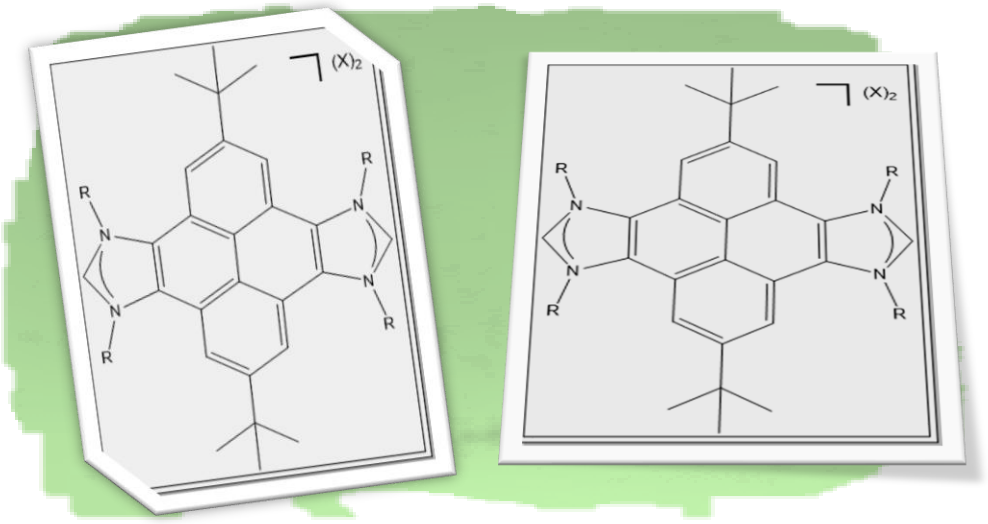
Synthesis of bis-NHC precursors and study of their coordination capabilities



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Final Degree Project

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Nomenclature:

The nomenclature employed to name the compounds described in this work is:

The starting organic material and the organic intermediates in the synthesis of the bis-imidazolium salts: letters of the alphabet (**A**, **B** and **C**).

Precursors salts of the bis-NHC ligands: the ligand letter with the acidic protons and its counter-ions. In our case, **[DH$_2$](I)$_2$** and **[EH$_2$](I)$_2$** are the precursor salts of the ligands **D** and **E**, respectively, which contain two acidic C-H bonds and two iodides as counter-ions.

List of abbreviations:

Δ	refluxing temperature
NHC	N-heterocyclic carbene
$CDCl_3$	deuterated chloroform
DMSO-d_6	deuterated dimethylsulfoxide
DMF	N,N-dimethylformamide
n-BuI	n-butyl iodide
MeCN	acetonitrile
DMSO	dimethylsulfoxide
KHMDS	potassium bis(trimethylsilyl)amide
NMR	Nuclear Magnetic Resonance
δ	chemical shift
s	singlet
d	doublet
t	triplet
m	multiplet
ppm	part per million
MHz	megahertz
Me	methyl
nBu	n-butyl
g	gram
mg	milligram
h	hour

min	minutes
µL	microlitres
mL	millilitre
mmol	millimole
ºC	degree Celsius
%	percent
eq.	equivalent
pyr	pyrene
Cq	quaternary carbon atom
THF	tetrahydrofuran
OTf	triflate
AgOAc	silver acetate
LDA	lithium diisopropylamine
cod	1,5-cyclooctadiene
*t*BuOK	potassium *tert*-butoxide

INDEX:

1. GENERAL INTRODUCTION

1.1. N-Heterocyclic carbenes (NHCs)

N-Heterocyclic carbenes (from now on NHCs) are neutral compounds containing a divalent carbon atom with six valence electrons and being part of a nitrogen atom containing heterocycle. Four electrons are involved in σ-bonds and the other two remain at the central carbon.

Their incomplete electron octet and their coordinative unsaturation, render free carbenes unstable. Indeed, they were considered only as highly reactive transient intermediates for decades.

The first stable free N-heterocyclic carbene 1,3-di(adamantyl)imidazol-2-ylidene (Figure 1.1) was isolated by Arduengo[1] in 1991 inspired by earlier studies by Wanzlick[2] and Ofele[3] on metal-carbene complexes. Four years later, in 1995, Herrmann stated that N-heterocyclic carbenes constitute "a new structural principle for the design of catalysts in homogeneous catalysis".[4] These facts led to the synthesis and analysis of several NHCs.

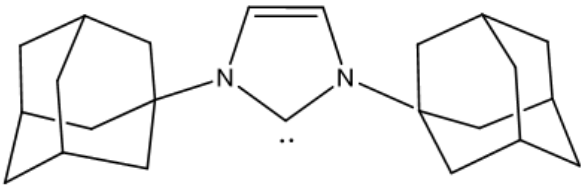


Figure 1.1. The first stable free NHC

The success of NHC ligands could be attributed to the relatively easy preparation of their precursors (normally imidazolium salts) that allows for the synthesis of a wide variety of structures.

The major applications of NHCs involves their coordination to transition metals, either in the area of homogeneous catalysis or as organometallic or metallopharmaceutical materials.

1.1.1. Different types of NHCs

As already mentioned, the general structure of NHCs consists of a divalent carbon and at least one nitrogen inside the heterocycle. Within these characteristics, we can find a large number of types of NHCs.

The imidazolylidene **(A)** ligands, are the type of NHCs more widely used and normally referred as normal NHCs. Despite that, there are a wide variety of this type of carbenes as can be seen in Figure 1.2.

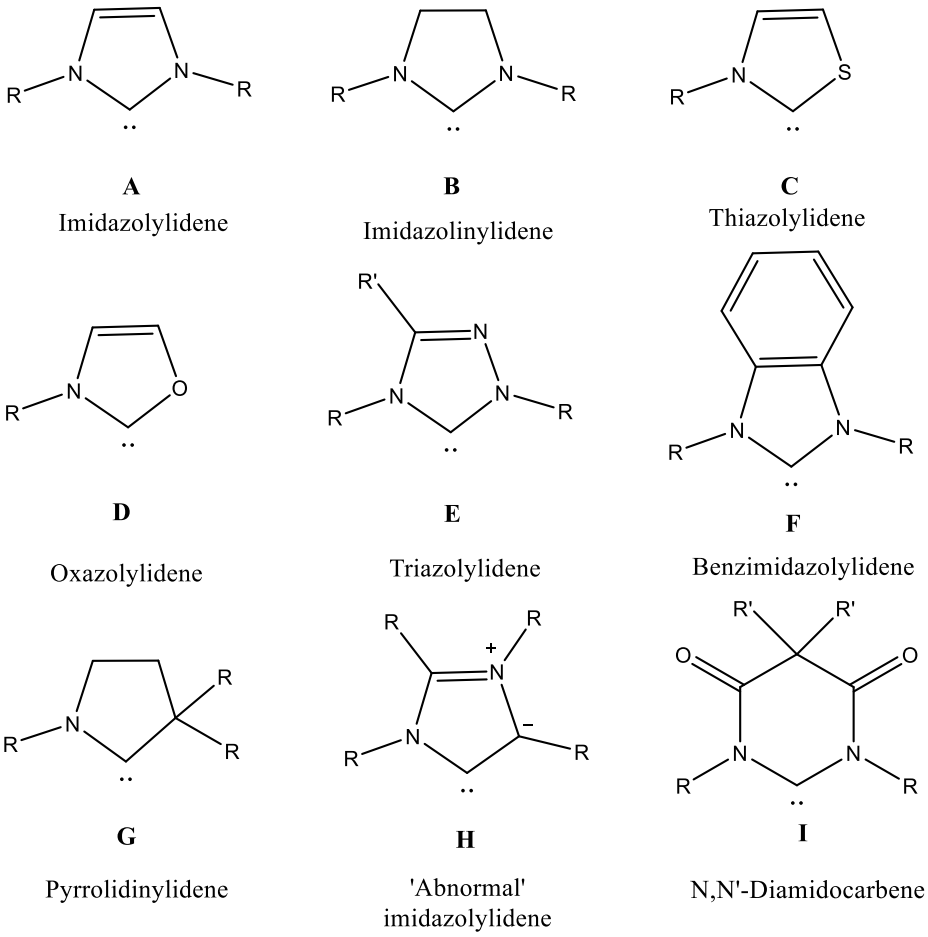


Figure 1.2 Structures of the most typical N-heterocyclic carbene ligands

We can find carbenes with different steric properties, changing the group that we have called R or R' in this work (Figure 1.2) and with different electronic properties by changing the backbone or the ring size, giving rise not only to five-membered ring carbenes but also six and even four and seven membered rings.

1.2 Poly-NHCs

Attending to their composition, NHC ligands can be classified as bis-NHC, tris-NHC and tetra-NHC. Since NHCs can admit other donor functional groups, the coordination abilities of these poly-NHCs are not restricted only to the carbene fragments. For instance, we can find tricoordinate compounds because the ligand contains a coordinating group (pyridine, amino, phosphine, alkoxy, aryl or any other coordinating group).

