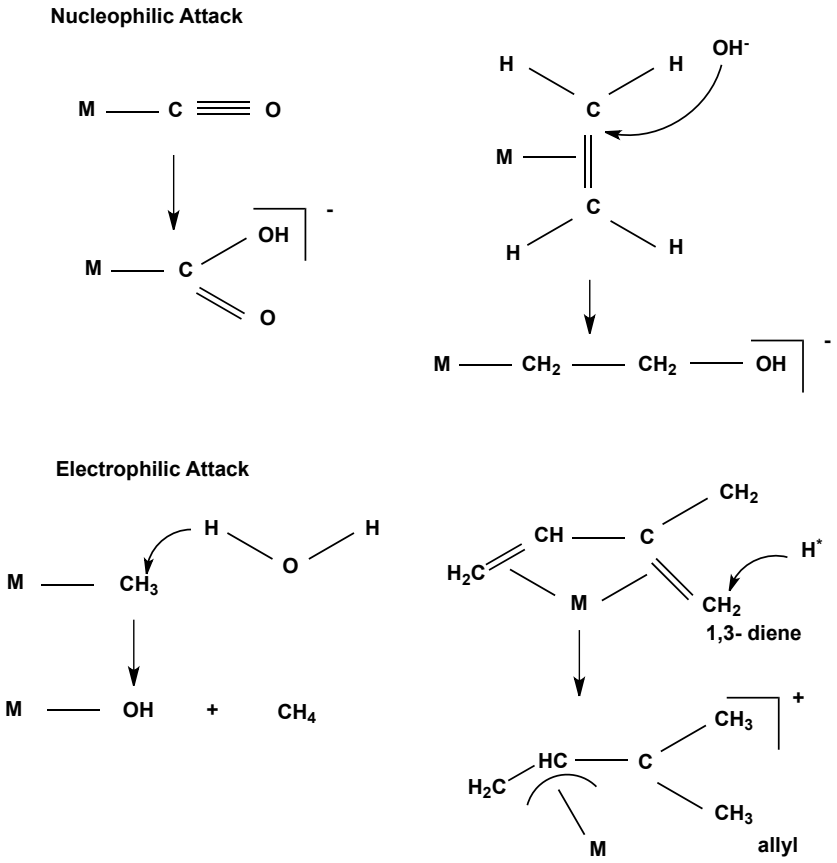
(2) in water-promoted reactions, mild conditions can be sufficient and yields and selectivities can therefore be largely improved;

(3) water-soluble compounds can be used directly without the need for the tedious protection – deprotection process;

(4) water-soluble catalyts can be re-used after filtration, decantation or extraction of the water – insoluble products [64 - 68].

A remarkable feature of water - promoted reactions is that the reactants only need to be sparingly water. However, a challenge often associated with catalysis in water is the need for water-soluble and water stable ligand / catalyst systems and the decrease in catalytic activity and / or stereoselectivity when going from organic solvents to water. Water-solubility of catalysts is often achieved by introduction of polar groups in the ligands such as sulfonate, quaternized aminoalkyl, hydroxyalkyl, polyether, carboxylated groups [69 - 70].

2.3.2 Organometallic Reactions in Water



Scheme 2.1 Basic reactions of organometallic compounds in aqueous systems

Metal – carbon (M-C) bonds are thermodynamically unstable with regard to their hydrolysis products. Water can attack M-C bonds either by proton transfer (H^+, electrophilic reaction) or via the oxygen (OH_2 or OH^-, nucleophilic reaction). Scheme 2.1 shows the example. Ligands

such as carbon monoxide and ethylene are activated toward nucleophilic attack upon coordination to (low valent) metals, e.g. Pd^{+2}. A number of C-C bond forming reactions are derived from this activation.

Allyl ligands are generated by proton attack to the terminal 1,3-diene carbon groups. In other cases, protonation of heteroatoms of metal-attached ligands is followed by elimination steps; for example, the allyl alcohol ligand $H_2C=C(CH_3)CH_2OH$ (η^2) is converted by H $[BF_4]$ into the allyl cation $[H_2CC\text{-}(CH_3)=CH_2]^+$, which standard route of making metal – allyl complexes [71 - 74].

2.4 Hydrogenation Reaction in Aqueous System

Hydrogenation is one of the most intensively studied fields of metal complex catalyzed homogeneous transformations. There are several reasons for such a great interest in this reaction. First of all, there are numerous important compounds that can be produced through hydrogenation, such as pharmaceuticals, herbicides, flavors, fragrances, etc. H_2 is rather reactive molecule and its reaction can be followed relatively easily with a number of widely available analysis techniques for product identification and quantification. There are some important points related to hydrogenations in water. First, the activation of hydrogen molecule. H_2 can be split either by homolysis or heterolysis.

$$H_2 \rightleftharpoons H^{\circ} + H^{*}$$

$$H_2 \rightleftharpoons H^{+} + H^{-}$$

Scheme 2.2 Hydrogenation in water

In the gas phase homolytic splitting requires 436 kJ mol^{-1} and therefore the first reaction is much more probable than heterolytic splitting which is accompanied by enthalpy change of 1674 kJ mol^{-1}. However, hydration of both H^+ and H^- is strongly exothermic (-1090 kJ mol^{-1} and -435 kJ mol^{-1}) in contrast to the hydration of H° (-4 kJ mol^{-1}). Therefore, heterolytic activation becomes more favourable in water than hemolytic splitting of H_2, requiring 156 kJ mol^{-1} and 423 kJ mol^{-1}.

The major difference between aqueous and most organic solvent is the low solubility of H_2 in water. As a result, in aqueous system 2-5 times higher is needed in order to run a hydrogenation at the same concentration of dissolved hydrogen as in the organic solvent under atmospheric pressure.

Table 2.1. Solubility of H_2 in water and organic solvents [75]

Solvent	$10^3[H_2]/M$	Temperature/°C
Water	0.81	20.0
Methanol	3.75	20.0
Ethanol	2.98	20.0
Ethyl acetate	3.40	21.0
Dimethylformamide	1.78	25.0
Benzene	2.94	20.0
Toluene	3.50	20.0
Chlorobenzene	2.46	21.2

Additionally, in a fast reaction the stationary concentration of dissolved hydrogen can be even lower than equilibrium solubility. Not only the rate but also the selectivity of catalytic

hydrogenation can be influenced by the concentration of H_2 in solution. Therefore, comparison of analogous aqueous and non-aqueous systems should be made carefully.

2.4.1 Mechanistic Features of Hydrogenation Reaction of Olefins in Aqueous Systems

It is very instructive to compare the kinetics and plausible mechanisms of reactions catalyzed by the same or related catalyst in aqueous and non-aqueous systems. A catalyst which is sufficiently soluble both in aqueous and in organic solvents (rare situation) can be used in both environments without chemical modifications which could alter its catalytic properties. Even then there may be important differences in the rate and selectivity of a catalytic reaction on going from an organic to an aqueous phase. The most important properties of water in this context are the following: polarity, capability of hydrogen bonding, and self-ionization (amphoteric acid-base nature).

It is often suggested that the cativation of molecular hydrogen may take place via formation of molecular hydrogen complex $[M(H_2)]^{n+}$ [75 – 77] which may further undergo either oxidative addition giving a metal dihydride, $[M(H)(H)]^{n+}$, or acid dissociation to $[M(H)]^{(n-1)+} + H^+$. Both pathways are influenced by water.

Table 2.2 Hydrogenation with water-soluble catalysts in homogeneous solution and in aqueous – organic two phase system

Catalyst	Substrates	Solvent	Condition	Ref
[{RhCl(cyclohexene)$_2$}$_2$] + P (CH_2OH)$_3$	1-octene	EtOH	Isomerization	[78]
[RhCl(TPPMS)$_3$]	hexenes, cyclohexene maleic, fumaric, crotonic acids 1-octene	H_2O H_2O H_2O / MeOH H_2O/benzene H_2O	25°C, 3 bar H_2 35°C, P_{tot}= 1 bar H_2 Bu_4NBr added	[79] [80]
$RhCl_3$ + TPPMS, 1:3	cyclohexene	H_2O	35°C, P_{tot}=1 bar Co-solvents: MeOH, EtOH, DMA, ($MeOCH_2$)	[81]
[RhCl(COD)$_2$] + DSPrPE, 1:1.5 [RhCl(COD)$_2$] + DHPrPE, 1:1.5	1-hexene crotonaldehyde	H_2O/THF 6:1	60°C 3.5 bar H_2	[82]
[RhCl(COD)$_2$] + P	1-hexene	H_2O	40 – 80 °C, 1 – 5 bar H_2 pH effects Isomerization to ketone	[83] [84]

[Rh(SULPHOS)(COD)] [Rh(SULPHOS)(CO)$_2$]	Styrene	methanol/n-heptane 1/1	65 °C, 30 bar H_2 Addn. Of H_2O gives two-phase product mixture	[85]
[RhCl(PTA)$_3$]	cinnamaldehyde allylbenzene	H_2O	50° C, P_{tot} = 1 bar Selective C=C hydrogenation Isomerization	[86] [87] [88]
[Rh(acac)(CO)PR_3]	1-hexene cyclohexene	H_2O	30°C, 1 bar H_2	[89]
PR_3 = PTA, TPPTS, Cyep [RhH(MePTA$^+$I$^-$)$_4$] [RhH(EtPTA$^+$I$^-$)$_4$]	allyl alcohol allyl alcohol maleic, fumaric, itaconic acid, acrylamide cinnamaldehyde	H_2O	Isomerization 20°C, 1 bar H_2 Selective C=C reduction Isomerization Strong effect of Co^{2+}	 [90] [91]
[Rh(amphos)$_2$(MeOH)$_2$]$^{3+}$	maleic acid fumaric acid styrene, 1-hexene	H_2O	r.t., P_{tot} = 1 bar Co-solvents: CH_2Cl_2, Et_2O, Pentane	[92] [93]
[Rh(NBD)(n-phosphos)]$^{3+}$ n = 2,3,6, 10	1-hexene maleic acid	H_2O	r.t., P_{tot} = 1 bar	[94]

$[Rh(COD)_2BF_4$ + DPDP, 1:3	1-hexene cyclohexene	H_2O	r.t., P_{tot} = 1 bar	[95]
$[RhCl(DPUP)_3]$	Unsaturated phospholipids	H_2O, buffered to pH 6.9	37 °C, P_{tot} = 1.2 bar	[96]
$Rh(COD)_2]PF_6$ + NORBOP, 1:2 $[RuClH(TPPMS)_3]$ $[RuH(CO)(TPPMS)_3]$ $[RuCl(CO)(Cp^*)(PR_3)]$ $[Ru(CO)(Cp^*)(PR_3)CF_3SO_3]$ R=CH_2OH, $(CH_2)_3OH$, C_6H_4-3-SO_3Na	α-acetamido-cinnamic acid, hexenes, cyclohexene, styrene, cyclohexene sorbic acid	H_2O,/MeOH ¼ H_2O H_2O/decalin H_2O/n-heptane	r.t., 3 bar H_2 80°C, 50 bar H_2 Max. 86% selectivity to cis- and trans-3-hexenoic acid	[97] [98] [99]
$[Ru_3(CO)_{l2-x}(PR_3)_2]$ R = $(CH_2)_3OH$	sorbic acid	H_2O/ethyl-acetate (buffered aq. Phase, pH 7	80°C, 50 bar H_2 Max. 90 % selectivity to 4-hexenoic acid	[100]

$[Ru_3(CO)_{12-x}(TPPTS)_x]$ $[Ru_4H_4(CO)_{11}(TPPTS)]$	1-octene, 1-decene, cyclohexene, styrene Benzene	H_2O	60 °C, 60 bar H_2 Styrene to ethylbenzene Benzene to cyclohexane	[101]
$[Ru\{HB(pz)_3\}(PPh_3)_2(CH_3CN)]^+$ $[Ru\{HB(pz)_3\}(PPh_3)_2(CH_3CN)_2]^+$	1-octene,1-decene, styrene 1-dodecene, cyclohexene, norbornene, cyclohex-1-ene-2-one, dimethylmaleate ,benzylideneace-tone	H_2O/THF	110°C, 40 bar H_2	[102]
[Pd(OH)(CH3COO)(TPPMS)]	allyl alcohol	H_2O	20°C, Ptot = 1 bar	[103]
$[Pd(OH)_2(CH3COO)(TPPMS)]$	Propargyl alcohol 1,3-pentadiene		Selective reduction of alkynes and dienes to olefins	[104]
$[Rh(acac)_2(CO)_2]$ + $Ph_2P(CH2)3PO3Na2$ 1 : 2.5	2,5-dimethoxy-2,5-dihydrofuran	H_2O	70°C, 30 bar syngas, C=C hydrogenation	[105]

2.5 Transfer Hydrogenations

Transfer hydrogenation is a reaction in which hydrogen is catalytically transferred from a suitable hydrogen donor (DH_2) to a reducible substrate (S) yielding to hydrogenated product (SH_2) and the oxidized form of donor molecule (D) [106 - 109].

$$DH_2 + S \rightleftharpoons SH_2 + D$$

Scheme 2.3 Transfer Hydrogenation

Some of the most common hydrogen donors, such as formic acid and formates, ascorbic acid, EDTA or 2 – propanol are well or at least sufficiently soluble in water. As written in the equation above, the hydrogen transfer reaction is often reversible.

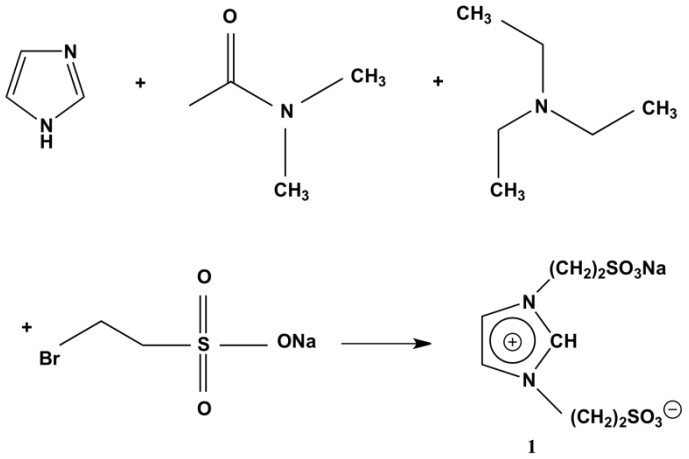
Reductions with hydrogen transfer are attractive because of two reasons. First, the concentration of DH_2 in the reaction mixture can be much higher than that of H_2 under high pressure. This may be beneficial for a faster reaction. Second, the use of a soluble or liquid hydrogen donor also eliminates the safety hazard of handling high-pressure hydrogen.

Hydrogen transfer to ketones from 2-propanol was developed into an efficient method of obtaining secondary alcohols [110 - 113] and the use of chiral N-(p-tolylsulfonyl) diamines allow the reduction of prochiral ketones with extraordinary streoselectivity [113].

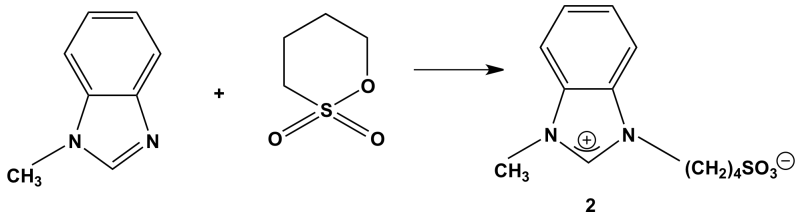
3 Water-soluble Sulfoalkyl-Substited Azolium-Derived NHC Complexes

The synthesis of water-soluble Rh(I), Ir(I), and Ru(II) *N*-heterocyclic carbene complexes is described as well as their application as catalysts for aqueous phase hydrogenation reactions. The complexes display good hydrogenation activities under ca. 40 atm pressure H_2 at room temperature. In this work, we report on the preparation and catalytic properties of sulfoalkyl-substituted azolium-derived NHC complexes in the hydrogenation of aromatic ketones in aqueous media.

For the synthesis of water-soluble NHC complexes, sulfonated N-alkylazolium salts were applied to prepare the ligands. Ligand **1** (see scheme 3.1) was obtained by reaction of imidazole with dimethylacetamide, triethylamine, and the sodium salt of 2-bromoethanesulfonic acid according to a method described earlier [114]. Ligand **2** (see scheme 3.2) was synthesized via the reaction of methyl benzimidazole and 1,4 butane sultone at room temperature, similar to a previously published procedure, using a different azolium salt, however (see experimental part and ref. [114]).



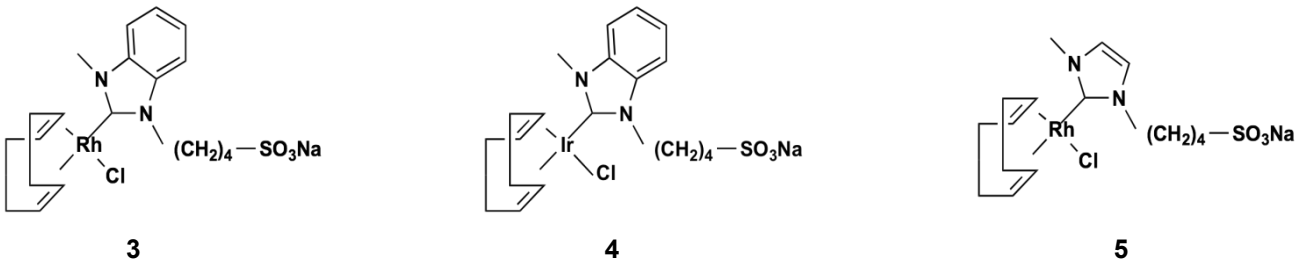
Scheme 3.1. Synthesis of Ligand **1**



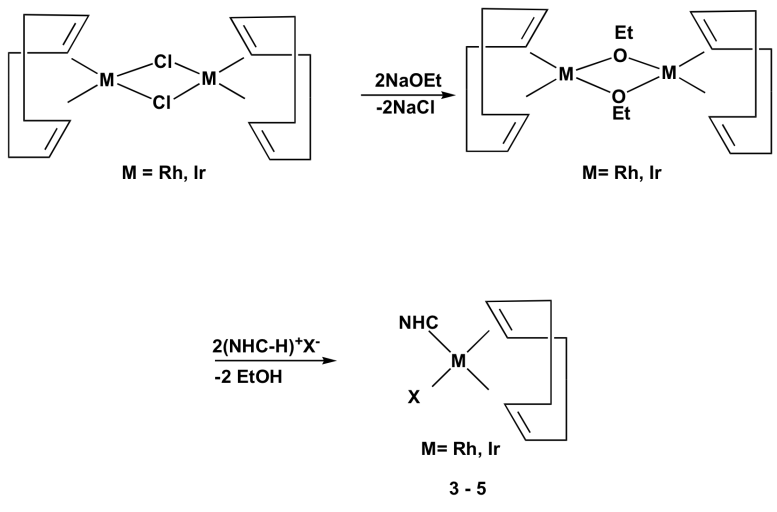
Scheme 3.2. Synthesis of Ligand **2**

3.1 Synthesis of Rhodium and Iridium Complexes

The new complexes **3** - **5** (see scheme 3) were prepared by in situ deprotonation of azolium salts and subsequent reaction of rhodium/iridium precursors $(Rh(COD)Cl)_2$/$(Ir(COD)Cl)_2$ with the sulfonated ligands **2** at ambient temperature (see scheme 3.4). Complexes **3** - **5** are readily soluble and stable in H_2O.



