



SYNTHESIS AND CHARACTERIZATION OF PYRENE-BASED TETRANUCLEAR Ir(I) COMPLEXES

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Nomenclature

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

The starting material and the intermediate in the synthesis of the tetra-imidazolium salt are named with letters **A** and **B**, respectively. The precursor tetra-imidazolium salt is labelled as **C**. Finally, the metallic complexes are named **1** and **2**.

List of abbreviations

Δ	refluxing temperature
NHC	N-heterocyclic carbene
CDCl_3	deuterated chloroform
$\text{DMSO-}d_6$	deuterated dimethylsulfoxide
COD	1,5-cyclooctadiene
NaOAc	sodium acetate
DMF	N,N-dimethylformamide
nBuI	n-butyl iodide
ACN	acetonitrile
$[\text{IrCl}(\text{COD})]_2$	bis(1,5-cyclooctadiene) diiridium (I) dichloride
NEt_3	triethylamine
NMR	Nuclear Magnetic Resonance
δ	chemical shift
s	singlet
d	doublet
m	multiplet
ppm	parts per million
MHz	megahertz
ESI-MS	Electrospray Ionization Mass Spectrometry
m/z	mass to charge
Cq	quaternary carbon atom
g	gram
mg	milligram
h	hour
mL	millilitre
mmol	millimol

°C	degree Celsius
%	percent
eq	equivalence
imi	imidazole
py	pyrene

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1.- GENERAL INTRODUCTION

N-Heterocyclic carbene ligands (NHCs) are heterocyclic species, which contain a carbene carbon and at least one nitrogen atom inside the ring structure.

There are two main reasons why these ligands became widespread in Organic and Organometallic Chemistry. The first one was the successful use of NHC-based complexes in catalysis by Herrmann and co-workers.¹ The other reason is their use in the preparation of Grubbs' second generation catalyst,² which undoubtedly had its contribution in the award of the Nobel Prize for Chemistry in 2005. In the late 70s, Öfele³ and Wanzlick⁴ described the first examples of NHC-based complexes. They remained almost unexplored until 1991, when Arduengo was able to isolate the first thermally stable carbene (Figure 1.1).⁵ A few years later, in 1995, Herrmann stated that the use of N-heterocyclic carbenes constituted "a new structural principle for catalysis design in homogeneous catalysis", establishing a new renaissance for these ligands.¹

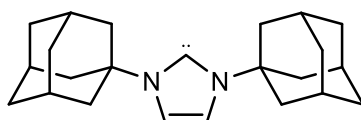


Figure 1.1. First isolated stable NHC ligand (1,3-di-1-adamantyl-imidazol-2-ylidene)

Chemical stability and coordination versatility are two of the main properties of NHCs that may have helped their great development. Furthermore, the easy preparation of NHC-precursors, typically imidazolium salts, has allowed an almost infinite access to new organometallic topologies.

1.1. APPLICATIONS OF NHCs

Many of the applications of NHCs are related to their coordination to a transition metal. The particularity of this bond can be explained by the capability of NHCs as σ -donor of two electrons from the carbene's carbon to the metal and in its capability to accept electrons from the metal.

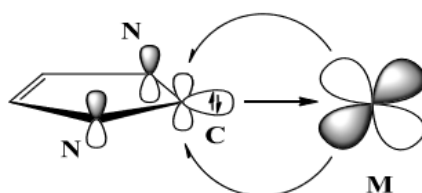


Figure 1.2. Bond between a NHC ligand and a transition metal

The characteristics of NHCs as ligands have led to several uses in different fields of Chemistry for example in areas like metallopharmaceuticals, but the main use is in homogeneous catalysis.