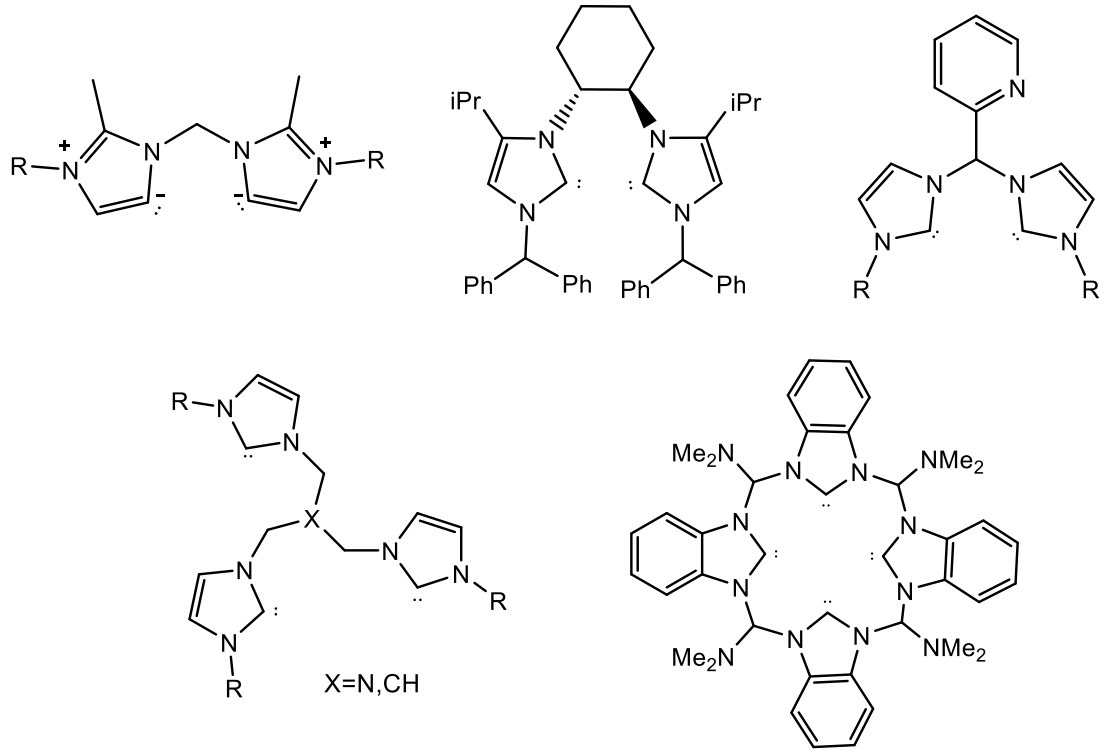


Figure 1.3 Examples of poly-NHC ligands

Poly-NHCs are of great interest because they allow the preparation of organometallic compounds with a variety of geometries.

1.2.1- *Janus*-type bis-NHCs

Bis-NHCs are the most abundant type of poly-NHCs. A particular class of bis-NHCs ligands are those normally referred to as *Janus*-type. These ligands contain two NHC fragments in a facially-opposed disposition. Their name is attributed to its analogy with the representation of the Roman God *Janus* (Figure 1.4), who had two faces looking at opposite directions.

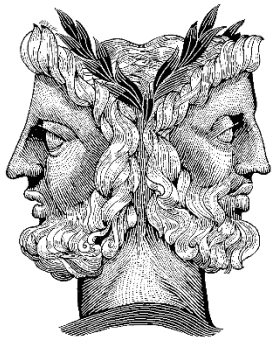


Figure 1.4 Representation of the Roman God *Janus*

In a similar way, *Janus*-type bis-NHC ligands show facially opposite coordination abilities, so they can be bound in principle to two different metals, giving rise to bimetallic complexes.

The first reported *Janus*-type bis-NHC ligand was 1,2,4-triazole-3,5-dylidene **A** (Figure 1.5) also called *ditz* ligand. Figure 1.5 depicts other two interesting examples of *Janus*-type ligands, **B** and **C**, which consist in an aromatic or polyaromatic system that joins the two carbene moieties, also called aromatic-linked *Janus*-type bis-NHCs.

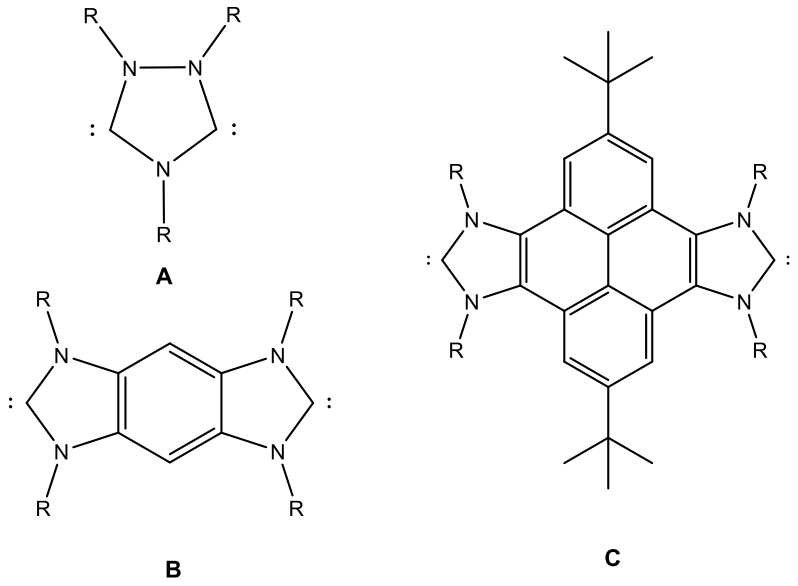
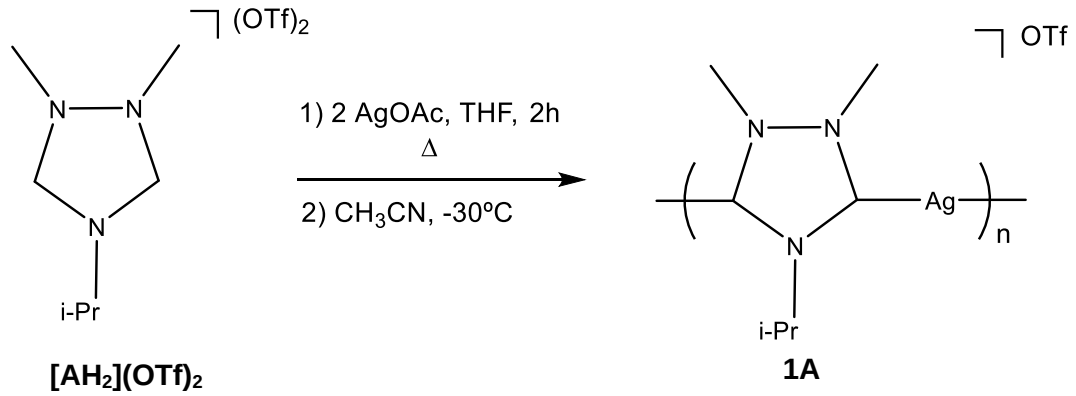


Figure 1.5 Examples of *Janus*-type bis-NHC ligands

In general, this type of ligands allows the preparation of an important variety of homo-bimetallic complexes. Now, we will see examples of possible coordination of these ligands.

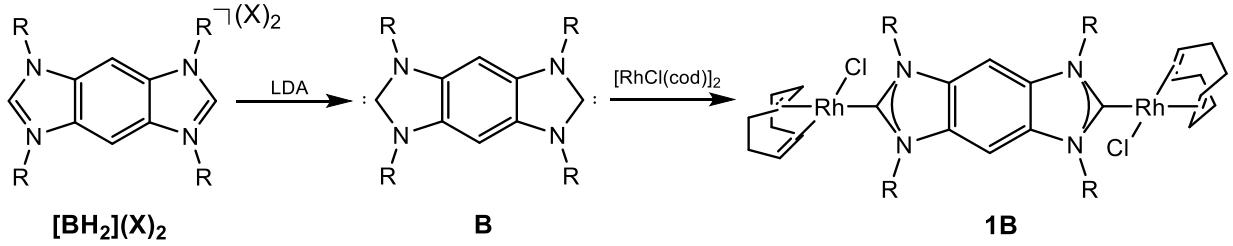
Ligand **A** was first used in 1997 by Bertrand and co-workers[5] as building block for the synthesis of organometallic polymers. The dicationic heterocycle **[AH$_2$](OTf)$_2$** was treated with 2 eq. of silver(I) acetate in refluxing THF. Single crystals of the organometallic Ag(I)-based polymer **1A** were obtained at -30ºC in CH_3CN.



Scheme 1.1 Synthesis of organometallic polymer based on *ditz* ligand

Ligands **B** and **C** were coordinated to a wide range of metals fragments. Unlike other ligands, such us P- or N-donor ligands, NHC ligands require the prior activation of their precursors, normally azolium-based salts. In the case of imidazolium salts, this activation implies the deprotonation with a base.

Rh(I) complex **1B**, bearing bis-NHC ligand **B** was synthesized by Bielawski and co-workers in 2006.[6] The deprotonation of the salt **[BH$_2$](X)$_2$** was carry out with LDA, providing the free *Janus*-type ligand **B**. Then, this ligand reacted with $[RhCl(cod)]_2$, giving the desired bimetallic complex **1B**.



