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N-Heterocyclic carbene ligands and their Rh(I) complexes
Mechanochemical and solvent synthesis and catalytic applications

PhD thesis

Sourav De

Supervisor: Dr. Ferenc Joó

Declaration

I, Sourav De, have prepared This Dissertation within the Reaction Kinetics and Catalysis (K/1) Program of the Doctoral School of Chemistry of the Doctoral Council of Natural Sciences and Information Technology of the University of Debrecen with the aim of obtaining the Doctor of Philosophy (PhD) degree in Sciences from the University of Debrecen. Herewith I declare, that the results included in This Dissertation are not included in other PhD dissertation(s).

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                                                          Signature of the applicant

Herewith I, Ferenc Joó, attest that the applicant, Sourav De has carried out his research in the period of 2016-2020 under my supervision within the Reaction Kinetics and Catalysis (K/1) Program of the Doctoral School of Chemistry. With his independent and ingenious research activity, the applicant made decisive contributions to the results contained in This Dissertation. Herewith I declare, that the results included in This Dissertation are not included in other PhD dissertation(s). I recommend the approval of the Dissertation.

Debrecen, 2020 …….....   ………………………………………..
                                                          Signature of the supervisor

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Dissertation submitted in partial fulfilment of the requirements for the
doctoral degree (PhD)
in Chemistry

Written by
Sourav De
(MSc in Chemistry)

Prepared in the framework of the Doctoral School of Chemistry of the
University of Debrecen
(K/1 Reaction Kinetics and Catalysis programme)

Dissertation advisor: Dr. Ferenc Joó, Professor Emeritus

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The date of the dissertation defence: ……………............... 2020

<u>Contents</u>

<u>Abbreviations</u>

°C	Degree Celsius
COD	1,5-Cyclooctadiene
CsOH	Caesium hydroxide
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
EtOAc	Ethyl acetate
ESI-MS	Electrospray ionization mass spectrometry
GC	Gas Chromatography
GPC	Gel Permeation Chromatography
HOMO	Highest Occupied Molecular Orbital
IMes	1,3-Dimesityl-1,3-dihydro-2H-imidazol-2-ylidene
IPr	1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene
MALDI-TOF	Matrix-Assisted Laser Desorption/Ionization-Time of Flight
*m*tppms	meta-triphenyphosphine monosulfonate
NHC	N-heterocyclic carbene
NMR	Nuclear magnetic resonance
PA	Phenylacetylene
PIN	1-isopropyl-3-(5,7-dimethyl-1,8-naphthyrid-2-yl) imidazol-2-ylidene
PPA	Polyphenylacetylene
PTA	1,3,5-Triaza-7-phosphaadamantane
SIMes	1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene
SIPr	1,3-Bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene
THF	Tetrahydrofuran
TLC	Thin-layer chromatography
TOF	Turnover Frequency
XRD	X-ray diffraction

1. General introduction and objectives

Carbenes are neutral compounds with a divalent carbon atom having six electrons in the valence shell. The very first assumption about the existence of carbenes was made by Hermann and Geuther in the year 1855 [1]. Next in 1897, Nef from the University of Chicago told about carbene intermediate for the transformation of pyrrole in chloroform to α-chloropyridine and the Reimer-Tiemann reaction [2]. However, at that time, due to lack of proper evidence, most of the scientists didn't believe the existence of free radicals. Three years after that, Gomberg characterized the very first example of free radical tri-phenyl-chloromethylene (scheme 1a) [3] and then, finally the scientific community welcomed this legendary discovery [1].
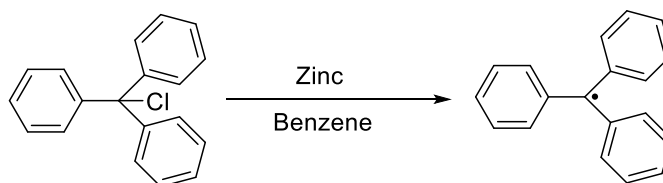
Scheme 1a: First stable radical generation.

Still, there was a misconception that carbenes are impossible to isolate and they can only be caught by a trapping agent [1,4,5]. Because of this, the field of carbene chemistry remained dormant until the end of the twentieth century. Bertrand, in 1988, for the first time in history, reported the synthesis of free carbene called phosphinosilyl carbene [6]. Three years later, Arduengo and coworkers synthesized the first and one of the best-known examples of persistent carbene, a cyclic diamino carbene called *N-hetero*cyclic carbene or NHC [4,7].

Apart from the most available NHCs featuring 5-membered ring, significant researches have been accomplished on the synthesis of larger heterocycle NHCs. The first stable NHC with six-membered aliphatic heterocycle **1.1** (fig. 1a) [8] was discovered in 1999. Very soon, this was followed by the discovery of several N,N'- substituted **1.1** [9–11].
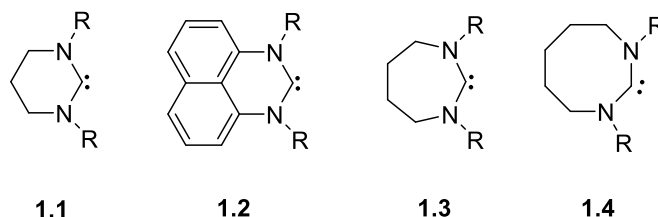

| 1.1 | 1.2 | 1.3 | 1.4 |

Fig. 1a: Stable NHCs with more than five-membered heterocycles.

Again, in search of making novel NHC ligands, two of more NHC units have been fused with a linker to form poly N-heterocyclic carbenes and the unique bonding characteristics of such poly NHCs have also opened up a new horizon in the domain of organometallic chemistry [4,12]. Even though mono NHCs are rich in example with variable ring size, di-NHCs are only available with five-membered heterocyclic rings [13].

Free di N-heterocyclic carbenes are also air, temperature and moisture sensitive. The very straightforward way to prepare a di-NHC is the direct reaction between imidazole and alkyl/aryl dihalide, followed by the alkylation (Scheme 1b).
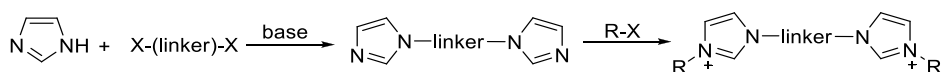
Scheme 1b: General synthetic procedure of di-NHCs.

Di-NHCs are well recognized to form stable and isolable complexes with various transition metal complexes with different oxidation states and have application in the field of material science, pharmacological field and catalysis. For this reason, a variety of transition metal complexes of rhodium, ruthenium, palladium, iron, chromium, nickel, iridium and copper, with a few examples with lanthanides and actinides have been synthesized [13–15].

Aims and objectives

Even though NHC complexes with rhodium are very well known, we checked that there are still no reports presented on the Rh-di(NHC) complexes. Therefore, our main aim was to synthesize and characterize Rh-di(NHC) complexes, first with the classical methods in the organic solvents. We extended our investigation to the mechanochemical synthesis of such complexes to compare the two different types of synthetic methods. The traditional solvent synthesis most often involves many steps, needs long reaction time and involves high energy costs. In addition, such procedures most often have negative impact on the environment due to the prevalent usage of volatile organic solvents. On the other hand, the reaction using mechanical energy is a viable alternative to classical solution method as it is capable of producing better yields in lesser time in a greener way. Moreover, the opportunity to adjust several instrumental parameters makes the procedures more flexible. The relative lack of application of Rh(I)-NHC complexes as catalysts in selective hydration of nitriles in aqueous media or in the polymerization reaction of alkynes also encouraged us to further extend our research work in those directions.

2. Bibliographic review

2.1. Chemistry of carbenes

Carbenes are neutral compounds containing a bivalent carbon atom with six electrons valency [16,17]. Amongst them, four electrons are involved in making σ-bonds, while the other two electrons stay with the central carbon, thereby, not following the 'octet rule'. Depending on electronic spins, carbenes can be divided into two classes- singlet and triplet (fig. 2a). In case of the first one, the remaining two electrons on the carbon centre are spin paired in HOMO σ-orbital, thereby, keeping the p_π-orbital vacant. Therefore, they have both electrophilic and nucleophilic nature. On the other hand, for the triplet carbenes, each of these electrons stays in each degenerated p- orbitals (e.g. p_x and p_y in fig. 2a) [16,18].
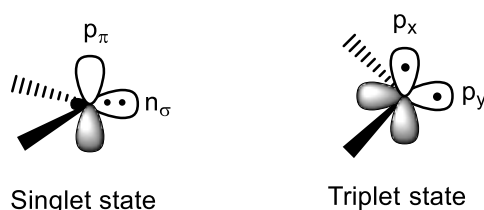

Fig. 2a: The two different states of carbenes.

Stabilization of carbenes is always a big deal for scientists. Even though triplet carbenes are more unstable comparing to singlet carbenes, they both are highly reactive and hard to isolate. Kinetically, singlet carbenes can be stabilized by introducing a bulky functionalization on the α-position of the carbene carbon. Thermodynamically, stabilization is possible by interacting the σ and p_π orbitals by introducing proper substituents. σ-electron-withdrawing and π- electron-donating substituents like OR, NR_2,

SR etc. (R=alkyl group) can stabilize the carbene centre like in fig. 2b [16,19,20].
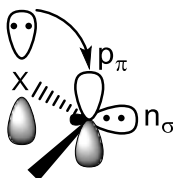

Fig. 2b: Stabilization of p_π-orbital with π- electron-donating group.

Before 1960, carbenes were originally thought to be extremely reactive and short-lived species to use as a catalyst. At the beginning of 1960, the first attempts to isolate carbene were made by α- elimination of chloroform from imidazole precursor and by deprotonating imidazolium salt utilizing strong bases by Wanzlick. However, in the absence of proper trapping agents, carbenes were only isolated as carbene dimers [4,5]. Thus, isolation of free carbenes was remained unsuccessful till in 1988, Bertrand and coworkers reported the synthesis of first free carbene – phosphinosilyl carbene (fig. 2c(i)) [6]. And, three years later, in 1991, Arduengo and coworkers isolated the first crystalline bottleable cyclic diaminocarbene, the first N-heterocyclic carbene or NHC (fig. 2c(ii)) [4,7].
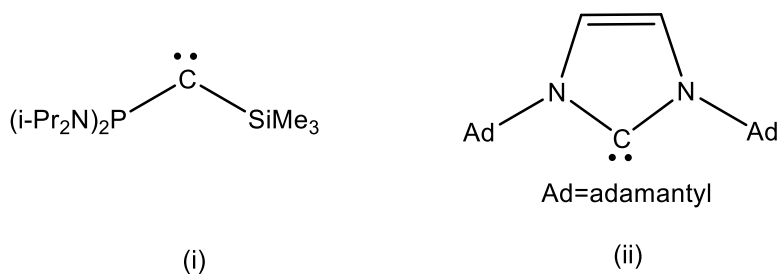

(i)   (ii)

Fig. 2c: First stable carbenes reported.

2.2. N-heterocyclic carbenes

N-heterocyclic carbenes or NHCs are cyclic carbenes with at the minimum one nitrogen atom present in the ring-structure [4]. After the first report of NHC by Arduengo [7], several other stable NHCs have been reported [1,16,21–23]. Fig. 2d represents some of the typical N-heterocyclic carbenes. This includes the most widely studied NHCs generated from imidazole moiety. Such NHCs are stabilized by the interaction of lone pairs of two nitrogen atoms with the p_π-orbital of carbene carbon like in fig. 2e [17,24]. NHCs derived from imidazole moiety can be functionalized very easily on both of their nitrogen atoms like in scheme 2a [25–27].

Imidazole-2-ylidenes

Imidazoline-2-ylidenes

N,N'-diamidocarbenes

Thiazol-2-ylidenes

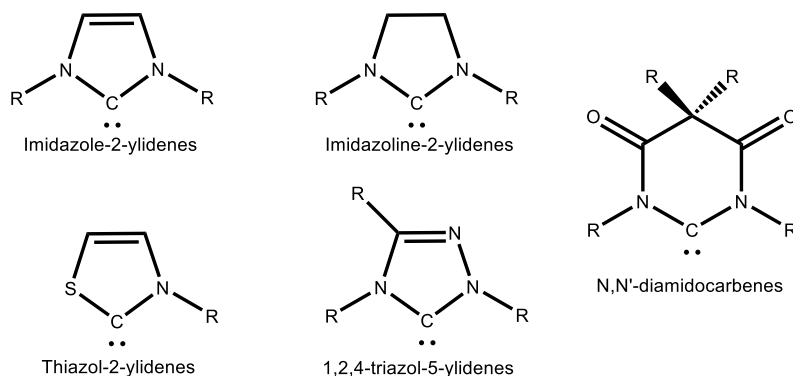1,2,4-triazol-5-ylidenes
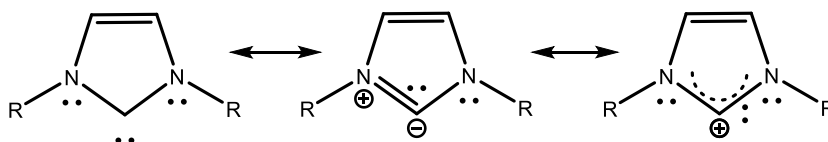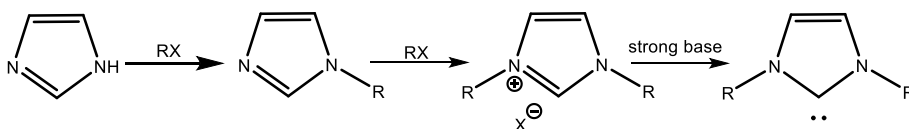
Fig 2d: Structure of typical NHCs.

Fig 2e: Stabilization of NHCs derived from imidazole.

Scheme 2a: Typical synthesis of NHCs.

Introduction of functional groups to N-heterocyclic carbenes is not something very easy to do. Even though NHCs are stable, they are very reactive and strong bases are required during their preparation as they tend to protonate easily. As they accept protons, we can call them Bronsted bases. Again, a Bronsted base can be seen as a nucleophile that can react with an electrophile. So, they can be termed as Lewis base i.e. σ-donor as well. The reactions presented in scheme 2b definitely prove the σ-donor nature of the NHCs. This reactivity is not only limited to Lewis acidic transition metals but also with any electrophiles, thereby limiting the possible functional groups to be introduced [25].
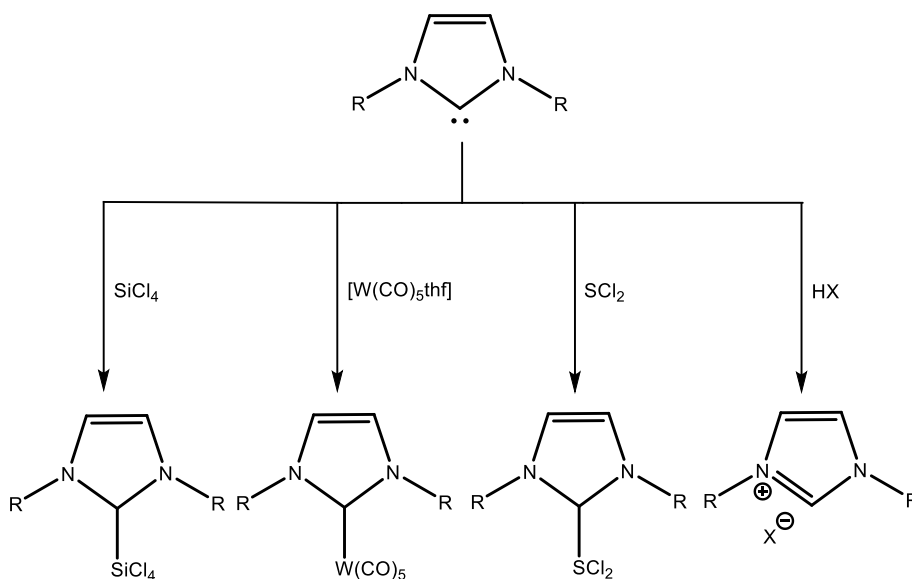
Scheme 2b: NHCs as σ-donor ligands.

Before the invention of N-heterocyclic carbenes, phosphines used to be the mostly used ligands in the field of organometallic chemistry. Due to their week π acceptor and strong σ-donor properties, NHCs are analogous to phosphines, therefore, initially NHCs were used to mimic the similar transition metal-phosphine complexes [28]. However, there are some differences between these two types of ligands. In general, NHCs are more electron-donating than phosphines, thereby leading to stronger metal-ligand bond which is reflected in the shorter bond distance and higher bond-dissociation energies for NHCs over the phosphines. Moreover, complexes of NHCs are more air and moisture-stable and display high catalytic activities [4,29–31], therefore, NHCs nowadays rival the phosphines in the domain of organometallics [4]. In the present day, N-heterocyclic carbene complexes are available with all transition metals [23], alkali earth [32] and f-block metals [33] in various oxidation states.