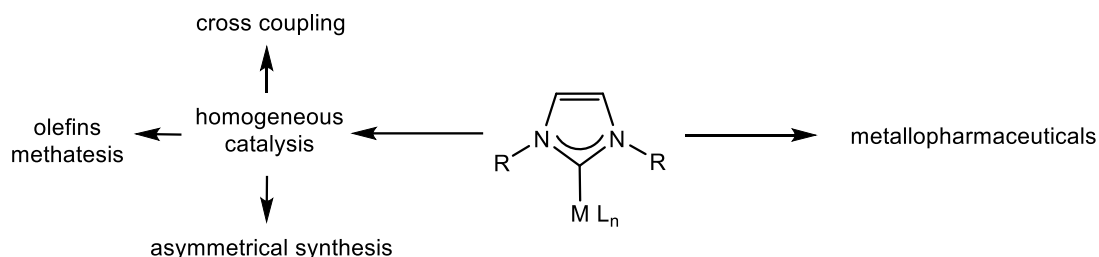


Figure 1.3. Main applications of NHC ligands

Within the field of metallopharmaceuticals, NHC ligands have been used as carrier molecules for metals in biological applications. A multitude of transition metals have been used in conjugation with NHCs including copper, silver, gold, platinum, palladium, ruthenium, etc.⁶

Their ability to bind different types of metals, as well as the multitude of chemical modifications that exist, makes them useful in many areas of scientific study, including new antibacterial and anticancer compounds. Specially, Ag-NHC complexes have shown promising outcomes in both of these areas.

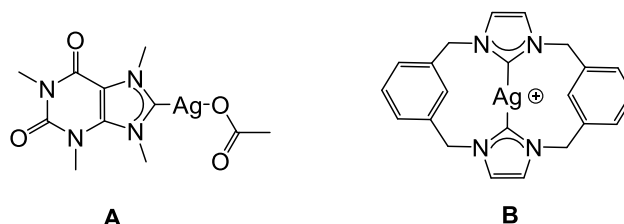


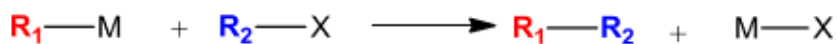
Figure 1.4. Ag-NHC complexes used as antibacterial (A) and anticancer agents (B)

Although, the main application of NHC-complexes is in the field of homogeneous catalysis.⁷ The three most extensively studied classes of catalytic reactions are asymmetric synthesis, cross coupling and olefins metathesis.

Asymmetric Synthesis: involves a procedure used to obtain stereoselective compounds from non-chiral compounds. Within the asymmetric synthesis framework, asymmetric catalysis is of great interest. These catalysts work interacting in a reversible way with the substrate creating a “chiral pocket” in the transition state, in this way, favouring the formation of one enantiomer instead of the other. NHCs stand out in the benzoin condensation, hydrogenation of alkenes or asymmetric reduction reactions.

Cross Coupling: involves the reaction between two hydrocarbon fragments that are attached to form a molecule; this reaction is normally carried out with a palladium catalyst. The most

important are Heck, Suzuki and Negishi reactions. In these reactions, there is a formation of a carbon-carbon bond and other carbene-heteroatom bond (Figure 1.5). NHC ligands can improve each phase of the cycle. As it is shown in Figure 1.6, the cycle consists of three steps. The first one involves an oxidative addition that is enhanced by the strong σ -donation of NHCs. The high steric influence of these ligands improves the last step of the cycle.