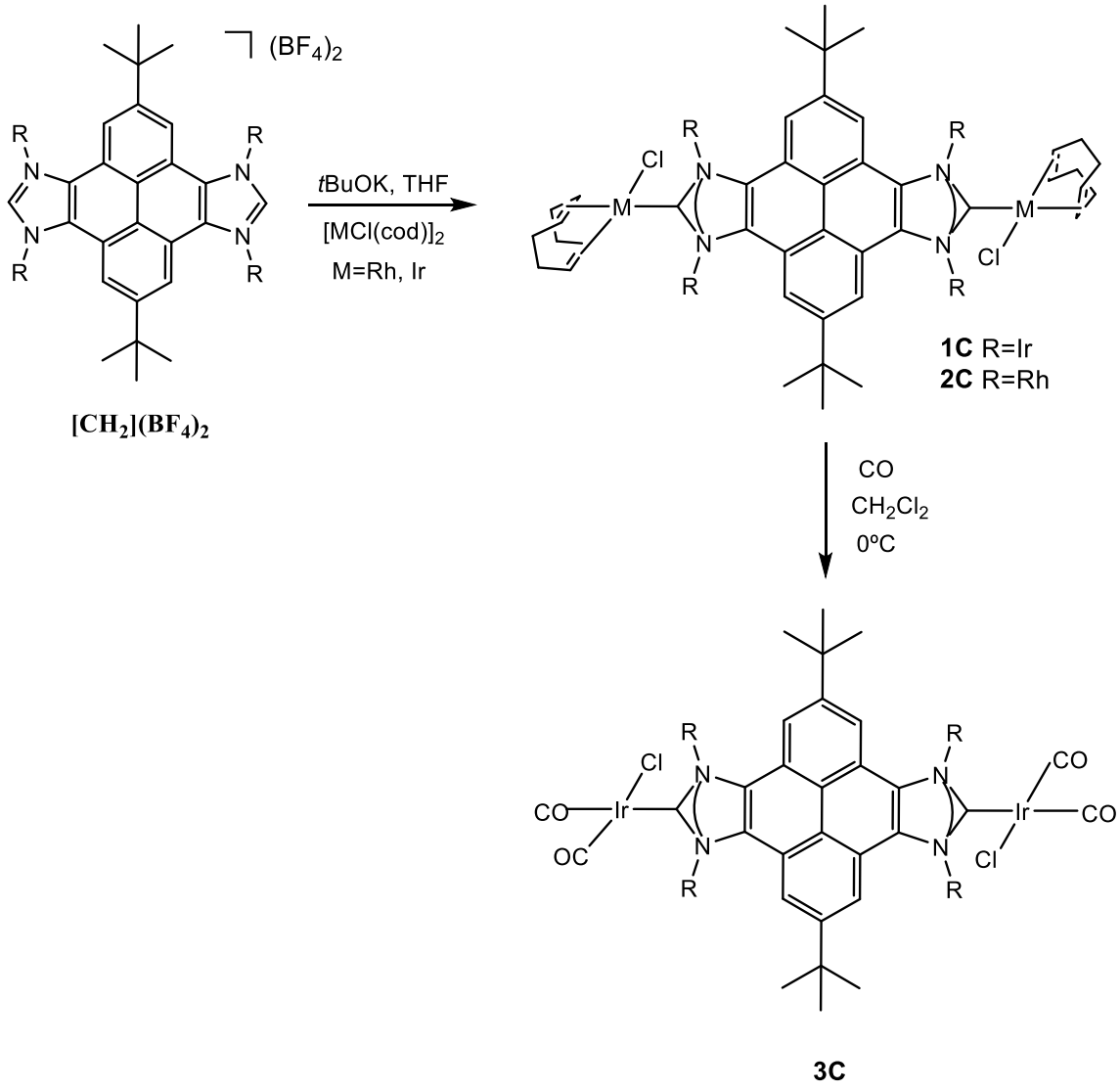
Scheme 1.2 Synthesis of complex **1B**

Ligand **C** was coordinated to Ir(I) and Rh(I)[7] and later to Ru(II)[8] by the group of research of Prof. Peris.

The procedure involves the deprotonation of the corresponding salt **[CH$_2$](BF$_4$)$_2$** with *t*BuOK and subsequent coordination to $[MCl(cod)]_2$ (M = Rh and Ir), giving the desired

bimetallic complexes **1C** and **2C**. Then, complex **1C** was carbonylated with CH_2Cl_2 to obtain complex **3C** (Scheme 1.3).

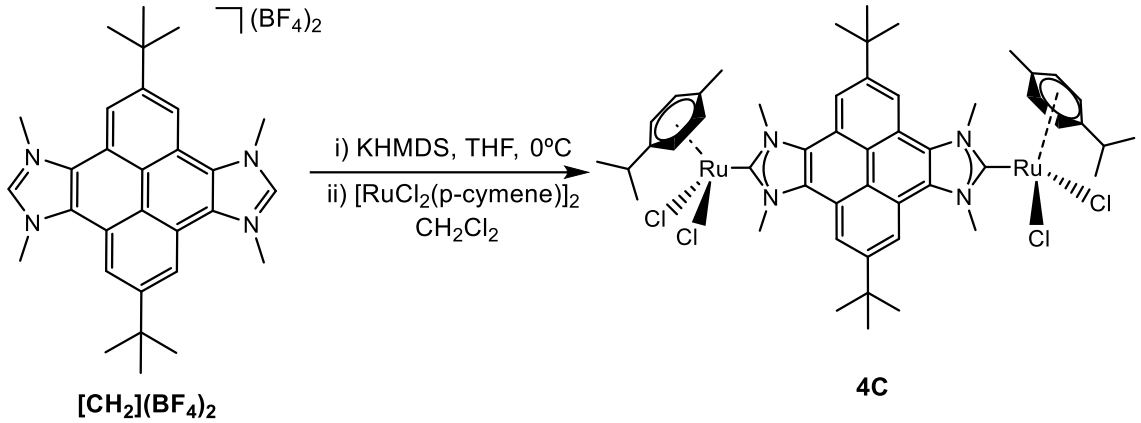
For the synthesis of the Ru(II) complex, the procedure is similar. The deprotonation of the salt **$[CH_2](BF_4)_2$** was carry out by KHMDS and then, reacted with $[RuCl_2(p\text{-cymene})]_2$ to yield the desired bimetallic complex **4C** (Scheme 1.4).



$[CH_2](BF_4)_2$

3C

Scheme 1.3 Synthesis of Rh(I) and Ir(I) pyrene-based complexes **1C**, **2C** and **3C**



[CH2](BF4)2 **4C**

Scheme 1.4 Synthesis of Ru(II) pyrene-based complex **4C**

2. OBJECTIVES

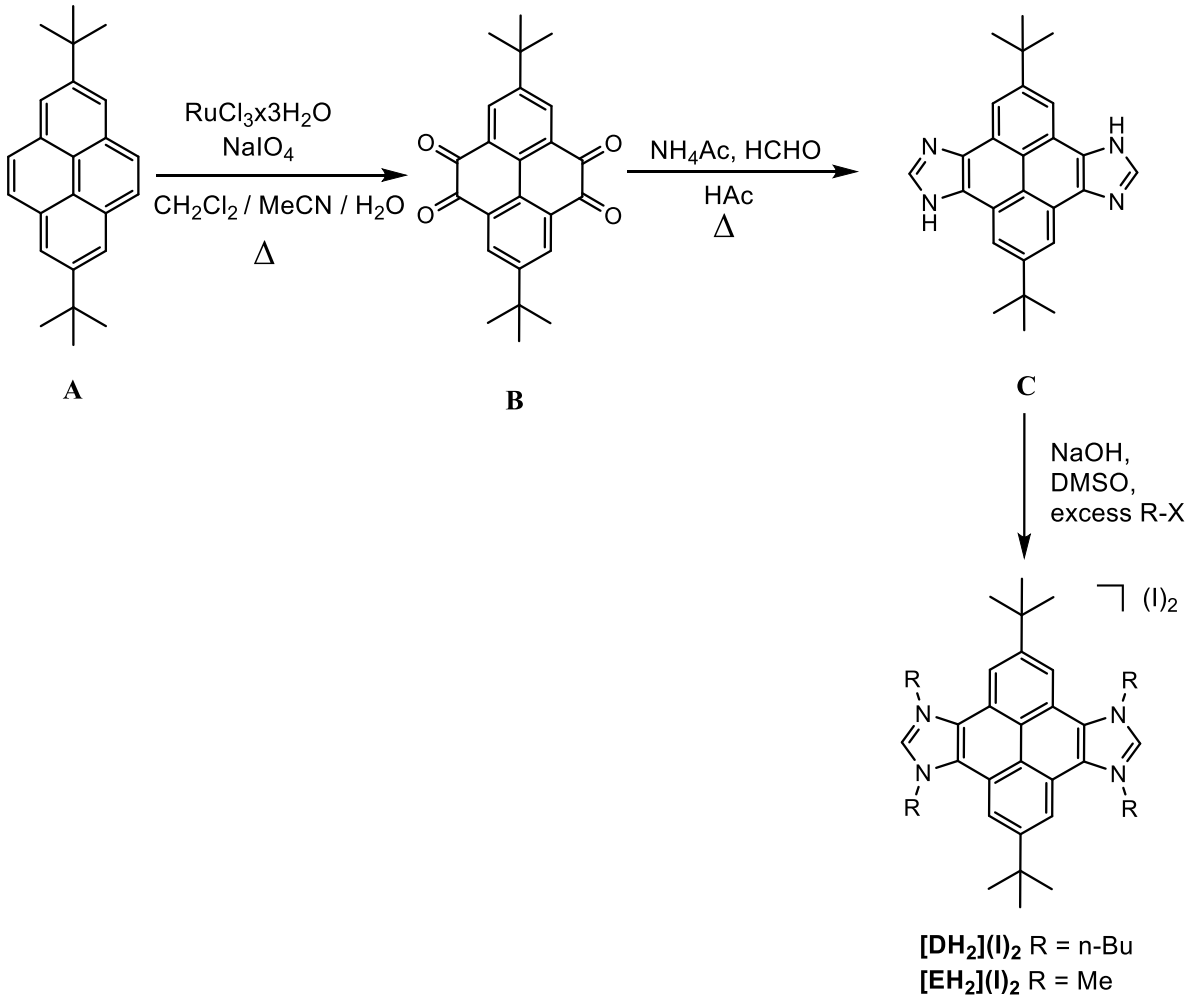
The general objective of this work is to explore the coordination versatility of a pyrene-based bis-NHC ligand. This general objective can be divided in two main objectives that are:

- Synthesis and characterization of two pyrene-based bis-imidazolium salts, starting from 2,7-di-*tert*-butylpyrene.
- Synthesis and characterization of a homo-bimetallic Ru(II)-NHC complex.