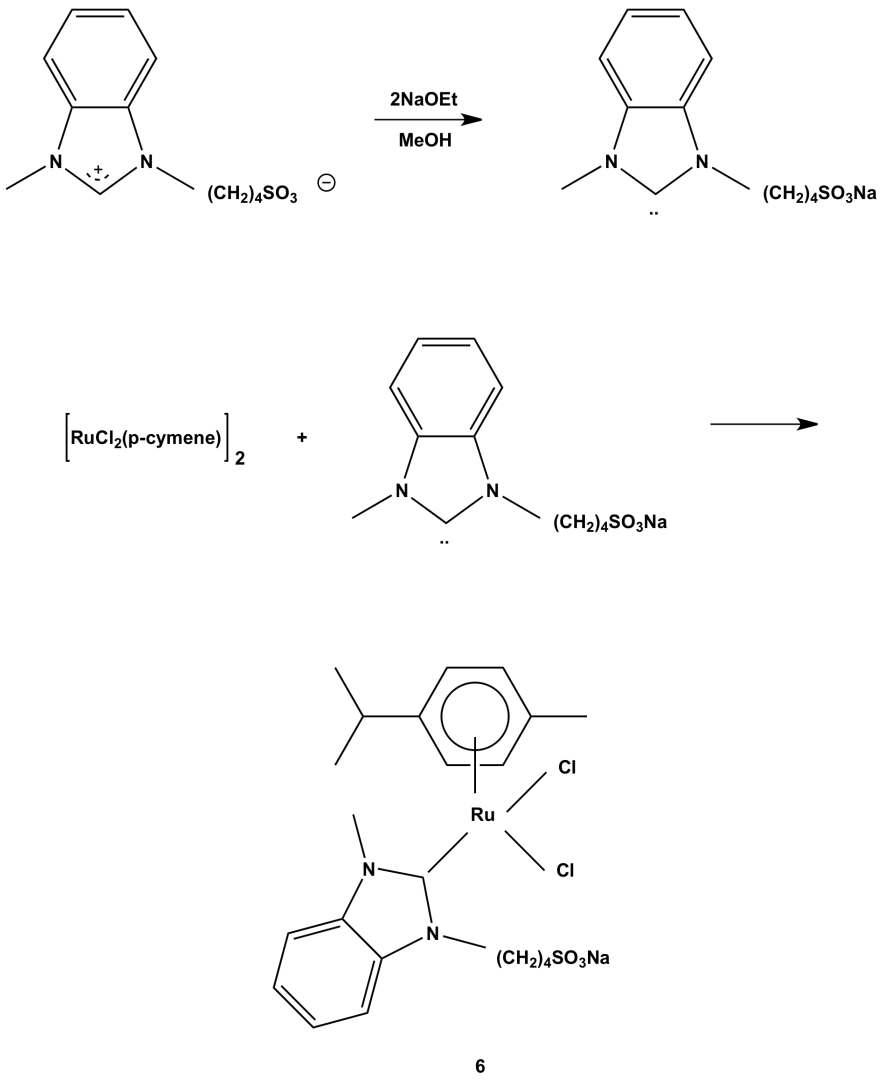
Scheme 3.3. Rhodium – NHC and Iridium – NHC complexes **3** – **5**



Scheme 3.4. Synthesis route for Rhodium – NHC and Iridium – NHC complexes **3** – **5**

3.1 Synthesis of Ruthenium Complexes

In situ deprotonation of azolium salt to form free carbene and subsequent reaction of Ruthenium precursors $[RuCl_2(p\text{-cymene})]_2$ were used to prepare the new complex **6** (see scheme 3.5).



Scheme 3.5. Synthesis route for Ruthenium – NHC complexes **6**

In the ^1H NMR spectrum of complex **3,** pseudo-quintets are observed at $\delta(^1H)$ = 2.32 and 2.45 ppm and triplets are seen at 3.05 and 4.52 ppm . They are assigned to the non-equivalent CH_2 protons. The signals at $\delta(^1H)$ = 1.91, 3.23 and 3.58 ppm are indicative for the COD protons. The signal at 4.11 ppm stems from the CH_3 methyl substituent. The CH signals of the

benzimidazole ring are observed at 7.26 and 7.41 ppm, respectively. In the ^{13}C NMR spectrum of complex **3**, the signal at $\delta(^{13}C)$ = 195.5 ppm originates from the Rh-C carbene carbon atom, whereas the signals at $\delta(^{13}C)$ = 31.4, 69.6, 92.3, and 99.5 ppm are caused by the COD carbons. The N-CH_3 signal is observed at 51.1 ppm and the CH_2 signals of the ligand are found at 24.3, 35.8, and 51.2 ppm.

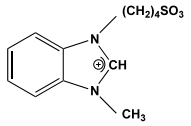
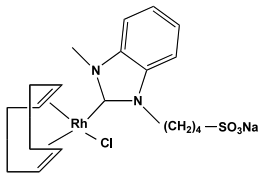
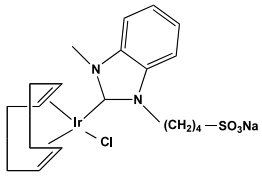
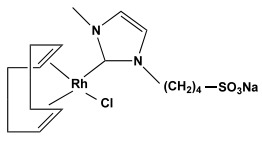
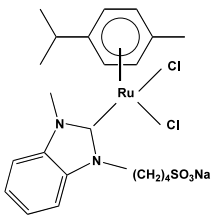
For the ^{1}H NMR spectrum of complex **4,** the non-equivalent CH_2 protons are observed at $\delta(^{1}H)$ = 2.11, 2.93, and 4.48 ppm, showed pseudo-quintets and triplets, while the signals at $\delta(^{1}H)$ = 1.79, 3.85, and 4.34 ppm are assigned to the COD protons. The signal at 4.06 ppm comes from the CH_3 methyl substituent. The CH signals of the benzimidazole ring are found at 7.62, 7.77, and 7.83 ppm, respectively. In the ^{13}C NMR spectrum of complex **4**, the signal at $\delta(^{13}C)$ = 191.7 ppm stems from the Rh-C carbene carbon atom, whereas the signals at $\delta(^{13}C)$ = 30.7 and 85.7 ppm are due to the COD carbons. The N-CH_3 signal is observed at 48.3 ppm and the CH_2 signals of the ligand can be seen at 23.8, 26.3, 34.1 and 50.8 ppm.

The ^{1}H NMR spectrum of complex **5** shows pseudo-quintets at $\delta(^{1}H)$ = 2.42 and 2.87 ppm and triplets at 3.98 and 4.50 ppm, which are assigned to the non-equivalent CH_2 protons. The signals at $\delta(^{1}H)$ = 1.71, 3.55 and 3.67 ppm are indicative for the COD protons. The signal at $\delta(^{1}H)$ = 4.15 ppm stems from the CH_3 methyl substituent. The CH signals of the benzimidazole ring are observed at 7.12 and 7.16 ppm. For the ^{13}C NMR spectrum of complex **5**, the signal at $\delta(^{13}C)$ = 180.6 ppm originates from the Rh-C carbene carbon atom, while the signals at $\delta(^{13}C)$ = 31.6, 67.3, 89.6, and 96.6 ppm come from the COD carbons. The N-CH_3 signal is seen at 51.9 ppm and the CH_2 signals of the ligand are observed at 23.9, 30.7 and 39 and 57.7 ppm.

Derived from a different metal precursor, complex **6** has NMR signals differing from

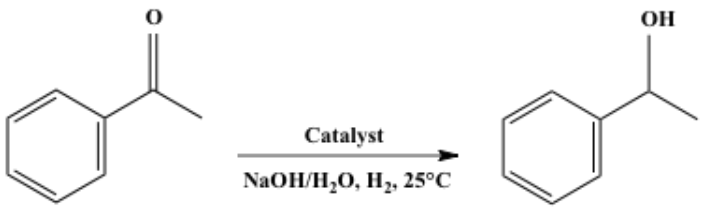
complexes **3** - **5**. The non – equivalent CH_2 protons for complex **6** are found at $\delta(^1H)$ =1.85, 2.19, 2.87 and 4.57 ppm. The signals at 1.85 and 2.19 ppm are seen as pseudo-quintets, whereas the signals at 2.87 and 4.57 ppm are triplets. The CH_3 signals of the isopropyl group, being attached to the *p*-cymene ring are seen at 1.31 and 1.33 ppm. The signal at $\delta(^1H)$ = 2.17 ppm is referred to the CH_3 methyl substituent of *p*-cymene ring. The signal at $\delta(^1H)$ = 4.14 ppm stems from the CH_3 methyl substituent of benzimidazole. The CH signals of the benzimidazole ring are observed at 7.70 and 7.92 ppm, respectively. For the ^{13}C NMR spectrum of complex **6**, the signal at $\delta(^{13}C)$ = 180.09 ppm stems from the Ru-C carbene carbon atom. The signals at $\delta(^{13}C)$ = 17.35 come from the isopropyl carbons. The CH_3 methyl substituent of *p*-cymene ring occurs at 20.90 ppm. The CH substituent of p-cymene ring is seen at 31.16 ppm. Substituted C atoms of *p*-cymene ring result in the signal at 76.26 and 78.27 ppm. The N-CH_3 signal is seen at 46.47 ppm and the CH_2 signals of the ligand are observed at 21.35, 27.44, 31.32 and 49.84 ppm respectively. For the better understanding of NMR, Table 3.2 gives an overview of the signals of the ligands and the complexes.

Table 3.2 NMR Results

	^{1}H	^{13}C
Ligand 2 	1.81 (pq, 2H, CH_2), 2.14 (pq, 2H, CH_2), 2.94 (t, 2H, CH_2), 4.09 (s, 3H, CH_3), 4.53 (t, 2H, CH_2), 7.69 (d, 2H, CHCHarom), 7.83, 7.9 (d, 2H, CHCHarom), 9.28 (s, 1H, NCHN).	21.13 (CH$_2$), 27.06 (CH$_2$), 32.78 (CH$_2$), 46.26 (NCH$_3$), 49.98 (CH$_2$), 112.89, 126.62, 130.86 (CHCHCHCHarom), 132.02 (NCCNarom), 141.07 (NCHN).
Complex 3 	1.91 (m, COD allyl), 2,32 (pq, 2H, CH_2), 2.45 (pq, 2H, CH_2), 3.05 (t, 2H, CH$_2$), 3.23, 3.58 (COD vinyl), 4.11 (3H, CH_3), 4.52 (t, 2H, CH_2), 7.26 (d, 2H, CHCHarom), 7.41 (d, 2H, CHCHarom).	24.3 (CH_2), 31.4 (COD allyl), 35.8 (CH_2), 51.1 (N-CH_3), 51.2 (CH$_2$) 69.6 (COD allyl), 92.3, 99.5(COD vinyl), 115 (CHCHarom), 122.8 (CHCHarom), 135.5 (NCCNarom), 195.5 (NC_{carb}N).
Complex 4 	1.79, (m, COD allyl), 2.11 (pq, 4H, CH$_2$), 2.93 (t, 2H, CH_2), 3.85 (COD vinyl), 4.06 (3H, CH_3), 4.34 (COD vinyl), 4.48 (t, 2H, CH_2), 7.62 (d, 2H, CHCHarom), 7.77 (d, 1H, CHarom), 7.83(d, 1H, CHarom).	23.8(CH_2), 26.3(CH_2), 30.7 (COD allyl), 34.1 (CH_2), 48.3 (N-CH_3), 50.8 (CH_2), 85.7 (CODvinyl), 111.4 (CHCHarom), 124.7 (CHCHarom), 135.5 (NCCNarom), 191.7 (NC_{carb}N).
Complex 5 	1.71 (m, COD allyl), 2.42 (pq, 2H, CH_2), 2.87 (pq, 2H,CH_2), 3.55, 3.67 (COD vinyl), 3.98 (t, 2H, CH_2), 4.15 (3H, CH_3), 4.50 (t, 2H, CH_2), 7.12 (d, 1H, NCHN), 7.16 (d, 1H, NCHN).	23.9 (CH_2), 30.7 (CH_2), 31.6 (COD allyl), 39.0 (CH_2), 51.9 (N-CH_3), 57.7(CH_2), 67.3, 89.6, 96.6 (COD vinyl), 124.0 (NCHCHN), 180.6 (NC_{carb}N).
Complex 6 	1.31 (d, 6H, CH (CH_3)), 1.85 (pq, 2H, CH_2), 2.17 (s, 3H, C (CH_3)), 2.19 (pq, 2H, CH_2), 2.76 (sept, 1H, CHCH$_3$), 2.87 (t, 2H, CH_2), 4.14 (s, 3H, NCH_3), 4.57 (t, NCH_2), 5.29 (m, 2H, C$_6$H$_4$),	17.35 (CH(CH$_3$)), 20.90 (C(CH_3)), 21.35 (CH$_2$), 27.44 (CH$_2$), 31.16 (CH(CH$_3$), 31.32(CH$_2$), 46.47 (NCH$_3$), 49.84 (NCH$_2$), 76.26 (2C, C$_6$H$_4$), 78.27 (2C, C$_6$H$_4$), 93.54 (1C, CMe, *p*-cymene), 97.28 (1C,

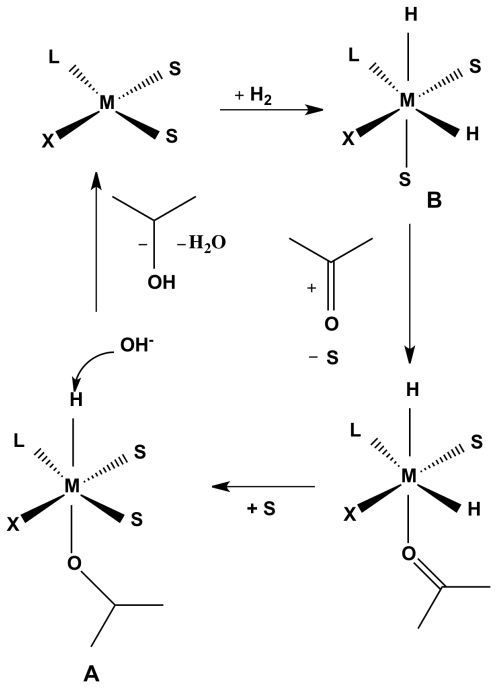
	5.54 (m, 2H, C_6H_4), 7.70 (d, 2H, C*H*C*H*arom), 7.92 (d, 2H, C*H*C*H*arom).	C*i*Pr, *p*-cymene), 112.87 (*C*H*C*Harom), 126.89 (*C*H*C*Harom), 131.53, 132.15 (N*CC*Narom), 180.09 (NC_{carb}N).

3.3 Aqueous Hydrogenation of Acetophenone



Scheme 3.6. Aqueous Hydrogenation of Acetophenone

The catalytic activities of complexes **3** - **5** were examined in the hydrogenation of acetophenone in water under a hydrogen pressure of 40 atm H_2 at room temperature. In order to be able to compare the activity of the catalysts, a fixed reaction time of 21 h was applied. Complexes **3** - **5** show remarkable activities in basic media in the aqueous hydrogenation of acetophenone under hydrogen pressure without any phase-transfer agent. In situ formed complexes of Ru and Rh with ligands **1** - **2** also show good activities for aqueous hydrogenation of acetophenone.



Scheme 3.7. Proposed mechanism for aqueous hydrogenation of acetophenone; S = H_2O, M = Ir, Rh, X = Anion, L = Ligand

The mechanism of these Rh, Ir – catalyzed hydrogenation is not well examined at present. Based on the commonly accepted mechanism together with observations made in the literature by Bujoli et al. [115] and Zhang et al. [116] (see scheme 6), the main role of the added base is to deprotonate the intermediate A, while water can protonate the alkoxide ligand. **A** is obtained from the insertion of the ketone into one of the M-H bonds. A push-pull process would favor the reductive elimination of **A**, allowing the oxidative addition of hydrogen to generate **B**.

The catalytic reaction results of hydrogenation are summarized in table 3.1. Conversion, yield and selectivity are defined as:

a Conversion = (moles acetophenone reacted) / (moles acetophenone fed)

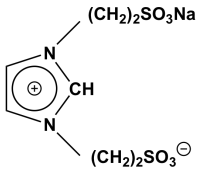
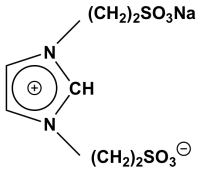
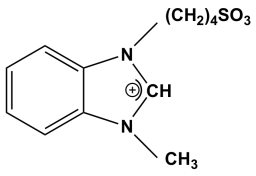
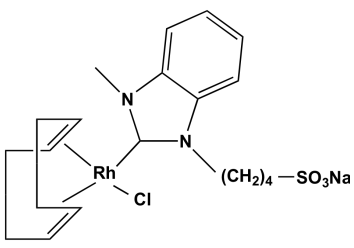
b Yield = (moles 1-Phenylethanol formed) / (moles acetophenone fed)

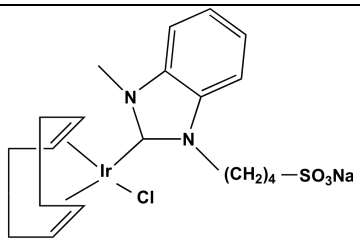
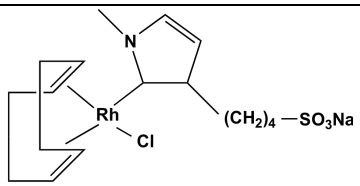
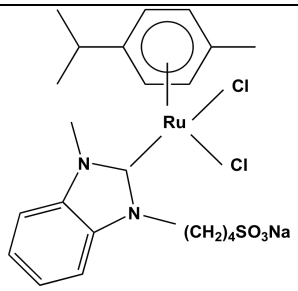
c Selectivity = (moles 1-Phenylethanol formed) / (moles acetophenone reacted)

With the same carbene ligand, the Rh complex **3** produces a higher yield, conversion, and selectivity than compound **4** with the larger Ir as central atom. Furthermore, **3**, as benzimidazole derived complex, leads to higher yield and selectivity, but almost the same conversion, when compared to the imidazole derived complex **5**. An explanation might be the influence of the steric bulk of the carbene ligand on directing the reaction. Particularly in octahedral intermediates the steric bulk of the carbene ligand could be decisive for the selectivity of the catalyst. An in situ formed complex derived from Rhodium (III) acetate (**1a)** shows higher catalytic activity compared to the in situ formed complex derived from $[RuCl_2(p\text{-cymene})]_2$ (**1b**) although the same ligand was used. Using the same catalytic reaction condition, the isolated complex **6** shows higher activity compared to the in situ formed compound **2**. A possible reason for this might be the higher purity of the isolated (and purified) complex prior to catalytic application.

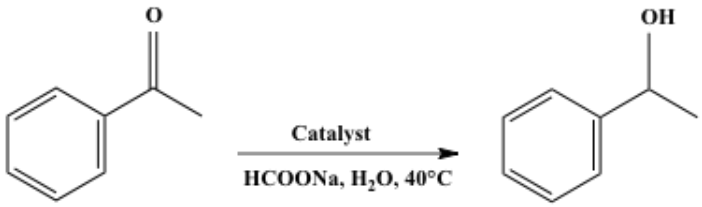
With respect to by-products, beside 1-phenylethanol as the main product, the hydrogenation of acetophenone also produces cyclohexylethanol. The formation of the latter compound has been reported in the literature [117 - 121]. Cheng et al. mention that product formation follows the route: acetophenone ⟶ 1-phenyethanol ⟶ cyclohexylethanol, with the reaction selectivity towards 1-phenylethanol being increased with decreasing formation of cyclohexylethanol as its follow-up product [122].