R and R' = aryl, vinyl, alkyl; X = halide; M = metal

Figure 1.5. Cross coupling reaction

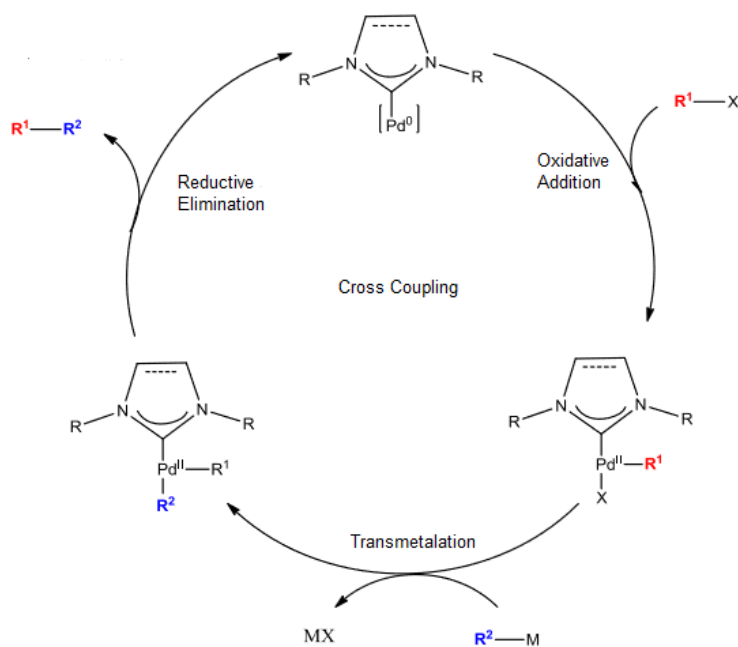


Figure 1.6. Catalytic cycle of the cross coupling reaction using an NHC-based palladium catalyst

Olefin Metathesis: This type of reaction is based on the exchange of substituent groups between two alkene units to yield two olefins with exchanged substituents.

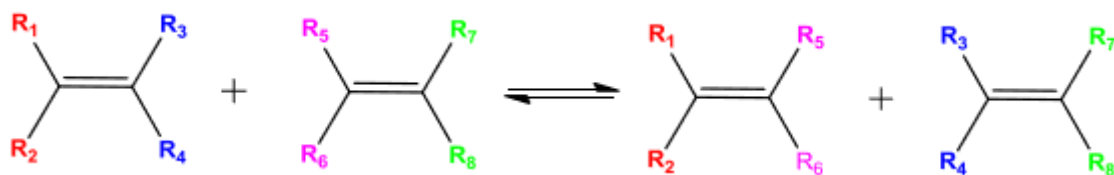


Figure 1.7. Olefin Metathesis reaction

Prof. Natta reported the use of ruthenium compounds as catalysts for olefin metathesis in 1965, using ruthenium trichloride. Years later, in 1992, Prof. Grubbs developed a family of catalysts bearing phosphine ligands. In 1996, Prof. Grubbs developed a generation of catalysts named as first generation catalysts (Grubbs I). These complexes are characterized by short activations periods, tolerance to different functional groups, stability and resistance to decomposition in air and wet atmosphere.

In 1999, Grubbs' second generation catalysts were obtained (Grubbs II). This generation of catalysts consists in replacing one of the olefins of the Grubbs I catalyst by a NHC ligand, thus obtaining an increase in the catalytic activity.²

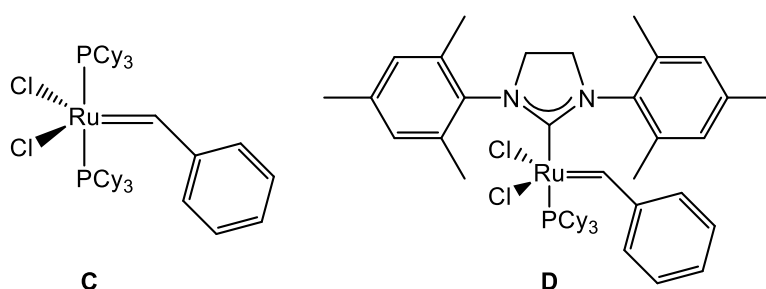


Figure 1.8. Examples of Grubbs I (C) and Grubbs II (D) catalysts

1.2. Poly-NHCs

Poly-N-heterocyclic carbenes (poly-NHCs) are ligands that contain more than one NHC unit in their structure. These ligands have attracted great attention because they allow the preparation of organometallic compounds with bis-, tris-, and tetra- NHCs that can act as bischelating, pincer, tripodal or bridging ligands.^{7b,8}

Bis-NHCs: The most abundant are bis-NHCs due to the easy preparation of their imidazolium precursors. Bis-NHCs also admit changes in the linker between the two NHC units yielding different compounds with structural and reactive properties. The first ones to be obtained were those in which the two NHC fragments are bonded with an aliphatic linker. Nowadays, bis-NHCs with other linkers such as ethers, amines or aromatic rings that provide some rigidity to the bridge, have been reported.