3. RESULTS AND DISCUSSION:

3.1 Synthesis of the pyrene-based bis-imidazolium salts

As depicted in Scheme 3.1, the pyrene-based bis-imidazolium salts **[DH$_2$](I)$_2$** and **[EH$_2$](I)$_2$** were prepared following a three-step synthetic procedure starting from 2,7-di-*tert*-butylpyrene **(A)**. Compound **A** can be prepared in large scale (*ca*. 10 g) from commercially available pyrene, so we employed a common batch of the group.



Scheme 3.1 Synthesis of the bis-imidazolium salts

The first step involves the oxidation of **A** with $RuCl_3x3H_2O$ and $NaIO_4$ in CH_2Cl_2, water and MeCN under very mild conditions to yield tetra-ketone **B**. The resulting dark-brown solution was stirred at 40ºC overnight. The solid was extracted from the dark-brown mixture with CH_2Cl_2. The volatiles were removed under vacuum. After that, an orange solid was isolated. Then, compound **B** was purified by column chromatography eluting with ethyl acetate/hexane mixture (2:5). After purification, compound **B** was isolated as

orange crystalline solid in 34% yield. The two *tert*-butyl groups were introduced at the Kappa positions of pyrene (2,7) in order to obtain the oxidation of pyrene at the desired positions and increase the solubility of the final products.

The second step involves the condensation of **B**, formaldehyde and ammonium acetate in glacial acetic acid. The brown-orange suspension was heated to reflux overnight. The resulting mixture was treated with water and neutralized with aqueous ammonia. After that, the so-formed solid was isolated by filtration. Compound **C** was isolated as beige solid in 57% yield.

The third step involves the tetraalkylation of **C** by treatment with NaOH dissolved in DMSO followed by the addition of the corresponding alkyl halide. The brown solution was stirred at 37ºC overnight. After this time, the solvent was removed under vacuum distillation (Chart 3.1). This step is crucial to achieve the desired salts in high level of purity and high yields, so it is very important to remove the remaining DMSO. Giving that DMSO has a very high boiling point (189 ºC), vacuum distillation is the best way to remove it. Upon vacuum distillation, the crude solid was dissolved in CH_2Cl_2 and filtered through a pad of Celite. The solvent was removed under vacuum and the yellow solid was put in a Schlenk tube fitted with a Teflon tap with an excess of the corresponding alkyl halide. This solution was stirred at 130ºC for 3d. During this time, the desired products precipitated and were collected by filtration and washed with diethyl ether. Salts **[DH_2](I)$_2$** and **[EH_2](I)$_2$** were isolated as beige solids in approximately 20% yield.

Chart 3.1 Vacuum distillation

The two salts **[DH$_2$](I)$_2$** and **[EH$_2$](I)$_2$** were purified by precipitation with CH_2Cl_2 and diethyl ether.

All the already known compounds (**B** to **[EH$_2$](I)$_2$**) were identified according to previously reported spectroscopic data.

Characterization of compound B

*^{1}H NMR spectrum of **B** in $CDCl_3$*

Figure 3.1 shows the ^{1}H NMR spectrum in $CDCl_3$ of 2,7-di-*tert*-butylpyrene-4,5,9,10-tetraone (**B**). The number of signals and their integration are consistent with the two-fold symmetry of the compound. The signal assigned to the four aromatic protons of the pyrene core is observed as a singlet at 8.47 ppm (**a**). The signal corresponding to the eighteen protons of the *tert*-butyl groups appears as a singlet at 1.42 ppm (**b**).

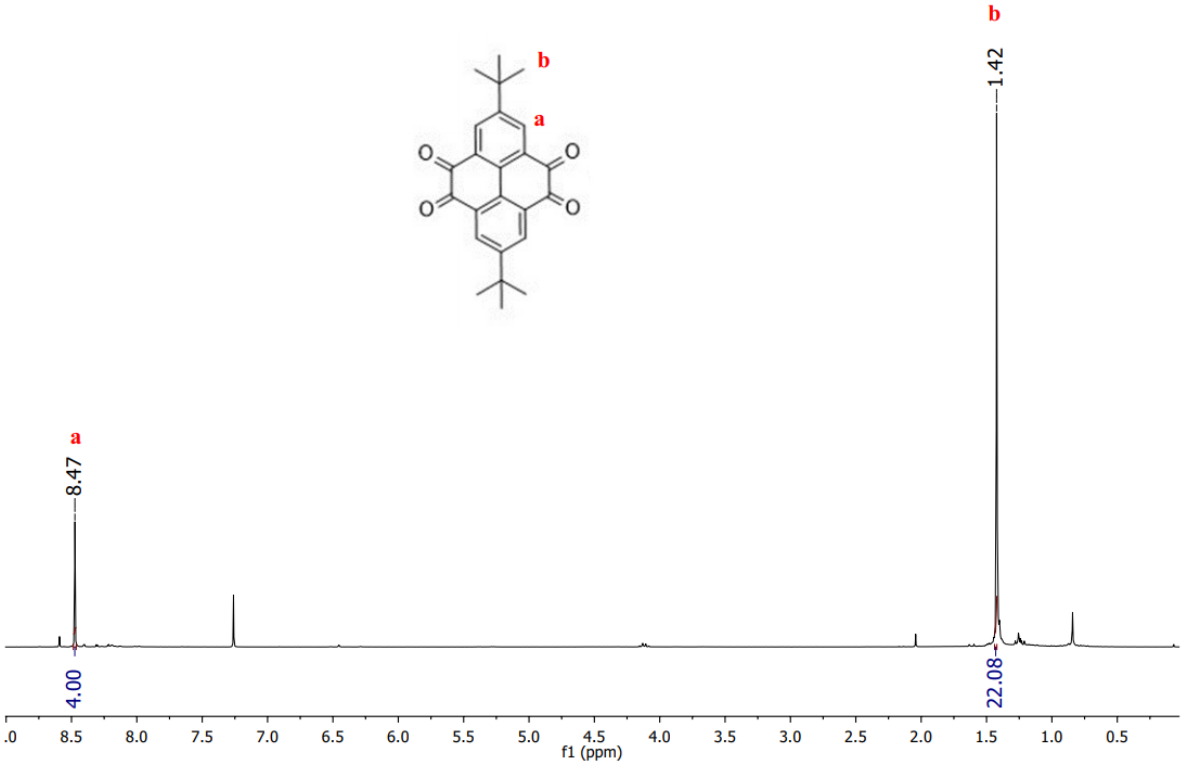


Figure 3.1 ^{1}H NMR spectrum of **B** in $CDCl_3$

Characterization of compound C:

*^{1}H NMR spectrum of **C** in DMSO-d_6*

Figure 3.2 shows the ^{1}H NMR spectrum in DMSO-d_6 of compound **C**. The number of signals and their integration are consistent with the two-fold symmetry of the compound. The signal assigned to the four aromatic protons of the pyrene core is observed as a singlet at 8.69 ppm (**a**). The protons corresponding to the two NC*H*N groups appear as a singlet at 8.41 ppm (**c**). Finally, the signal corresponding to the eighteen protons of the *tert*-butyl groups is displayed as a singlet at 1.61 ppm (**b**).