Table 3.3 Aqueous hydrogenation of acetophenone catalyzed by water-soluble carbene complexes

No	Catalyst	Catalyst loading (mol %)	Conversion (%)	Yield (%)	Selectivity (%)
1	**a)**  **+ Rh (III) Acetate**	2.5	92	74	81
	b)  **+[$RuCl_2$ (*p*-cymene)]$_2$**	2.5	75	58	78
2	 **+[$RuCl_2$ (*p*-cymene)]$_2$**	2.5	68	65	95
3		2.5	95	89	94

4		2.5	51	37	71
5		2.5	98	46	47
6		2.5	90	87	96

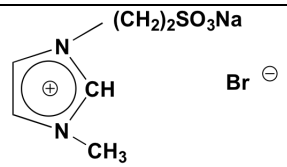
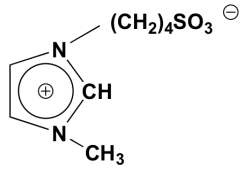
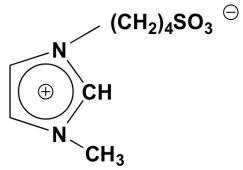
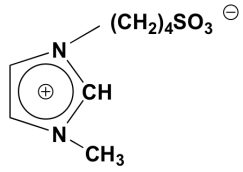
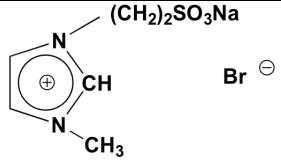
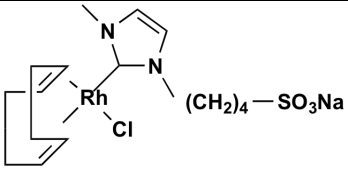
3.4 Transfer Hydrogenation of Acetophenone in Water

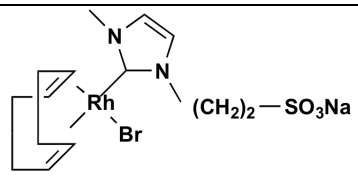


Scheme 3.7. Transfer hydrogenation of acetophenone in water

For transfer hydrogenation experiments in aqueous solution, HCOONa has a function as the hydrogen transfer reagent to reduce acetophenone. The reaction was carried out at 40°C for 21 hours. After cooling to room temperature, the organic phase was extracted with Et_2O and analyzed by gas chromatography coupled with a mass spectrometer to determine the conversion, the yield and the selectivity which are listed in the table below (see table 3.4)

Table 3.4. Transfer hydrogenation of acetophenone

No	Catalyst	Catalyst loading (mol%)	Conversion (%)	Yield (%)	Selectivity (%)
1	 **+ Rh (III) acetate**	1	28.10	0.31	1.10
2	 **+ Rh (III) acetate** **+ SDS (as surfactant)**	5	46.23	5.93	12.83
3	 **+ Rh (III) acetate**	5	16.89	8.12	48.06
4	 **+ Rh (III) acetate**	1	13.94	2.91	20.86
5	 **+ Rh (III) acetate**	1	53.79	0.17	0.32
6		1	68.85	0.13	0.18

7		1	42.41	0.14	0.32

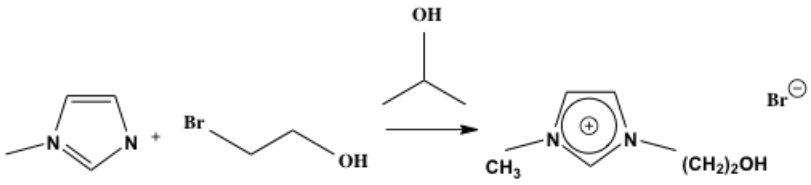
3.5 Crystallization of Water-soluble NHC Precursor and Complexes

Several attempts have been made for the crystallization of water-soluble carbene complexes. Et_2O-MeOH with ratio 1:3, 2:2, and 1:1 were used to form the crystals. Besides that, THF-water and THF-methanol system has been tried too. All gave either small crystals in needle form, which are difficult to be measured or the crystals could not be formed. The crystals for water-soluble carbene complexes are still very rare founded in the literature.

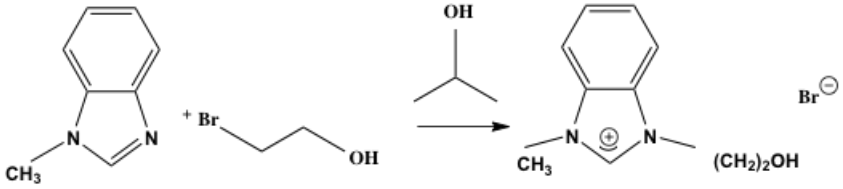
4 Water-Soluble Carbene Complexes with Hydroxy Group

4.1 Synthesis of Imidazolium and Benzimidazolium Salts with Hydroxy Group

N-alkylazolium salts were synthesized as ligands. 1-Methyl-3-(2-hydroxyethyl) imidazolium bromide was obtained by reaction of methyl imidazole with 2-bromoethanol, and isopropanol at temperature of 80°C according to a method described earlier [123] (Scheme 4.1). Modified azolium salt was applied to synthesize new ligand of 1-Methyl-3-(2-hydroxyethyl) benzimidazolium bromide in a similar way (Scheme 4.2)

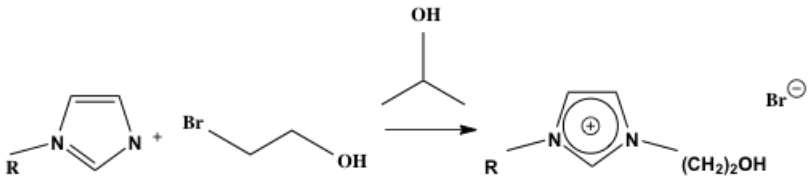


Scheme 4.1 Synthesis of 1-Methyl-3-(2-hydroxyethyl) imidazolium bromide

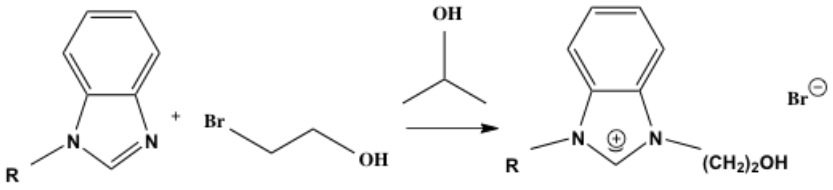


Scheme 4.2 Synthesis of 1-Methyl-3-(2-hydroxyethyl) benzimidazolium bromide

Additionally, the side chain was modified too using the same reaction condition (Scheme 4.3 and 4.4).



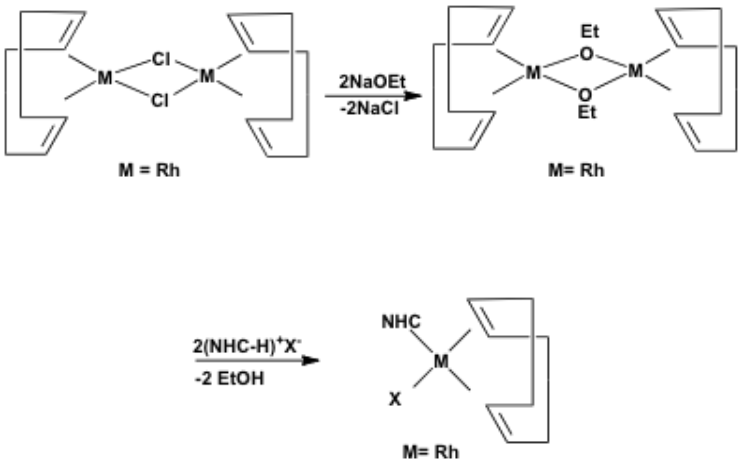
Scheme 4.3 Synthesis of 1-R-3-(2-hydroxyethyl) imidazolium bromide (to be continued)



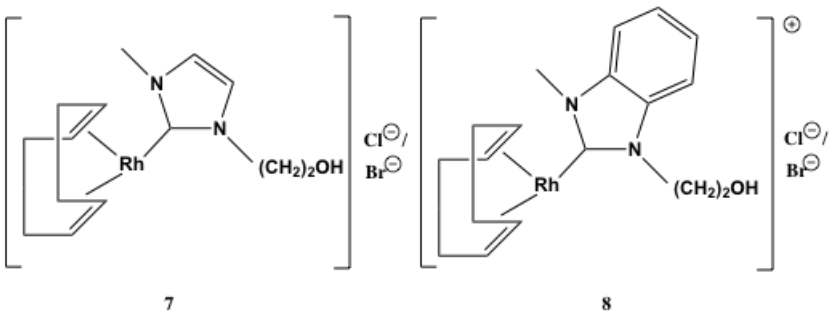
Scheme 4.4 Synthesis of 1-R-3-(2-hydroxyethyl) benzimidazolium bromide

4.2 Synthesis of Rhodium Complexes

The new complexes **7 - 8** were prepared by in situ deprotonation of azolium salts and subsequent reaction of rhodium/iridium precursors $(Rh(COD)Cl)_2$/$(Ir(COD)Cl)_2$ with the sulfonated ligands **2** at ambient temperature (see Scheme 4.5). Complexes **7 - 8** are readily soluble and stable in H_2O.



Scheme 4.5 Synthesis route for Rhodium – NHC complexes **7** – **8**



Scheme 4.6 Rhodium – NHC complexes **7** – **8**

For the ^{1}H NMR spectrum of complex **7,** the COD protons are observed at $\delta(^{1}H)$ = 1.84, 2.13 , and 4.39 – 4.94 ppm , while the signals at $\delta(^{1}H)$ = 3.81 and 4.27 ppm are assigned to the non-equivalent CH_2 protons. The signal at 3.93 ppm comes from the CH_3 methyl substituent. The CH signal of the imidazole ring is found at 7.24 ppm, respectively. In the ^{13}C NMR spectrum of complex **7**, the signal at $\delta(^{13}C)$ = 180.35 ppm stems from the Rh-C carbene carbon atom, while the signals at $\delta(^{13}C)$ = 27.47 – 33.80 and 55.88 ppm are due to the COD carbons. The N-CH_3 signal is observed at 51.98 ppm and the CH_2 signals of the ligand can be seen at 35.90 and 59 ppm. The CH signals of the benzimidazole ring found at 115 and 122.8 ppm. The signal at $\delta(^{13}C)$ = 128.59 and 137.02 are indicative to *tert* - C, respectively.

For the ^{1}H NMR spectrum of complex **8,** the COD protons are seen at $\delta(^{1}H)$ = 1.99, 2.44 , and 2.57 ppm, while the signals at $\delta(^{1}H)$ = 3.49 and 3.88 ppm are indicative for the non-equivalent CH_2 protons. The signal at 4.27 ppm stems from the CH_3 methyl substituent. The CH signal of the benzimidazole ring is found at 7.31 and 7.58 ppm, respectively. In the ^{13}C NMR spectrum of complex **8**, the signal at $\delta(^{13}C)$ = 180.35 ppm comes from the Rh-C carbene carbon atom, while the signals at $\delta(^{13}C)$ = 28.42 – 33.19, 68.90 and 98.13 ppm are due to the COD carbons. The N-CH_3 signal is found at 59.99 ppm and the CH_2 signals of the ligand can be seen at 34.42 and 49.88 ppm. The CH signals of the benzimidazole ring come at 110, 122.04, 126.26 and 134.76 ppm. The signal at $\delta(^{13}C)$ = 143.02 refers to *tert* - C, respectively.

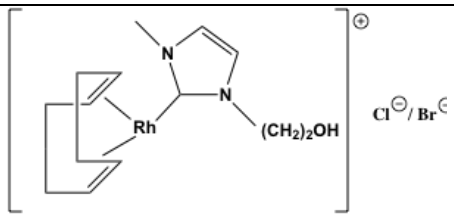
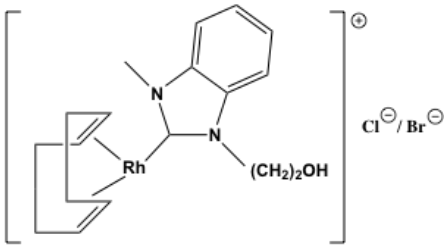
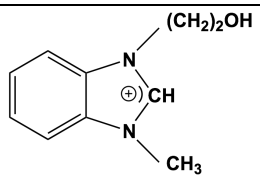
MS-FAB measurement showed clean spectra for imidazolium complex **7** with 371.8 as molecular weight of $C_{14}H_{22}N_2ORhCl$ and 415.7 as molecular weight of $C_{14}H_{22}N_2ORhBr$. The same observation is found for the benzimidazolium complex **8**. Molecular weight of 421.7 is referred to $C_{18}H_{24}N_2ORhCl$ and 467.6 is indicative for $C_{18}H_{24}N_2ORhBr$. Since it is not possible to analyze quantitatively the ratio of Cl^- and Br^- by available MAS FAB, ESI,

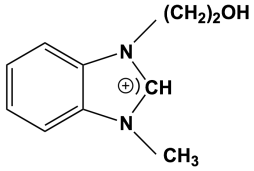
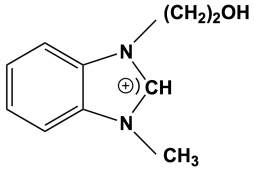
MALDI-TOF, and GC-MS method, the stoichiometric method is used to calculate the ratio of the anion.

4.3 Hydrogenation Reaction Catalyzed by NHC Complexes with Hydroxide Functional Group

The catalytic activities of complexes **7 - 11** were examined in the hydrogenation of acetophenone in water under a hydrogen pressure of 40 atm H_2 at room temperature. In order to be able to compare the activity of the catalysts, a fixed reaction time of 21 h was applied.

Table 4.1. Aqueous hydrogenation of acetophenone catalyzed by water-soluble carbene complexes using hydroxy functional groups as polar substituents

No	Catalyst	Catalyst loading (mol %)	Conversion (%)	Yield (%)	Selectivity (%)
7		2.5	100	18	18
8		2.5	64	57	90
9	 **+ [Rh(COD)Cl]$_2$**	2.5	93	41	44

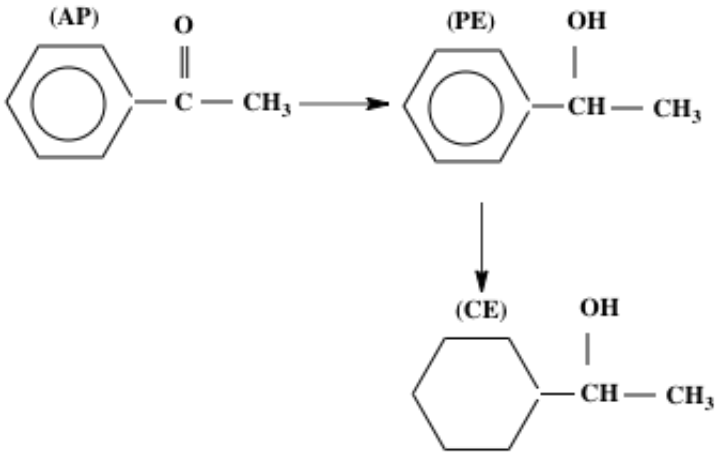
10	 + **[RuCl$_2$ (*p*-cymene)]$_2$**	2.5	99	99	100
11	 + **[Ir(COD)Cl]$_2$**	2.5	100	78	78

An in situ formed complex derived from [RuCl$_2$(*p*-cymene)]$_2$ (**10)** shows higher catalytic activity compared to the in situ formed complex derived from (Rh(COD)Cl)$_2$) (**9)** and (Ir(COD)Cl)$_2$ (**11**) although the same ligand was used. Using the same catalytic reaction condition, the isolated complex **7** shows higher yield and selectivity but lower conversion compared to the in situ formed compound **9**. The reason for the lower yield, and selectivity of compound **9** might be the presence of excess of water before and during the formation of the complex in the in situ system.

There is quite significant difference between the product obtained on imidazole derived complex and the benzimidazole derived one **7**. 1-phenylethanol is more dominated as the product on hydrogenation catalyzed by **7** and cyclohexylethanol is formed more on catalysis by **8**. Mass spectra analysis of acethophenone hydrogenation catalyzed by **8** shows that the ratio between cyclohexylethanol to 1-phenylethanol is 1.5. Not like **7**, which is more selective towards 1-phenylethanol, **8** is more selective towards cyclohexylethanol.

Cheng et al. mentioned that there could be competitive hydrogenation between phenyl and carbonyl groups in one molecule. Acetophenone is one of the simplest molecules; it contains

two kind of functional groups. So far, this competitive reaction between these two functional groups was not yet significantly studied and discussed in published articles. It has been found that enhancement of hydrogenation of phenyl group may depend on the electron effect of promoter and the rate of carbonyl hydrogenation [121 - 122]. Activation of carbonyl group should be prior to that of phenyl group to form phenylethanol. Cyclohexlethanol can be formed at room temperature through further hydrogenation process. In other words, cyclohexyethanol is formed through phenyl hydrogenation group of phenylethanol. Therefore, Cheng et al. mentioned that formation of products is proposed to follow the route acetophenone ⟶ 1-phenyethanol ⟶ cyclohexylethanol, with the reaction selectivity of 1-phenylethanol is boosted with decreasing formation of cyclohexylethanol [122].

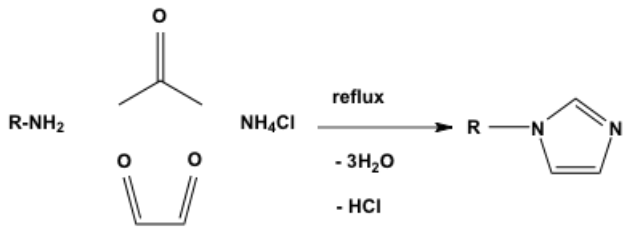


Scheme 4.6 Reaction pathway of hydrogenation of acetophenone

5 Sulfoalky-Substituted and Hydroxy-Substituted Azolium-Derived NHC Ligands with Variation on the R-Subtitutents, Chain Length and Coordinating Anion

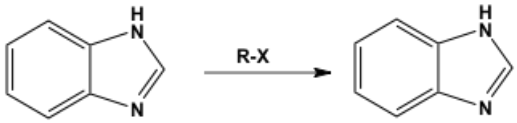
In order to synthesize other library of imidazolium and benzimidazolium salts, in this chapter, the synthesis will be focused on the variation of the substitutents R on sulfonate and hydroxy functional group. It is acknowledged that the variation of substituent R will change the electronic properties and the strength of ligand's σ-donor.

The substituted imidazole precursors are accessible via one-pot synthesis route related to a method reported by Gridnev et al. (Scheme 5.1) [124]. The products can be purified by sublimation, extraction, recrystallization, distillation, bulb-to-bulb distillation or column chromatography [124 - 127].



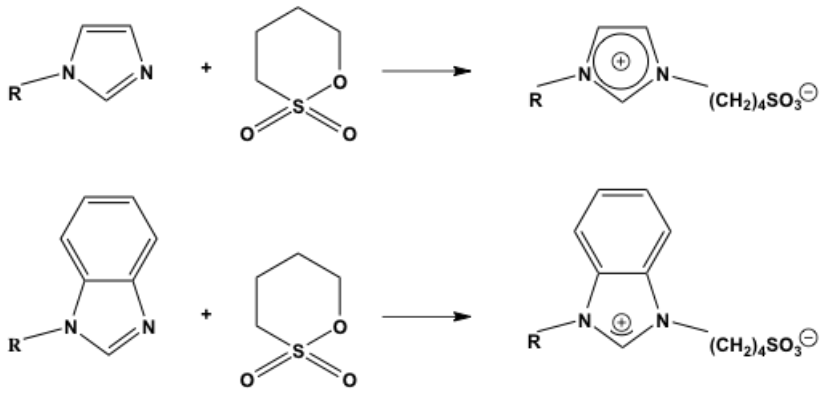
Scheme 5.1. Synthesis of R-imidazole

The reaction of benzimidazole and R-iodide in acetonitrile solution was used to synthesize the substituted benzimidazole precursors. The obtained product is purified through extraction.