Most of the applications of the N-heterocyclic carbenes engage their coordination to transition metals. Majority of the applications of the NHC-metal complexes are in the field of catalysis. Herrmann and coworkers reported the first catalytic application of NHC by applying Pd-NHC complex of imidazole-2-ylidene in Mizoroki-Heck reaction [30]. Nowadays, NHCs are available with various transition metals and applied as catalysts not only in academia but in commercial fields also [31,34]. Ruthenium and iridium NHC complexes are very popular in the field of hydrogenation and hydrogen transfer reactions [35]. The NHC complexes of gold are widely used in the field of π-bond activation [36]. Rhodium and platinum with NHCs are really good for hydrosilylation reactions [37]. The two mostly studied catalytic reactions are cross-coupling (NHC complexes of palladium and other transition metals) [38–40] and ruthenium-NHC catalyzed olefin metathesis reaction [41,42].

Despite catalysis, NHCs, in recent days are utilized in the field of medicine and materials. NHC complexes of silver(I) and gold(I) display excellent anti-cancer and anti-bacterial activities [29,43]. Many imidazoline-2-ylidene and imidazole-2-ylidene silver complexes display anti-bacterial activity against both gram-positive and gram-negative bacteria [43]. The cationic complex of Au(I) in fig. 2f(i) displays selective inhibition against selenoenzyme thioredoxin reductase, which is very often found in human cancers [44].

On the other hand, the thermal stability and ability to tune the electronic and steric properties makes the NHC-transition metal complexes ideal for the development as organometallic materials [45]. NHC-metal complexes are very often incorporated into the main or side chains of polymers. The platinum(II) and palladium(II) organometallic polymer in fig. 2f(ii) displays self-healing characteristics and shows promise as electrical conductor [46,47].
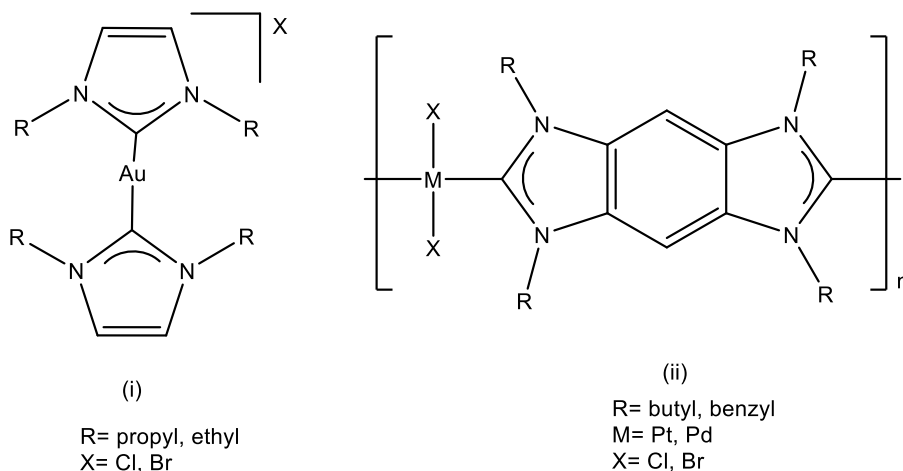

(i)

R= propyl, ethyl
X= Cl, Br

(ii)

R= butyl, benzyl
M= Pt, Pd
X= Cl, Br

Fig. 2f: NHC complexes with application in medicine and materials.

2.3. Poly-N-heterocyclic carbenes and their complexes

In the domain of NHCs, poly-N-heterocyclic carbenes are of greatest interest as they allow the preparation of various organometallic compounds with different geometries. Poly-NHCs are polytopic ligands containing more than one NHC units. In the present time, there are a number of poly-NHC complexes available with di-, tri-, tetra-dentate NHCs and they can act as bridging, chelating, tripodal, tetrapodal or pincer ligands [4].

Amongst poly-NHCs, di-NHCs are most common. Two NHC units are joined together with a linker to prepare a di-NHC unit. This linker can be aromatic rings [48,49], aliphatic chains [30,50–52], amines [53] etc. and relatively easy to prepare. Also, the properties of di-NHCs are easily modifiable by altering the linker or changing the linker size [54–57]. In some cases, a di-NHC can have a linker which can act as an electron-donating species (e.g. pyridine), thereby forming a tris coordinating di-NHC ligand, like the pincer ligands shown in fig. 2g [58–62].
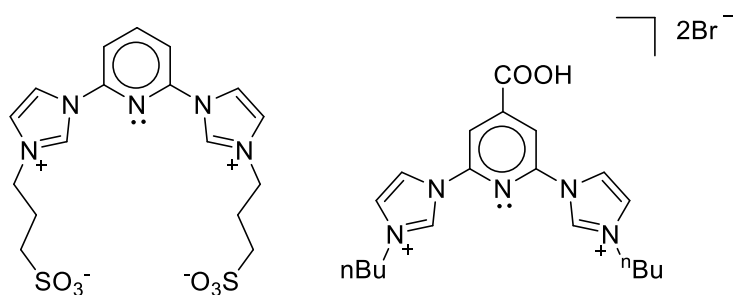

Fig. 2g: Example of pincer ligands.

Now, let's come to the coordination fashion of di-NHCs to a transition metal. A bidentate di-NHC can coordinate to metal centre(s) in two possible modes. The ligand can coordinate to one metal centre in a

chelating fashion as shown in fig. 2h(i). On the other hand, one NHC ligand can coordinate to two metal ions forming a bridge between the two metal ions as shown in fig. 2h (ii, iii, iv). In the case of this bridging coordination, there are three different possibilities. It can either form a 2:1 metal/ligand complex (fig. 2h(ii)) or 1:1 metal/ligand complex (fig. 2h(iii)) or can form polymeric chain like in fig. 2h(iv) [4,63–68].
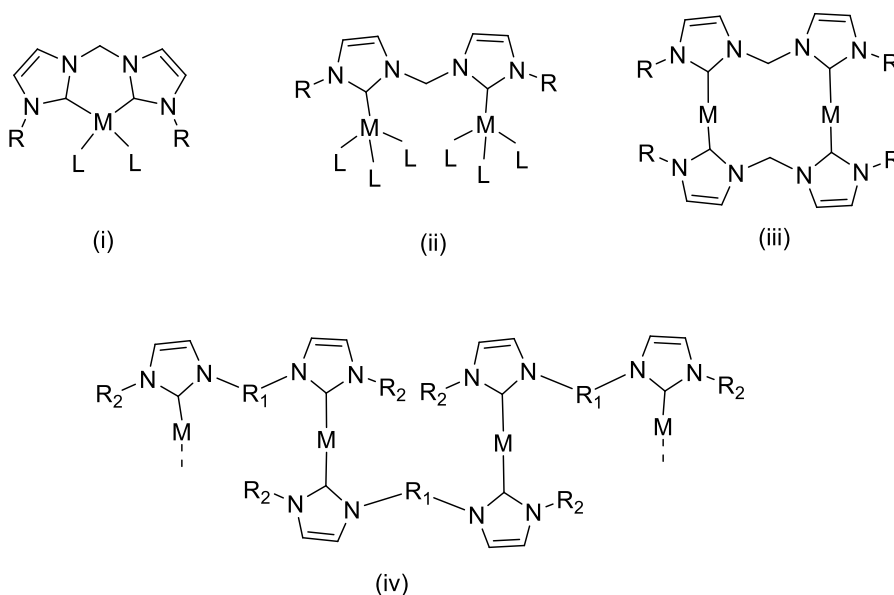

(i)   (ii)   (iii)

(iv)

Fig. 2h: Coordination modes of di-NHC ligands.

The tris- or tetra-NHCs are less common as their synthetic procedure is difficult, involves a lot of steps and hard purification procedure because of their limited solubilities. Only a few such *N*-heterocyclic carbenes are known to us. Some of them are presented in fig. 2i [69–72].
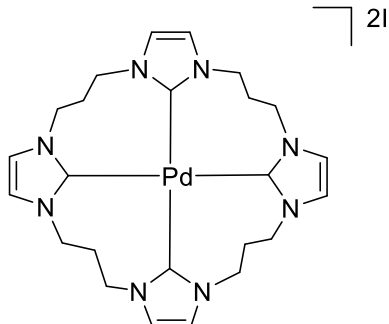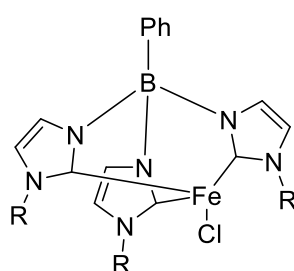
Fig. 2i: Example of tris- and tetra-NHC metal complexes.

Several factors work behind the formation of a metal-di (NHC) complex and their possible outcomes are presented in scheme 2d. The steric factor is the main reason behind such coordination fashions. However, it is not only enough to explain all the examples. The nature of anion present in the system also does matter [4].
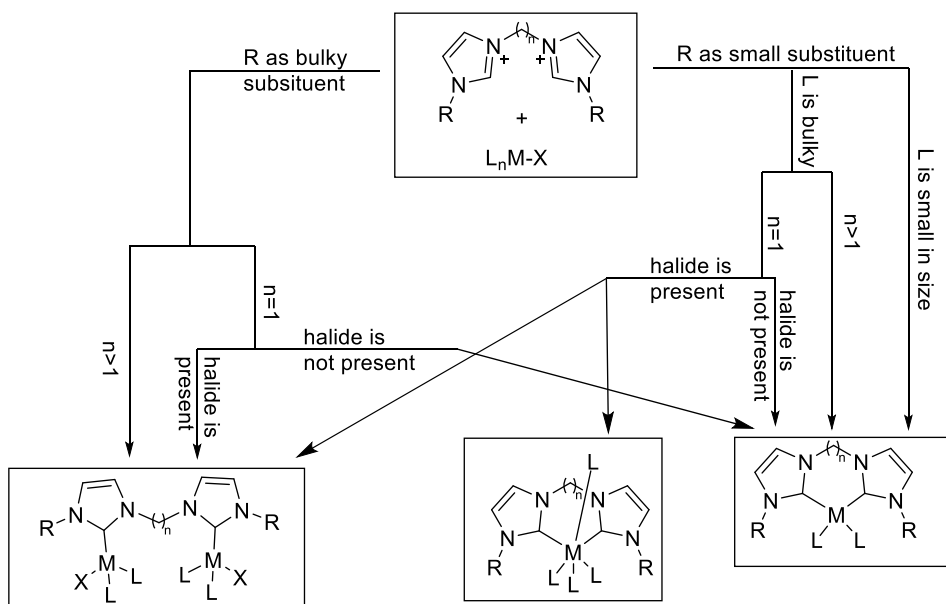
Scheme 2d: Scheme representing several factors behind the formation of metal-di (NHC) complexes.

2.4.Polymerization of acetylenes

For the last twenty years, one of the main fields of research in the field of catalysis is the polymerization of the unsaturated substrates with a special concern towards π-conjugated polymers. And, this is because of their unique physicochemical properties which makes them applicable in several fields. Within the group of these polymeric materials, polymers of acetylenes are of significant interest as they can offer some noble properties like ferromagnetism, conductivity, humidity sensor, oxygen permeability etc. [73].

The polymerization reaction of unsubstituted acetylene is possible to be promoted by various catalytic systems, however, the application of the system is restricted by the nature of polyacetylene as it very often has less stability, poor solubility and hard to be processed [73,74].
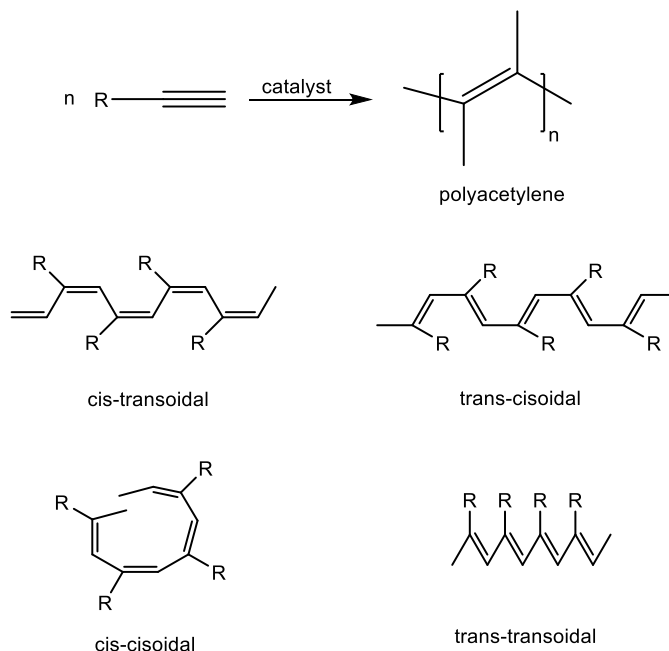
Scheme 2e: Polymerisation of monosubstituted acetylene and the outcomes.

On the other hand, for the monosubstituted acetylenes, the polymerization reaction can in principle develop four isomeric polyenes presented in scheme 2e. This depends on the configuration of carbon-carbon double bond and the conformation of carbon-carbon single bond of the main chain (cisoidal or transoidal). Polymerization of such monomers of acetylene was first reported in the year 1969 [75]. Two main classes of catalysts are capable of polymerizing such monomers:

(i) Group 6 metal compounds

(ii) Organometallic derivatives of rhodium

Complexes of molybdenum and tungsten are main amongst the first type catalysts and they process the polymerization reaction in metathesis mechanism. In some cases, such catalytic systems have shown the ability to polymerize di-substituted acetylene as well [73].

In contrast, the second type of catalytic system i.e. the rhodium complexes polymerize the monosubstituted acetylene monomers via insertion mechanism, producing stereoselective products [73,76–79]. Some nickel and palladium complexes have also displayed the alkylene polymerization activity, however, proceeding through the same mechanism. Therefore, we can keep them in the same group with rhodium catalytic systems [80–82].

2.5. Hydration of nitriles

Amides are very important compounds because of their crucial use in the field of industry and medicine. Even though, the method for synthesis of amides is quite straightforward, in practical cases it can still be tricky [83]. There are a number of methods available to convert nitriles to amides [84–86]. Amongst them, the hydration reaction is completely atom economic. However, this classic transformation is challenging to achieve, even with the number of accessible catalysts. The conventional method of hydration

of nitriles happens utilizing strong bases (e.g. sodium hydroxide) or strong acids (e.g. sulfuric acid) under harsh conditions, which most often lead to overhydrolysis as well as byproduct formation because of functional group incompatibility (scheme 2f) [83].

Scheme 2f: Selective hydration of nitriles to amides.

To overcome this difficulty, a number of astonishing catalytic systems have been designed till date. Several homogeneous and heterogeneous catalytic systems [84,87–89], nanoparticles of several metal complexes [90–92], NHC complexes of several metals [84] and biocatalytic enzymes like nitrile hydratase [93] deserve special mention amongst them. Till date, metal complexes of nickel [94], gold [95], osmium [96], ruthenium [97–100] and rhodium [84,99,101] have been applied as catalysts for hydration reaction of nitriles.

Several catalytic systems in the absence of transition metals have also been applied for this reaction. Sodium hydroxide [102], dried potassium *tert*-butoxide [103], CsOH-DMSO superbase systems [104] are amongst them. Nitrile hydratases are effectively utilized to hydrate the nitriles to amides under milder conditions [93], however, they are costly and unstable at elevated temperature (>30 °C). Several homogeneous organometallic catalytic systems have also yielded amides with high selectivity, most often these systems require very high reaction temperature (>150 °C) [105] or some particular experimental environments such as micro-wave,

inert atmosphere etc. Therefore, this field of research is still under development and scientists, from all over the world, are still searching towards a new and more effective catalytic system.

In the case of transition metal complexes, ruthenium is the most used transition metal for the hydration reaction of nitriles [84]. There are only a few cases reported till date about the usage of rhodium metal complex as a catalyst for the hydration reaction of nitriles to amides. In 2000, Djoman et al. mentioned about the water soluble complex of rhodium synthesized in-situ from P(m-C$_6$H$_4$SO$_3$Na)$_3$ ($m$tppts) and [RhCl(COD)]$_2$ to be efficient as a catalyst [106]. Eight years later, in 2008, Goto and coworkers reported the in situ synthesis of a rhodium(I) complex from PCy$_3$ and [Rh(OMe)(COD)]$_2$, which was successfully used in the hydration reaction at room temperature [107]. In 2012 and 2014, Daw et al. and Cadierno et al. reported two rhodium complexes [RBr(COD)(κC$_2$-PIN)] (used with a base) and [RhCl(COD){P(NMe$_2$)$_3$}] (used without any additives), respectively, as catalyst [101,108]. Very recently, in 2020, we have reported the application of the first [RhCl(COD)(NHC)] type complexes for the hydration of nitriles to amides in aqueous or partly aqueous medium [84].