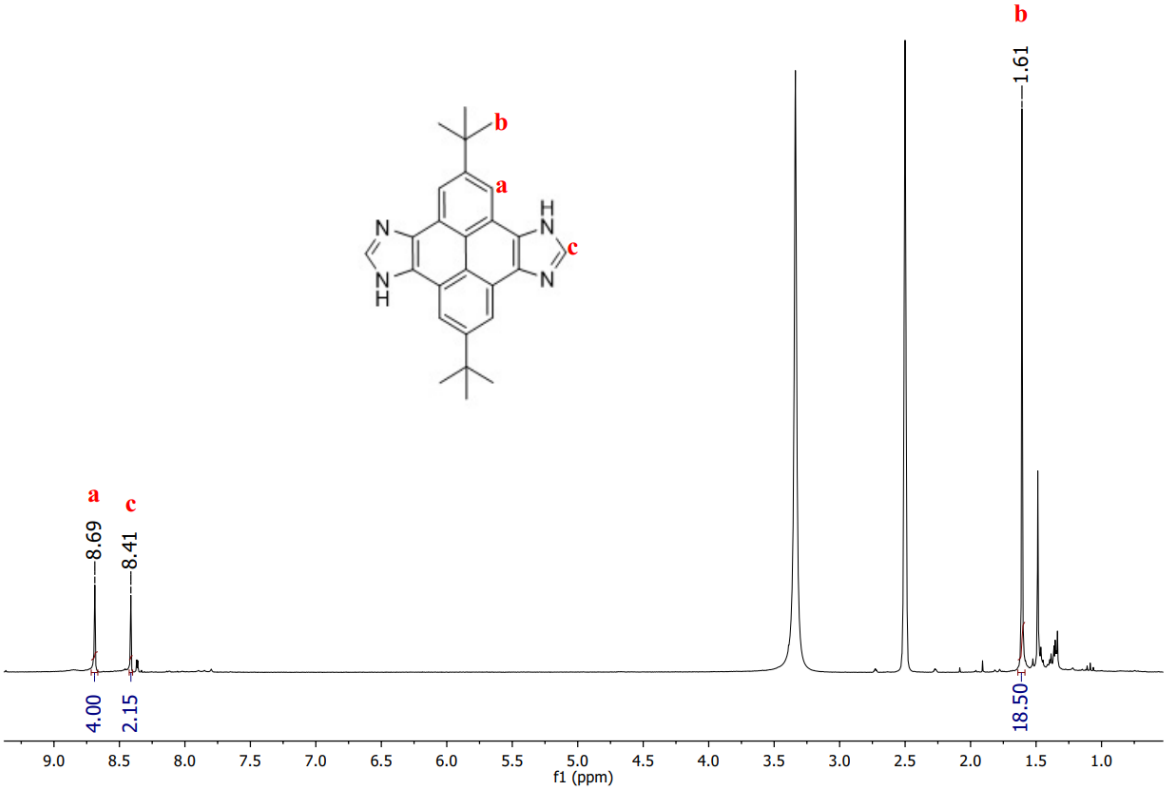


Figure 3.2 ^{1}H NMR spectrum of **C** in DMSO-d_6

*^{13}C NMR spectrum of **C** in DMSO-d_6*

Figure 3.3 shows the ^{13}C NMR spectrum in DMSO-d_6 of compound **C**. The signals observed at 176.66, 149.04, 139.55 and 118.23 ppm (**$C_{q\ pyr}$**) are attributed to the quaternary carbons of the pyrene core. The signal attributed to the N*C*HN carbons is displayed at 172.41 ppm (**4**). The signal due to the aromatic CH groups of the pyrene core appears at 114.91 ppm (**1**). Finally, the signals corresponding to the carbon atoms of the *tert*-butyl groups appear at 35.72 (**2**) and 32.21 ppm (**3**).

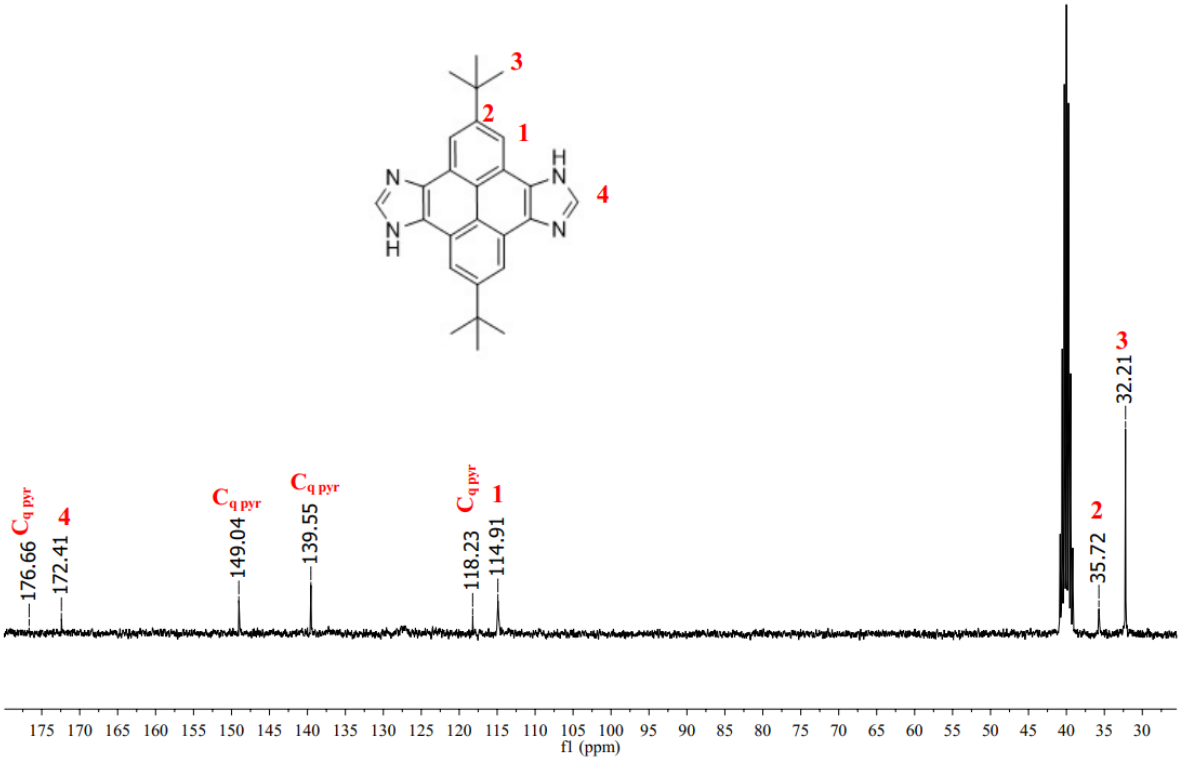


Figure 3.3 ^{13}C NMR spectrum of **C** in DMSO-d_6

Characterization of salts $[DH_2](I)_2$ and $[EH_2](I)_2$:

*^{1}H NMR spectrum of **$[DH_2](I)_2$** in DMSO-d_6*

Figure 3.4 shows the ^{1}H NMR spectrum in DMSO-d_6 of compound **$[DH_2](I)_2$**. The number of signals and their integration are consistent with the two-fold symmetry of the compound. The most characteristic signal, namely the signal attributed to the protons of NC*H*N appears as a singlet at 10.02 ppm (**c**). The protons corresponding to the pyrene core are displayed as a singlet at 8.90 ppm (**a**). The signal corresponding to the protons of the *tert*-butyl groups is displayed as a singlet at 1.70 ppm (**b**). Finally, in the aliphatic region, we can find four signals corresponding to the *n*-butyl substituents (**nBu**), two of them as triplets at 5.18 and 1.03 ppm, and the other two as multiplets at 2.16 and 1.59 ppm.

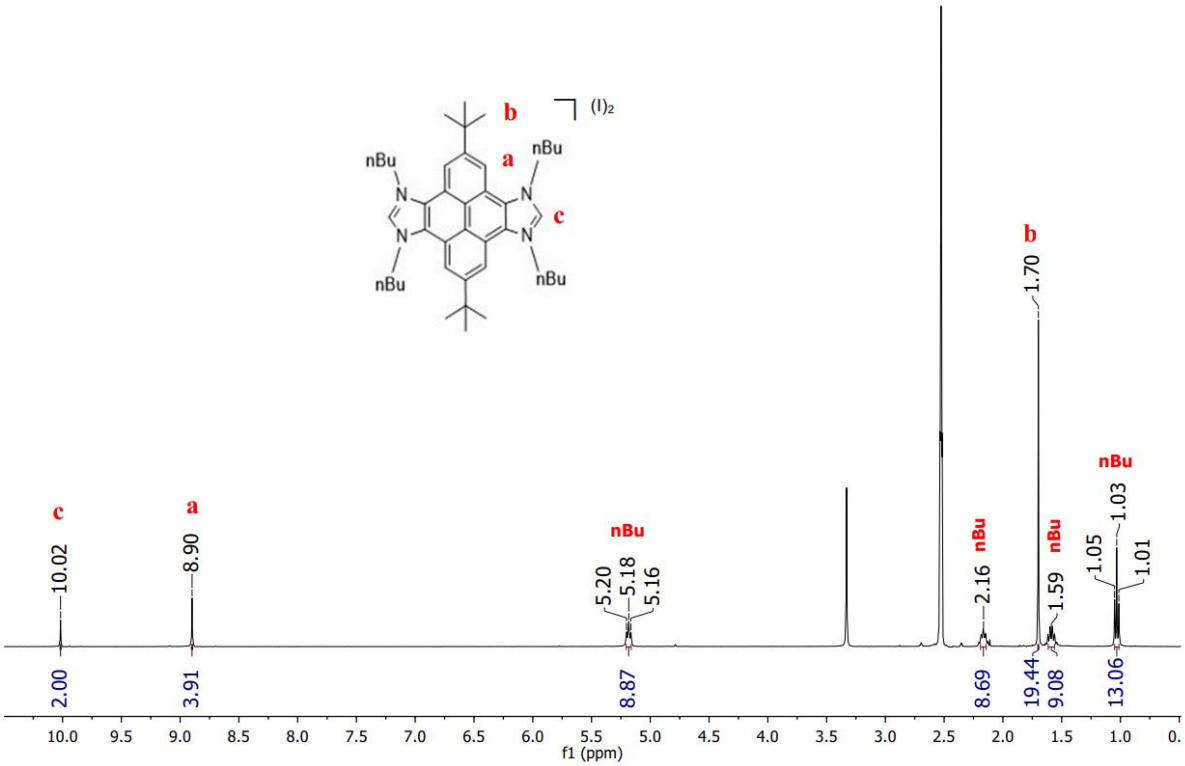


Figure 3.4 ^{1}H NMR spectrum of **[DH$_2$](I)$_2$** in DMSO-*d*$_6$

*^{13}C NMR spectrum of **[DH$_2$](I)$_2$** in DMSO-d$_6$*

Figure 3.5 shows the ^{13}C NMR spectrum in DMSO-*d*$_6$ of **[DH$_2$](I)$_2$**. The resonances due to the quaternary carbon atoms of the pyrene core appear at 150.48, 126.75, 120.55, 120.19 (**C$_{q\ pyr}$**). The signal attributed to the N*C*HN carbons is displayed at 142.73 ppm (**4**). The signal due to the aromatic CH groups of the pyrene core appears at 118.62 ppm (**1**). The signals attributed to the carbons of the n-butyl groups are observed at 50.57, 31.07, 19.83 and 13.49 ppm (**nBu**). Finally, the signal of the carbons of the *tert*-butyl groups appears at 35.68 (**1**) and 30.51 (**2**) ppm.