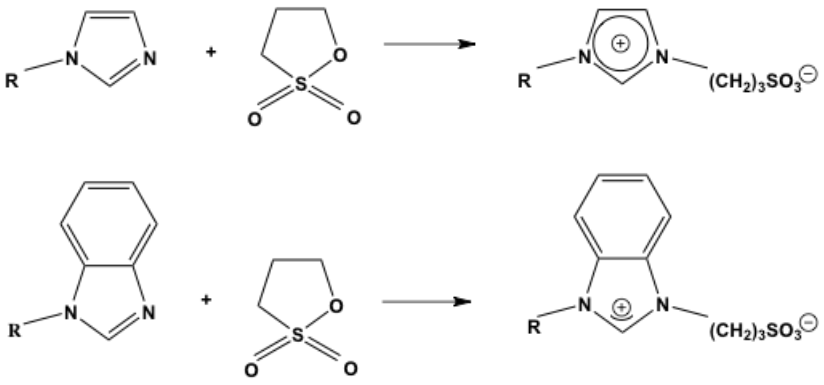
Scheme 5.2. Synthesis of R-benzimidazole

The obtained modified R-imidazole and benzimidazole was reacted further to sulfoalkyl-substituted azolium salts as explained on Scheme 5.3.



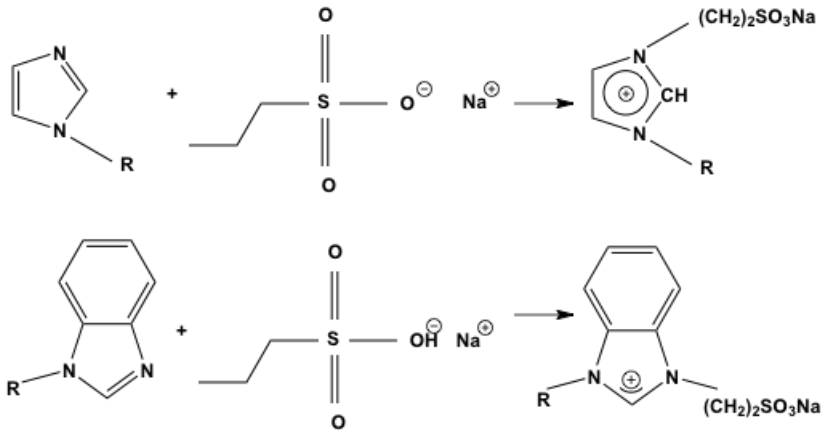
Scheme 5.3. Synthesis of 1-R-3(butyl-4-sulfonate) azolium betaine

The reaction of R-azolium with 1,4-butane sultone will give 1-R-3(butyl-4-sulfonate) azolium betaine. While the reaction of R-azolium with 1,3-propane sultone will give 1-R-3(propyl-3-sulfonate) azolium sulfonate (Scheme 5.4).



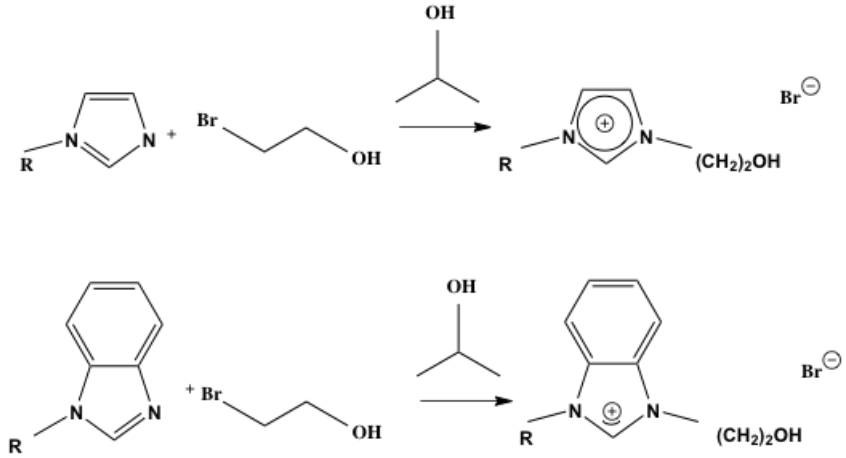
Scheme 5.4. Synthesis of 1-R-3(propyl-4-sulfonate) azolium betaine

1-R-3(ethylsulfonic acid sodium salt) azolium bromide obtained by reaction of R-azolium with 2-bromoethanesulfonic acid sodium salt as shown on Scheme 5.5.



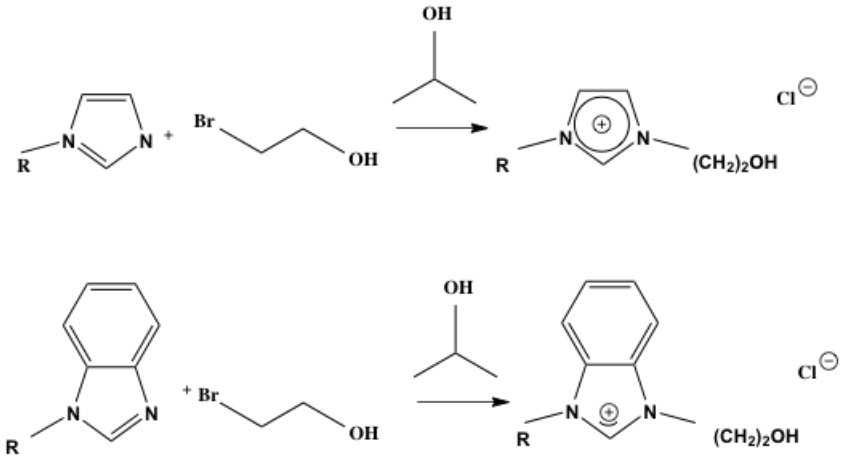
Scheme 5.5. Synthesis of 1-R-3(propyl-4-sulfonate) azolium betaine

Hydroxy substituent is prepared by reaction of R-azolium with 2-bromoethanol in isopropanol (see Scheme 5.6).

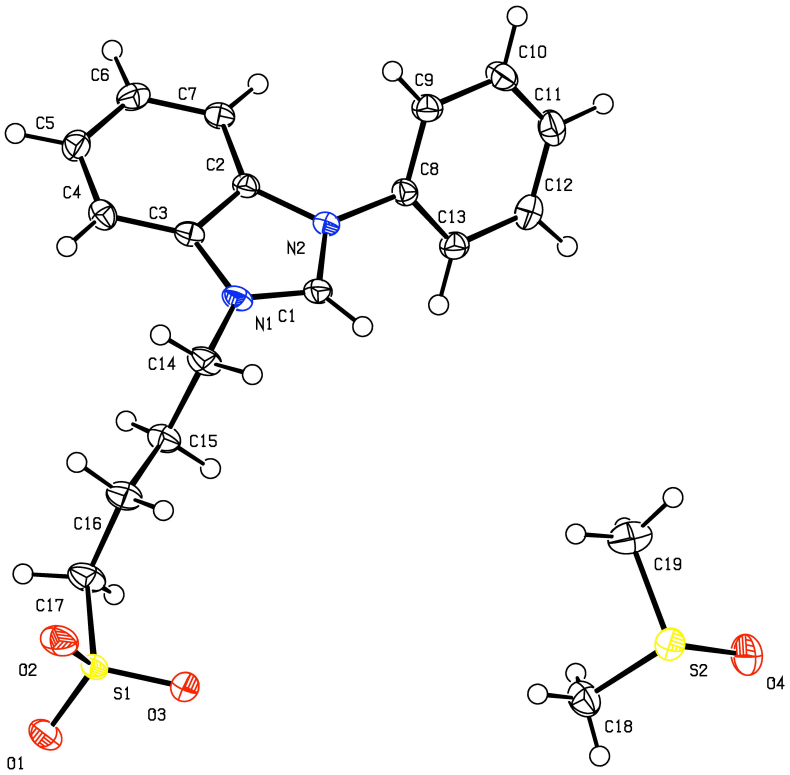


Scheme 5.6. Synthesis of 1-R-3-(2-hydroxyethyl) azolium bromide

Additionally, in order, to vary the coordinating anion, 1-R-3-(2-hydroxyethyl)-azolium chloride is synthesized with similar procedure using 2-chloroethanol counterpart (Scheme 5.7)



Scheme 5.7. Synthesis of 1-R-3-(2-hydroxyethyl)-azolium chloride



Scheme 5.8 Crystal Structure of 1-Phenyl-3(propyl-4-sulfonate) benzimidazolium betaine

1-Phenyl-3(propyl-4-sulfonate) benzimidazolium betaine crystallizes in the orthorhombic space group (Scheme 5.8). A clear light yellow fragment like specimen of $C_{19}H_2N_2O_4S_2$ ($C_{17}H_{18}N_2O_3S$ as desired compound and C_2H_6OS as solvent), approximate dimensions 0.230 mm x 0.380 mm x 0.800 mm, was used for the X-ray crystallographic analysis.

Crystal was grown from a concentrated solution of DMSO. Torsion angle between phenyl substituent and benzimidazole (C(9) .. C (8) .. N(2) .. C(2)) is 53.7 (2). Selected bond lengths (Å) angles: N1-C1 1.325 (2), N2-C1 1.340 (2), N1-C1-N2 110.9 (3), C9-C8-N2-C2 53.7(2). There are multiple hydrogen bonds, starting from sulfonate group to the neighbouring cations, which are O to H on $CH_{benzimidazole}$, O to H on CH_{phenyl}, and O to H on the backbone of benzimidazole ring. Those OH bonds lengths are in the range of 2.2 – 2.72 Å.

6 Summary

The primary focus of this dissertation is on the synthesis, characterization and catalytic applications of new water-soluble *N*-heterocyclic carbene ligands. In the first part of the thesis, some new water-soluble complexes containing Ir, Rh, Ru and an NHC ligand have been synthesized using sulfonate moieties as polar substituents.

Synthesis of water-soluble complexes using hydroxy functional group and rhodium as metal precursor is represented in the second part of the thesis.

To synthesis other catalyst library, in the last part of the thesis, the synthesis was broadened on the variation of the substitutents R on sulfonate and hydroxy functional group. It is acknowledged that the variation of substituent R will change the electronic properties and the strength of ligand's σ-donor. Additionally, side chain length and coordinating anion were varied too.

These catalysts used for the hydrogenation of acetophenone in water under 40 bar hydrogen pressure and transfer hydrogenation. The Rh, Ir, and Ru complexes show good catalytic activities in basic media, in the absence of phase-transfer agent for aqueous hydrogenation. The NHC-based catalysts contain a hydrophilic functionality allow a homogeneously catalyzed hydrogenation reaction in water.

7 Experimental

7.1 General Techniques and Methods

All syntheses, storage and characterization of organometallic compounds were performed under the atmosphere of argon, using thoroughly heated standard Schlenk-technique. Distillation, sublimation, removal of the solvents and drying of the solid materials were performed under vacuum pump. Sealed equipment was secured against the penetration of air with paraffin security valves. Solvents were dried by standard procedures using Grubbs solvent purification system. Deionised water was degassed by using freeze pump thaw technique for several hours. All other materials were obtained from commercial resources (Acros Organics, Sigma Aldrich, Fluka, Merck, Deutero, Alfa Aesar, ABCR, and Strem Chemicals) and were used as received, except as noted.

7.2 Characterization of Substances

7.2.1 Nuclear Magnetic Resonance Spectroscopy

NMR spectra were measured on JEOL-JNM-GX270, JEOL-JNM-GX-400 and Bruker AMX-400 spectrometers operating on following frequencies:

	^{1}H-NMR	^{13}C-NMR	^{19}F-NMR	^{31}P-NMR
Bruker Avance DPX 400	400.13 MHz	100.61 MHz	376 MHz	161.98 MHz
Jeol-JNM-GX-270	270.16 MHz	67.93 MHz	-	109.37 MHz
Jeol-JNM-GX-400	399.80	100.51 MHz	376 MHz	161.83 MHz
Bruker Avance 300	300.130 MHz	75.468 MHz	-	-

7.2.1.1 Liquid State NMR

The substances were dissolved in pure deuterated solvents purchased from Fa. Deutero GmbH, which were, if necessary dried over molecular sieve and degassed by freeze pump thaw method. The chemical shift σ in ppm is specified comparatively to the working frequency of the spectrometer.

The solvent residual signal ($CDCl_3$: 7.25/77.2 ppm; DMSO-d_6: 2.5/39.52 ppm; D_2O: 4.8/- ppm) was used as an internal standard for ^1H and ^{13}C (1H coupled/decoupled)-NMR under the given frequencies. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, sept = septet, m = multiplet, br = broad signal. Coupling constants are given in Hz.

7.2.1.2 Solid State NMR

MAS – NMR spectra were recorded on a Bruker Avance 300 with 4 mm ZrO_2 rotor and rotation frequencies of 10 and 15 kHz, respectively. Adamantane was used as external standard. The chemical shift was specified relative to TMS, 2 ppm for ^1H and 29.472 ppm for ^{13}C. The techniques, which used for measuring spectra, were single pulse technique for ^1H and cross polarization (CPMAS) for ^{13}C.

7.2.2 Elemental Analysis

Elemental analysis (C, H, N) was performed by the Microanalytical Laboratory of the Technische Universität München.

7.2.3 Mass Spectroscopy

Mass spectra were measured on either MAT-90 OR MAT-311 instrument-311 instrument of Fa. Finnigan. They were used for the characterization using EI-, Cl-(Isobutene, positive and negative ions) and Fast Atom Bombardment technique (FAB, solvent: 4-nitrobenzylalkohol).

7.2.4 Gas Chromatography

Hewlett-Packard HP 5970 mass spectrometer was used in connection with HP 5890 gas chromatograph for separation, identification and characterization of fluid reaction samples. For chromatographic separations, a HP-1 column (50 m, 0.2 mm, 0.33 μm) was used with helium as carrier gas. For routine uses several different programmed temperature gradients (60 ºC to 240 ºC, heating rate between 15 ºC/min and 35 ºC/min) were employed. The mass spectra are given in the form X (Y, [m + nZ^+/n). This corresponds to the detection of the molecular mass X with the intensity Y %, as the mass of studied molecule m with the cation Z^+.

7.2.5 X- Ray Crystallographic

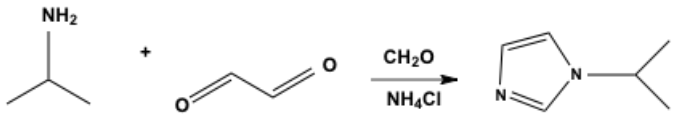
The X-ray intensity data were measured. Preliminary examination and data collection was carried out on area detecting system (APEX II) at the window of sealed tube and graphite monochromated radiation Mo Kα (λ = 0.71 Å). It was performed at 123 K. Total of 3242 frames were collected. The total exposure time was 4.50 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 38861 reflections to a maximum θ angle of 25.53° (0.82 Å resolution), of which 3591 were independent (average redundancy 10.822, completeness = 99.7%, Rint = 2.54%, Rsig = 1.30%) and 3481 (96.94%) were greater than 2σ(F2). The final cell constants of a = 9.7005(2) Å, b = 24.9649(4) Å, c = 7.97990(10) Å, volume = 1932.51(6) Å3, are based upon the refinement of the XYZ-centroids of 9944 reflections above 20 σ(I) with 5.104° < 2θ < 50.97°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.910. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7933 and 0.9324.

7.3 Working Procedures

7.3.1 Synthesis of Monocarbene Precursors

7.3.1.1 Synthesis of mono (alkyl/aryl) imidazolium salts

1-Isopropyl imidazole



A flask cooled at 0-5°C was charged with formaldehyde (37 wt %, 9.42 g, 1.16 mol), isopropylamine (99.37ml, 1,16 mol), ammonium carbonate (55.73 g, 0.58 mol), glyoxal (168.4 g, 1.16 mol), and 70 mL of CH_3OH. The mixture was stirred at room temperature overnight. After evaporating the volatiles, the crude brown material was purified by vacuum distillation to give a clear liquid.

^{1}H – NMR (400 MHz, d_6-DMSO, 25°C), δ [ppm]: 1.39 (d, 6H, ^{3}J(H, H) = 1.3Hz, CH(C*H*$_3$)$_2$), 4.41 (m, 1H, C*H*(CH$_3$)$_2$), 6.88 (s, 1H, NC*H*CH), 7.22 (s, 1H, NCHC*H*), 7.67 (s, 1H, NC*H*N).

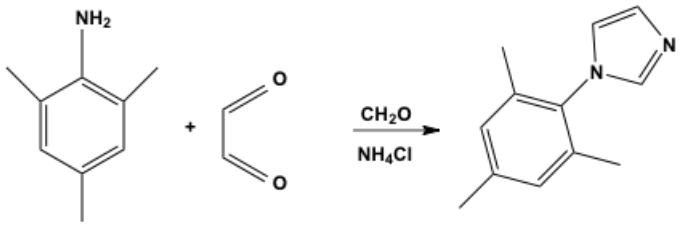
^{13}C-NMR (100.5 MHz, d_6-DMSO, 25°C), δ [ppm]: 22.1 (C(*C*H$_3$)$_2$), 46.1 (C(*C*H$_3$)$_2$), 120.5 (CH*C*HN), 126.3 (N*C*HCH), 138.9 (s, N*C*HN).

Elemental Analysis ($C_6H_{10}N_2$), Mw = 110.157

Calculated: C: 65.42 H: 9.15 N: 25.43.

Found: C: 64.15 H: 9.06 N: 25.22.

1-Mesitylimidazole or 1-(2,4,6-Trimethylphenyl)-1H-imidazole



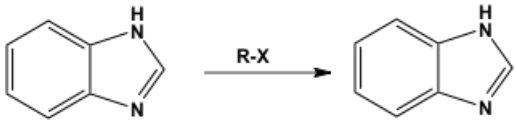
Glacial acetic acid (50ml), aqueous formaldehyde (15ml), and aqueous glyoxal (23 mL) were transferred to a round bottom flask (250mL) and heated at 70°C. A solution of glacial acetic acid, ammonium acetate in water (15.4 g in 10 mL), and mestylamine (28 mL) was then added dropwise over a period of 30 min. The solution was continuously stirred and heated at 70°C for 18h. The mixture was then cooled to room temperature, and the mixture was added dropwise to a stirred solution of $NaHCO_3$ (147 g) in water (1.5 L) when the target product precipitated. The precipitate was isolated on a filter frit, washed with water (3 x 100 mL), and air dried to obtain a brown yellow solid (25.9 g). The crude product was sublimated at temperature 110°C and Pressure of 5 x 10^{-2} bar to obtain target product 1-(2,4,6-trimethylphenyl)-1H-imidazole.

^{1}H – NMR (400 MHz, $CDCl_3$, 25°C), δ [ppm]: 1.99 (s, 6H, C*H*$_3$), 2.34 (s, 3H, C*H*$_3$), 6.89 (s, 1H, C*H*), 6.97 (s, 2H, C*H*$_{ar}$), 7.23 (m, 1H, C*H*), 7.44 (m, 1H, C*H*).

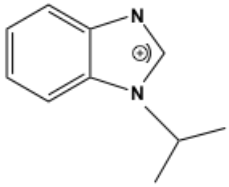
^{13}C-NMR (100.5 MHz, $CDCl_3$, 25°C), δ [ppm]: 17.3 (C(*C*H$_3$)$_2$), 21.0 (C(*C*H$_3$)$_2$), 120.0 (N*C*H*C*HN), 128.9, 129.5, 133.4, 135.4, 137.4 (*C*H$_{mes}$), 138.8 (s, N*C*HN).

7.3.1.2 Synthesis of Mono (Alkyl/Aryl) Benzimidazolium Salts

Synthesis of substituted benzimidazole



1-Isopropyl benzimidazole



A mixture of benzimidazole (50 mmol, 5.9 g) in 25 ml acetonitrile and 15 ml of 30wt% solution of NaOH was added with isopropyl iodide (50 mmol, 5.0 ml). The pale yellow solution was stirred for 5 days at room temperature. The reaction mixture was diluted with 100 ml water and extracted with 3 x 50 ml dichloromethane. The combined organic layers were dried over $MgSO_4$ and the solvent removed in vacuo. The pale yellow oil was distilled to yield 1-isopropyl benzimidazole as colorless oil (bp. 136 – 137° C @2.0 mbar, 106°C @0.2 mbar)

^{1}H- NMR (400 MHz, $CDCl_3$), δ [ppm]: 7.94 (s, 1H, NC*H*N), 7.75 (m, 1H, C*H*arom), 7.36 (m, 1H, C*H*arom), 7.22 (m, 2H, C*H*arom), 4.56 (s, 1H, C*H*$(CH_3)_2$), 1.55 (d, 6H, CH_3).