3. Experimental Section

3.1. Materials and general information

All the solvents and chemicals were purchased from well-known commercial distributors like Sigma-Aldrich, Alfa Aesar, Merck, Molar Chemicals Kft. and VWR International and employed as received without further purification. Analytical thin-layer chromatography (TLC) was carried out on Kieselgel 60 F254 plates from Merck and the plates were visualised under UV light at 254 nm. The column chromatography was executed on silica gel from Sigma-Aldrich (70-230 mesh, 63-200 µm). The Rh-metal precursors [RhCl(COD)]$_2$ [109], [Rh(OH)(COD)]$_2$ [110], the ligands $m$tppms-Na [111] and PTA [112] were prepared following the methodology described in literature. Synthesis of di-NHC ligand precursors 1,1′-bis(imidazole-1-yl)methane (**1a**) and 1,4-bis(imidazole-1-yl)butane (**1b**) were done following the procedure described in literature [113,114]. The purity of the prepared compounds were examined by correlating their respective ^{1}H-NMR, ^{13}C-NMR and ESI-MS spectra to those available in the literature.

NMR spectra were recorded at room temperature on a Bruker DRX 360 instrument and well-established solvent peaks were taken as the internal standard. High-resolution electrospray ionization mass spectra (HR ESI-MS) were recorded on a Bruker maXis II MicroTOF-Q type Qq-TOF-MS instrument, controlled by Compass Data Analysis 4.4 software from Bruker. CHN elemental analysis was done using Elementar Vario Micro microanalyzer, solid-state single crystals were examined by Bruker D8 Venture diffractometer (SCXRD) and data processing managed by Olex^2 software [115] including SHELXT program [116] and the molecular images established by Mercury CSD-4.3.0 software [117]. The MALDI-TOF MS

measurements were done using Bruker Autoflex Speed MALDI-TOF instrument. Gas chromatographic measurements were done with the use of an Agilent Technologies 7890 A instrument (HP-5, 0.25µm x 30 m x 0.32 mm, FID 300 °C; carrier gas: nitrogen 1.9 mL/min). The GPC was recorded in Waters 2695 separator module with UltraStyroGel, HR1-2-3-4 column and THF as eluent.

Reactions in ball mill were carried out utilizing a planetary milling instrument model 'RETSCH PM 100' with stainless steel jar (12.5 mL) and G100 ball bearings (Ø 5 mm and Ø 8 mm) at room temperature (fig. 3a).

Fig. 3a: Ball mill and milling jar with stainless steel balls.

In the following section, for our convenience, the di-NHC precursors are numbered as **1**, **2** and the metal complexes as **3**.

3.2. Synthesis of di-NHC ligand precursors
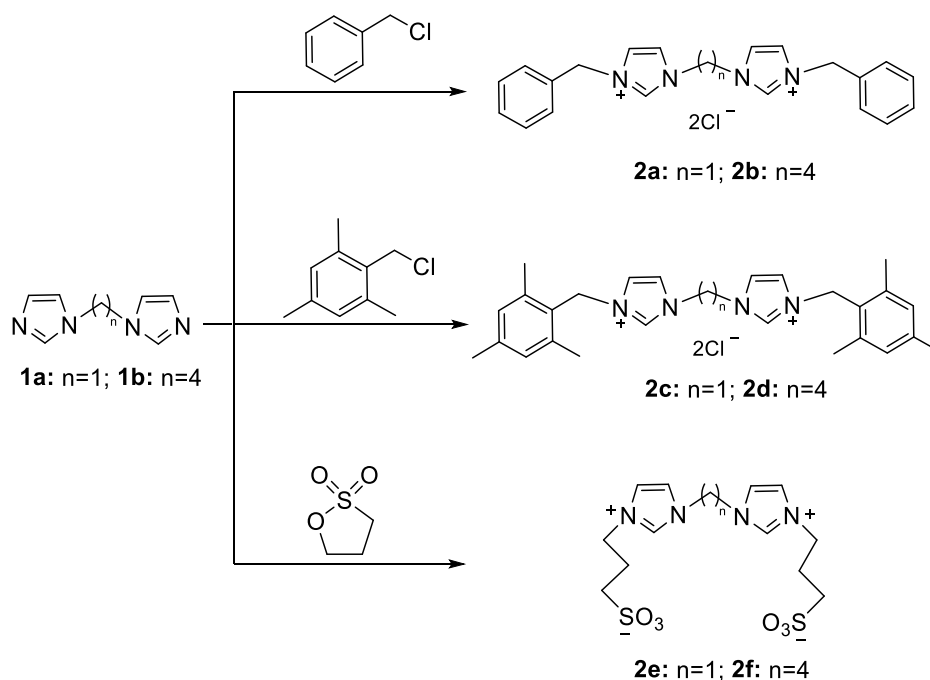
Scheme 3a: Synthesis of the di-NHCs (**2a-f**)

3.2.1. 1,1'-methylene-bis(3-benzyl-imidazolium)dichloride (2a) and 1,1'-(butane-1,4-diyl)bis(3-benzyl-imidazolium)dichloride (2b)

Both the compounds (**2a** and **2b**) are known from the literature [118,119], however, in our study, we have prepared them in a more straightforward and convenient way. The actual analytical data presented refer to the products of the solution synthesis method.

Classical solvent method

A mixture of **1a** (100 mg, 0.675 mmol) or **1b** (100 mg, 0.526 mmol) and benzyl chloride (for **1a**: 155 µL, 1.35 mmol; for **1b**: 121 µL, 1.052 mmol) was dissolved in dry CH$_3$CN (5 mL) in a dry Schlenk tube and stirred overnight at

reflux temperature until the appearance of white precipitation. The resulting hot solution was then filtered and the precipitate was washed twice with 5 mL cold CH_3CN, once with 5 mL acetone, respectively, and then dried under vacuum. The obtained yield was 78% for **2a** (211 mg) and 76% for **2b** (177 mg). White powders.

Mechanochemical method

A dry 12.5 mL ball milling jar was charged with 10 Ø 5 mm and 10 Ø 8 mm stainless steel balls, **1a** (100 mg, 0.675 mmol) or **1b** (100 mg, 0.525 mmol) and benzyl chloride (for **1a**: 155 µL, 1.35 mmol; for **1b**: 121 µL, 1.052 mmol) were milled over a period of 90 cycles (1 cycle= 2 min milling + 2 min pause) at 550 rpm. Afterwards, the jar and the bearing balls were washed twice with 5 mL methanol and the resulting solution was filtered through hyflo supercel. Evaporation of methanol yielded **2a** (74%, 199 mg) or **2b** (71%, 165 mg) as a white powders.

2a: $^{13}C\{^{1}H\}$ NMR (90 MHz, MeOD), δ/ppm: 139.26 (NCN_{imid}), 134.50 ($C_{Ar-ipso}$), 130.70 ($CH_{Ar-meta}$), 130.59 ($CH_{Ar-ortho}$), 130.20 ($CH_{Ar-para}$), 124.85 (CH_{imid}), 123.93 (CH_{imid}), 60.17 (NCH_2N_{bridge}), 54.84 ($ArCH_2N$).
^{1}H NMR (360 MHz, MeOD), δ/ppm: 9.46 (s, 2H, NCHN), 7.88 (s, 2H, CH_{imid}), 7.64 (s, 2H, CH_{imid}), 7.32-7.36 (m, 10H, CH_{Ar}), 6.62 (s, 2H, NCH_2N), 5.37 (s, 4H, $ArCH_2N$).
HRMS(ESI), m/z for [M-2Cl]: Calculated: 165.0917, Found: 165.0917.
2b: $^{13}C\{^{1}H\}$ NMR (90 MHz, MeOD), δ/ppm: 137.56 (NCN_{imid}), 135.30 ($C_{Ar-ipso}$), 130.58 ($CH_{Ar-meta}$), 130.3 ($CH_{Ar-ortho}$), 129.85 ($CH_{Ar-para}$), 124.21 (CH_{imid}), 124.06 (CH_{imid}), 54.42 ($ArCH_2N$), 50.30 (CH_2-butane bridge), 27.97 (CH_2-butane bridge).

^{1}H NMR (360 MHz, MeOD), δ/ppm: 9.12 (s, 2H, NCHN), 7.53-7.59 (d, 4H, CH_{imid}), 7.30-7.33 (m, 10H, CH_{Ar}), 5.33 (s, 4H, $ArCH_2N$), 4.19 (s, 4H, CH_2-butane bridge), 1.83 (s, 4H, CH_2-butane bridge).

HRMS(ESI), m/z for [M-Cl]: Calculated: 407.1997, Found: 407.1992.

3.2.2. *1,1'-methylene-bis(3-(2,4,6-trimethylbenzyl)imidazolium)dichloride (2c) and 1,1'-(butane-1,4-diyl)bis(3-(2,4,6-trimethylbenzyl) imidazolium)dichloride (2d)*

2d is known from the literature, however, was synthesized as a part of a rotaxane and with diiodide as counter anion [120]. In our study, we have synthesized **2c** and **2d** as azolium salts and the method of synthesis in the solvent method is straightforward and simple. The actual analytical data presented refer to the products of the solution synthesis method.

Classical solvent method

A mixture of **1a** (100 mg, 0.675 mmol) or **1b** (100 mg, 0.526 mmol) and α^2-chloroisodurene (for **1a**: 228 mg, 1.35 mmol; for **1b**: 177 mg, 1.052 mmol) were dissolved in dry CH_3CN (5 mL) in a dry Schlenk tube and stirred overnight under reflux until the appearance of a white precipitation. The resulting hot solution was then filtered and the precipitate was washed with 2×5 mL CH_3CN, once with 5 mL acetone respectively and dried under vacuum. White powders. Yield: 70 % for **2c** (228 mg) and 86% for **2d** (238 mg).

Mechanochemical method

A dry 12.5 mL ball milling jar was charged with 10 Ø 5 mm and 10 Ø 8 mm stainless steel balls, **1a** (100 mg, 0.675 mmol) or **1b** (100 mg, 0.526 mmol) and α^2-chloroisodurene (for **1a**: 228 mg, 1.35 mmol; for **1b**: 177 mg, 1.052 mmol) were milled over a period of 90 cycles (1 cycle= 2 min milling + 2 min pause) at 550 rpm. Afterwards, the jar and the bearing balls were washed with

2×5 mL methanol and the resulting solution was filtered through hyflo supercel. Evaporation of methanol yielded **2c** (68%, 222 mg) or **2d** (78%, 216 mg) as a white powders.

2c: $^{13}C\{^1H\}$ NMR (90 MHz, MeOD), δ/ppm: 141.59 (NCN$_{imid}$), 139.82 (C$_{Ar\text{-}ipso}$), 131.10 (CH$_{Ar\text{-}meta}$), 126.73 (C$_{Ar\text{-}para}$), 124.57 (C$_{Ar\text{-}ortho}$),121.13 (CH$_{imid}$), 120.61 (CH$_{imid}$), 59.02 (NCH$_2$N$_{bridge}$), 49.84 (ArCH$_2$N), 21.25 (CH$_3$), 19.81 (CH$_3$).

^1H NMR (360 MHz, MeOD), δ/ppm: 9.15 (s, 2H, NCHN), 7.92 (s, 2H, CH$_{imid}$) 7.50 (s, 2H, CH$_{imid}$), 6.94 (s, 4H, CH$_{Ar}$), 6.59 (s, 2H, NCH$_2$N), 5.45 (s, 4H, ArCH$_2$N), 2.24 (s, 18H, CH$_3$).

HRMS(ESI), m/z for [M-2Cl-H]: Calculated: 413.2700, Found: 413.2700

Anal. Calc. for C$_{27}$H$_{34}$N$_4$Cl$_2$ × 4.5H$_2$O: C, 57.24; H, 7.65; N, 9.89. Found: C, 57.38; H, 6.89; N, 11.56.

2d: $^{13}C\{^1H\}$ NMR (90 MHz, MeOD), δ/ppm: 141.47 (NCN$_{imid}$), 139.88 (C$_{Ar\text{-}ipso}$), 137.28 (CH$_{Ar\text{-}meta}$), 131.26 (C$_{Ar\text{-}para}$), 127.53 (C$_{Ar\text{-}ortho}$), 124.33 (CH$_{imid}$), 123.90 (CH$_{imid}$), 50.47 (CH$_2$-butane bridge), 48.67 (ArCH$_2$N), 28.35 (CH$_2$-butane bridge), 21.50 (CH$_3$), 20.07 (CH$_3$).

^1H NMR (360 MHz, MeOD), δ/ppm: 8.73 (s, 2H, NCHN), 7.57 (s, 2H, CH$_{imid}$) 7.30 (s, 2H, CH$_{imid}$), 6.87 (s, 4H, CH$_{Ar}$), 5.34 (s, 4H, ArCH$_2$N), 4.14 (s, 4H, CH$_2$-butane bridge), 2.17 (s, 18H, CH$_3$), 1.77 (s, 4H, CH$_2$-butane bridge).

HRMS(ESI), m/z for [M-Cl]: Calculated: 491.2936, Found: 491.2935.

Anal. Calc. for C$_{30}$H$_{40}$N$_4$Cl$_2$ × 4.5H$_2$O: C, 59.20; H, 8.11; N, 9.21. Found: C, 59.27; H, 8.05; N, 9.41.

X-ray quality crystals of **2d** were obtained from methanolic solution layered with diethyl ether. Details can be found in the Results and Discussion chapter.

3.2.3. *3,3'-(1,1'-methylenebis(1H-imidazole-3-ium-3,1-diyl))bis(propane-1-sulfonate) (2e) and 3,3'-(1,1'-(butane-1,4-diyl)bis(1H-imidazole-3-ium-3,1-diyl))bis(propane-1-sulfonate) (2f)*

Both the zwitterionic azolium salts are known [60,66,121] and the synthesis were performed following the procedure by Papini et al. [66]. 2 mmol of **1a**/**1b** was reacted with 4.4 mmol of 1,3-propansultone in 30 mL acetone for 5 days at room temperature. Next, the solvent was removed and the white solid was recrystallized from methanol. Yield 68% for **2e** (533 mg), 71% for **2f** (617 mg).

2e: $^{13}C\{^1H\}$ NMR (90 MHz, D_2O), δ/ppm: 137.2 (NCN$_{imid}$), 123.8 (CH$_{imid}$), 122.3 (CH$_{imid}$), 59.0 (CH$_2$), 48.6 (CH$_2$), 47.2 (CH$_2$), 24.8 (CH$_2$).

^1H NMR (360 MHz, D_2O), δ/ppm: 9.20 (s, 2H, NCHN), 7.68 (d, 2H, CH$_{imid}$), 7.49 (d, 2H, CH$_{imid}$), 6.55 (s, 2H, CH$_2$), 4.33 (m, 4H, CH$_2$), 2.82 (m, 4H, CH$_2$), 2.24 (m, 4H, CH$_2$).

HRMS(ESI), m/z for [M-H]: Calculated: 391.071, Found: 391.075.

2f: $^{13}C\{^1H\}$ NMR (90 MHz, D_2O), δ/ppm: 135.6 (NCN$_{imid}$), 122.5 (CH$_{imid}$), 122.4 (CH$_{imid}$), 48.8 (CH$_2$), 47.9 (CH$_2$), 47.1 (CH$_2$), 26.1 (CH$_2$), 24.9 (CH$_2$).

^1H NMR (360 MHz, D_2O), δ/ppm: 8.82 (s, 2H, NCHN), 7.53 (s, 2H, CH$_{imid}$), 7.46 (s, 2H, CH$_{imid}$), 4.33 (m, 4H, CH$_2$), 4.21 (m, 4H, CH$_2$), 2.85 (m, 4H, CH$_2$), 2.25 (m, 4H, CH$_2$), 1.86 (m, 4H, CH$_2$).

HRMS(ESI), m/z for [M+H]: Calculated: 435.1359, Found: 435.1367.

X-ray quality crystals of **2f** were obtained by slow cooling of its hot dimethylformamide solution. Details can be found in the Results and Discussion chapter.