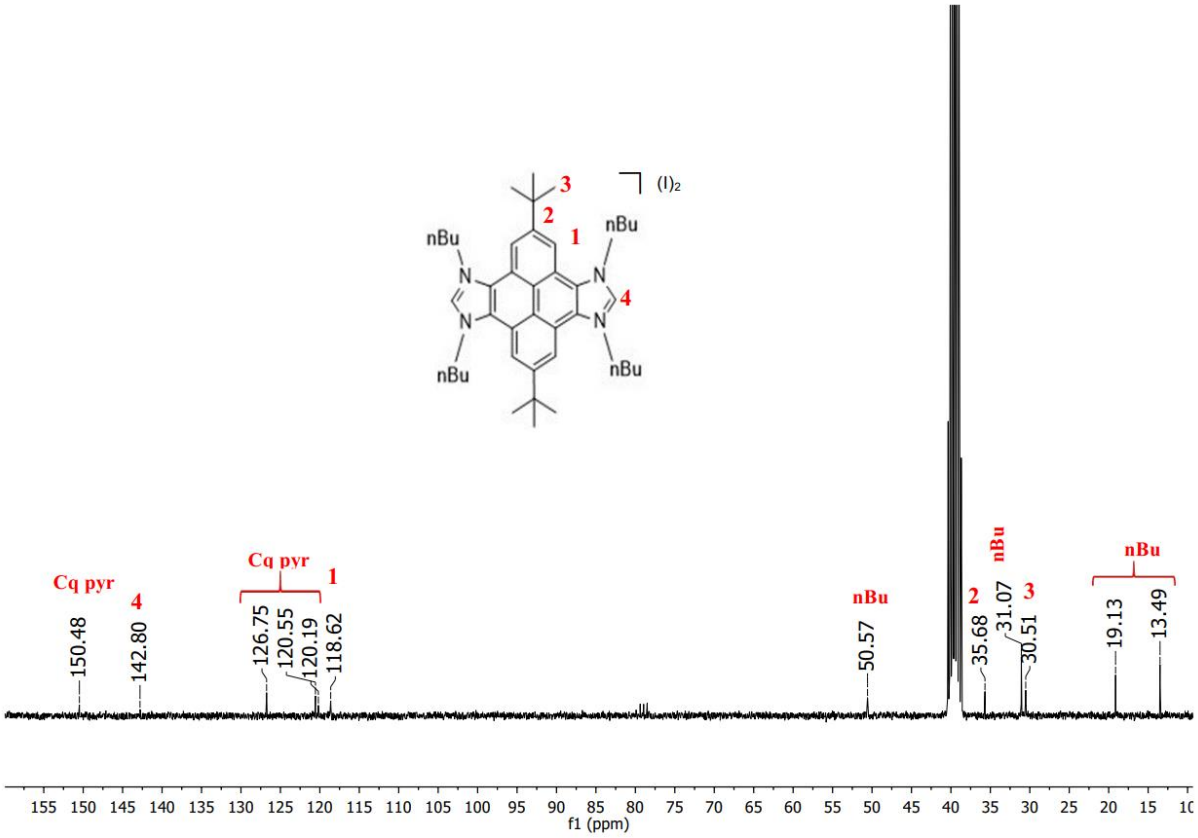


Figure 3.5 ^{13}C NMR spectrum of **[DH$_2$](I)$_2$** in DMSO-*d*$_6$

*^{1}H NMR spectrum of **[EH$_2$](I)$_2$** in DMSO-d$_6$*

Figure 3.6 shows the ^{1}H NMR spectrum of **[EH$_2$](I)$_2$**. The protons corresponding to the NC*H*N groups appears as a singlet at 9.88 ppm (**c**). The resonance attributed to the aromatic protons of the pyrene core is observed as a singlet at 9.07 ppm (**a**). The signal due to the protons of the methyl groups appears as a singlet at 4.79 ppm (**d**). Finally, the signal corresponding to the protons of the *tert*-butyl groups is displayed as a singlet at 1.72 ppm (**b**).

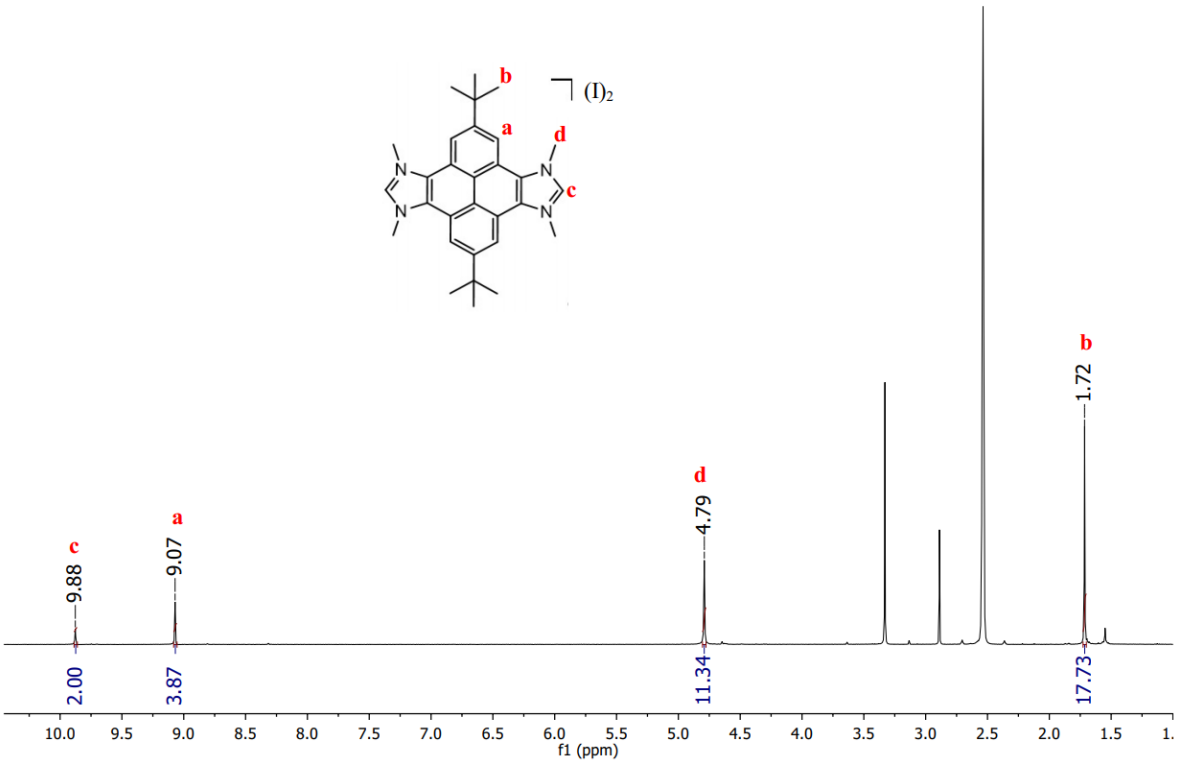


Figure 3.6 ^{1}H NMR spectrum of **[EH$_2$](I)$_2$** in DMSO-d$_6$

3.2 Attempts to activate salt [DH$_2$](I)$_2$

Once the pyrene-based imidazolium salts were prepared and conveniently characterized we decided to explore the capability of the salt **[DH$_2$](I)$_2$** to be used as the precursor of bis-NHC ligand **D** in the preparation of a di-ruthenium complex. To achieve the coordination of a bis-NHC ligand precursor to a metal fragment it is necessary the previous activation of the corresponding salt. The most widely method to activate imidazolium salts is their deprotonation with a strong base, such as NaH, *t*BuOK or KHMDS (Potassium bis(trimethylsilyl)amide).

The bis-imidazolium salt **[DH$_2$](I)$_2$** was reacted with [RuCl$_2$(*p*-cymene)]$_2$ in the presence of KHMDS under nitrogen atmosphere, using the Schlenk technique (Chart 3.2). Based on previous findings of the group, we expected to synthesize the homo-bimetallic Ru(II) complex displayed in Scheme 3.2, in which two chloride and a *p*-cymene ligands complete the coordination sphere about each of the two ruthenium atoms.