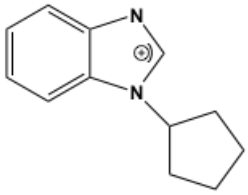
^{13}C – NMR (100 MHz, $CDCl_3$), δ [ppm]: 143.86(NC*H*N), 140.03 (N*C*CN), 133.1 (NC*C*N), 122.46, 121.87, 120.20, 109.97 (CH_{arom}), 47.51 (*C*H $(CH_3)_2$), 22.43 (CH(*C*$H_3)_2$).

Elemental Analysis ($C_{10}H_{12}N_2$), Mw = 160.10

Calculated: C: 74.97 H: 7.55 N: 17.48.

Found: C: 73.34 H: 7.37 N: 17.6

1-Cyclopentyl benzimidazole



A mixture of benzimidazole (50 mmol, 5.9 g) in 25 ml acetonitrile and 15 ml 30wt% solution of NaOH was added with cyclopentylbromide (50 mmol, 5.36 ml). The pale yellow solution was stirred for 5 days at room temperature. The reaction mixture was diluted with 100 ml water and extracted with 3 x 50 ml EtOAc. The combined organic layers were dried over $MgSO_4$ and the solvent removed in vacuo. The off white residue was extracted with boiling pentane. The pentane phase was evaporated in vacuo to yield colorless oil, which crystallizes slowly. Alternatively the pentane extract was immersed in bath of liquid nitrogen or put in the freeze to give a white precipitate.

^{1}H- NMR (400 MHz, $CDCl_3$), δ [ppm]: 7.96 (s, 1H, NC*H*N), 7.78 (m, 1H, C*H*arom), 7.42 (m, 1H, C*H*arom), 7.27 (m, 2H, C*H*arom), 4.73 (s, 1H, C*H*$(CH_3)_2$), 2.26 (m, 2H, CH_2), 2.04 (m, 2H, CH_2), 1.91 (m, 2H, CH_2) , 1.80 (m, 2H, CH_2).

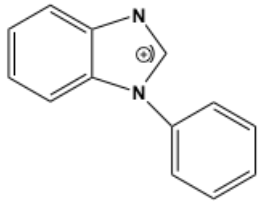
^{13}C – NMR (100 MHz, $CDCl_3$), δ [ppm]: 143.97 (N*C*HN), 140.56 (N*C*CN), 133.56 (NC*C*N), 122.52, 121.77, 120.23. 110.27 (CH_{arom}), 56.94 (*C*H$(CH_2)_2$), 32.3, 24.02 (CH(*C*$H_2)_2$) ppm.

Elemental Analysis ($C_{12}H_{14}N_2$), Mw = 186.25

Calculated C: 77.38 H: 7.58 N: 15.04.

Found: C: 77.13 H: 7.59 N: 14.89.

1-Phenyl benzimidazole



A mixture of benzimidazole (100 mmol, 11-80 g), phenyliodide (100 mmol, 8.62 ml), potassium carbonate (200 mmol, 27.60 g) in 100 ml dimethylformamide, was added (20 mmol, 3.80 g) with copper iodide and stirred at 120°C for 24 h. The red mixture was reduced in volume in vacuo, diluted with 100 ml dichloromethane, filtered over a plug of celite and eluted with 100 ml dichloromethane to yield a clear yellow solution. The solvents were removed in vacuo and the residue extracted several times with boiling pentane. After removal of the solvent of the solvent in vacuo, a white solid was obtained.

^{1}H- NMR (400 MHz, $CDCl_3$), δ [ppm]: 8.12 (s, 1H, NC*H*N), 7.90 – 7.88 (m, 1H, C*H*arom), 7.60 – 7.47 (m, 5H, C*H*arom), 7.37 – 7.3 (m, 2H, CH_{arom}).

^{13}C – NMR (100 MHz, $CDCl_3$), δ [ppm]: 144.09 (N*C*HN), 142.31 (N*C*CN), 136.38 (NC*C*N), 130.08 (C_{Ph}), 128.05 (C_{Ph}), 124.14, 123.70 (*C*Harom), 122.87 (C_{Ph}) 120.73 (*C*Harom), 110.65 (*C*Harom).

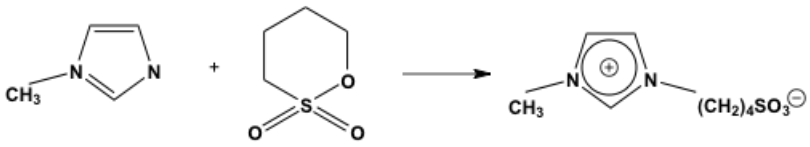
Elemental Analysis ($C_{13}H_{10}N_2$), Mw = 194.23.

Calculated: C: 80.39 H: 5.19 N: 14.42.

Found: C: 80.13 H: 5.33 N: 14.20.

7.3.1.3 Synthesis of Sulfoalkyl-substited Azolium Salts

1-Methyl-3(butyl-4-sulfonate) imidazolium betaine



1-Methylbenzimidazole (30 mmol) was stirred without solvent with 1,4-butanesultone (30 mmol) at room temperature for 3 days. After solidification of the mass, it was washed 3 times with toluene and dried under high vacuum. The white solid was readily soluble in water

^{1}H – NMR (400 MHz, D_2O, 25°C), δ [ppm]: 1.77 (pq, 2H, CH_2), 2.05 (pq, 2H, CH_2), 2.95 (t, 2H, CH_2), 3.92 (s, 3H, CH_3), 4.26 (t, 2H, CH_2), 7.46, 7.52 (m, 2H, C*H*C*H*), 8.67 (s, 1H, NC*H*N)

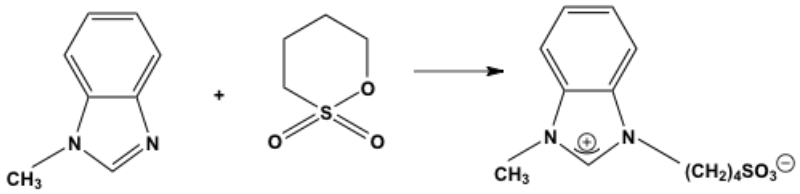
^{13}C – NMR (100.5 MHz, D_2O, 25°C), δ [ppm]: 20.84 (*C*H_2), 28.0 (*C*H_2), 35.38(*C*H_2), 48.41 (N*C*H_3), 49.82 (*C*H_2), 121.96 (*C*HCH), 123.82 (CH*C*H), 135.88 (N*C*HN)

Elemental Analysis ($C_8H_{14}N_2O_3S$), Mw = 218.27

Calculated: C: 44.02 H: 6.46 N: 12.83 S: 14.69

Found: C: 43.58 H: 6.52 N: 12.29 S: 15.6

Synthesis of 1-Methyl-3(butyl-4-sulfonate) benzimidazolium betaine



1-Methylbenzimidazole (1.32 g, 10 mmol) was stirred with 1,4-butanesultone (1361 g, 10 mmol) at room temperature for 3 days under solvent free condition. After solidification of the mass, it was washed 3 times with toluene and dried under high vacuum. The white solid was readily soluble in water.

^{1}H – NMR (400 MHz, D_2O, 25°C), δ[ppm]: 1.81 (pq, 2H, C*H*$_2$), 2.14 (pq, 2H, C*H*$_2$), 2.94 (t, 2H, C*H*$_2$), 4.09 (s, 3H, C*H*$_3$), 4.53 (t, 2H, C*H*$_2$), 7.69 (d, 2H, C*H*C*H*arom), 7.83, 7.9(d, 2H, C*H*C*H*arom), 9.28 (s, 1H, NC*H*N).

^{13}C-NMR (100.5 MHz, D_2O, 25°C), δ[ppm]: 21.13 (*C*H$_2$), 27.06 (*C*H$_2$), 32.78 (*C*H$_2$), 46.26 (N*C*H$_3$), 49.98 (*C*H$_2$), 112.89, 126.62, 130.86 (*C*H*C*H*C*H*C*Harom), 132.02 (N*CC*N), 141.07 (N*C*HN).

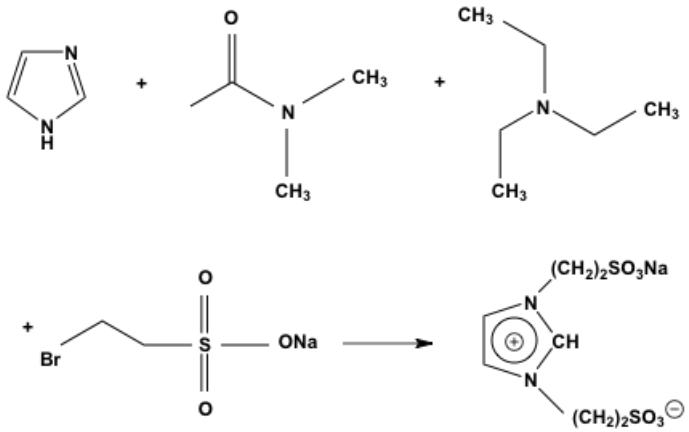
Elemental Analysis calcd. for ($C_{12}H_{16}N_2SO_3$)

Calculated: C: 53.71 H: 6.01 N: 10.44 S: 11.95.

Found: C: 53.14 H: 6.19 N: 10.15 S: 11.34.

MS-FAB: m/z (%) = 268.7 (M^+)

1-(Ethyl-2-sulfonic acid sodium salt)-3-(ethyl-2-sulfonate) imidazolium betaine



557 mg (8.2 mmol) of imidazole, dissolved in 20 ml of dimethylacetamide, is mixed with 1.5 ml (10.25 mmol) of triethylamine and 3.45 g (16.3 mmol) of 2-bromoethanesulfonic acid sodium salt. On heating to 120°C, the original suspension become clear. After further heating to 160°C, a white precipitate began to form. To achieve complete reaction, the mixture was heated for 4 hours under reflux. After cooling the solution to room temperature, the white precipitate was filtered off and washed twice with 20 ml of ethanol and ether each time.

^{1}H – NMR (400 MHz, D_2O, 25°C), δ[ppm]: 3.40 (t, 4H, C*H*$_2$C*H*$_2$), 4.58 (t, 4H, C*H*$_2$C*H*$_2$), 7.55 (s, 2H, NC*H*), 9.18 (s, 1H, NC*H*N).

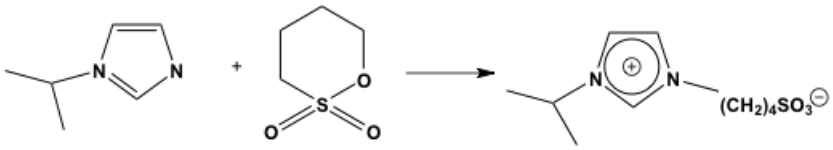
^{13}C-NMR (100.5 MHz, D_2O, 25°C), δ[ppm]: 45.15 (*C*H$_2$*C*H$_2$), 49.77 (*C*H$_2$*C*H$_2$), 32.78 (*C*H$_2$), 122.59 (N*C*H), 136.76 (NCHN).

Elemental Analysis for ($C_7H_{11}NaO_6S_2$)

Calculated: C: 27.40 H: 3.62 N: 9.14 S: 20.94.

Found: C: 26.85 H: 3.67 N: 8.82 S: 20.31.

1-Isopropyl-3-(butyl-4-sulfonate) imidazolium betaine



1-Methylimidazole (30 mmol) was stirred without solvent with 1,4-butanesultone (30 mmol) at room temperature for 3 days. After solidification of the mass, it was washed 3 times with toluene and dried under high vacuum. The white solid was readily soluble in water.

^{1}H – NMR (400 MHz, D_2O, 25°C), δ [ppm]: 1.54 (d, 6H, C*H*$_3$C*H*$_3$), 1.73 (pq, 2H, C*H*$_2$), 2.02 (pq, 2H, C*H*$_2$), 2.93 (t, 2H, C*H*$_2$), 4.23 (t, 2H, C*H*$_2$), 4.63 (sept, 1H, C*H*), 7.56 (d, 2H, C*H*), 8.83 (s, 1H, NC*H*N).

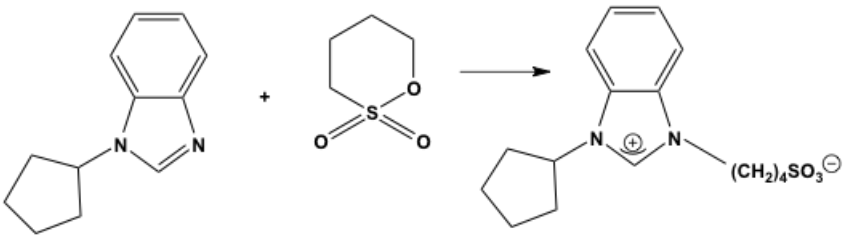
^{13}C – NMR (100.5 MHz, D_2O, 25°C), δ [ppm]: 21.01 (*C*H$_3$), 21.78 (*C*H$_3$), 28.09 (*C*H$_2$), 48.13 (*C*H$_2$), 50.99 (*C*H$_2$), 53.25 (*C*H$_2$), 76.34 (*C*H), 120.66 (NC*C*HCHN), 122.30 (NCH*C*HN), 133.47 (N*C*HN).

Elemental Analysis ($C_{10}H_{18}N_2O_3S$), Mw = 246.327

Calculated: C: 48.76 H: 7.37 N: 11.37 S: 13.02.

Found: C: 47.09 H: 7.82 N: 11.29 S: 12.18.

1-Cyclopentyl-3(butyl-4-sulfonate) benzimidazolium betaine



1-Cyclopentylbenzimidazole (10 mmol) was stirred without solvent with 1,4-butanesultone (10mmol) at room temperature for 3 days. After solidification of the mass, it was washed 3 times with toluene and dried under high vacuum. The white solid was readily soluble in water.

^{1}H – NMR (400 MHz, D_2O, 25°C), δ [ppm]: 1.88 (m, 6H, CH_2), 2.05 (pq, 2H, CH_2), 2.13 (pq, 2H, CH_2), 2.37 (m, 2H, CH_2), 2.95 (t, 2H, CH_2) 4.52 (t, 2H, CH_2), 5.06 (m, 1H, C*H*) 7.65 (d, 2H, C*H*C*H*), 7.86 (d, 2H, C*H*C*H*), 9.31 (s, 1H, NC*H*N).

^{13}C – NMR (100.5 MHz, D_2O, 25°C), δ [ppm]: 21.32 (*C*H_2), 23.09 (*C*H_2), 27.25 (*C*H_2), 31.67 (*C*H_2), 46.52 (*C*H_2), 49.97 (*C*H_2), 57.44 (*C*H_2), 59.61 (*C*H_2), 76.19 (*C*H), 113.11 (*C*H*C*H), 113.72 (*C*H*C*H), 126.60 (N*C*CN), 131.84 (NC*C*N), 138.77 (N*C*HN).

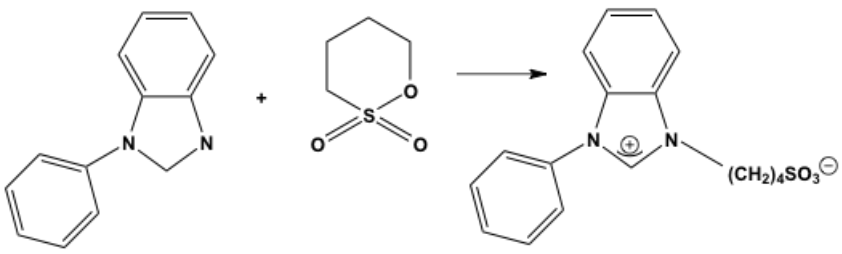
Elemental Analysis ($C_{16}H_{22}N_2O_3S$), Mw = 322

Calculated: C: 59.60 H: 6.88 N: 8.69 S: 9.95.

Found: C: 59.09 H: 6.85 N: 8.82 S: 9.76.

MS-FAB: m/z (%) = 322

1-Phenyl-3(butyl-4-sulfonate) benzimidazolium betaine



1-Phenylbenzimidazole (10 mmol) was stirred without solvent with 1,4-butanesultone (10 mmol) at room temperature for 3 days. After solidification of the mass, it was washed 3 times with toluene and dried under high vacuum. The white solid was readily soluble in water.

^{1}H – NMR (400 MHz, D_2O, 25°C), δ [ppm]: 1.75 (pq, 2H, CH_2), 2.08 (pq, 2H, CH_2), 3.29 (t, 2H, CH_2), 4.45 (t, 2H, CH_2), 7.32 (m, 2H, C*H*C*H*), 7.49 (m, 1H, C*H*), 7.63 (m, 6H, C*H*), 7.80 (m, 1H, C*H*), 8.56 (s, 1H, NC*H*N).

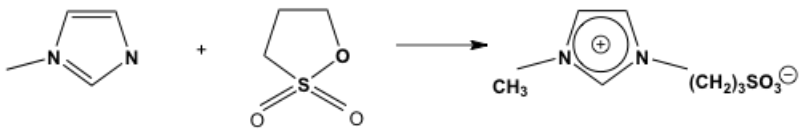
^{13}C – NMR (100.5 MHz, D_2O, 25°C), δ [ppm]: 22.46 (*C*H_2), 22.97 (*C*H_2), 27.40 (*C*H_2), 47.95 (*C*H_2), 73.48 (*C*H), 110.77 (*C*H), 119.90 (*C*H), 122.44 (*C*H), 127.70(*C*H), 130.04 (*C*H), 133.11 (*C*H), 135.91 (N*C*CN), 143.20 (NC*C*N), 143.74 (N*C*HN).

Elemental Analysis ($C_{17}H_{18}N_2O_3S$), Mw = 330.40

Calculated: C: 61.80 H: 5.49 N: 8.48 S: 9.70

Found: C: 60.70 H: 5.61 N: 8.44 S: 8.8

1-Methyl-3(propyl-3-sulfonate) imidazolium betaine



30 mmol 1-methylimidazole was added to 30 mmol 1,3-propanesultone. After stirring for 3 days, the white powder was obtained. The solid was washed with toluene and dried under vacuum.

^{1}H – NMR (400 MHz, **d**$_4$-MeOH, 25°C), δ [ppm]: 2.43 (pq, 2H, C*H*$_2$), 3.01 (t, 2H, C*H*$_2$), 3.99 (s, 3H, C*H*$_3$), 4.45 (t, 2H, ^{3}J(H, H) = 7Hz, C*H*$_2$), 7.54 (d, 1H, ^{3}J(H,H) = 6Hz, NC*H*), 7.63 (d, 1H, NC*H*), 8.84 (s,1H, NC*H*N).

^{13}C – NMR (100.5 MHz, **d**$_4$-MeOH, 25°C), δ [ppm]: 27.72 (*C*H$_2$), 38.25 (*C*H$_2$), 49.56 (*C*H$_3$), 50.42 (*C*H$_2$), 124.55 (*C*H), 126.19 (*C*H), 138.84 (NCHN).

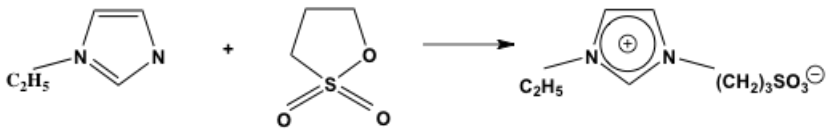
Elemental Analysis ($C_7H_{12}N_2O_3S$), Mw = 204.25

Calculated: C: 41.16 H: 5.92 N: 13.72 S: 15.70

Found: C: 40.85 H: 5.93 N: 13.88 S: 15.53

MS-FAB: m/z (%) = 203

1-Ethyl-3(propyl-3-sulfonate) imidazolium betaine



30 mmol 1-ethylimidazole was added to 30 mmol 1,3-propanesultone. After stirring for 3 days, the white powder was obtained. The solid was washed with toluene and dried under vacuum.