3.3. Synthesis of Rh-NHC complexes

3.3.1. Bridging di-nuclear Rh(I) complexes of 2a-d (3a-d)

2a: n=1; **2b:** n=4

3a: n=1; **3b:** n=4

2c: n=1; **2d:** n=4

3c: n=1; **3d:** n=4
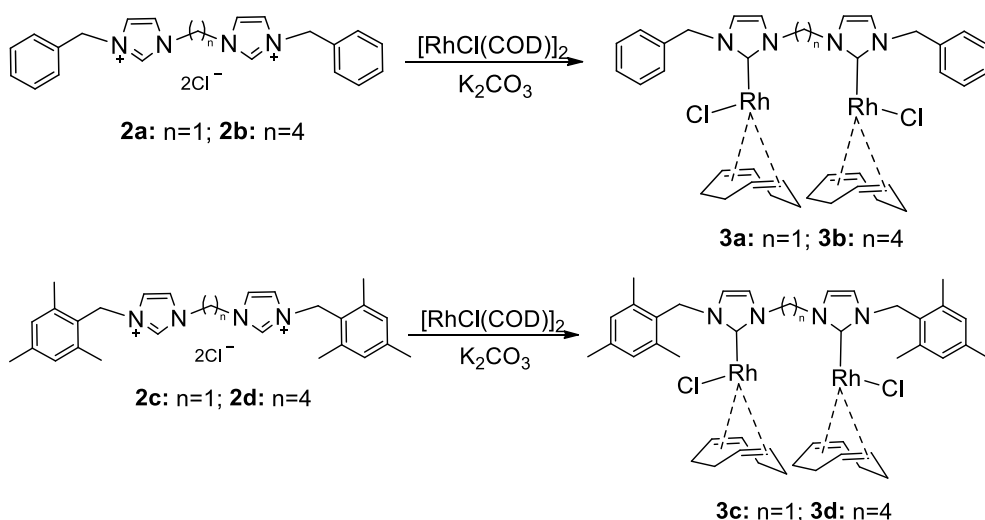
Scheme 3b: Synthesis of metal complexes **3a-d**

Classical solvent method

150 mg of **2a** (0.374 mmol) or **2b** (0.338 mmol) or **2c** (0.309 mmol) or **2d** (0.284 mmol) was dissolved in 10 mL of toluene in a Schlenk tube under inert atmosphere followed by the addition of [RhCl(COD)]$_2$ (for **2a**: 184 mg, 0.374 mmol; for **2b**: 167 mg, 0.338 mmol; for **2c**: 152 mg, 0.309 mmol; for **2d**: 140 mg, 0.284 mmol) and dry K$_2$CO$_3$ (for **2a**: 517 mg, 3.74 mmol; for **2b**: 467 mg, 3.38 mmol; for **2c**: 427 mg, 3.09 mmol; for **2d**: 392 mg, 2.84 mmol) in one portion. The solution was next stirred overnight at 80 °C and the course of the reaction was checked using TLC. The resulting solution was then filtered, washed twice with 5 mL toluene and the filtrate was collected. Next, the solvent was removed, the solid was purified using silica gel column chromatography with CH$_2$Cl$_2$ and EtOAc mixture (1:1) as eluent and dried

under vacuum. Yellow powders. Yield 80% for **3a** (245 mg), 77% for **3b** (224 mg), 51% for **3c** (143 mg) and 65% for **3d** (174 mg).

Mechanochemical method

A dry 12.5 mL ball milling jar was charged with 10 Ø 5 mm and 10 Ø 8 mm stainless steel balls, 150 mg of **2a** (0.374 mmol) or **2b** (0.338 mmol) or **2c** (0.309 mmol) or **2d** (0.284 mmol), [RhCl(COD)]$_2$ (for **2a**: 184 mg, 0.374 mmol; for **2b**: 167 mg, 0.338 mmol; for **2c**: 152 mg, 0.309 mmol; for **2d**: 140 mg, 0.284 mmol) and dry K$_2$CO$_3$ (for **2a**: 517 mg, 3.74 mmol; for **2b**: 467 mg, 3.38 mmol; for **2c**: 427 mg, 3.09 mmol; for **2d**: 392 mg, 2.84 mmol) were milled over a period of 45 cycles (1 cycle= 2 min milling + 2 min pause) at 550 rpm. Afterwards, the jar and the bearing balls were washed twice with 5 mL dichloromethane and the resulting solution was filtered. Next, the filtrate was collected, purification of the mixture was done using silica gel column chromatography with CH$_2$Cl$_2$ and EtOAc mixture (1:1) as eluent and dried under vacuum. Yellow powders. Yield 71%, for **3a** (218 mg), 74% for **3b** (215 mg), 58% for **3c** (162 mg) and 69% for **3d** (185 mg).

The actual analytical data presented underneath refer to the products of the solution synthesis method.

3a: ^{13}C{^{1}H} NMR (90 MHz, CD$_2$Cl$_2$), δ/ppm: 184.74 (d, *J*= 54.82 Hz , NCN$_{imid}$), 136.94 (C$_{Ar-ipso}$), 129.34 (CH$_{Ar-meta}$), 128.65 (CH$_{Ar-ortho}$), 128.56 (CH$_{Ar-para}$), 122.60 (CH$_{imid}$), 122.04 (CH$_{imid}$), 100.42 (d, *J*= 7.75Hz, COD-CH$_{vinyl}$), 99.75 (d, *J*= 7.75 Hz, COD-CH$_{vinyl}$), 70.28 (d, *J*= 13.34 Hz, COD-CH$_{vinyl}$), 69.19 (d, *J*= 13.33 Hz, COD-CH$_{vinyl}$), 63.84 (NCH$_2$N$_{bridge}$), 55.11 (ArCH$_2$N), 34.17 (COD-CH$_{allyl}$), 32.71 (COD-CH$_{allyl}$), 29.76 (COD-CH$_{allyl}$), 28.94 (COD-CH$_{allyl}$).

^{1}H NMR (360 MHz, CD$_2$Cl$_2$), δ/ppm: 7.96 (s, 2H, CH$_{imid}$), 7.54 (s, 2H, CH$_{imid}$), 7.34-7.37 (m, 10H, CH$_{Ar}$), 6.71 (s, 2H, NCH$_2$N), 5.95-5.99 (m, 2H,

COD-CH), 5.62-5.66 (m, 2H, COD-CH), 4.96-5.07 (m, 4H, COD-CH), 2.11 (s, 4H, ArCH$_2$N), 1.95-2.36 (m, 16H, COD-CH$_2$).

HRMS(ESI), m/z for [M-Cl]: Calculated: 785.1359, Found: 785.1357.

Anal. Calc. for C$_{37}$H$_{44}$N$_4$Cl$_2$Rh$_2$: C, 54.10; H, 5.40; N, 6.82. Found: C, 54.22; H, 5.55; N, 6.76.

X-ray quality crystals of **3a** were obtained from the benzene solution layered with diethyl ether. Details can be found in the Results and Discussion chapter.

3b: ^{13}C{^{1}H} NMR (90 MHz, CD$_2$Cl$_2$), δ/ppm: 183.33 (d, *J*= 54.68 Hz , NCN$_{imid}$), 182.85 (d, *J*= 50.58 Hz , NCN$_{imid}$), 137.49 (C$_{Ar-ipso}$),129.29 (CH$_{Ar-meta}$), 128.96 (CH$_{Ar-ortho}$), 128.55 (CH$_{Ar-para}$), 121.88 (CH$_{imid}$), 120.94 (CH$_{imid}$), 98.83 (d, *J*= 6.51 Hz, COD-CH$_{vinyl}$), 98.55 (d, *J*= 6.66 Hz, COD-CH$_{vinyl}$), 69.20 (d, *J*= 13.81 Hz, COD-CH$_{vinyl}$), 68.52 (d, *J*= 13.57 Hz, COD-CH$_{vinyl}$), 55.09 (ArCH$_2$N), 50.85 (CH$_2$-butane bridge), 33.46 (COD-CH$_{allyl}$), 30.25 (COD-CH$_{allyl}$), 29.62 (COD-CH$_{allyl}$), 29.28 (COD-CH$_{allyl}$), 28.11 (CH$_2$-butane bridge)

^{1}H NMR (360 MHz, CD$_2$Cl$_2$), δ/ppm: 7.33-7.41 (m, 14H, CH$_{imid}$ and CH$_{Ar}$), 5.94-5.98 (m, 2H, COD-CH), 5.51-5.65 (m, 2H, COD-CH), 4.94 (s, 4H, ArCH$_2$N), 4.78-4.88 (m, 2H, COD-CH), 4.27-4.41 (m, 2H, COD-CH), 3.29 (s, 4H, CH$_2$-butane bridge), 2.12 (s, 4H, CH$_2$-butane bridge), 1.94-2.29 (m, 16H, COD-CH$_2$).

HRMS(ESI), m/z for [M-Cl]: Calculated: 827.1829, Found: 827.1828.

Anal. Calc. for C$_{40}$H$_{50}$N$_4$Cl$_2$Rh$_2 \times 0.5$H$_2$O: C, 55.06; H, 5.89; N, 6.42. Found: C, 55.26; H, 5.81; N, 6.30.

Single crystals of **3b** were obtained from the benzene solution layered with diethyl ether and subjected to X-ray diffraction analysis. Details can be found in the Results and Discussion chapter.

3c: $^{13}C\{^1H\}$ NMR (90 MHz, CD_2Cl_2), δ/ppm: 183.94 (d, J= 51.86 Hz , NCN_{imid}), 139.13 ($C_{Ar-ipso}$), 138.89 ($CH_{Ar-meta}$), 129.84 ($C_{Ar-para}$), 128.49 ($C_{Ar-ortho}$), 121.08 (CH_{imid}), 120.65 (CH_{imid}), 100.04 (d, J= 7.31 Hz, COD-CH_{vinyl}), 99.52 (d, J= 7.00 Hz, COD-CH_{vinyl}), 70.22 (d, J= 13.81 Hz, COD-CH_{vinyl}), 68.32 (d, J= 13.96 Hz, COD-CH_{vinyl}), 64.41 (NCH_2N_{bridge}), 49.26 ($ArCH_2N$), 34.11 (COD-CH_{allyl}), 32.93 (COD-CH_{allyl}), 29.70 (COD-CH_{allyl}), 29.00 (COD-CH_{allyl}), 21.25 (CH_3), 20.32 (CH_3).

^1H NMR (360 MHz, CD_2Cl_2), δ/ppm: 7.75 (s, 2H, CH_{imid}), 7.51 (s, 2H, CH_{imid}), 6.92 (s, 4H, CH_{Ar}), 6.20 (s, 2H, NCH_2N), 5.81-5.85 (m, 2H, COD-CH), 5.43-5.49 (m, 2H, COD-CH), 4.96-5.08 (m, 4H, COD-CH), 3.50 (s, 4H, $ArCH_2N$), 2.45-2.52 (m, 4H, COD-CH_2), 2.34-2.37 (m, 2H, COD-CH_2), 2.25 (s, 18H, CH_3), 1.96-2.14 (m, 10H, COD-CH_2).

HRMS(ESI), m/z for [M-Cl]: Calculated: 869.2298, Found: 869.2303.

Anal. Calc. for $C_{43}H_{56}N_4Cl_2Rh_2 \times 4.5H_2O$: C, 52.34; H, 6.64; N, 5.68. Found: C, 52.10; H, 5.64; N, 5.74.

3d: $^{13}C\{^1H\}$ NMR (90 MHz, CD_2Cl_2), δ/ppm: 182.39 (d, J= 50.67 Hz , NCN_{imid}), 182.16 (d, J= 49.19 Hz , NCN_{imid}), 138.99 ($C_{Ar-ipso}$), 129.76 ($CH_{Ar-meta}$), 128.92 ($C_{Ar-para}$), 120.50 ($C_{Ar-ortho}$), 119.50 (CH_{imid}), 119.41 (CH_{imid}), 98.45 (d, J= 7.89 Hz, COD-CH_{vinyl}), 98.34 (d, J= 6.10 Hz, COD-CH_{vinyl}), 68.46 (d, J= 12.48 Hz, COD-CH_{vinyl}), 68.34 (d, J= 12.39 Hz, COD-CH_{vinyl}), 50.98 (CH_2-butane bridge), 49.24 ($ArCH_2N$), 33.84 (COD-CH_{allyl}), 33.32 (COD-CH_{allyl}), 29.70 (COD-CH_{allyl}), 29.16 (COD-CH_{allyl}), 28.32, 21.30 (CH_3), 20.30 (CH_3).

^1H NMR (360 MHz, CD_2Cl_2), δ/ppm: 6.87-6.93 (m, 8H, CH_{imid} and CH_{Ar}), 5.79-5.86 (m, 2H, COD-CH), 5.41-5.46 (m, 2H, COD-CH), 4.93 (s, 4H, CH_{Ar}), 4.73-4.84 (m, 2H, COD-CH), 4.29-4.38 (m, 2H, COD-CH), 3.49 (s, 4H, CH_2-butane bridge), 2.24-2.37 (m, 16H, COD-CH_2), 2.12 (s, 18H, CH_3), 1.96 (s, 4H, CH_2-butane bridge).
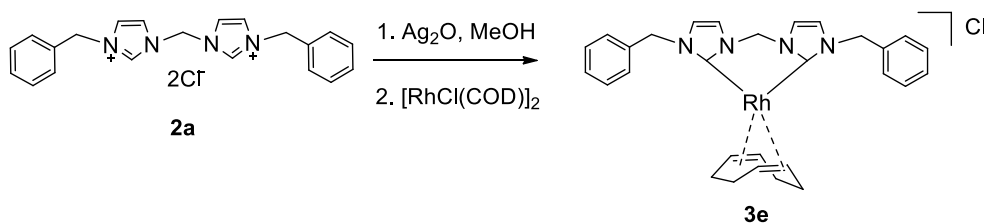
HRMS(ESI), m/z for [M-Cl]: Calculated: 911.2768, Found: 911.2751.

Anal. Calc. for $C_{46}H_{62}N_4Cl_2Rh_2 \times 0.5H_2O$: C, 57.75; H, 6.64; N, 5.86. Found: C, 57.61; H, 6.54; N, 5.68.

Single crystals of **3d** were obtained by slow evaporation of its solution in dichloromethane and subjected to X-ray diffraction analysis. Details can be found in the Results and Discussion chapter.

3.3.2. Chelating Rh(I) complex of 2a (3e)

Scheme 3c: Synthesis of metal complex **3e**

A mixture of 100 mg of ligand **2a** (0.25 mmol) and 128 mg of Ag_2O (0.55 mmol) in 2 mL methanol was taken into a dry Schlenk tube under an inert atmosphere. The whole mixture was then stirred at reflux temperature for 2 h in the dark and filtered through hyflo supercel pad.

The filtrate was collected and reacted with 61 mg of $[RhCl(COD)]_2$ (0.125 mmol) under inert atmosphere at room temperature for 15 h. The yellow liquid was evaporated in vacuum to get solid complex **3e**, which was stored under inert atmosphere. Yellow powder. Yield 42% (60 mg).

$^{13}C\{^1H\}$ NMR (90 MHz, CD_2Cl_2), δ/ppm: 181.6 (d, J= 50.1 Hz , NCN_{imid}), 136.0 ($C_{Ar-ipso}$), 129.0 ($CH_{Ar-meta}$), 128.4 ($CH_{Ar-ortho}$), 127.1 ($CH_{Ar-para}$), 121.9 (CH_{imid}), 121.1 (CH_{imid}), 92.45 (d, $COD-CH_{vinyl}$), 87.19 (d, $COD-CH_{vinyl}$), 63.6 (NCH_2N_{bridge}), 54.0 ($COD-CH_{allyl}$), 30.5 ($COD-CH_{allyl}$).
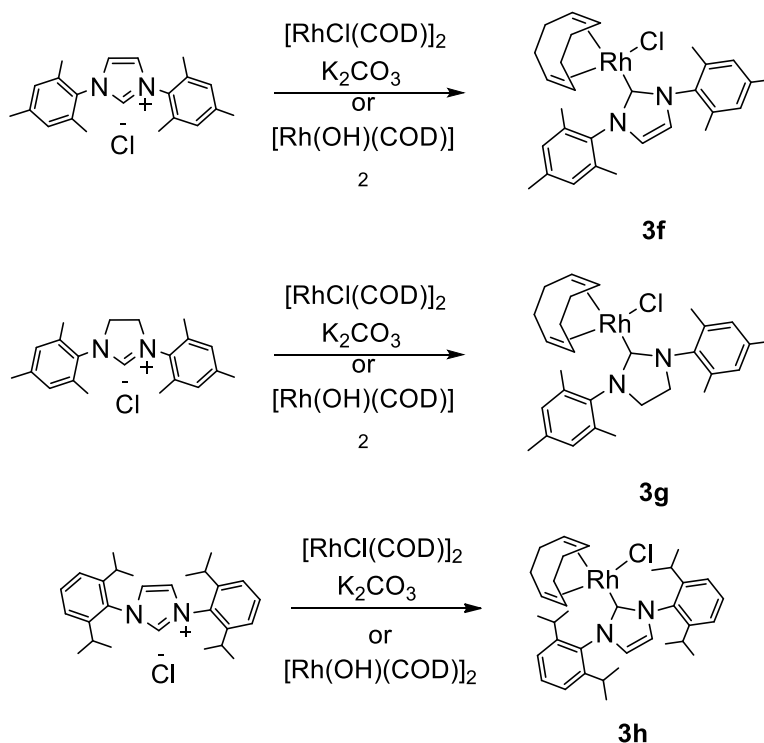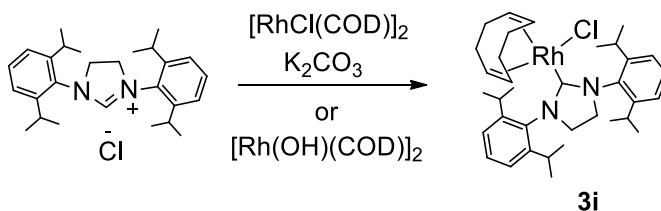
Scheme 3d: Synthesis of metal complexes **3f-i**

Method A

0.88 mmol of the corresponding imidazolium/imidazolinium salt was dissolved in 30 mL of toluene, followed by the addition of 0.44 mmol of [RhCl(COD)]$_2$ (220 mg) and 8.88 mmol of K$_2$CO$_3$ (1.228 g) in one portion. The whole mixture was then stirred at 70 °C for 3-24 h and the course of the reaction was followed by TLC. Finally, the solvent was removed, purification of the product was performed using column chromatography with dichloromethane/ethyl acetate (1:1) as eluent and later by evaporation, the final product was collected. Yellow powders. Yield 71% for **3f** (345 mg), 71% for **3g** (350 mg), 88% for **3h** (494 mg), 70% for **3i** (400 mg).