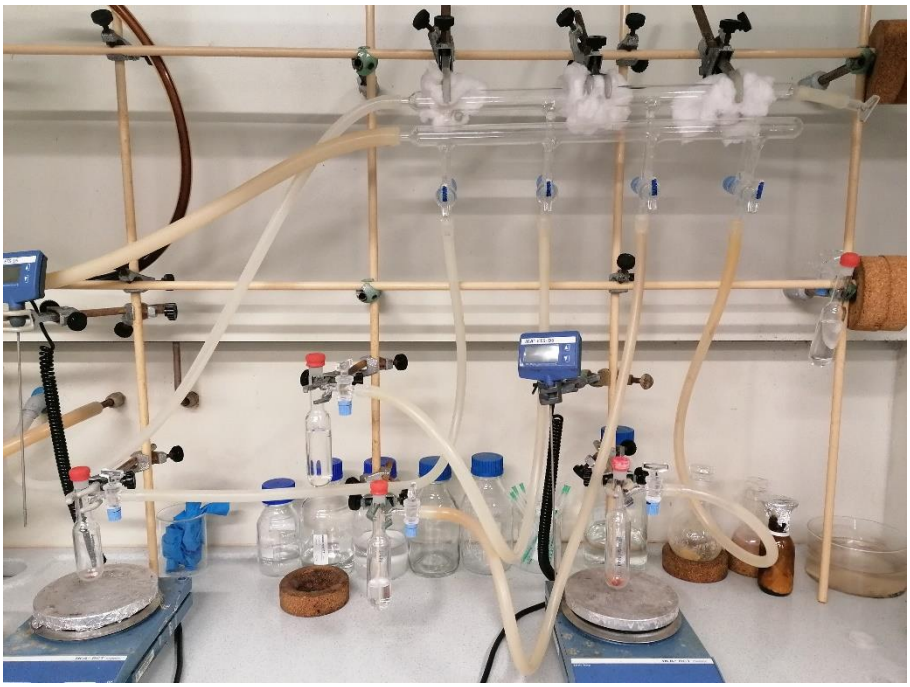
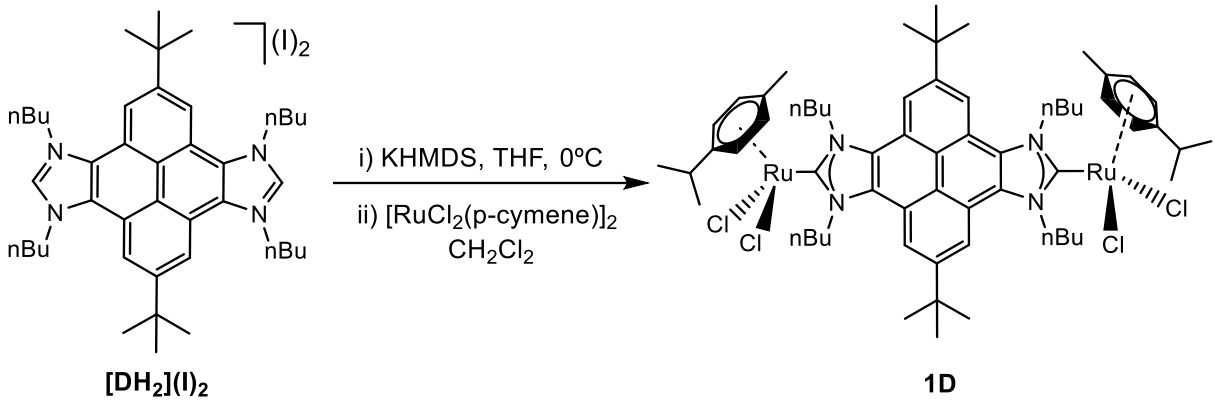


Chart 3.2 Experimental setup working under nitrogen atmosphere

Unfortunately, the coordination of ligand **D** to Ru(II) was unsuccessful. Using the methodology described in the literature,[8] we were not able to completely activate salt **[DH$_2$](I)$_2$**, as demonstrated bellow.



[DH$_2$](I)$_2$ **1D**

Scheme 3.2 Synthesis of the Ru(II)-based homo-dimetallic complex

Despite the spectra being made in different solvents, (**[DH$_2$](I)$_2$** in DMSO-d_6 and the crude solid after reaction in $CDCl_3$), we can observe the same pattern of signals. A clear sign of this is that the signal that corresponds to the acidic protons of the salt (at δ 10 ppm) remains in the ^{1}H NMR spectrum of the crude solid after the work-up, so we can conclude that the salt was not activate using this methodology.

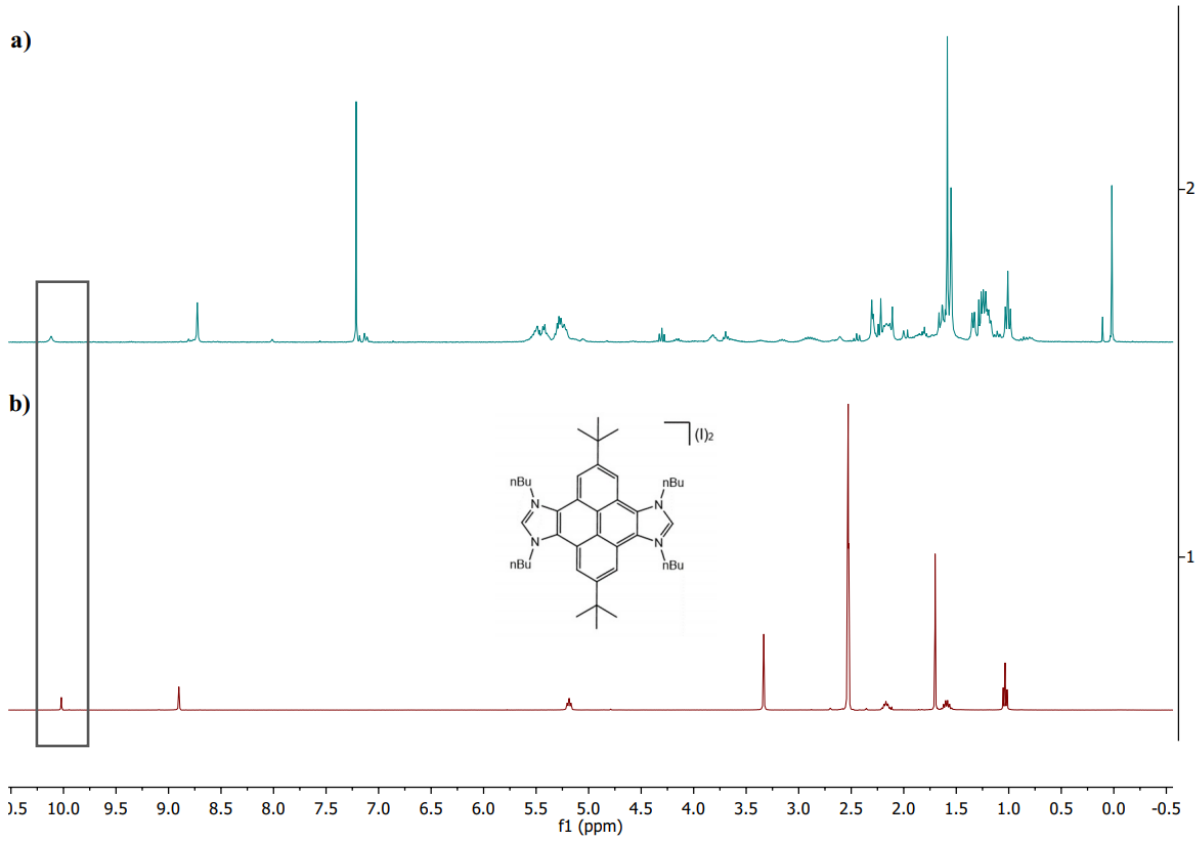


Figure 3.7 ^{1}H NMR pile up spectra of the crude solid isolated after the activation attempt (a) and the salt **[DH$_2$](I)$_2$** (b)

4. CONCLUSIONS:

In this work, first we synthetized two pyrene-based bis-imidazolium salts **[DH$_2$](I)$_2$** and **[EH$_2$](I)$_2$** as precursors of two *Janus*-type bis-NHC ligands, through a three-step synthetic route starting from 2,7-di-*tert*-butylpyrene.

The synthetic route to the bis-imidazolium salts involves the oxidation of 2,7-di-*tert*-butylpyrene to obtain compound **B**, and its subsequent purification. Then, the condensation of compound **B**, and subsequent tetralkylation of the resulting compound **C** with the corresponding alkyl halide, yielded the desired salts **[DH$_2$](I)$_2$** and **[EH$_2$](I)$_2$**.

With the ligand precursors in hand, we explore the coordination capabilities of the salt **[DH$_2$](I)$_2$** towards ruthenium, using [RuCl$_2$(*p*-cymene)]$_2$ as metal precursor in the presence of KHMDS.

As can be seen in the introduction, it is possible to carry out the coordination of a very similar bis-imidazolium salt to a Ru(II), as described by Peris and Gonell in 2014.[8] To study the coordination capabilities of the salt **[DH$_2$](I)$_2$**, we followed the same synthetic procedure, but in our hands the activation of the salt was unsuccessful. It is possible that the activation did not work because our bis-imidazolium salt differs from the already described in the substituents of the nitrogen atoms (n-butyl instead of methyl groups) and the counterions (iodide instead of tetrafluoroborate).

5. EXPERIMENTAL SECTION

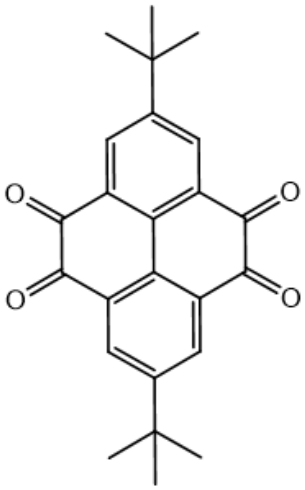
5.1 General methods

Compounds **B**, **C** and the bis-imidazolium salts **[DH$_2$](I)$_2$** and **[EH$_2$](I)$_2$** were prepared according to literature methods.[9,10] The synthesis of compounds **B** and **C** was performed under aerobic conditions. The synthesis of salts **[DH$_2$](I)$_2$** and **[EH$_2$](I)$_2$** was carried out in a thick-walled Schlenk tube fitted with a Teflon cap. In the case of the attempt to activate salt **[DH$_2$](I)$_2$**, the reaction was carried out by using Schlenk tube techniques under nitrogen atmosphere. Anhydrous solvents were dried using a Solvent Purification System (SPS MBRAUN). All other reagents were used as received from commercial suppliers. Column chromatography was performed in silica gel Merck 60, 63-200 μm unless otherwise stated using the mixture of solvents indicated.