^{1}H – NMR (400 MHz, D_2O, 25°C), δ [ppm]: 1.59 (m, 3H, C*H*$_3$), 2.43 (pq, 2H, C*H*$_2$), 3.01 (t, 2H, C*H*$_2$), 4.33 (m, 2H, C*H*$_2$), 4.45 (t, 2H, NC*H*$_2$), 7.62 (d, 1H, NC*H*), 7.63 (d, 1H, NC*H*), 8.94 (s, 1H, NC*H*N).

^{13}C-NMR (100.5 MHz, D_2O, 25°C), δ[ppm]: 14.28 (*C*H_3), 24.90 (*C*H_2), 44.82 (*C*H_2), 47.17, (*C*H_2), 123.60 (N*C*H*C*HN), 134.88 (N*C*HN)

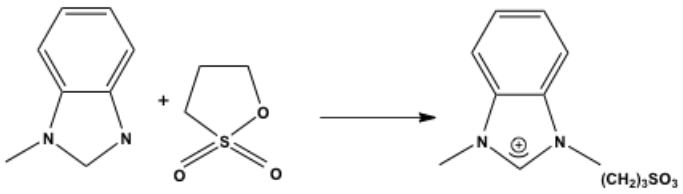
Elemental Analysis ($C_8H_{14}N_2O_3S$), Mw = 218.27

Calculated: C: 44.02 H: 6.46 N: 12.83 S: 14.69.

Found: C: 43.44 H: 6.74 N: 13.57 S: 14.33.

MS-FAB: m/z (%) = 217

1-Methyl-3(propyl-3-sulfonate) benzimidazolium betaine



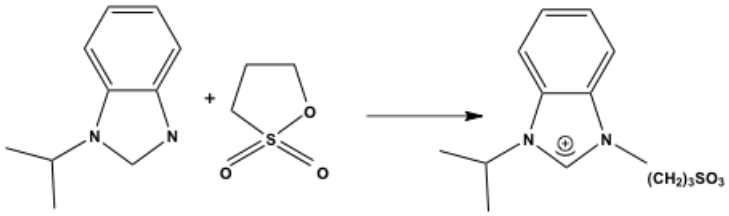
30 mmol 1-methylbenzimidazole was added to 30 mmol 1,3-propanesultone. After stirring for 3 days, the white powder was obtained. The solid was washed with toluene and dried under vacuum.

^{1}H – NMR (400 MHz, D_2O, 25°C), δ [ppm]: 2.41 (pq, 2H, C*H*$_2$), 2.97 (t, 2H, C*H*$_2$), 4.08 (s, 3H, C*H*$_3$), 4.62 (m, 2H, C*H*$_2$), 7.67 (C*H*), 7.81 (C*H*), 7.86 (C*H*), 9.28 (s, 1H, NC*H*N).

^{13}C-NMR (100.5 MHz, D_2O, 25°C), δ[ppm]: 24.20 (*C*H_2), 32.84 (*C*H_2), 45.26 (N*C*H_3), 47.29 (*C*H_2), 112.61, 126.80, 130.67, 131.99 (*C*H*C*H*C*H*C*Harom), 141.07 (N*C*HN).

MS-FAB: m/z (%) = 253

1-Isopropyl-3(propyl-3-sulfonate) benzimidazolium betaine



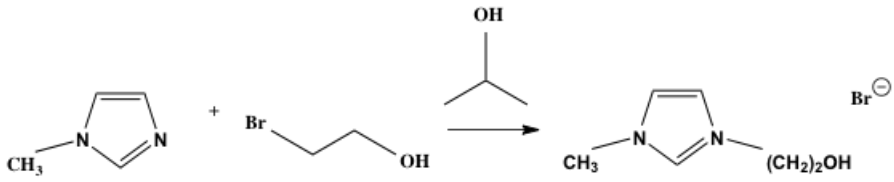
10 mmol 1-isopropylbenzimidazole was added to 10 mmol 1,3-propanesultone. After stirring for 3 days, the white powder was obtained. The solid was washed with Toluene and dried under vacuum.

^{1}H – NMR (400 MHz, D_2O, 25°C), δ [ppm]: 1.82, 2.15 (d, 6H, C*H*$_3$C*H*$_3$), 2.94 (pq, 2H, C*H*$_2$), 3.31 (sept, 1H, C*H*), 4.1 (t, 2H, C*H*$_2$), 4.54 (t, 2H, C*H*$_2$), 7.69 (d, 2H, C*H*C*H*), 7.85, 7.91 (d, 2H, C*H*C*H*), 9.14 (s, 1H, NC*H*).

^{13}C – NMR (100.5 MHz, D_2O, 25°C), δ [ppm]: = 21.23 (*C*H$_3$*C*H$_3$), 27.36 (*C*H$_2$), 32.80 (*C*H$_2$), 46.41 (*C*H$_2$), 50.07 (*C*H$_2$), 76.20 (*C*H), 112.99 (*C*Harom), 126.61 (*C*Harom), 131, 132.11 (N*CC*N), 141.05 (N*C*HN).

7.3.1.4. Snthesis of Hydroxy-Substited Azolium-Derived

1-Methyl-3-(2-hydroxyethyl) imidazolium bromide



3 ml 1-methylimidazole (3.1 g, 38 mmol) and 5 g 2-bromoethanol were added to 20 ml isopropanol. The mixture was stirred at 80°C for 24 hours and the resulting clear solution was obtained. After evaporation of the solvent, the white powder was obtained.

^{1}H – NMR (400 MHz, d_6-DMSO, 25°C), δ [ppm]: 3.71 (t, 2H, ^{3}J(H, H) = 5Hz, C*H*$_2$), 3.87 (s, 3H, NC*H*$_3$), 4.23 (t, 2H, ^{3}J(H, H) = 5Hz, C*H*$_2$), 5.13 (s, 1H, O*H*), 7.72 (s, 1H, NC*H*CHN), 7.75 (s, 1H, NCHC*H*N), 9.14 (s, 1H, NC*H*N).

^{13}C-NMR (100.5 MHz, d_6-DMSO, 25°C): δ [ppm]: 35.7 (s, N*C*H$_3$), 51.45, 59.2 (each s, *C*H$_2$*C*H$_2$), 122.5, 123.2 (each s, N*C*H*C*HN), 136.7 (s, N*C*HN).

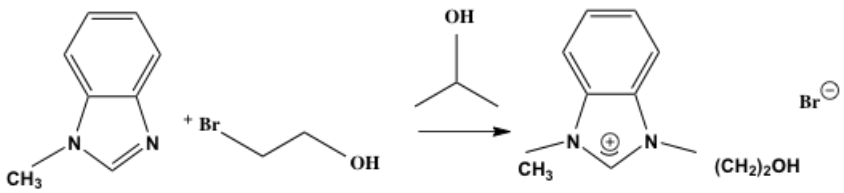
Elemental Analysis ($C_6H_{10}N_2OBr$)

Calculated: C: 34.97 H: 4.89 N: 13.59.

Found: C: 34.55 H: 5.59 N: 13.54.

MS-FAB: m/z (%) = 127 (M^+)

1-Methyl-3-(2-hydroxyethyl) benzimidazolium bromide



1.5 ml 1-methylbenzimidazole (19 mmol) and 2.5 g 2-bromoethanol were added to 10 ml isopropanol. After the mixture was stirred for 24 hours at 80°C, the resulting clear solution was obtained. The solvent was evaporated and the white powder was obtained. The white

solid was then washed with chloroform, THF, and diethyl ether and dried under vacuum.

^{1}H – NMR (400 MHz, d_6-DMSO, 25°C), δ [ppm]: 3.83 (t, 2H, C*H*$_2$), 4.12 (s, 3H, C*H*$_3$), 4.59 (t, 2H, C*H*$_2$), 5.19 (s, 1H, O*H*), 7.69 (d, 2H, C*H*C*H*arom), 8.04 (d, 1H, C*H*arom), 8.12 (d, 1H, C*H*arom), 9.80 (s, 1H, NC*H*N).

^{13}C-NMR (100.5 MHz, D_2O, 25°C), δ [ppm]: 33.17 (*C*H$_2$), 49.37 (*C*H$_3$), 58.64 (*C*H$_2$), 1113.47 (*C*H), 126.32 (*C*H), 131.24(*C*H), 131.81 (*C*H), 143.17 (N*CC*N).

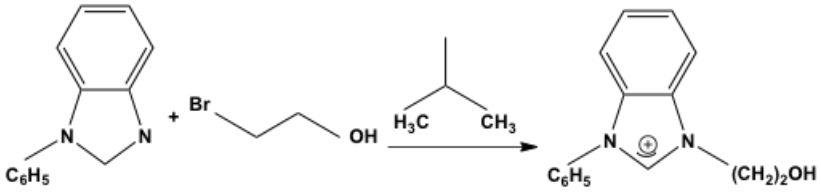
Elemental Analysis ($C_{10}H_{13}N_2OBr$), Mw = 257.13

Calculated: C: 46.71 H: 5.10 N: 10.89

Found: C: 46.72 H: 5.20 N: 11.42

MS-FAB: m/z (%) = 177 (M^+)

1-Phenyl-3-(2-hydroxyethyl) benzimidazolium bromide



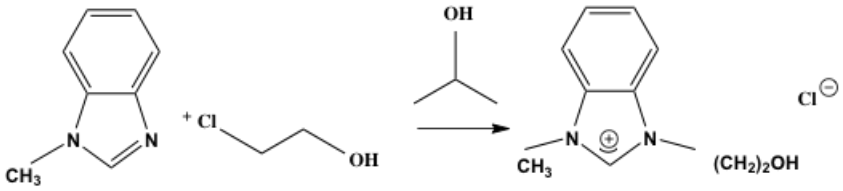
1-Phenylbenzimidazole (1.843 g, 9 mmol) and 1.25 g 2-bromoethanol were added to 5 ml isopropanol. The mixture was stirred at 80°C for 24 hours and the clear solution was obtained. After evaporation of the solvent, the white powder was obtained.

^{1}H – NMR (400 MHz, d_6-DMSO, 25°C), δ [ppm]: 4.10 (t, 2H, C*H*$_2$), 4.78 (t, 2H, C*H*$_2$), 7.65

(m, 5H, C*H*phenyl), 7.80 (d, 2H, C*H*arom), 8.16 (d, 2H, C*H*arom), 9.96 (s, 1H, NC*H*N).

^{13}C-NMR (100.5 MHz, d_6-DMSO, 25°C), δ [ppm]: 51.27 (*C*H_2), 60.42 (*C*H_2), 114.66 (*C*H_{arom}), 115.31 (*C*H_{arom}), 120.43 (CH_{phenyl}), 125.13 (CH_{phenyl}), 128.61 (CH_{arom}), 131.78 (CH_{phenyl}), 133.32 (N*C*CN), 134.60 (NC*C*N), 137.49(s, N*C*HN), 143.73 ($C_{tertphenyl}$).

1- Methyl-3-(2-hydroxyethyl) benzimidazolium chloride

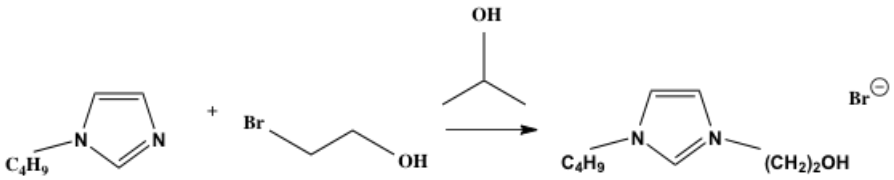


2.5 g 2-chloroethanol was added to 1.5 ml 1-methylbenzimidazole (19 mol) in 10 ml isopropanol. After stirring for 24 hours at 80°C and the reaction was cooled down to room temperature, the solvent was removed under vacuum. The white solid was then washed with chloroform, THF, and diethyl ether and dried under vacuum.

^{1}H – NMR (400 MHz, d_6-DMSO, 25°C), δ [ppm]: 4.02 (t, 2H, C*H*$_2$), 4.19 (s, 3H, C*H*$_3$), 4.64 (t, 2H, C*H*$_2$), 7.75 (d, 2H, C*H*arom), 7.97, 8.02 (d, 2H, C*H*arom), 9.95 (s, 1H, NC*H*N).

^{13}C-NMR (100.5 MHz, D_2O, 25°C), δ [ppm]: 33.91 (*C*H_2), 50.84 (*C*H_3), 60.12 (*C*H_2), 114.29 (*C*Harom), 114.60 (*C*Harom), 128.17 (*C*Harom), 132.72, 133.66 (N*CC*N), 145.32 (N*C*HN)

1-Butyl-3-(2-hydroxyethyl) imidazolium bromide

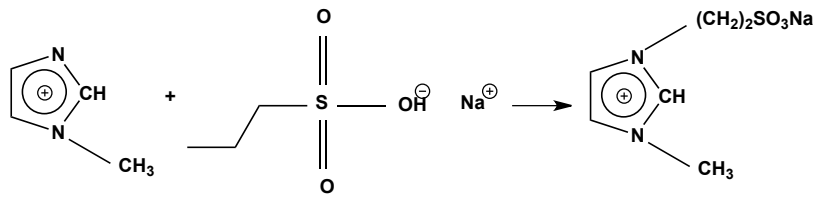


5 g 2-Bromoethanol was added to 3 ml 1-butylimidazole (3.1 g, 38 mol) in 20 ml isopropanol. After stirring for 24 hours at 80°C, the rmixture was cooled down to room temperature, and the solvent was removed under vacuum. The white solid was then washed with chloroform, THF, and diethyl ether and dried under vacuum.

^{1}H – NMR (400 MHz, d_4.MeOH, 25°C), δ [ppm]: 1.65 (t, 3H, C*H*$_3$), 2.99 (m, 2H, C*H*$_2$), 2.53 (m, 2H, C*H*$_2$), 4.22 (t, 2H, C*H*$_2$), 4.98 (t, 2H, C*H*$_2$), 5.01 (m, 2H, C*H*$_2$), 8.58 (d, 2H, C*H*arom), 8.64 (d, 2H, C*H*arom), 10.11 (s, 1H, NC*H*N).

^{13}C-NMR (100.5 MHz, d_6-DMSO, 25°C), δ [ppm]: 13.25 (*C*H$_3$), 18.80 (*C*H$_2$), 31.17 (*C*H$_2$), 48.42 (*C*H$_2$), 51.39 (*C*H$_2$), 59.19 (*C*H$_2$), 121.95, 122.74 (N*CC*N), 136.28 (s, N*C*HN).

1-Methyl-3-(ethylsulfonic acid sodium salt) imidazolium bromide



205 mg (2.5 mmol) of 1-methylimidazole was stirred without a solvent with 210 mg (1mmol) of 2-bromoethanesulfonic acid sodium salt for three days at 70°C. After cooling, the residue

was washed three times with 30 ml of diethyl ether to remove excess methylimidazole. A white solid obtained after drying under high vacuum.

^{1}H – NMR (400 MHz, d_6-DMSO, 25°C), δ [ppm]: 4.05 (t, 2H, C*H*$_2$), 4.51 (s, 3H, C*H*$_3$), 5.22 (t, 2H, C*H*$_2$), 8.05 (NC*H*CHN), 8.17 (NCHC*H*N), 9.95 (s, 1H, NC*H*N).

^{13}C-NMR (100.5 MHz, D_2O, 25°C), δ [ppm]: 35.66 (*C*H_3), 44.98 (*C*H_2), 49.78 (*C*H_2), 122.28, 123.55 (N*C*H*C*HN), 136.65 (N*C*HN).

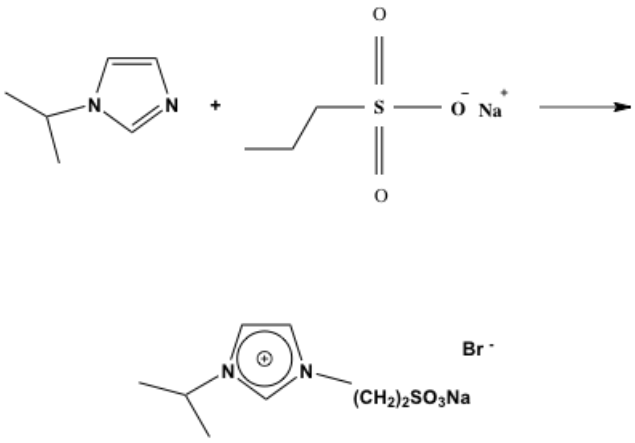
Elemental Analysis ($C_8H_{14}N_2O_3S$), Mw = 292

Calculated: C: 25 H: 3.44 N: 9.56 S: 10.94.

Found: C: 26.92 H: 4.17 N: 10.72 S: 10.09.

MS-FAB: m/z (%) = 212.8 (M^+).

1-Isopropyl-3-(ethylsulfonic acid sodium salt) imidazolium bromide



2.765 g (25.1 mmol) of 1-isopropylimidazole was stirred without a solvent with 2 g (9.5 mmol) of 2-bromoethanesulfonic acid sodium salt for three days at 70°C. The mixture was

cooled down and washed three times with 30 ml of diethyl ether to remove excess 1-isopropylimidazole. After drying under high vacuum, a white solid obtained.

^{1}H – NMR (400 MHz, D_2O, 25°C), δ [ppm]: 1.38 (d, 6H, C*H*$_3$C*H*$_3$), 3.26 (t, 2H, C*H*$_2$), 4.44 (t, 2H, C*H*$_2$), 4.6 (sept, 1H, C*H*), 7.39 (m, 2H, C*H*$_2$), 8.83 (s, 1H, NC*H*N).

^{13}C – NMR (100.5 MHz, D_2O, 25°C), δ [ppm]: 21.91 (*C*H$_3$), 45.06 (*C*H$_2$), 49.82 (*C*H$_2$), 53.09 (*C*H), 120.57 (*C*H), 122.17 (CH), 134.87 (N*C*HN).

Elemental Analysis for ($C_8H_{14}BrN_2NaO_3S$), Mw = 321.17

Calculated: C: 30.95 H: 4.82 N: 9.92 S: 9.11

Found: C: 29.92 H: 4.39 N: 8.72 S: 9.98

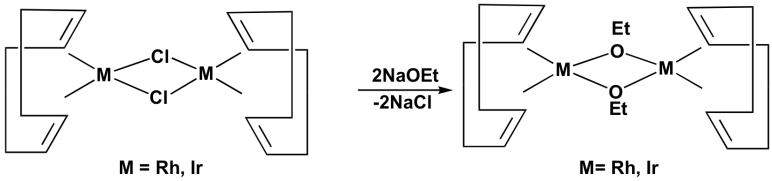
MS-FAB. m/z (%) = 241

7.3.2 Synthesis of Carbene Complexes

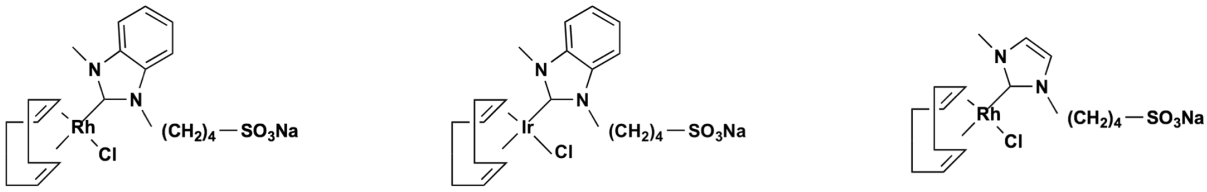
General Synthesis Procedure for of the carbene complexes (3 - 5):

1.6 ml of 1M NaOEt/EtOH solution was dissolved in 10 ml ethanol and slowly added to a suspension of (M(COD)Cl)$_2$. After the mixture was stirred for 30 min at room temperature, the azolium precursor (1.2 mmol) was added. The suspension was stirred at room temperature for 72 h. Ethanol was removed in vacuo, and the residue was washed with diethyl ether and dried under high vacuum. the carbene ligand (2.4 mmol) was added and dried under high vacuum. The rhodium/iridium precursor (Ir(COD)OEt)$_2$/(Rh(COD)OEt)$_2$ was prepared from (Rh(COD)Cl)$_2$/(Ir(COD)Cl)$_2$ by reaction with sodium ethanolate in ethanol at ambient temperature. Substitution of the chloro bridge in the dimeric precursor (Rh(COD)Cl)$_2$ by an ethoxy bridge allows the coordinated base to deprotonate the azolium in situ, leading to the

desired carbene complexes.