Method B

0.88 mmol of the corresponding imidazolium/imidazolinium salt was dissolved in 30 mL of toluene, followed by the addition of 0.44 mmol of [Rh(OH)(COD)]$_2$ (202 mg). The whole mixture was then stirred at 70 °C and the course of the reaction was followed by TLC. Finally, the solvent was removed, purification of the product was performed using column chromatography with dichloromethane/ethyl acetate (1:1) as eluent and later by evaporation, the final product was collected. Yellow powders. Yield 83% for **3f** (399 mg), 88% for **3g** (428 mg), 69% for **3h** (389 mg), 68% for **3i** (386 mg).

3f: $^{13}C\{^1H\}$ NMR (90 MHz, CD_2Cl_2), δ/ppm: 183.2 (d, J = 52.3 Hz, NCN_{imid}), 138.6 ($C_{Ar-para}$), 137.4 ($C_{Ar-ortho}$), 136.5 ($C_{Ar-ipso}$), 134.5 ($CH_{Ar-meta}$), 129.3 (CH_{imid}), 128.3 (CH_{imid}), 123.7 (COD-CH), 95.7 (d, J = 7.2 Hz, COD-CH), 68.1 (d, J = 14.3 Hz, COD-CH), 32.6 (COD-CH), 28.3 (COD-CH), 20.8 (COD-CH), 19.5 (CH_3), 17.9 (CH_3).

^1H NMR (360 MHz, CD_2Cl_2), δ/ppm: 7.12-7.11 (m, 4H, H_{Ar}), 7.04 (s, 2H, NCH), 4.48 (br, 2H, H_{COD}), 3.38 (br, 2H, H_{COD}), 2.46-2.42 (m, 12H, Me), 2.18 (s, 6H, Me), 1.92-1.89 (m, 4H, H_{COD}), 1.63-1.59 (m, 4H, H_{COD}).

HRMS(ESI), m/z for [M-Cl]: Calculated: 515.1928, Found: 515.1928.

3g: $^{13}C\{^1H\}$ NMR (90 MHz, CD_2Cl_2), δ/ppm: 212.4 (d, J= 48.4 Hz, , NCN_{imid}), 138.2 ($C_{Ar-para}$), 137.7 ($CH_{Ar-ortho}$), 136.6 $C_{Ar-ipso}$), 135.4 ($C_{Ar-meta}$), 129.6 (CH_2-imid), 128.5 (CH_2-imid), 96.8 (d, J= 6.4 Hz, COD-CH), 67.8 (d, J= 14.3 Hz, COD-CH), 51.47 (COD-CH), 32.6 (COD-CH), 28.1 (COD-CH), 20.8 (COD-CH), 19.7 (CH_3), 18.2 (CH_3).

^1H NMR (360 MHz, CD_2Cl_2), δ/ppm: 7.09-7.06 (m, 4H, H_{Ar}), 4.43 (br, 2H, H_{COD}), 3.89 (br, 4H, NCH_2), 3.46 (br, 2H, H_{COD}), 2.62 (s, 6H, Me), 2.41-2.38 (m, 12H, Me), 1.85-1.80 (m, 4H, H_{COD}), 1.64-1.55 (m, 4H, H_{COD}).

HRMS(ESI), m/z for [M-Cl]: Calculated: 517.2085, Found: 517.2085.

3h: $^{13}C\{^1H\}$ NMR (90 MHz, $CDCl_3$), δ/ppm: 186.1 (d, J= 52.2 Hz, NCN_{imid}), 147.9 ($C_{Ar-ortho}$), 145.3 ($C_{Ar-ipso}$), 136.4 ($C_{Ar-para}$), 129.8 ($C_{Ar-meta}$), 124.6 (CH_{imid}), 122.9 (CH_{imid}), 96.4 (d, J= 7.2 Hz, COD-CH), 67.8 (d, J= 14.4 Hz, COD-CH), 32.7 (COD-CH), 28.8 (CH_3), 28.3 (COD-CH), 26.6 (CH), 22.8(CH).

^1H NMR (360 MHz, dmso-d6), δ/ppm: 7.62 (s, 2H, NCH), 7.54 (t, J = 7.7 Hz, 2H, H_{Ar}), 7.39 (br, 4H, H_{Ar}), 4.33 (br, 2H, H_{COD}), 3.51 (br, 2H, CH(CH$_3$)$_2$), 3.23 (s, 2H, H_{COD}), 2.35–2.31 (br, 2H, CH(CH$_3$)$_2$), 1.71–1.27 (m, 8H, H_{COD} +12H, CH(CH$_3$)$_2$), 1.06 (d, J = 6.8 Hz, 12H, CH(CH$_3$)$_2$).

HRMS(ESI), m/z for [M-Cl]: Calculated: 599.2867, Found: 599.2867.

X-ray quality crystals of **3h** were obtained from benzene and the details of the X-ray analysis can be found in our published article. [84].

3i: $^{13}C\{^1H\}$ NMR (90 MHz, CD$_2$Cl$_2$), δ/ppm: 214.9 (d, J= 47.7 Hz, NCN$_{imid}$), 149.3 (C$_{Ar-ortho}$), 146.4 (C$_{Ar-ipso}$), 136.9 (C$_{Ar-para}$), 128.8 (C$_{Ar-meta}$), 124.8 (CH$_2$-imid), 123.3 (CH$_2$-imid), 96.4 (d, J= 7.1 Hz, COD-CH), 67.8 (d, J= 13.9 Hz, COD-CH), 53.4 (COD-CH), 32.4 (COD-CH), 28.9 (CH$_3$), 28.6 (COD-CH), 27.9 (COD-CH), 26.6 (CH$_3$), 24.0 (CH), 22.7 (CH).

^{1}H NMR (360 MHz, C$_6$D$_6$), δ/ppm: 7.31-7.24 (m, 4H, H$_{Ar}$), 7.15 (d, J= 6.8 Hz, 2H, H$_{Ar}$), 4.99 (br, 2H, H$_{COD}$), 4.43-3.36 (m, 4H, NCH$_2$), 3.73-3.68 (m, 2H, H$_{COD}$), 3.43-3.39 (m, 2H, CH(CH$_3$)$_2$), 3.10-3.03 (m, 2H, CH(CH$_3$)$_2$), 1.82-1.70 (m, 10H, H$_{COD}$), 1.45-1.18 (m, 18H, CH(CH_3)$_2$), 1.05 (d, J= 6.8 Hz, 6H, CH(CH_3)$_2$).

HRMS(ESI), m/z for [M-Cl]: Calculated: 601.3024, Found: 601.3025.

X-ray quality crystals of **3i** were obtained from benzene and the details of the X-ray analysis can be found in our published article. [84].
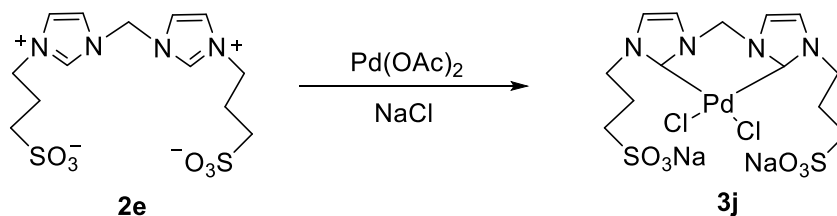
3.3.4. *Chelating Pd(II)-NHC complex of 2e (3j)*

Scheme 3e: Synthesis of metal complexes **3j**

Following the procedure of Asensio et al. [64], the chelating complex **3j** was prepared to utilize in Suzuki and Sonogashira coupling reactions. 0.45 mmol (177 mg) of the ligand **2e** was mixed with 0.49 mmol (110 mg) of Pd(OAc)$_2$

and 0.9 mmol (53 mg) of NaCl in 10 mL DMSO and stirred for an hour at 50 °C. For the next one hour, the reaction temperature was increased by 10 °C steps each after every 20 minutes. Finally, the reaction was run at 90 °C for another 1 hour. The whole solution was filtered through hyflow supercel and dry acetone was added to the filtrate till pale yellow precipitation. This solution was filtered and the residue was collected and dried in vacuum. Pale yellow powder. Yield 68%.

$^{13}C\{^1H\}$ NMR (90 MHz, D_2O), δ/ppm: 150.2 (NCN_{imid}), 122.3 (CH_{imid}), 122.2 (CH_{imid}), 62.9 (NCH_2N), 48.7 ($NCH_2CH_2CH_2SO_3$), 47.9 ($NCH_2CH_2CH_2SO_3$), 26.0 ($NCH_2CH_2CH_2SO_3$).

HRMS(ESI), m/z for [M-Na]: Calculated: 588.8983, Found: 588.8988.

3.4. General methods of the catalytic experiments performed

3.4.1. *Polymerization of phenylacetylene*

The polymerization reaction of phenylacetylene (PA) was carried out utilizing the metal complexes **3a** and **3b**. 0.01 mmol of **3a**/**b** were dissolved in 0.65 mL of chloroform. 1 mmol of phenylacetylene (102 mg) was then added and the whole mixture was taken into a NMR tube and the course of the reaction was followed by ^1H NMR for 30 minutes. Yield 99% with **3a**, 94% with **3b** in relation to the starting molar amount of the monomer (phenylacetylene).

Finally, the mixture was treated with excess methanol till the precipitation of polyphenylacetylene (PPA) appeared. The whole solution was then filtered through a P4 glass filter and then dried under vacuum.
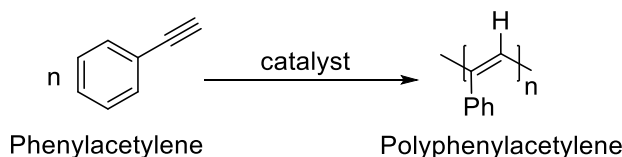
Scheme 3f: Polymerization reaction of phenylacetylene.

3.4.2. Selective hydration reaction of benzonitrile

Metal complexes **3f-i** were applied as catalysts for the hydration reaction of benzonitrile to benzamide. All the reactions were carried out in open-air conditions and the reaction temperature was kept fixed throughout the reaction using a thermostat. The identification of the product was done by comparing their retention time with known standard compounds.
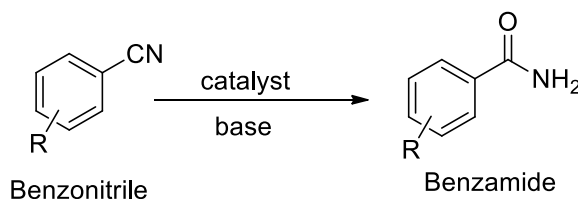
Scheme 3g: Selective hydration of benzonitrile

Hydration of benzonitrile without the isolation of the product

1 mmol of benzonitrile (100 µL), 0.01 mmol of **3f** (5.5 mg), 0.01 mmol of NaOH (0.4 mg) and 0.1 mmol of naphthalene (12.8 mg) (used as internal standard) were dissolved in 3 mL water/2-propanol (1:1) mixture and stirred at 80 °C for 2 h. Next, 100 µL of the resulting hot solution was extracted with dichloromethane (2 mL), passed through a $MgSO_4$ column and subjected to gas chromatography. Yield 98%.

Hydration of benzonitrile with the isolation of the product

2 mmol of benzonitrile (200 µL), 0.02 mmol of **3f** (11 mg) and 0.02 mmol of NaOH (0.8 mg) were dissolved in 3 mL water/2-propanol (1:1) mixture and stirred at 80 °C for 3 h. The resulting solution was then dried under vacuum and the residue was subjected to silica gel column chromatography using ethyl acetate as eluent. Yield 89% (217.3 mg).

4. Results and discussion

4.1. General discussion about the synthetic procedure

To prepare the $(-CH_2-)_n$ bridged (n=1,4) substituted di-imidazole ligand precursors (**2a-f**), the corresponding unsubstituted di-imidazoles (**1a, b**) were first synthesized following the literature [113,114]. Next, to prepare **2a-f**, the di-imidazoles (**1a, b**) were reacted with the corresponding chlorides (in case of **2a-d**) or 1,3-propansultone (in case of **2e-f**) in 1:2 ratio as depicted in scheme 3a (Experimental Section). All the bridging di-nuclear Rhodium(I) complexes (**3a-d**) were prepared by reacting the di-imidazolium chloride salts with $[RhCl(COD)]_2$ and K_2CO_3 in 1:1:10 ratio (scheme 3b). The chelating Rh(I)-di(NHC) complex **3e** was synthesized by transmetallating the corresponding silver-NHC complex with $[Rh(COD)Cl]_2$ (scheme 3c). The other four Rh(I)-mono(NHC) complexes **3f-i** were prepared by reacting the corresponding imidazolium/imidazolinium salt with $[RhCl(COD)]_2$ or $[Rh(OH)(COD)]_2$ in 2:1 ratio (scheme 3d). All the prepared Rh(I)-NHC complexes (**3a-i**) were purified using column chromatography on silica gel with dichloromethane/ethyl acetate (1:1) as eluent. Finally, the products were isolated by evaporation of the eluent to dryness.

4.2. Stirring or milling

The azolium salts **2a-d** and metal complexes **3a-d** were synthesized both via traditional solvent method of stirring and mechanical method using ball mill and the results were compared to see which method is better for synthesis.

Initially, the influence of ball milling conditions like milling time, frequency of milling and size of bearing balls were investigated (table 4.1 and 4.2). To do so, a milling cycle of 2 minutes milling, followed by another 2 minutes pause to avoid the overheating, was used. **2b** (table 4.1) was taken as reference, 10 Ø 5 mm bearing balls were employed to check the effects of frequency and milling time. The yield was found to be increased with the raise of frequency (table 4.1, entries 2, 4) and it intended to remain more or less the same with longer milling time (table 4.1, entries 2, 3). Next, the effect of stainless-steel bearing balls was examined and the experiment revealed that the amount and the size of balls influenced significantly the yield (table 4.1, entries 4-8). It was finally found out that the mixture of 10 Ø 5 mm and 10 Ø 10 mm balls yielded the best after 90 cycles at 550 rpm frequency (table 4.1, entry 8). In case of the metal complexes, **3b** was taken as a reference (table 4.2) with 10 Ø 5 mm and 10 Ø 10 mm balls and the best yield was observed after 45 cycles at 550 rpm frequency (table 4.2, entry 4).

Table 4.1: Optimization of milling conditions for the synthesis of ligand **2b**[a].

Entry	Diameter of balls (mm)	Number of balls	Frequency (rpm)	Cycles[b]	Yield (%)[c]
1	5	10	350	45	42
2	5	10	350	90	58
3	5	10	350	135	59
4	5	10	550	90	65

5	5	20	550	90	68
6	8	10	550	90	67
7	8	20	550	90	70
8	5 +8	10 + 10	550	90	71

[a]Synthesis was performed with 0.526 mmol of **1b** and 1.05 mmol of benzyl chloride in air. [b]1 cycle= 2 min milling + 2 min pause. [c]Isolated yield.

Table 4.2: Optimization of milling conditions for the synthesis of metal complex **3b**[a].

Entry	Diameter of balls (mm)	Number of balls	Frequency (rpm)	Cycles[b]	Yield (%)[c]
1	5 + 8	10 + 10	350	45	69
2	5 + 8	10 + 10	350	90	71
3	5 + 8	10 + 10	350	135	72
4	5 + 8	10 + 10	550	45	74

[a]Synthesis was performed with 0.338 mmol of **2b**, 0.338 mmol of $[Rh(COD)Cl]_2$ and 3.38 mmol of K_2CO_3 in air. [b]1 cycle= 2 min milling + 2 min pause. [c]Isolated yield.

As the volume of the milling jar was fixed (12 mL), the influence of the amount of starting material for the preparation of **2b** and metal complex **3b** was examined (table 4.3 and 4.4). It was observed that 100 mg of **1b** and 150 mg of **2b** as reactant yielded the best (table 4.3, entry 2; table 4.4, entry 3). The drop of yield in the cases of increasing reactant amount might be due to inefficient mixing (table 4.3, entries 3,4; table 4.4, entry 4).

Table 4.3: Effect of the reactant amount for the formation of ligand **2b**[a].

Entry	Amount of **1b** (mg)	Yield (%)[b]
1	50	58
2	100	71
3	150	68
4	200	62

[a]Reactions were performed with **1b** and benzyl chloride (2 mol equivalent), ball mill, 550 rpm 90 cycles. [b] Isolated yield.

Table 4.4: Effect of the reactant amount for the formation of metal complex **3b**[a].

Entry	Amount of **2b** (mg)	Yield (%)[b]
1	50	61
2	100	67
3	150	74
4	200	70

[a]Reactions were performed with **2b**, [Rh(COD)Cl]$_2$ (1 mol equivalent) and K$_2$CO$_3$ (10 mol equivalent), ball mill, 550 rpm 90 cycles. [b] Isolated yield.