NMR spectra were recorded on a Bruker 300 or 400 MHz using $CDCl_3$ or DMSO-d_6 as solvents.

5.2 Synthesis and characterization of the pyrene-based bis-imidazolium salts

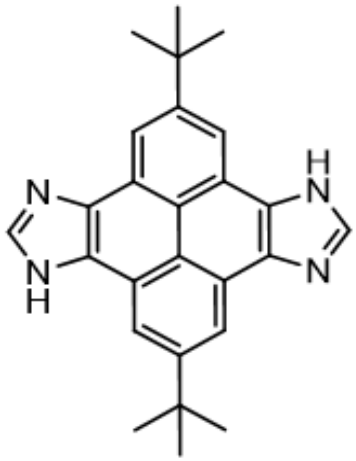
*Synthesis of compound **B***



In a round-bottom flask, 2,7-di-*tert*-butylpyrene (**A**, 3.15 g, 10 mmol, 1 eq.) was dissolved in a mixture of MeCN (40 mL) and CH_2Cl_2 (40 mL). The oxidizing agent, $NaIO_4$ (17.50 g, 81.8 mmol, 8 eq.) and water (50 mL) were subsequently added to the resulting mixture. The reaction mixture was initially orange and turned to dark after adding the catalyst, $RuCl_3 \cdot 3H_2O$ (0.32 g, 1.2 mmol, 0.1 eq.). The resulting mixture was stirred at 40°C overnight. After this time, the mixture was allowed to reach room temperature with stirring. Water (200 mL) was added to the resulting solution. After that, the mixture was filtered through a pad of Celite, giving a dark green solution. The solution was poured into a separation funnel and extracted with DCM (3x50 mL). The organic layers were combined and dried with anhydrous $MgSO_4$. After that, the solution was filtered and the solvent was removed under vacuum. The desired product was purified by column chromatography. Elution with a mixture 5:2 ethyl acetate/hexane afforded the separation of an orange band that contained the desired compound. The desired product **B** was

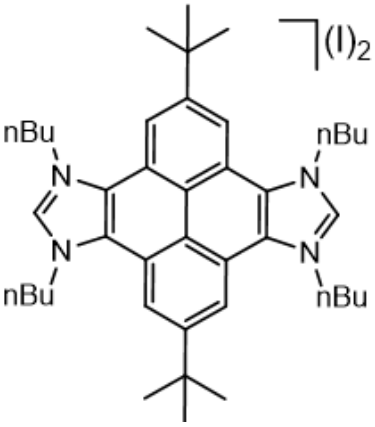
isolated as a yellow solid. Yield: 1.29 g, 34%. ^{1}H NMR: (300MHz, $CDCl_3$): δ = 8.47 (s, 4H, CH_{pyr}), 1.42 (s, 18H, C(CH_3)$_3$).

*Synthesis of compound **C***



2,7-Di-*tert*-butylpyrene-4,5,9,10-tetraone (**B**, 0.50 g, 1.33 mmol, 1 eq.) and NH_4Ac (4.2 g, 53.48 mmol, 40 eq.) were dissolved in glacial acetic acid (20 mL). Formaldehyde (0.22 mL, 2.94 mmol, 2.2 eq.) was added dropwise to the reaction mixture and the resulting mixture was heated to reflux overnight. Once at room temperature, the reaction mixture was treated with water (400 mL) and neutralized with NH_4OH. The solid so formed was filtrated and washed successively with water and cold diethyl ether. After that, compound **C** was isolated as a beige solid. Yield: 0.34 g, 57%. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 8.69 (s, 4H, CH_{pyr}), 8.42 (s, 2H, NCHN), 1.61 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 176.66 ($C_{q\ pyr}$), 172.41 (NCHN), 149.04 ($C_{q\ pyr}$), 139.55 ($C_{q\ pyr}$), 118.23 ($C_{q\ pyr}$), 114.91 (CH$_{pyr}$), 35.72 (C(CH$_3$)$_3$), 32.21 (C(CH$_3$)$_3$).

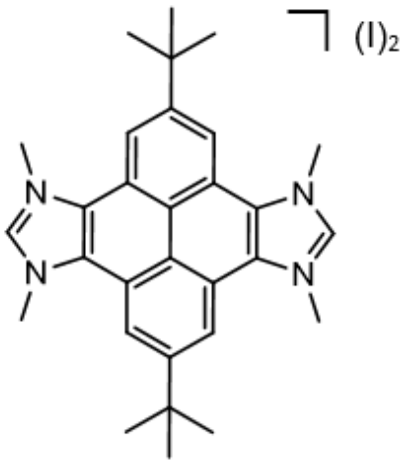
*Synthesis of compound **[DH$_2$](I)$_2$***



Compound **C** (0.10 g, 0.25 mmol, 1 eq.) and NaOH (0.02 g, 0.51 mmol, 2 eq.) were dissolved in DMSO (2mL). The suspension was stirred at room temperature for 2 h. After that, the suspension becomes a brown solution. n-Butyl iodide (58 µL, 0.51 mmol, 2 eq.) was then added and the solution was stirred at room temperature for 30 min and thereafter at 37°C overnight. After this time, the solvent was removed by vacuum distillation. The residue was dissolved in CH_2Cl_2 and filtered over Celite to remove insoluble salts washing with CH_2Cl_2. The solvent was removed under vacuum and the isolated orange solid was placed in a high pressure Schlenk with n-butyl iodide (1.68 mL, 10.15 mmol, 40.6 eq.). The reaction mixture was stirred at 130°C for 3 days. After that, diethyl ether was added to precipitate the desired product as a yellow-orange solid. This solid was collected by filtration and washed with diethyl ether. Yield: 0.03 g, 17%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.02 (s, 2H, NCHN), 8.90 (s, 4H, CH$_{pyr}$), 5.18 (t, $^{3}J_{H,H}$ = 5.25 Hz, 8H,

$NCH_2CH_2CH_2CH_3$), 1.70 (s, 18H, $C(CH_3)_3$, 1.03 (t, $^3J_{H,H}$ = 8.70 Hz, 12H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 150.48 ($C_{q\ pyr}$), 142.73 (N*C*HN), 126.75 ($C_{q\ pyr}$), 120.55 ($C_{q\ pyr}$), 120.19 ($C_{q\ pyr}$), 118.62 (CH_{pyr}), 50.57 ($NCH_2CH_2CH_2CH_3$), 35.68 ($C(CH_3)_3$), 31.07 ($NCH_2CH_2CH_2CH_3$), 30.51 ($C(CH_3)_3$), 19.83 ($NCH_2CH_2CH_2CH_3$), 13.49 ($NCH_2CH_2CH_2CH_3$).

Synthesis of compound ***[EH₂](I)₂***



Compound **C** (0.10 g, 0.25 mmol, 1 eq.) and NaOH (0.02 g, 0.51 mmol, 2 eq.) were dissolved in DMSO (2mL). The suspension was stirred at room temperature for 2 h. After that, the suspension becomes a brown solution. Methyl iodide (32 µL, 0.51 mmol, 2 eq.) was the added and the resulting solution was stirred at room temperature for 30 min and thereafter at 37°C overnight. After this time, the solvent was removed by vacuum distillation. The residue was dissolved in CH_2Cl_2 and filtered over Celite to remove insoluble salts washing with CH_2Cl_2. The solvent was removed under vacuum and the isolated orange solid was placed in a high pressure Schlenk with methyl iodide (0.64 mL, 10.15 mmol, 40.6 eq.). The reaction mixture was stirred at 130°C for 3 days. After that, ether was added to precipitate the desired product as a red-orange solid. This solid was collected by filtration and washed with diethyl ether. Yield: 0.03 g, 18%. ^1H NMR (400 MHz, DMSO-d_6): δ = 9.88 (s, 2H, NC*H*N), 9.07 (s, 4H, CH_{pyr}), 4.79 (s, 12H, NCH_3), 1.72 (s, 18H, C(CH_3)$_3$).

5.3 Attempts to activate salt [DH₂](I)₂

Salt **[DH₂](I)₂** (0.03 g, 0.04 mmol, 1 eq.) and $[RuCl_2(p\text{-cymene})]_2$ (0.02 g, 0.04 mmol, 1 eq.) were placed in two different Schlenk tubes. The tubes were evacuated and filled with nitrogen three times. After that, 5 mL of dry THF were added at 0ºC to the Schlenk tube containing the salt, giving a brown solution. In the other hand, 5 mL of dry CH_2Cl_2 were added at 0ºC to the Schlenk tube containing the metal precursor, giving an orange solution. KHMDS (0.5 M in toluene, 0.15 mL, 0.07 mmol, 2 eq.) was added dropwise to the solution of the salt, giving a yellow solution and the resulting mixture was stirred at 0ºC for 10 min. The latter solution was then added through an oven-dried cannula to the

solution of the metal precursor, giving a red-brown solution. The resulting mixture was stirred at 45ºC for 1 h, and after that was refluxed for 20 min. The solution was filtered through a pad of Celite eluting with CH_2Cl_2. The solvent was removed under vacuum. The evolution of the reaction was monitored by ^1H NMR, as mentioned in the Results and Discussion section.

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