Synthesis route for Rhodium – NHC and Iridium – NHC complexes **3** – **5** (to be continued)



Rhodium – NHC and Iridium – NHC complexes **3** – **5**

Complex 3 ($C_{20}H_{27}ClN_2NaO_3RhS$)

^{1}H-NMR: (400 MHz, D_2O, 20°C, ppm), δ[ppm]: 1.91 (m, COD allyl), 2,32 (pq, 2H, CH_2), 2.45 (pq, 2H, CH_2), 3.05 (t, 2H, CH_2), 3.23, 3.58 (COD vinyl), 4.11 (s, 3H, CH_3), 4.52 (t, 2H, CH_2), 7.26 (d, 2H, C*H*C*H*arom), 7.41 (d, 2H, C*H*arom).

^{13}C-NMR (15kHz, ^{13}C-CPMAS, 25°C), δ[ppm]: 24.3(CH_2), 31.4 (COD allyl), 35.8 (CH_2), 51.1 (N-CH_3), 51.2 (*C*H$_2$) 69.6 (COD allyl), 92.3, 99.5 (COD vinyl), 115 (*C*H*C*Harom), 122.8 (*C*H*C*Harom), 135.5 (N*CC*Narom), 195.5 (NC_{carb}N).

Elemental Analysis ($C_{20}H_{27}ClN_2NaO_3RhS$), Mw = 536.85

Calculated: C: 44.74 H: 5.07 N: 5.22 S: 5.97.

Found: C: 42.96 H: 5.28 N: 5.60 S: 6.65.

MS-FAB: m/z (%) = 512.1 (M^-).

Complex 4 ($C_{20}H_{27}ClIrN_2NaO_3S$)

^{1}H-NMR: (400 MHz, D_2O, 25°C), δ[ppm]: 1.79 (m, COD allyl), 2.11 (pq, 4H, C*H*$_2$), 2.93 (t, 2H, C*H*$_2$), 3.85 (COD vinyl), 4.06 (s, 3H, C*H*$_3$), 4.34 (COD vinyl), 4.48 (t, 2H, C*H*$_2$), 7.62 (d, 2H, C*H*C*H*arom), 7.77, 7.83 (d, 2H, C*H*C*H*arom).

^{13}C-NMR (10kHz, ^{13}C-CPMAS, 25°C), δ [ppm]: 23.8 (C*H*$_2$), 26.3 (C*H*$_2$), 30.7 (COD allyl), 34.1 (C*H*$_2$), 48.3 (N-C*H*$_3$), 50.8 (C*H*$_2$), 85.7 (CODvinyl), 111.4 (*C*H*C*Harom), 124.7 (*C*H*C*Harom), 135.5 (N*CC*Narom), 191.7 (N*C*$_{carb}$N).

Elemental Analysis ($C_{20}H_{27}ClN_2NaO_3IrS$), Mw = 626.16

Calculated: C: 38.36 H: 4.35 N: 4.47 S: 5.12.

Found: C: 37.89 H: 4.68 N: 4.97 S: 6.02.

MS-FAB: m/z (%) = 602 (M^-).

Complex 5 ($C_{16}H_{25}N_2RhClNaO_3S$)

^{1}H – NMR (400 MHz, D_2O, 25°C), δ[ppm]: 1.71 (m, COD allyl), 2.42 (pq, 2H, C*H*$_2$), 2.87 (pq 2H, C*H*$_2$), 3.55, 3.67 (COD vinyl), 3.98 (t, 2H, C*H*$_2$), 4.15 (s, 3H, C*H*$_3$), 4.50 (t, 2H, C*H*$_2$), 7.12 7.16, (d, 2H, C*H*C*H*arom).

^{13}C-NMR (15kHz, ^{13}C-CPMAS, 25°C), δ[ppm]: 23.9 (C*H*$_2$), 30.7 (C*H*$_2$), 31.6 (COD allyl), 39.0 (C*H*$_2$), 51.9 (N-C*H*$_3$), 57.7(C*H*$_2$), 67.3, 89.6, 96.6 (COD vinyl), 124.0 (N*C*H*C*HN), 180.6 (N*C*$_{carb}$N).

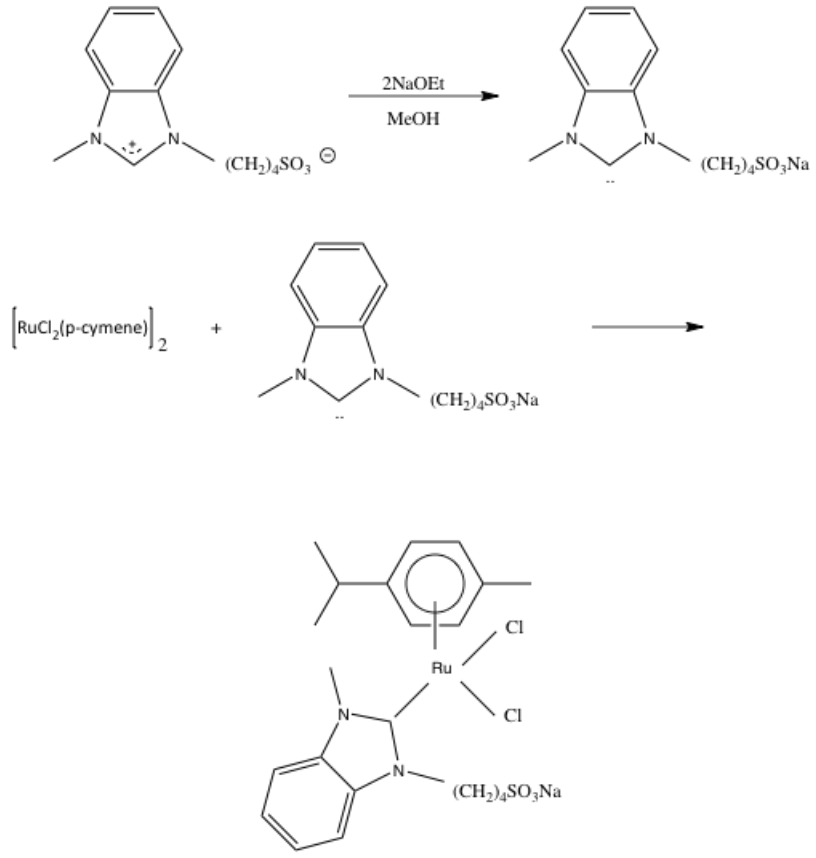
Elemental Analysis ($C_{16}H_{25}N_2RhClNaO_3S$), Mw = 486.79

Calculated: C: 39.48 H: 5.18 N: 5.75 S: 6.59

Found: C: 38.04 H: 5.36 N: 6.18 S: 7.97.

MS-FAB: m/z (%) = 462.9 (M^-).

Complex 6



1 ml of 1M NaOEt/MeOH solution was slowly added to a suspension of carbene ligand in 15 ml methanol. After the mixture was stirred for 24 h at room temperature and free carbene was formed, the ruthenium precursor was added. The suspension was stirred at room temperature for another 24 h. Methanol was removed under vacuum. And then washed with diethyl ether and dried under high vacuum.

Complex 6 ($C_{22}H_{29}Cl_2RuN_2NaO_3S$)

^{1}H – NMR (400 MHz, CD_3OD, 25°C), δ[ppm]: 1.31 (d, 6H, CH (C*H*$_3$)), 1.85 (pq, 2H, C*H*$_2$), 2.17(s, 3H, C(C*H*$_3$)), 2.19(pq, 2H, C*H*$_2$), 2.76 (sept, 1H, C*H*CH$_3$), 2.87 (t, 2H, C*H*$_2$), 4.14 (s, 3H, NC*H*$_3$), 4.57(t, NC*H*$_2$), 5.29(m, 2H, C_6H_4), 5.54 (m, 2H, C_6H_4), 7.70(d, 2H, C*H*C*Harom*), 7.92 (d, 2H, C*H*C*Harom*).

^{13}C– NMR (CD_3OD, 25°C), δ[ppm]: 17.35 (CH(*C*H$_3$)), 20.90 (C(*C*H$_3$)), 21.35 (*C*H$_2$), 27.44 (*C*H$_2$), 31.16 (*C*H(*C*H$_3$), 31.32(*C*H$_2$), 46.47 (N*C*H$_3$), 49.84 (N*C*H$_2$), 76.26 (2C, C_6H_4), 78.27 (2C, C_6H_4), 93.54 (1C, *C*Me, *p*-cymene), 97.28 (1C, C*i*Pr, *p*-cymene), 112.87 (*C*H*C*Harom), 126.89 (*C*H*C*Harom), 131.53, 132. 15 (N*CC*Narom), 180.09 (N*C*$_{carb}$N).

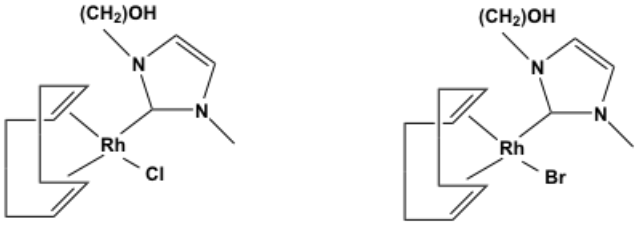
Elemental Analysis for ($C_{22}H_{29}Cl_2RuN_2NaO_3S$):

Calculated C: 44.30 H: 4.90 N: 4.70 S: 5.38 Cl: 11.89 Na: 3.85

Found: C: 44.07 H: 5.30 N: 5.03 S: 5.42 Cl: 12.13 Na: 3.5.

MS-FAB: m/z (%) = 573 (M^-)

Complex 7



1.2 ml of 1M NaOEt/EtOH solution was slowly added to a suspension of $(Rh(COD)Cl)_2$ in 15 ml ethanol. After stirring for 30 min at room temperature, 1-Methyl-3-(2-ethanol)-imidazolium bromide (1.2 mmol) was added. The suspension was stirred at room temperature

for 72 h. Ethanol was removed under vacuum, and the residue was washed with diethyl ether and dried under high vacuum.

^{1}H-NMR (400 MHz, D_2O, 20°C, ppm), δ[ppm]: 1.84 (COD allyl), 2.13 (COD allyl), 3.81 (t, 2H, C*H*$_2$), 3.93 (s, 3H, C*H*$_3$), 4.27 (t, 2H, C*H*$_2$), 4.39 – 4.94 (COD vinyl), 7.24 (m, N*C*H*C*HNarom).

^{13}C-NMR (15kHz, ^{13}C-CPMAS, 25°C)), δ[ppm]: 27.47 – 33.80 (COD allyl), 35.90 (*C*H$_2$), 51.98 (NCH$_3$), 55.88 (COD allyl), 59 (CH$_2$), 82.37, 96.16 (COD vinyl), 115 (*C*H*C*Harom), 122.8 (N*C*H*C*HNarom), 128.59 (N*C*CNarom), 137.02 (NC*C*Narom), 180.35 (N*C*$_{carb}$N).

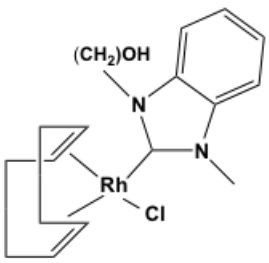
MS-FAB: m/z (%):

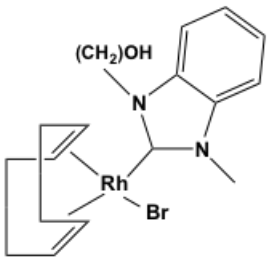
$C_{14}H_{22}N_2ORh$ = 336.9

$C_{14}H_{22}N_2ORhCl$ = 371.8

$C_{14}H_{22}N_2ORhBr$ = 415.7

Complex 8





1.2 ml of 1M NaOEt/EtOH solution was slowly added to a suspension of (Rh(COD)Cl)$_2$ in 15 ml ethanol. After stirring for 30 min at room temperature, 1-Methyl-3-(2- ethanol) benzimidazolium bromid (1.2 mmol) was added. The suspension was stirred at room

temperature for 72 h. Ethanol was removed under vacuum, and then the residue was washed with diethyl ether and dried under high vacuum.

MS-FAB: m/z (%):

$C_{18}H_{24}N_2ORh$ = 386.8

$C_{18}H_{24}N_2ORhCl$ = 421.7

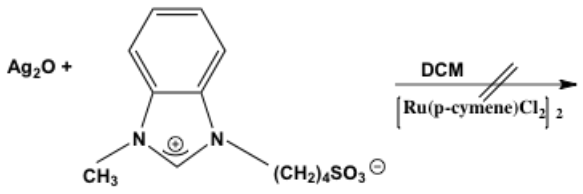
$C_{18}H_{24}N_2ORhBr$ = 467.6

^{1}H-NMR (400 MHz, D_2O, 20°C, ppm), δ[ppm]: 1.99 (COD allyl), 2.44 (COD allyl), 2.57 (COD allyl), 3.49 (t, 2H, C*H*$_2$), 3.88 (t, 2H, C*H*$_2$), 4.27 (s, 3H, C*H*$_3$), 4.63 – 5.04 (COD vinyl), 7.31 (C*H*C*H*arom), 7.58 (C*H*C*H*arom).

^{13}C-NMR (15kHz, ^{13}C-CPMAS, 25°C), δ[ppm]: 28.42 – 33.19 (COD allyl), 34.42 (*C*H$_2$), 49.88 (*C*H$_2$), 59.99 (*C*H$_3$), 68.90, 98.13 (COD vinyl), 110 (*C*Harom), 122.04 (*C*Harom), 126.26 (*C*Harom), 134.76 (*C*Harom), 143.02 (N*CC*N) 180.35 (N*C*$_{carb}$N).

7.3.2.1 Attempt to make Ru-NHC via Transmetalation Method

Synthesis to isolate the Ruthenium complex with 1-Methyl-3-(butyl-4-sulfonate) benzimidazolium betaine as the ligand.



Several methods has been attempted as explained below, but Ru-NHC complexes with sulfonate ligand could not be made via Transmetalation Method.

(1) 1-Methyl-3-(butyl-4-sulfonate) benzimidazolium betaine (0.99 mmol, 0.265 g) was dissolved in 20 mL of dichloromethane and transferred into a Schlenk vessel. Silver (I) oxide (0.49 mmol, 01135 g) was added, and the mixture was stirred for 2h at room temperature under Ar atmosphere. The unreacted Ag_2O was filtered off. [Ru(p-cymene)Cl_2]$_2$ 0.45 mmol, 0.2755g) was added to the solution. The mixture was stirred for 1 h at room temperature. After filtration, the solvent was removed in vacuo.

(2) 1-Methyl-3-(butyl-4-sulfonate) benzimidazolium betaine (0.49 mmol, 0.131 g) was dissolved in 8 mL of dichloromethane and transferred into a Schlenk vessel. Silver (I) oxide (0.3 mmol, 0.0695 g) was added, and the mixture was stirred for 3h at 50°C under Ar atmosphere. The unreacted Ag_2O was filtered off. The product was isolated by removing the solvent in vacuo. It was supposed to give silver carbene as the product.

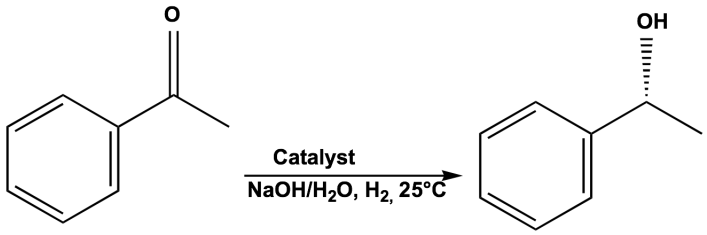
(3) [Ru(p-cymene)Cl_2]$_2$ (0.25 mmol, 0.153g), silver oxide (0.5 mmol, 0.116 g), 1-methyl-3(butyl-4-sulfonate) benzimidazolium betaine (0.5 mmol, 0.134 g), was dissolved in 30 ml of dichloromethane. The mixture was stirred for 24 h at -78°C under Ar atmosphere. The unreacted Ag_2O was filtered off and the product was isolated by removing the solvent in vacuo.

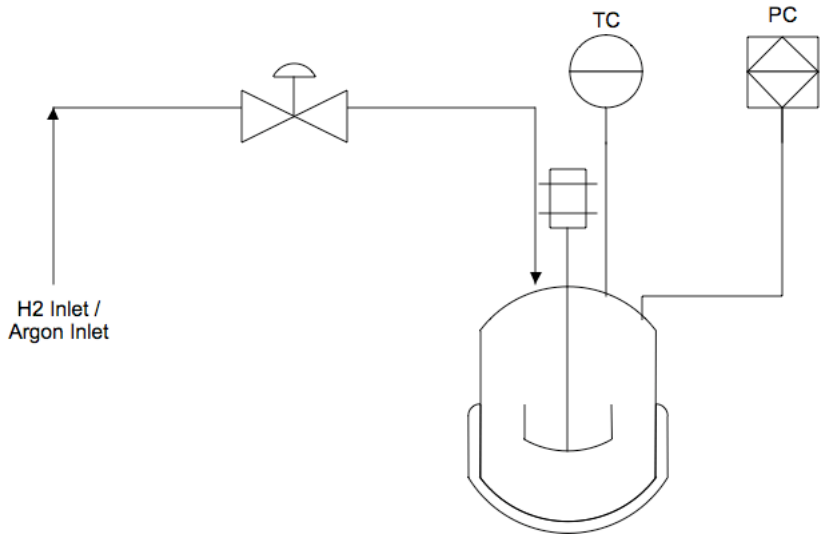
7.4 Catalytic Reaction

7.4.1 General Procedure for Hydrogenation [115]:

In a Schlenk tube 0.03 mmol catalyst and 0.96 ml of 1M aqueous sodium hydroxide solutions were added to 10 ml of water under argon and the mixture was degassed. After stirring for 24 hours at room temperature, the solution was transferred to a 50 ml stainless steel glass coated autoclave and 1.2 mmol of substrate was added. The autoclave was purged with hydrogen and final pressure was adjusted to 40 atm. The mixture was stirred at room temperature for 21 h and then analyzed by gas chromatography to determine the conversions and reaction yields

using diethylene glycol dibutyl ether as an internal standard.





TC = Temperature Controller

PC = Pressure Controller

7.4.2 Transfer Hydrogenation of Acetophenone in Aqueous Solution

After preparing the precatalyst, HCOONa (3.40 g, 50 mmol) and acetophenone (1.2 g, 10 mmol) were added to the solution. Following quick degassing (3X), the solution was allowed to react at 40°C for a certain period of time. After cooling to r.t., the organic phase was extracted with Et_2O (3x4 mL) and analyzed By GC and MS.

8. References

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

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

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

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

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

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

[7] F. E. Hahn, M. C. Jahnke, Angew. Chem. Int. Ed. 47 (2008) 3122.