In addition, the influence of the support of milling aids like silica, hyflo supercel, alumina and quartz were also investigated. However, no positive influence was observed.

Results and discussion

In the case of synthesis in solution, the impact of reaction time and temperature were initially checked for the preparation of ligand **2b** and metal complex **3b** taking as references (table 4.5 and 4.6). The result depicted that overnight reactions at high temperature (80 °C to reflux temperature) (table 4.5, entry 4; table 4.6, entries 4) provided the best yields. To compare the mechanochemical method with the classical solvent approach, the synthesis of ligand **2b** and metal complex **3b** were carried out maintaining reaction time the same i.e. 6h for the preparation of ligand (table 4.1, entry 8 vs table 4.5, entry 3) and 3h for metal complexes (table 4.2, entry 4 vs table 4.6, entry 3). The comparison study clearly shows the formation of higher yield (up to four times in the case of the metal complex) in ball mill synthesis.

Table 4.5: Effect of the reaction temperature and time for the synthesis of ligand **2b**[a].

Entry	Temperature (°C)	Time (h)	Yield (%)[b]
1	room temperature	6	0
2	50	6	6
3	reflux temperature	6	49
4	reflux temperature	overnight	76

[a] Reaction was performed in 5 mL acetonitrile with 0.526 mmol of **1b** and 1.05 mmol of benzyl chloride. [b] Isolated yield.

Table 4.6: Effect of the reaction temperature and time for the synthesis of metal complex **3b**.

Entry	Temperature (°C)	Time (h)	Yield (%)
1	room temperature	3	0
2	50	3	0
3	80	3	18
4	80	overnight	77

[a] Reaction was performed in 10 mL toluene with 0.338 mmol of **2b**, 0.338 mmol of [Rh(COD)Cl]$_2$ and 3.38 mmol of K$_2$CO$_3$. [b] Isolated yield.

So, to sum up, we can say that the mechanochemical or ball mill method of synthesis performed better in shorter time without the use of organic solvents and lesser waste production, thereby leading to more environment friendly way of synthesis. Hence, we can definitely state this method to be superior in comparison to the classical solvent method of synthesis (at least, in the cases studied by us).

4.3. Characterization of the compounds

The successful formation of all the ligand precursors and metal complexes were validated by ^{1}H and ^{13}C NMR NMR spectroscopy, high resolution ESI-MS, elemental analysis and XRD study.

Characterization in solution

For the metal complexes, the typical appearance of characteristic doublet Rh-C$_{carbene}$ signal(s) at δ 180-215 ppm in ^{13}C NMR and the disappearance of the C2 proton signal from imidazole moiety in ^{1}H NMR proved the successful formation of metal-carbene carbon bond. The bridging mode of coordination and the presence of two rhodium centres were confirmed by the signals of two doublets each in the region of δ 98-101 ppm and δ 68-71 ppm which are assigned to Rh-C$_{vinyl}$ of coordinated COD. In case of the chelating metal complex **3e**, there was the signal of one doublet each in the same region. The high-resolution mass spectrometry also confirmed the synthesis of the complexes.

Characterization in the solid-state

The solid-state crystal structures of the azolium salts **2d**, **2f** and the metal complexes **3a**, **3b**, **3d, 3h** and **3i** were established by single-crystal X-ray diffraction study.

X-ray quality crystals of **2d** were obtained from a methanolic solution layered with diethyl ether. The compound crystallized as triclinic (P–1 space group). The asymmetric unit contains half of the molecule. In **2d**, the imidazole centroids are long apart (7.070 Å), their ring planes are parallel and in a distance of 3.877 Å while the distance of the mesityl groups is 3.649 Å. All of the bond lengths and bond angles in the imidazole rings are as expected. The supramolecular architecture is further stabilized by π-π stacking interactions between the five- and six-membered rings. Capped sticks representation of the solid-state structure of **2d** is shown in fig. 4a, while the packing diagram with stacking interactions can be seen in fig. 4b.
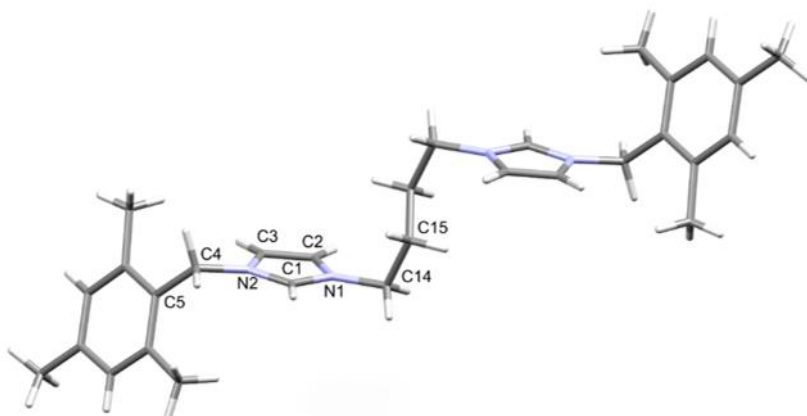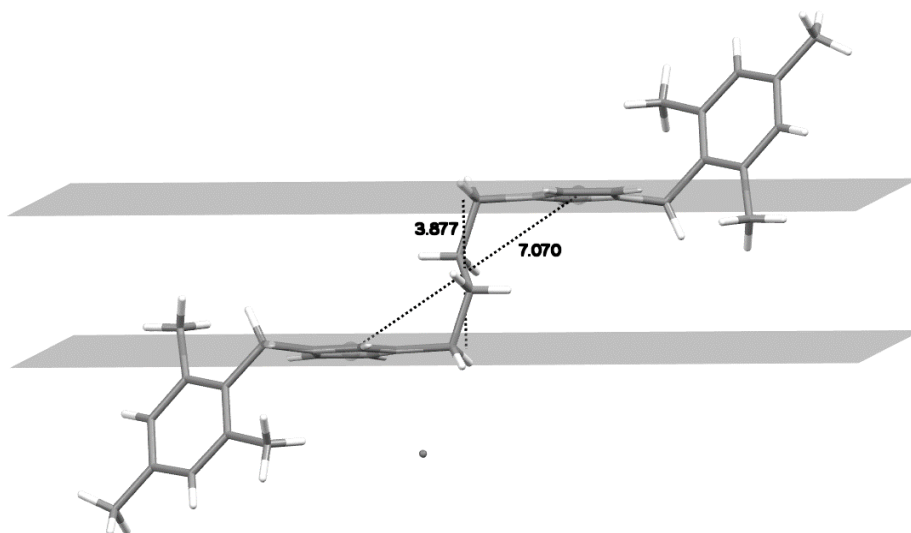
Fig. 4a: Capped sticks representation of the molecular structure of **2d** in the solid-state (counter ions are omitted for clarity). Selected bond lengths and angles of **2d**: N1–C1: 1.333 Å; N2–C1: 1.327 Å; C2=C3: 1.341; N1–C1–N2: 108.37°; N2–C4–C5: 112.08°; N1–C14–C15: 111.96°.
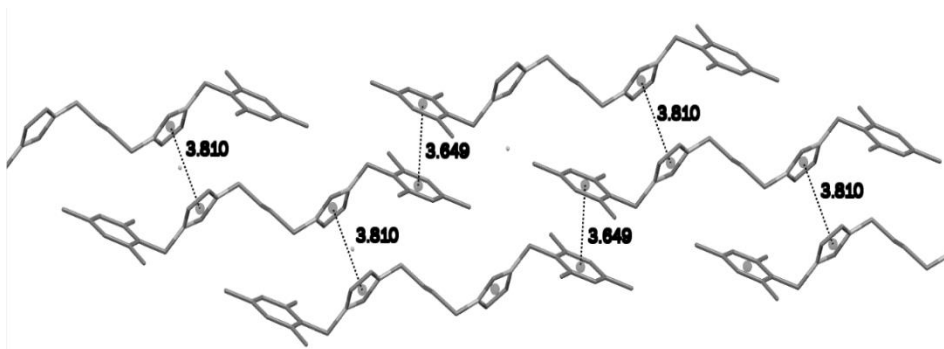
Fig. 4b: Intramolecular distances and partial packing diagram with π-π stacking interactions in **2d**.

2f was suspended in DMF and heated to approximately 100°C, left overnight for slow cool-down to room temperature and suitable crystals were obtained for X-ray analysis. **2f** crystallizes in the monoclinic $P2_1/c$ space group, the asymmetric unit contains half of the zwitterionic molecule (zwitterions) and one water molecule. (**2f** was also crystallized from water, the same unit cell was obtained.) In the di-NHC precursor, imidazole ring planes are almost parallel and in a distance of 2.741 Å. The supramolecular architecture of the solid-state structure is stabilized with strong hydrogen bonds between **2f** and the water molecules (O4w… H–O2: 2.819 Å, O4w…H–O3: 2.816 Å) and π-π stacking interactions between the five-membered imidazole rings (3.955 Å).
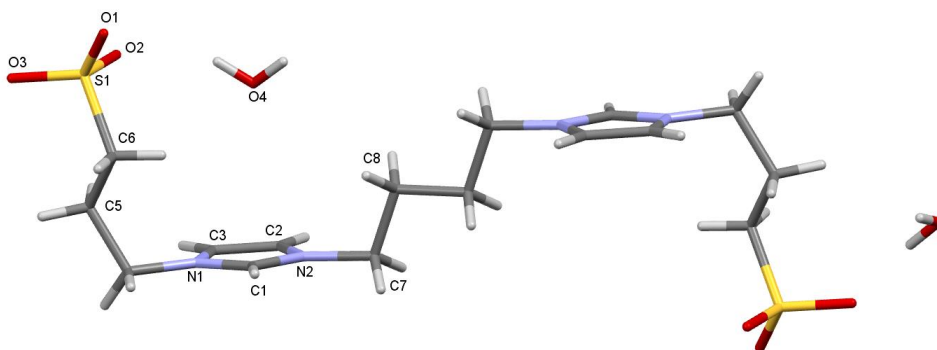
Fig. 4c: Capped sticks view of the molecular structure of **2f**. Selected bond lengths and angles of **2f**: N1–C1: 1.327 Å; N2–C1: 1.324; N1–C4: 1.472 Å; N2–C7: 1.477 Å; C2=C3: 1.345; N1–C4: 1.472 Å; S1–C6: 1.765 Å; S1–O1: 1.448 Å; S1–O2: 1.452 Å; S1–O3: 1.447 Å; O4w…H–O2: 2.819 Å; O4w…H–O3: 2.816 Å; N1–C1–N2: 108.73°; N2–C7–C8: 112.60°; N1–C4–C5: 111.67°; O1–S1–O2: 112.73°, O1–S1–O3: 111.98°, O2–S1–O3: 112.90°.

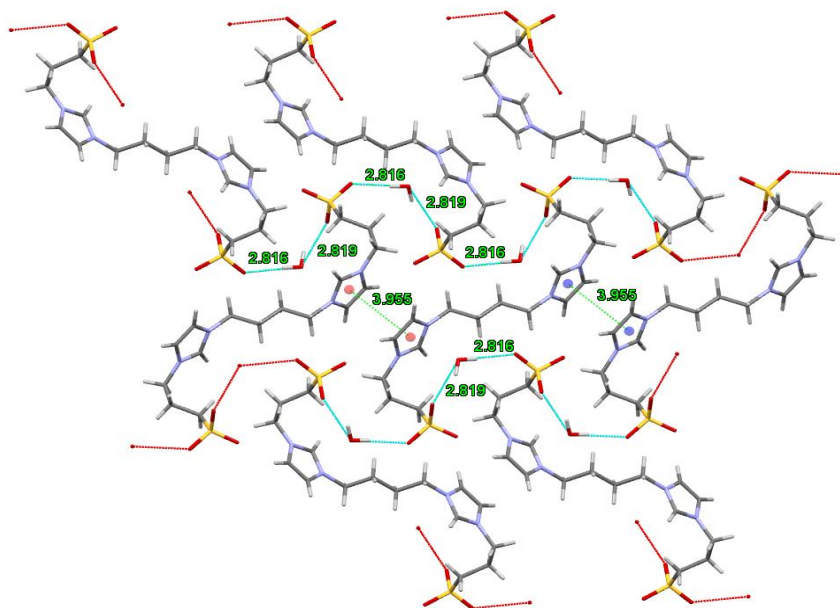
Fig. 4d: Partial packing diagram of **2f** showing hydrogen bonds and π-π stacking interactions.

Crystallization of **3d** (the dinuclear Rh(I) complex of **2d**) was attempted by several methods, unfortunately, the best crystals (obtained by slow evaporation of its solution in CH_2Cl_2) were still of rather bad quality. **3d** crystallized in the monoclinic $P2_1/n$ space group, the unit cell contains half of the molecule. After refinement of the best dataset, the error remained still too large ($R_1 = 17.51\%$, $wR_2 = 41.25\%$) so while the molecular model (fig. 4e) proved to be suitable, the bond distances and bond angles cannot be evaluated.
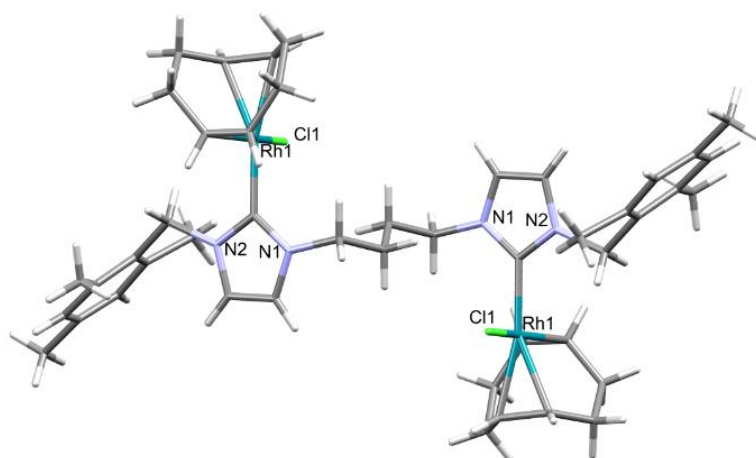
Fig. 4e: Capped sticks representation of the molecular structure of **3d** in the solid-state.

The Rh(I)-complexes **3a** and **3b** were crystallized from benzene solutions layered with diethyl ether and were isolated as yellow crystals, not sensitive to air and moisture. Both the complexes crystallize in the monoclinic crystal system; however, the space groups are different (c2/c for **3a**, and $P2_1/c$ for **3b**). Capped sticks representations of the molecular structures are shown in fig. 4f, while the selected bond distances and angles can be found in table 4.7.
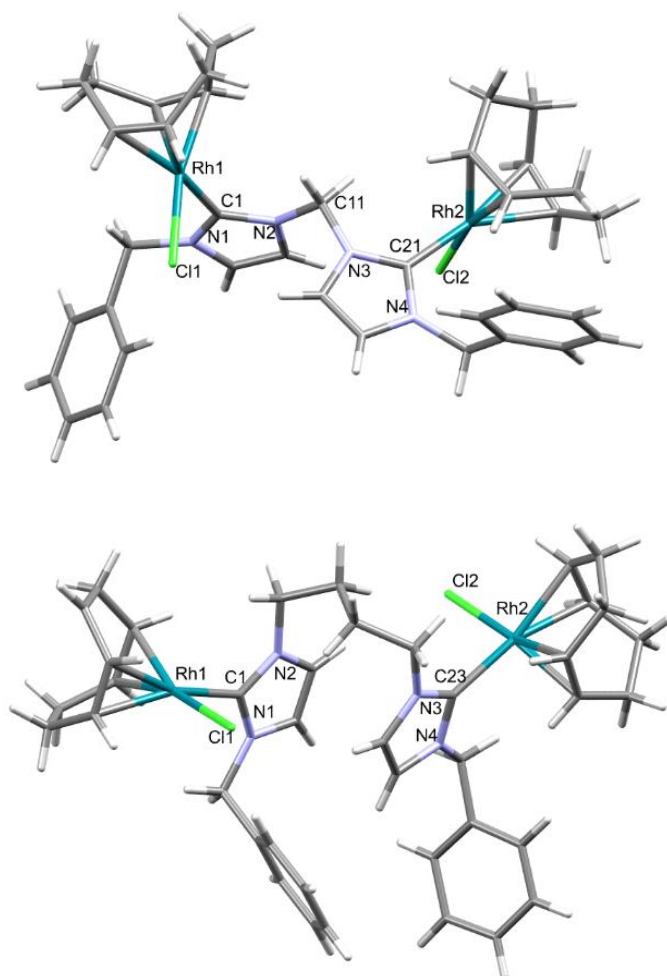
Fig. 4f: Capped sticks representation of the molecular structure of the Rh(I)-complexes **3a** (top) and **3b** (bottom) in the solid-state.

Table 4.7: Selected bond lengths and bond angles for the solid-state structures of the Rh(I)-complexes **4a** and **4b**.