[8] G. B. Schuster, Adv. Phys. Org. Chem. 22 (1986) 311.

[9] R. Hoffmann, G. D. Zeiss, G. W. Van Dine, J. Am. Chem. Soc. 90 (1968) 1485.

[10] J. F. Harrison, J. Am. Chem. Soc. 93 (1971) 4112.

[11] C. W. Bauschlicher, Jr., H. F. Schaefer II, P.S. Bagus, J. Am. Chem. Soc. 99 (1977) 7106

[12] J. F. Harrison, R.C. Liedtke, J. F. Liebman, J. Am. Chem. Soc. 101 (1979) 7162.

[13] D. Feller, W.T. Borden, E. R. Davidson, Chem. Phys. Lett. 71 (1980) 22.

[14] L. Tschugaef, M. Skanawy – Grigorjewa, A. Posnjak, Z. Anorg. Chem. 148 (1925) 37.

[15] A. Burke, A. L. Bach, J. M. Enemark, J. Am. Chem. Soc. 92 (1970) 2555.

[16] E. O. Fischer, A. Maasboel, Angew. Chem. 76 (1964) 645.

[17] K. Öfele, J. Organomet. Chem. 12 (1968) 42.

[18] H. W. Wanzlick, H. J. Schönherr, Angew. Chem., Int. Ed. 7 (1968) 141.

[19] R. R. Schrock, J. Am. Chem. Soc. 96 (1974) 6796.

[20] Denys Baskakov, Phd Thesis, Technische Universität München, 2007.

[21] C. Köcher, W. A. Herrmann, J. Organomet. Chem. 532 (1997) 261.

[22] K. Öfele, W. A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, W. Scherer, J. Mink, J. Organomet. Chem. 459 (1993) 177.

[23] D. Enders, H. Gielen, J. Runsink, K. Breuer, S. Brode, K. Böhn, Eur. J. Inorg. Chem. (1998) 913.

[24] A. A. D. Tulloch, A. A. Danopoulos, S.M. Cafferkey, S. Kleinhenz, M. B. Hursthouse, R.P. Tooze, Chem. Commun. (2000) 1247

[25] J. H. Davis, Jr., C.M. Lake, M. A. Bernard, Inorg. Chem. Chem. 37 (1998) 5412

[26] H. M. J. Wang, I. J. B. Lin, Organometallics. 17 (1998) 972.

[27] D. S. McGuinness, K. J. Cavell, Organometallics. 19 (2000) 741.

[28] A. Fürstner, G. Seidel, D. Kremzow, C. W. Lehmann, Organometallics. 22 (2003) 907.

[29] P. J. Fraser, W. P. Roper, F. G. Stone, J. Chem. Soc., Dalton Trans. (1974) 102.

[30] P. J. Fraser, W. P. Roper, F. G. Stone, J. Chem. Soc., Dalton Trans. (1974) 760.

[31] M. F. Lappert, J. Organomet. Chem. 100 (1975) 139.

[32] A. J. Arduengo III, S. F. Gaper, J. C. Calabrese, F. Davidson. J. Am. Chem. Soc. 116 (1994) 4391.

[33] P. L. Arnold, G. N. Cloke, T. Geldbach, P. B. Hitchcock, Organometallics 18 (1999) 3228.

[34] W. P. Fehlhammer, G. Beck, J. Organomet. Chem. 369 (1989) 105.

[35] K. Bartel, W. P. Fehlhammer, Angew. Chem. Int. Ed. Engl. 13 (1974) 599.

[36] D Rieger, S. D. Lotz, U. Kernbach, S. Schröder, C. André, W. P. Fehlhammer, Inorg. Chim. Acta 222 (1994) 275.

[37] S. D. Lotz, D. Rieger, U. Kernbach, J. Bertran Nadal, C. André, W. P. Fehlhammer, J. Organomet. Chem. 491 (1995) 135.

[38] H. Turkmen, R. Can, B. Cetinkaya, Dalton Trans. (2009**)** 7039.

[39] C. Fleckenstein, S. Roy, S. Leuthausser, H. Plenio, Chem. Commun. (2007) 2870.

[40] G. Papini, M. Pellei, G.G Lobbia, A. Burini, C. Santini, Dalton Trans. (2009**)** 6985.

[41] M. A. N.Virboul, M. Lutz, M.A. Siegler, A.L. Spek, G. van Koten, R. Gebbink, Chem. Eur. J. 15 (2009**)**, 9981.

[42] Y. Nagai, T. Kochi, K. Nozaki, Organometallics. 28 (2009), 6131.

[43] J. K. Huang, H.-J. Schanz, E. D. Stevens, S. P. Nolan, Organometallics. 18 (1999) 2370.

[44] K. Öfele, C. G. Kreiter, Chem. Ber. 105 (1972), 529.

[45] K. Öfele, M. Herberhold, Z. Naturforsch B. B 28 (1973), 306.

[46] P. Anastas, J.C. Warner (Eds.), Green Chemistry: Theory and Practice, Oxford University Press, Oxford, 1998.

[47] P. T. Anastas, T.C. Wiliamson (Eds.), Green Chemistry: Frontiers in Chemical Synthesis and Processes, Oxford University Press, Oxford, 1998.

[48] P. T. Anastas, M. M. Kirchhoff, Acc. Chem. Res. (35), 2002, 686, Wiliamson (Eds.), Green Chemistry: Frontiers in Chemical Synthesis.

[49] P. T. Anastas, L.G. Heine, T.C. Williamson (Eds.), Green Chemical Syntheses and Processes, American Chemical Society, Washington DC, 2000.

[50] P. T. Anastas, C. A. Farris (Eds.), Benign by Design : Alternative Synthetic Design for Pollution Prevention, ACS Symp. Ser. Nr. 577, American Chemical Society, Washington, Washington DC, 1994.

[51] J. H. Clark, D.J. Macquarrie, Handbook of Green Chemistry and Technology, Blackwell, Abingdon, 2002.

[52] A. S. matlack, Introduction to Green Chemistry, Marcel Dekker, New York, 2001.

[53] M. Lancaster, Green Chemistry: An Introductory Text, Royal Society of Chemistry, Cambridge, 2002.

[54] M. Lancaster, Green Chemistry: An Introductory Text, Royal Society of Chemistry, Cambridge, 2002.

[55] R. A. Sheldon, I. A. Arends, U. Hanefeld, Green Chemistry and Catalysis, Chimie / Chemistry. 3 (2000), 541.

[56] R. A. Sheldon, C. R. Acad. Sci. Paris, IIc, Chimie/Chemistry, 3 (2000) 541.

[57] T. Hudlicky, D.A. Frey, L. Koroniak, C.D. Claeboe, L.E. Brammer, Green Chem. 1999, 1, 57.

[58] D. J. C. Constable, A.D. Curzons, V.L. Cunningham, Green Chem. 4 (2002) 521 see also A. D. Curzons, D.J. C. Constable, D.N. Mortimer, V. L. Cunningham, Green Chem. 2001, 3, 1 – 6; D.J.C. Constable, A. D. Curzons, L. M. Freitas dos Santos, G. R. Green, R. E. Hannah, J.D. Haylet, J. Kitteringham, M.A. McGuire, J.E. Richardson, P. Smith, R.L. Webb, M. Yu, Green Chem. 3 (2001) 7.

[59] S. Kobayashi (Ed.), Special Issue on Water, Adv. Synth. Catal. 344 (2002) 219.

[60] X. Wu, J. Xiao, Chem. Commun. 24 (2007) 2449 .

[61] B. Cornils, W.A. Herrmann, Aqueous-Phase Organometallic Catalysis, Concepts and Application, second ed., Wiley-VCH, Wenheim, Germany, 1998.

[62] C. J. Li, L. Chen, Chem. Soc. Rev. 35 (2006) 68 .

[63] D. Sinou, Adv. Synth. Catal. 344 (2002) 221.

[64] E. G. Kuntz, Chemtech 17 (a) (1987) 570.

[65] B. Cornils, J. Falbe, Proc. 4th Int. Symp. On Homogeneus Catalysis, Leningrad, Sept. 1984, p. 487.

[66] H. Bach, W. Gick, E.Wiebus, B. Cornils, 1st IUPAC Symp. Org. Chemistry, Jerusalem 1986, Abstracts, p. 295.

[67] E. Wiebus, B. Cornils, Chem. –Ing.-Techn. (1994) 66.

[68] B. Cornils, E. Wiebus, Chemtech 25 (1995) 33.

[69] S. Otto, J.B.F.N. Engberts, Pure App. Chem. 72 (2000) 1365.

[70] P. N. Rylander, Catalytic Hydrogenation – over Platinum Metals, Academic Press: New York, 1967.

[71] J. P. Collman, L.S. Hegedus, J. R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987.

[72] Ch. Elschenbroich, A. Salzer, Organometallics, A Concise Introduction, 2nd ed, VCH, Weinheim, 1992.

[73] P. Powell, Principles of Organometallic Chemistry, 2nd ed., Chapman and Hall, London, 1988.

[74] R. H. Crabtree, The Organometallic Chemistry of the Transition Metals, John Wiley, New York, 1988.

[75] F. Joo, Aqueous Organometallic Catalysis, Kluwer Academic Publishers, 2001, p. 48.

[76] E. Rocchini, A. Mezzetti, H. Rüegger, U. Burckhardt, V. Gramlich, A. Del Zotto, P. Martinuzzi, P. Rigo, Inorg. Chem. 36 (1997) 711.

[77] G. Jia, C.P. Lau, Coord. Chem. Rev. 83 (1999) 190.

[78] J. Chatt, G. J. Leigh, R.M. Slade, J. Chem. Soc., Dalton Trans. (1973) 2021.

[79] A. F.Borowski, D.J. Cole – Hamilton, G. Wilkinson, Nouv. J. Chim. 2 (1978) 137.

[80] V. R. Parameswaran, S. Vancheesan, Proc. Indian Acad. Sci., Chem. Sci. 103 (1991) 1.

[81] Y. Dror, J. Manassen, J. Mol. Catal. 2 (1997) 219.

[82] G. T. Baxley, T. J. R. Weakly, W.K.Miller, D.K. Lyon, D.R. Tyler, J.Mol. Catal. A. 116 (1997) 191.

[83] E. Meczynska, A. M. Trzeciak, R. Grzybeck, J.J. Ziólkowsky, J. Mol. Catal.A. 132 (1998) 203.

[84] E. Meczynska, A. M. Trzeciak, J. J. Ziólkowsky, J. Mol.Catal. A. 148 (1999) 59

[85] C. Bianchini, P. Frediani, V. Sernau, Organometallics. 14 (1995) 5458.

[86] D. J. Darensbourg, F. Joó, M. Kannisto, Á. Kathó, J. H. Reibenspies, Organometallics. 11 (1992) 1990.

[87] D. J. Darensbourg, N.W. Stafford, F. Joó, J. H. Reibenspies, J. Organometal. Chem. 1995, 488, 99.

[88] F. Joó, L. Nádasdi, A. Cs. Bényei, D.J. Darensbourg, J. Organometal. Chem. 1998, 512, 45.

[89] F. P. Pruchnick, P. Smolénski, K. Wadja – Hermanowicz, J. Organometal. Chem. 570 (1998) , 63.

[90] F. P. Pruchnick, P. Smolénski, E. Galdecka, Z. Galdecki, Inorg. Chim. Acta 293 (1999) 110.

[91] F. P. Pruchnick, P. Smolénski, Appl. Organometal. C-hem. 1999, 13, 829.

[92] R. T. Smith, R. K. Ungar, M.C. Baird, Transition Met. Chem. 7 (1982) 288.

[93] R. T. Smith, R. K. Ungar, L.J. Sanderson, M. C. Baird, Organometallics 2 (1983) 1138.

[94] E. Renaud, R. B. Russel, S. Fortier, S. J. Brown, M. C. Baird, J. Organometal. Chem. 419 (1991) 403.

[95] T. L. Schull, R. Olano, D. A. Knight, Tetrahedron (2000) 56.

[96] F. Farin, H. L. M. Van Gaal, S. L. Bonting, F. J. M. Daemen, Biochim. Biophys. Acta 711 (1982) 336.

[97] S. Lèlievre, F. Mercier, F.Mathey, J. Org. Chem. 61 (1996) 3531.

[98] A. Andriollo, A. Bolivar, F. A. López, D. E. Páez, Inorg. Chim.Acta. 238 (1995) 187.

[99] B. Drießen-Hölscher, J. Heinen, J.Organometal. Chem. 570 (1998) 141.

[100] J. Heinen, M.S. Tupayachi, B. Drießen-Hölscher, Catal. Today. 48 (1999) 273.

[101] D. J. Ellis, P.A. Dyson, D.G. Parker, T. Welton, J. Mol. Catal. A. 150 (1999), 150, 71.

[102] W.-C. Chan, C.-P. Lau, Y.-Z. Chen, Y. –Q. Fang, S.-M. Ng, G. Jia, Organometallics 1997, 16, 34.

[103] A. S. Berenblyum, T.V. Turkova, I.I. Moiseev, Koord. Khim. 5 (1979) 773.

[104] A. S. Berenblyum, T.V. Turkova, I.I. Moiseev, Izv. A.N. S.S.S.R., Ser. Khim. (1981) 514.

[105] S. Bischoff, M. Kant, Catal. Today. 58 (2000) 241.

[106] S. Otto, J.B.F.N. Engberts, Pure App. Chem. 72 (2000) 1365.

[107] F. Joo, Aqueous Organometallic Catalysis, Kluwer Academic Publishers, 2001, p. 102.

[108] R. A. W. Johnstone, A.H. Wilby, I. D. Entwistle, Chem. Rev. 85 (1985) 129.

[109] G. Zassinovic, G. Mestroni, Chem. Rev. 92 (1992), 1051.

[110] M. J. Palmer, M. Wills, Tetrahedron Asymmetry. 10 (1999), 2045.

[111] R. L. Chodhury, J. E. Bäckvall, J. Chem. Soc., Chem. Commun. (1991) 1063.

[112] R. Noyori, S. Hashiguchi, Acc. Chem. Res. 30 (1997) 97.

[113] K. J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, Angew. Chem. Int. Ed. Engl. 36 (1997) 285.

[114] W. A. Herrmann, M. Elison, J. Fischer, C. Köcher. (Hoechst AG) US Patent 5,663,451.

[115] V. Pénicaud, C. Maillet, P. Janvier, P. Pipelier, B. Bujoli, Eur. J. Org. Chem. (1999), 1745.

[116] Q. Jiang, Y. Jiang. D. Xiao, P. Cao, X. Zhang, Angew. Chem. Int. Ed. 37 (1998) 1100.

[117] S. D. Lin, D. K. Sanders, M.A. Vannice, Appl. Catal. 113 (1994) 59.

[118] D. K. Sanders, S. D. Lin, M.A. Vannice, J. Catal. 147 (1994) 375.

[119] T. Koscielski, J.M. Bonnier, J.P. Damon, J. Masson, Appl. Catal. 49 (1989) 91.

[120] S. D. Lin, D. K. Sanders, M.A. Vannice, J. Catal. 147 (1994) 370.

[121] J. Masson, S. Vidal, P. Cividino, P. Fouilloux, J. Court, Appl. Catal. 99 (1993) 147.

[122] C.-S. Chen, H.-W. Chen, W.-H. Cheng, Appl. Catal. 248 (2003) 117.

[123] Christian Köcher, Phd Thesis, Technische Universität München, 1997.

[124] A. A. Gridnev, I. M. Mihaltseva, Synth. Commun. 24 (1994) 1547.

[125] T. Focken, J. Rudolph, C. Bolm, Synthesis. (2005) 429.

[126] J. Liu, J. Chen, J. Zhao, Y. Zhao, L. Liang, H. Zhang. Synthesis. (2003) 2661.

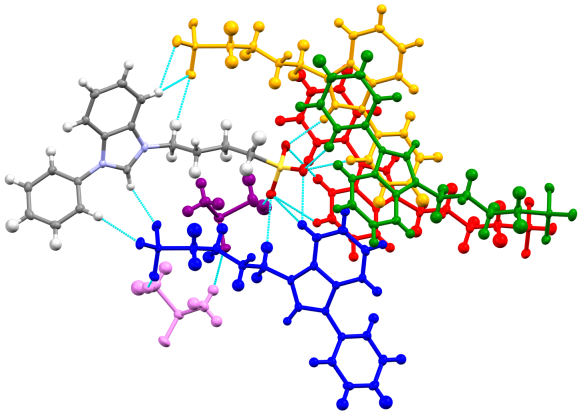
[127] Y. Genisson, N. L. Lauth-de Viguerie, C. Andre, M. Baltas, L. Gorrichon, Tetrahedron : Asymmetri. 16 (2005) 1017.

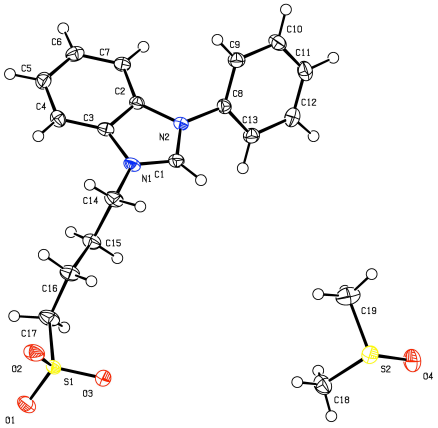
Appendix

Crystallographic Data for 1-Phenyl-3(butyl-4-sulfonate) benzimidazolium betaine

Formula	$C_{17}H_{18}N_2O_3S$, C_2H_6OS
Weight	408.54
Crystal System	Orthorhombic
Space group	Pna21(No. 33)
a [Angstrom]	9.7005(2)
b [Angstrom]	24.9649(4)
c [Angstrom)	7.9799(1)
V [Ang**3]	1932.51(6)
Z	4
D(calc) [g/cm**3]	1.404
Mu (MoKa) [/mm]	0.304
F(000)	864
Crystal Size [mm]	0.23x0.38x0.80
Temperature (K)	123
Radiation [Angstrom]	MoKa 0.71073
Theta Min-Max [Deg]	1.6, 25.5
Tot., Uniq. Data, R(int)	38861, 3591, 0.025
Observed data [I > 2.0 sigma(I)]	3481
Nref, Npar	3591, 340
R, wR2, S	0.0225, 0.0559, 1.07
w = 1/[\s^2^(Fo^2^)+(0.0279P)^2^+0.5819P] where P=(Fo^2^+2Fc^2^)/3	
Max. and Av. Shift/Error	0.00, 0.00
Flack x	-0.01(4)

Min. and Max. Resd. Dens. [e/Ang^3] -0.21, 0.23





O-H Bonds length (Å)

O1	H9	x,y,z	1.5-x,1/2+y,-1/2+z	2.426
O2	H7	x,y,z	1.5-x,1/2+y,1/2+z	2.699
O3	H6	x,y,z	1.5-x,1/2+y,1/2+z	2.716
O1	H4	x,y,z	-1/2+x,1/2-y,z	2.575
O3	H4	x,y,z	-1/2+x,1/2-y,z	2.642
O3	H14A	x,y,z	-1/2+x,1/2-y,z	2.518
H1	O2	x,y,z	-1/2+x,1/2-y,z	2.216
H13	O1	x,y,z	-1/2+x,1/2-y,z	2.362
O1	H13	x,y,z	1/2+x,1/2-y,z	2.362
O2	H1	x,y,z	1/2+x,1/2-y,z	2.216
H4	O1	x,y,z	1/2+x,1/2-y,z	2.575
H4	O3	x,y,z	1/2+x,1/2-y,z	2.642
H14A	O3	x,y,z	1/2+x,1/2-y,z	2.518
O3	H19A	x,y,z	1/2+x,1/2-y,z	2.524
H19A	O3	x,y,z	-1/2+x,1/2-y,z	2.524
H18A	O4	x,y,z	1/2+x,1/2-y,z	2.411