Bonds and Angles	4a	4b
Rh1–C1	2.012 Å	2.025 Å
Rh2–C21	2.026 Å	2.030 Å
Rh1–Cl1	2.378 Å	2.381 Å
Rh2–Cl21	2.383 Å	2.367 Å
Rh1–Rh2	6.938 Å	8.277 Å
C2–C3	1.336 Å	1.336 Å
C22–C23	1.339 Å	1.332 Å
N2–C11–N3	110.6°	–
N1–C1–N2	103.93°	104.36°
N3–C21–N4	103.52°	104.10°
N1–C4–C5	112.08°	112.14°
N4–C24–C25	114.17°	113.14°
C1–Rh1–Cl1	88.79°	91.28°
C21–Rh2–Cl21	89.76°	89.34°
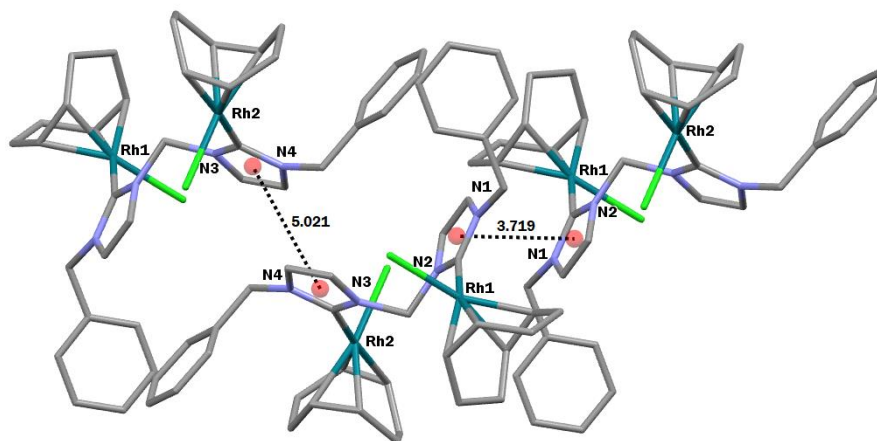
Fig. 4g: Intermolecular imidazole distances in **3a** (π- π stackings).

Fig. 4h: Intramolecular imidazole distances **3b** (π- π stackings).

Fig. 4i: Distances between the phenyl rings in **3b** (π- π stackings).

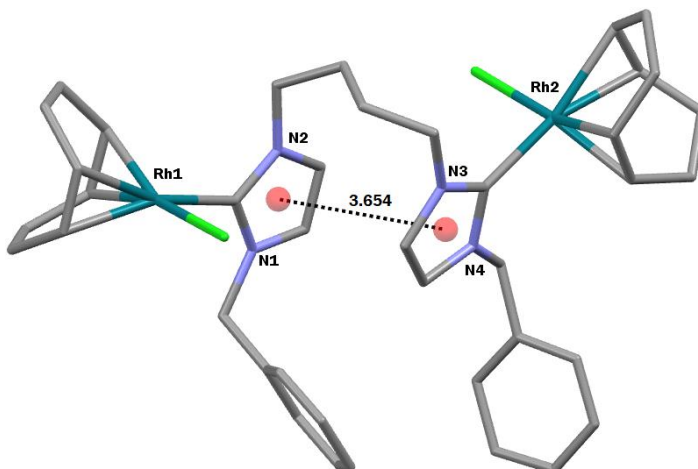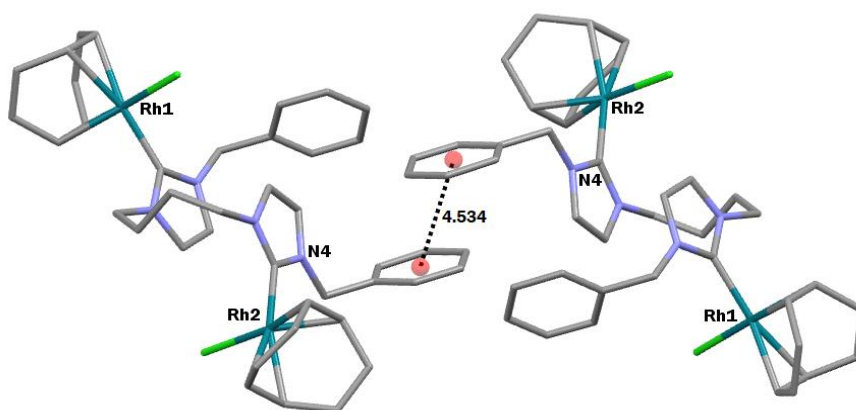The metal-NHC complexes **3h** and **3i** were crystallized from benzene and the details of X-ray analysis can be found in our published article. [84].

4.4. Catalysis experiments

Polymerization of phenylacetylene

In the field of homogeneous catalysis, polymerization of unsaturated substrates utilizing metal complexes is a hot topic for the last two decades. The reason behind this attention is their unique physico-chemical properties, which makes their widespread applied aspects. Among these polymers, poly-acetylenes is of great interest because of their unique properties like oxygen permeability, ferromagnetism, conductivity, humidity sensor etc. The polymerization of phenylacetylene is known to be possible by group 5 and 6 transition metal complex catalysts, also by nickel and palladium complexes. Rhodium(I) metal complexes have also attracted the attention because they are reactive towards the alkynes. Moreover, Rh based systems are well known for high tolerance of functional groups [74].

In our study, we applied the metal complexes **3a** and **3b** for the polymerization reaction of phenylacetylene (scheme 3e). The reaction was performed in chloroform ($CDCl_3$) using THF as internal standard maintaining substrate/catalyst ratio 100 at room temperature. ^{1}H NMR study clearly displayed that the intensity of the proton joined with the triple bond decreased, whereas, the same for the proton joined with double bond increased with respect to time, thereby proved the formation of polyphenylacetylene (fig 4j).
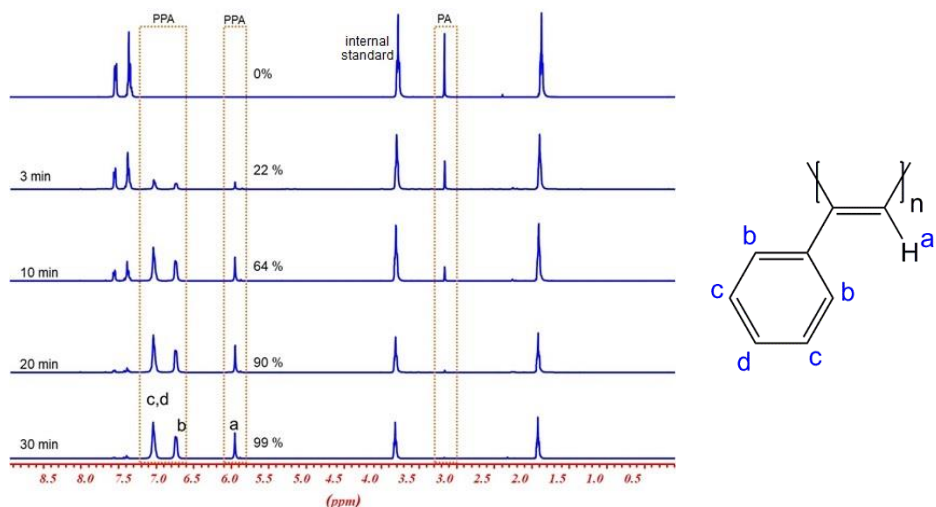
Fig. 4j: ^{1}H NMR spectrum showing the formation of polyphenylacetylene with the increase of time[a].

[a] Reaction conditions: PA/**3a** =100, **3a**=0.01 mmole, 1 mmol THF (int. std.), 0.65 mL chloroform, room temperature.

The same reaction conditions were applied using metal complex **3b** and metal precursor, [RhCl(COD)]₂ as catalyst and they both were found to be equally active in the polymerization reaction (fig 4k).
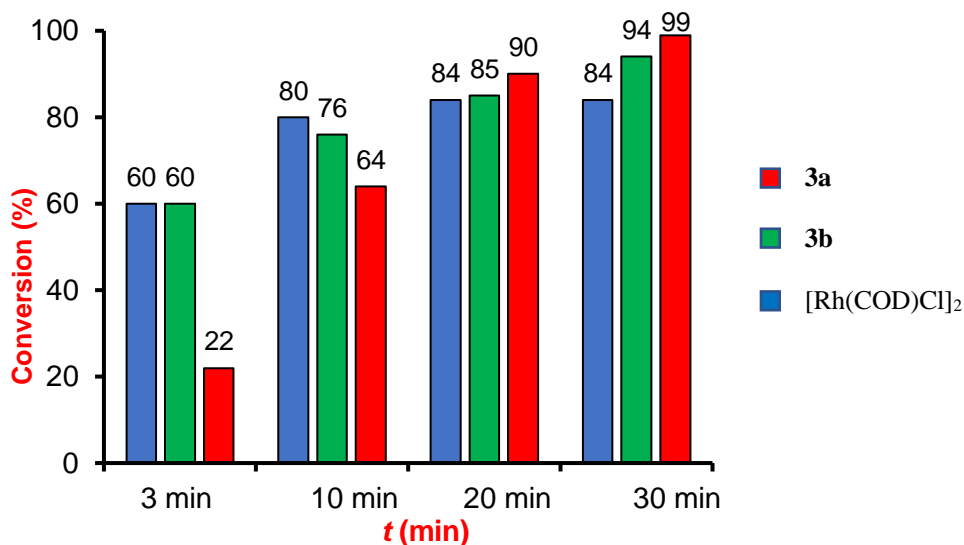
Fig. 4k: Formation of polyphenylacetylene with different catalysts in different time gaps[a].

[a] Reaction conditions: PA/Rh =100, Rh=0.01 mmole, 1 mmol THF (int. std.), 0.65 mL chloroform, room temperature.

Next, the reusability of the catalyst **3a** was checked. Excess methanol was added and polyphenylacetylene was separated out, the filtrate was evaporated and once again, the same volume of chloroform was added and the catalytic reaction was carried out following the same way. It was able to show excellent yield (89 %), even on its 3rd use (fig. 4l).
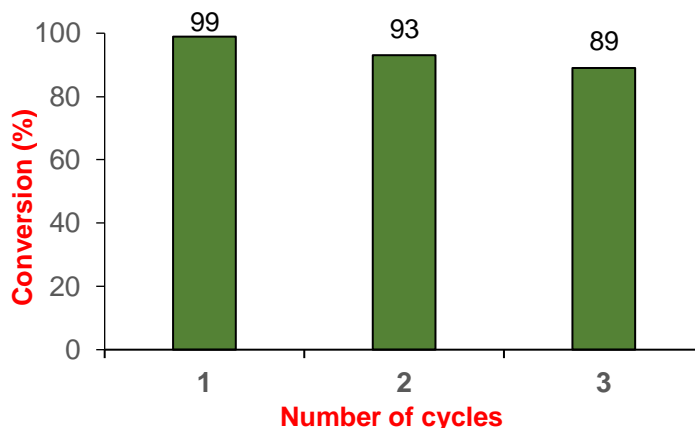
Fig. 4l: Formation of polyphenylacetylene in different cycles of reutilization of the catalyst[a].

[a] Reaction conditions: Rh=0.01 mmole, 1 mmol THF (int. std.), 0.65 mL chloroform, room temperature.

The MALDI-TOF MS measurement of the polymer formed, clearly indicated the mass difference between two successive peaks to be 102, which is a monomer unit of polyphenylacetylene (fig. 4m).
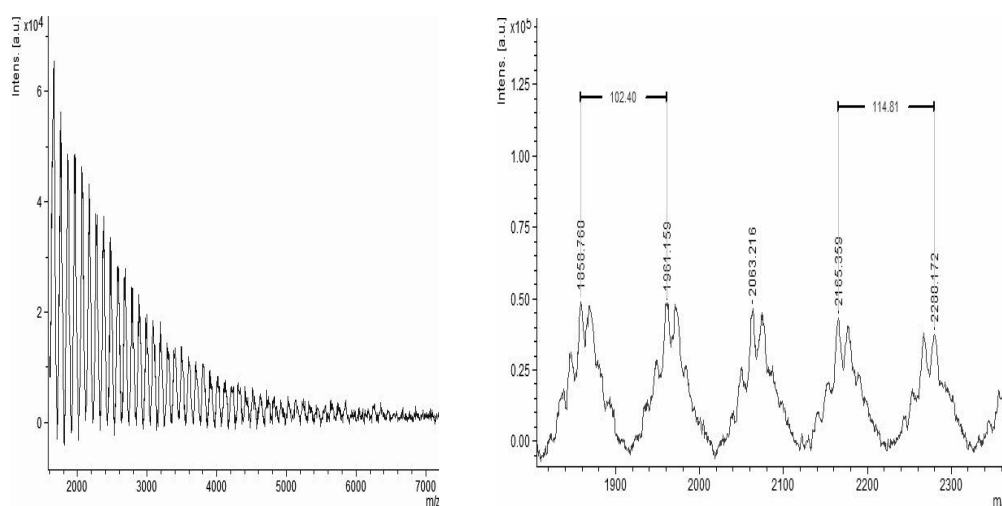
Fig. 4m: MALDI-TOF MS measurement of the polymer.

The molecular weight determination was always performed with freshly prepared polymer in chloroform solution (table 4.8.). However, the property of the polymer formed in different batches of preparation, was found not to be uniform. Moreover, they were polydisperse in nature.

Table 4.8: Table showing the GPC results.

Catalyst	RT (min)	M_n	M_w	M_p	M_w/M_n
3a	17.223	10416	34421	25838	3.305

Selective hydration of benzonitrile

In the field of pharmaceutical chemistry, amides are of great interest and because of this fact, development of new transition metal catalysts is very important, especially those, which are able to hydrate aliphatic as well as aromatic nitriles to corresponding amides under mild conditions and with high activity [84]. Metal complexes **3f-i** were applied as catalyst for the selective hydration reaction of benzonitrile to benzamide in water/isopropanol (1:1) mixture under mild conditions of ≤ 80 °C temperature (scheme 3f).

Fast hydration of benzonitrile to benzamide was not possible only with the metal complexes, therefore, at the very beginning, we checked the effect of various bases (table 4.9) [84].

Table 4.9: Effect of bases on the hydration reaction of benzonitrile[a].

Entry	Time	Base	Conversion (%)	TOF[b] (h^{-1})
1	1.5	-	0	0
2	2	-	3	4

3	1.5	*t*BuOK	52	69
4	1.5	K_2CO_3	56	75
5	1.5	KOH	52	69
6	1.5	NaOH	59	79

[a] Conditions: 1 mmol benzonitrile, 0.5 mol% **3f**, 0.005 mmol base, 3 mL H_2O/*i*-PrOH (1:1), 80 °C.

[b] TOFs were calculated from the conversion at indicated reaction times.

Next, the optimization process for the hydration reaction was carried out varying several reaction parameters using **3f** as the catalyst and the conversion was monitored using GC (table 4.10).

It is clearly visible from the data of Table 4.10 that the use of sodium hydroxide as a base yielded the best, therefore, it was opted for our further studies. When the same experimental conditions were applied without the use of any Rh-NHC complexes, only a trace amount of product (< 1%) was detected in gas chromatography, which confirmed that the base-catalyzed hydration reaction was really negligible to the corresponding metal complex catalysis.

Table 4.10: Effect of several reaction parameters on the hydration reaction of benzonitrile[a].

Entry	Cat. (mol%)	Phosphine	Temp. (°C)	Time (min)	Conv.[b] (%)	TOF[c]
1[d]	1	-	40	120	48 (0)	24
2[d]	1	-	50	120	72 (1)	36
3[d]	1	-	60	120	82 (1)	41
4[d]	1	-	70	120	91 (3)	45
5[d]	1	-	80	120	98 (6)	49
6[d]	1	-	80	10	46 (1)	276

7 [d]	1	-	80	20	63 (1)	189
8 [d]	1	-	80	30	74 (2)	148
9 [d]	1	-	80	60	86 (3)	86
10 [d]	1	-	80	90	94 (5)	63
11	5	-	reflux	60	0	0
12	5	-	reflux	120	18	2
13	5	-	reflux	180	26	2
14 [d]	5	-	reflux	10	86	115
15 [d]	5	-	reflux	20	97	58
16 [d]	5	-	reflux	60	>99	20
17	5	0.05 mmol PTA	reflux	60	17	3
18	5	0.15 mmol PTA	reflux	60	70	14
19	5	0.25 mmol PTA	reflux	60	78	16
20	5	0.05 mmol *m*tppms	reflux	60	75	15
21	5	0.15 mmol *m*tppms	reflux	60	76	15
22	5	0.25 mmol *m*tppms	reflux	60	94	19

[a]Conditions: 1 mmol benzonitrile, [NaOH]/[Rh]= 1, 3 mL H_2O/*i*-PrOH (1:1). [b]Only base (NaOH) catalyzed conversion in first bracket (entries 1-10). [c]TOFs were calculated from the conversion at indicated reaction times.[d] NaOH was used as a base.

Data in the table 4.10 depicts the effects of several parameters on the hydration reaction. Initially, the effect of temperature was checked. It was observed that with the increase of temperature, formation of benzamide increased reaching 98% at 80 °C (entry 5). Reactions were carried out using only the metal complex, as well as, only the base and the conversion was not that satisfactory even at reflux temperature after 3 h with 5 mol%

catalyst loading (entry 13). On the other hand, the combination of the metal complex **3f** and NaOH yielded 86% only after 10 min under the same conditions. The effect of addition of tertiary phosphines PTA and *m*tppms-Na salt were also checked, however, found to be inferior compared to the base NaOH (entry 18,21 vs. entry 14).

Next, all the four [RhCl(COD)(NHC)] complexes **3f-i** were applied as catalyst for the hydration reaction of benzonitrile for different reaction times (1-3 h) (table 4.11). It is clearly visible that, in the absence of the base NaOH, all the catalyst displayed low catalytic activities with hight conversion of only 26% after 3 h (entry 1). It was also noticed that catalyst **3f** and **3g** is more active compared to the other two metal catalysts (entries 2,4 vs. entries 6,8).

Table 4.11: Hydration reaction of benzonitrile using **3f-i** as catalyst[a].

Entry	Catalyst	Conversion (%)		
		1 h	**2 h**	**3 h**
1	**3f**	0	18	26
2	**3f** + NaOH	>99	-	-
3	**3g**	0	0	10
4	**3g** + NaOH	99	>99	-
5	**3h**	0	1	2
6	**3h** + NaOH	66	86	93
7	**3i**	0	0	12
8	**3i** + NaOH	94	98	-

[a] Conditions: 1 mmol benzonitrile, 5 mol% [RhCl(COD)(NHC)], [NaOH]/[Rh]= 1, 3 mL H_2O/i-PrOH (1:1), reflux temperature.

After picking **3f** as the best catalyst amongst the four, we checked the hydration reaction of various nitriles (benzonitriles with electron donating and electron withdrawing substituents) with catalyst **3f** and NaOH (table 4.12). Our catalyst was found to be active in all the cases even with low catalyst loading (1 mol%). However, findings revealed that the electron withdrawing substituents displayed better conversion, which matches with previously reported observations [88,92], and are explained with that the electron withdrawing substituents make the nitrile carbon more susceptible to nucleophilic attack by OH$^-$.

Table 4.12: Hydration reaction of various nitriles with catalyst **3f** and NaOH [a].

Entry	Nitrile	Time (h)	Conv. (%)	TOF [b] (h^{-1})
1	benzonitrile	1	93	93
2	benzonitrile	2	98	49
3	4-chlorobenzonitrile	1	88	88
4	4-chlorobenzonitrile	2	94	47
5	4-methylbenzonitrile	1	70	70
6	4-methylbenzonitrile	2	84	42
7	4-chlorophenyl-acetonitrile	1	58	58
8	4-chlorophenyl-acetonitrile	2	62	31

[a] Conditions: 1 mmol nitrile, 1 mol% [RhCl(COD)(IMes)], [NaOH]/[Rh]= 1, 2 mL H$_2$O/i-PrOH (1:1), 80 °C. [b] TOFs were calculated from the conversion at indicated reaction times.

Finally, the hydration of benzonitrile reaction was checked at 25 °C with catalyst **3f** and NaOH for different timings and different catalyst loadings (table 4.13). Catalyst **3f** was able to provide good conversion after 40 h

with only 1 mol% of loading (entry 3). But, with higher loading of catalyst (2.5 mol%), excellent conversion of 99% was reached in 24 h (entry 8). However, lowering the concentration of *i*-PrOH (50% *v/v* to 20% *v/v*) in the solvent mixture reduced the conversion (entries 9,10). The reason behind is unclear as *i*-PrOH itself is not involved in the reaction and lower concentration of *i*-PrOH still kept the reaction mixture homogeneous.

Table 4.13: Hydration of benzonitrile at 25 °C with catalyst **3f** and NaOH[a].

Entry	Cat. Load. (mol%)	Time (h)	Conv. (%)	TOF[b] (h^{-1})
1	1	17	73	4.3
2	1	22	79	3.6
3	1	40	94	2.4
4	2	17	84	2.5
5	2	22	85	1.9
6	2.5	17	94	2.2
7	2.5	19	96	2.0
8	2.5	24	99	1.7
9[c]	1	17	34	2.0
10[c]	1	34	60	1.8

[a] Conditions: 1 mmol benzonitrile, [NaOH]/[Rh]= 1, 2 mL H_2O/*i*-PrOH (1:1).
[b] TOFs were calculated from the conversion at indicated reaction times.
[c] 20% *v/v* *i*-PrOH.

The findings above didn't allow us to suggest the detailed mechanism of the reaction (scheme 4a). However, the high rate of conversion in the presence of base can support the formation of Rh(I)-OH hydroxo complex. Again, the complete selectivity of the hydration reaction to benzamide supports that most probably the nitrile group also coordinates to Rh(I) centre. However, the role and fate of COD is still unclear.
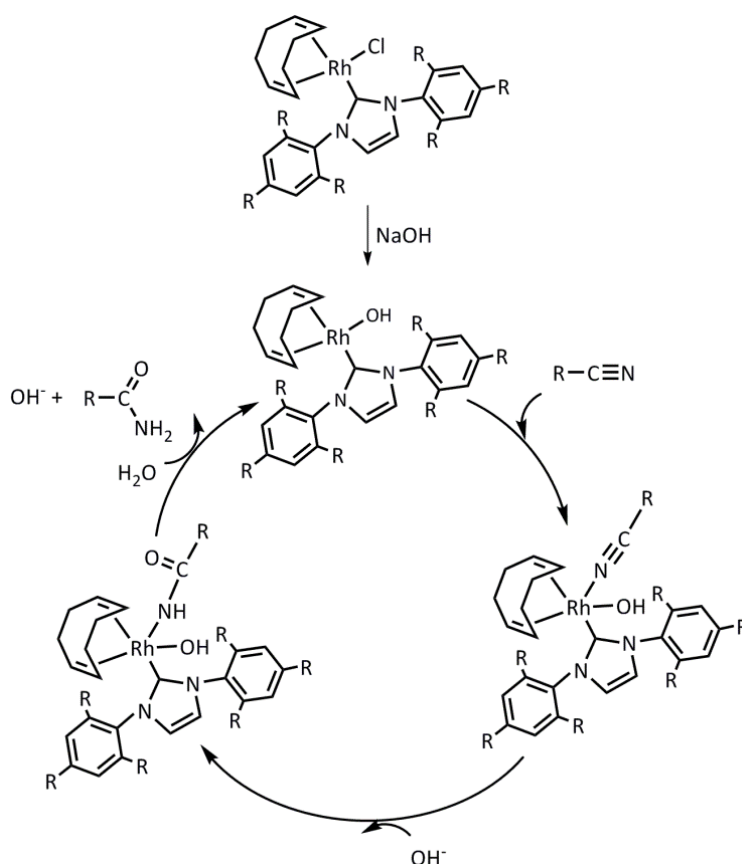
Scheme 4a: Suggested mechanism of the hydration reaction of nitrile catalysed by [RhCl(COD)(NHC)] complexes (**3f-i**).

Attempted use of 3j as catalyst for carbon–carbon coupling

The chelating metal complex **3j** was prepared to check its application on coupling reactions. Therefore, the complex was used in Suzuki and Sonogashira coupling reactions. However, the complex failed to display good activity in these reactions. The Suzuki coupling reaction between iodobenzene and phenylboronic acid always displayed the black metal

precipitation even at room temperature. On the other hand, the Sonogashira coupling reaction between iodobenzene and phenylacetylene yielded polyphenylacetylene instead of diphenylacetylene all the time.

5. Summary

This thesis presents the development of new di-N-Heterocyclic carbene ligands and their chelating and bridging transition metal complexes mainly with rhodium(I) metal. Both the ligand precursors and the complexes were prepared in the traditional stirring method in solution and by the environmentally green zero-solvent mechanochemical method and the results are compared. Novel methods of synthesis for four known rhodium(I)-mono(NHC) metals of [Rh(COD)Cl(NHC)] type complexes and their successful utilization for the hydration reaction of nitriles have also presented. Additionally, this dissertation describes the first examples of metal-di(NHC) complexes as well as Rh-NHC complexes synthesized in a ball mill without the use of solvent.

Chapter 1 and 2 of this dissertation deals with the introductory part about the basics of carbenes, N-Heterocyclic carbenes and their metal complexes and their applications. Chapter 2 is mainly about the detailed background information related to the *N*-Heterocyclic carbenes, transition metal complexes of NHCs and the catalytic experiments e.g. polymerization of phenylacetylene and hydration of nitriles.

Chapter 3 discusses the experimental part i.e. the methods of preparation and characterization techniques applied. In our work, we have prepared the precursor azolium salts of a total of six di-NHCs with methane and butane linkers between the two NHC units. Amongst them, four have benzyl N-substitution and they were initially prepared with the aim to make them water-soluble by sulfonation, which was not successful. However, those four ligands and their bridging di-nuclear rhodium(I) complexes were synthesized both in the solvent and solvent-free media.

Synthesis of a new chelating Rh(I)-NHC complex is also reported in this section. The other two reported di-NHCs have ω-sulfonatopropyl N-substituents and one of them was used to prepare a chelating palladium(II) metal complex. A new and straightforward method of synthesis has been described for four known [RhCl(COD)(NHC)] type complexes of IMes, SIMes, IPr, SIPr. All the above-mentioned ligands and complexes were characterized with ^{1}H NMR, ^{13}C NMR, HR-ESI-MS, elemental analysis and x-ray diffraction study. The Pd(II)-di(NHC) complex was utilized in Suzuki and Sonogashira coupling reactions, however, it failed to show good activity towards these reactions. Suzuki coupling reaction between iodobenzene and phenylboronic acid with the Pd(II)-di(NHC) complex as catalyst always yielded black metal precipitation. On the other hand, the Sonogashira coupling reaction between iodobenzene and phenylacetylene yielded polyphenylacetylene instead of diphenylacetylene. In contrast, two of four bridging di-nuclear Rh(I)-di(NHC) complexes were successfully utilized in the polymerization reaction of phenylacetylene and the four [RhCl(COD)(NHC)] type complexes displayed excellent catalytic activity toward the hydration reaction of nitriles.

The next and the final chapter tells about the results and discussions. The formation NHC-Rh(I) metal complexes were proved by the appearance of Rh-C$_{carbene}$ doublet peak(s) at 180-215 ppm in ^{13}C{^{1}H} NMR spectra. Also, in the ^{1}H NMR spectra, the disappearance of the imidazole proton peak from C-2 in the ligands supported the formation of the NHC-metal complexes. Furthermore, the high-resolution ESI-MS, elemental analysis and crystallography study confirmed the successful formation of all the compounds. We compared the synthesis of the poly-NHC precursors and the Rh(I)-NHC metal complexes in solvent and in zero-solvent media. The synthesis by the solvent method incorporated the use of flammable, toxic

volatile organic solvent(s) having a negative impact on the environment. Most of the times, this method required higher temperature and longer reaction time. In our cases, it always required $\geq$ 80 °C temperature and overnight reaction time. On the other hand, the mechanochemical method allowed the synthesis of the ligands and metal complexes at room temperature in shorter time without the use of any solvents (which were only used in smaller amounts for isolation of the products). It was possible to obtain good yields with only 3 hours of milling time. This method of synthesis is environment-friendly from the viewpoint of green chemistry. Here, we have reported the first metal-di(NHC) complexes (also the first rhodium NHC complexes) to be synthesized mechanochemically. The bridging di-nuclear Rh(I)-di(NHC) complexes were catalytically active for the polymerization of phenylacetylene. Utilizing these catalysts, it was possible to obtain 99% conversion after 30 minutes at room temperature with the catalyst loading as low as 1 mole% with respect to the substrate. Unfortunately, for some yet unknown reason(s), the prepared polyphenylacetylene failed to display uniform polymeric properties for different batches of preparations. The four Rh(I)-mono(NHC) complexes of the type [RhCl(COD)(NHC)] showed good catalytic activity towards the hydration of nitriles in presence of a base. Here, at the very beginning, the activity of several bases was determined and sodium hydroxide was found to be the best amongst them. Next, several experimental checks with benzonitrile as substrate and [RhCl(COD)(IMes)] as the catalyst yielded almost 100% with the substrate to catalyst ratio 20 with an equimolar amount of base to the catalyst in the water/2-propanol medium at reflux temperature. The same catalyst was applied for different sets of nitriles and responded well for all of them. The hydration reaction was checked at room temperature as well and the catalyst displayed the excellent yield of

99% with only 2.5% catalyst loading with respect to the substrate within 24 hours. A mechanism for the hydration reaction has also been suggested in this chapter.

Throughout our investigation of di-NHC ligands, trials to make them water-soluble, making their metal complexes and utilizing them in the field of catalysis allowed us to write a review article, which has been published in the *Coordination Chemistry Reviews* from Elsevier.

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List of Publications

1. **Title:** Poly-*N*-heterocyclic carbene complexes with applications in aqueous media

   Authors: *Sourav De*, Antal Udvardy, Csilla Enikő Czégéni and Ferenc Joó.

   Journal Details: Coordination Chemistry Reviews, **2019**, 400, 213038 **[IF:**13.48**]**

2. **Title:** Selective hydration of nitriles to corresponding amides in air with Rh(I)-N-heterocyclic complex catalysts

   Authors: Csilla Enikő Czégéni, *Sourav De*, Antal Udvardy, Nóra Judit Derzsi, Gergely Papp, Gábor Papp and Ferenc Joó.

   Journal Details: Catalysts, **2020**, 10(1), 125 **[IF: 3.44]**

3. **Title:** Stirring or milling? First synthesis of Rh(I)-di-*N*-heterocyclic carbene complexes both in solution and in a ball mill

   Authors: *Sourav De*, Ferenc Joó, Henrietta Horváth, Antal Udvardy and Csilla Enikő Czégéni

   Journal Details: Manuscript for the Journal of Organometallic Chemistry to be submitted.

4. **Title:** Crystal structure of zwitterionic 3,3'-(1,1'-(butane-1,4-diyl)bis(1H-imidazole-3-ium-3,1-diyl))bis(propane-1-sulfonate), a di-N-heterocyclic carbene precursor

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   Journal Details: Manuscript for the Acta Crystallographica Section E to be submitted.

Acknowledgements

During the last four years here at the University of Debrecen has been an experience that I will never forget. Debrecen, with a lot of memories, has got a special place in my heart and I am more than proud to be an alumnus of this great and historic university.

My highest gratitude goes to my supervisor Prof. Ferenc Joó for proving me this wonderful opportunity to become Dr. Sourav from Sourav. Ferenc, I still remember my homesickness in the beginning days and your endless support and care from having lunch or dinner together to taking me to the musical concerts slowly made Debrecen to be my second home. You deserve a lot more than just thanks for your contentious encouragement, advice and assistance throughout my PhD work. You are not just my guide, you are my friend, philosopher and second parent. You have been my role model for the last four years. I wish to achieve your patience, expertise and instant grip to handle any situation as a leading figure in future.

My PhD study has provided the opportunity to travel overseas for the first time, experience a diverse culture and meet new people. A big thanks go to the Government of India and Hungary for awarding me with the prestigious 'Stipendium Hungaricum' scholarship to obtain this fortune. It has also helped to fulfil my hobby as a traveller, by allowing me to visit more than twenty countries so far.

I am grateful to all the present and past members of the Department of Physical Chemistry for their great help in solving academic and language-related problems. Special thanks go to Dr. Antal Udvardy and Dr. Csilla Enikő Czégéni for their invaluable contributions to our joint papers, as well as continuous assistance and help in teaching me several new experimental techniques and making me a better chemist. I am grateful to Dr. Attila Bényei,

Dr. Attila Gáspár, Dr. Tibor Nagy, Dr. György Deák and Dr. Attila Kiss for their help in the measurement of crystal structures, ESI-MS, GPC and elemental analysis. Also, I acknowledge the unforgettable help at the very beginning from Ágnes Bertók by showing me the city, shopping malls, medicine stores and restaurants.

Bence Vadkerti – you definitely deserve a special mention. Thank you for making me one of your family members by calling 'brother', you have always been and will be my best friend in Hungary. Thank you for introducing me to your amazing family members and inviting me all the time to your house in the home parties and celebrations. I will never forget the fun we had in the camping at Kerekdomb. Thank you for making my Debrecen life smoother and more colourful.

Finally, my warmest appreciation goes to my wonderful family. To my wifey, Ipsita: Thank you for your patience and unwavering support throughout my doctoral study. Thanks for staying awake overnight just to take care of me during my illness. I know that I could not have come to this step without your support, care and love. I love you and thank you for everything. My dear brother Kumaresh, thank you for your assistance in my busy days (by saying "Can I be in some help?"). Thanks for the delicious chicken dishes that you always prepare for me and also, the 'best-ever' head-massages I get in my stressful days. You are one of the kindest and most helpful persons I have ever seen. The final word goes to my parents for their unconditional love, guidance and support.

I dedicate this thesis to my maternal grandparents, who play the biggest role in my life. See grandpa, I am about to fulfil your dream, on the way to be the first person from our family to be awarded a PhD degree.