An important class of bis-NHC ligands is in which the two NHC units are in a facially-opposed disposition.⁹ They can lead to homo- or hetero- bimetallic compounds. This situation avoids chelation over one metal, as typically happens when bis-NHCs with flexible linker are used. This class of complexes are referred to as Janus-Head ligands by their analogy with Roman God Janus.

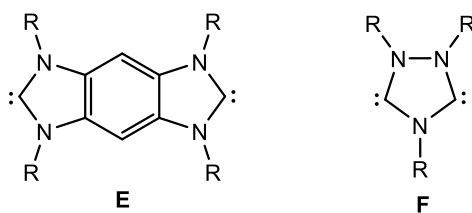


Figure 1.9. Examples of Janus-Head type ligands (benzobis(imidazolylidene), **E**, and 1,2,4-trimethyltriazol-3,5-diylidene ligands), **F**

Another important class of bis-NHCs is the one that results from introducing a donor-functional group between the two carbene edges. The potential donor atoms are P, O, S, N or C. These ligands can coordinate in a tridentate-*mer* (*pincer*) (Figure 1.11 **G**) or tridentate-*fac* (tripodal) (Figure 1.11 **H**) coordination fashion. This fact induces that the coordination capability of poly-NHCs is not restricted to the coordination by the carbene fragments since they can admit other donor-functional groups. For example, some bis-carbene ligands can be tri-coordinating ligands, because they contain a donor-functional group (Figure 1.10).

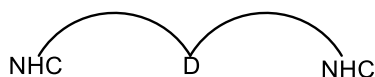


Figure 1.10. Scheme of bis-NHC that may be tris-coordinating

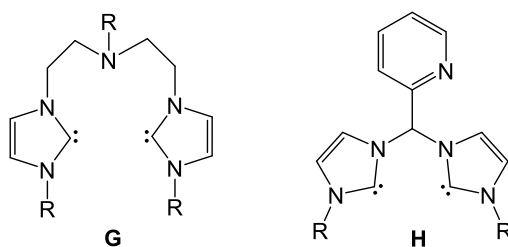


Figure 1.11. Bis-NHC ligands able to coordinate in a *pincer* (**G**) or tripodal (**H**) coordination fashion

Tris- and tetra-NHCs: These ones are less abundant than bis-NHCs, mainly due to their more complicated preparation. Their tris- and tetra-imidazolium precursors are difficult to purify due to their low solubility in most organic solvents. Whereas there are some examples of tris-NHCs, there are just two examples of tetra-NHCs.

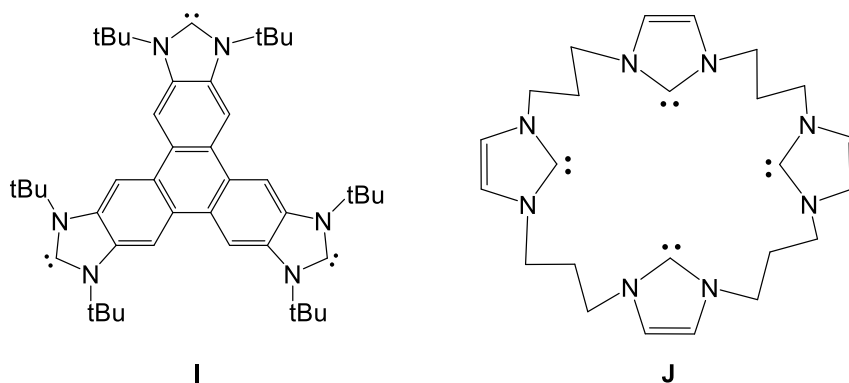


Figure 1.12. Tris-NHC (I) and tetra-NHC (J) ligands

Taking all these examples of poly-NHCs into account, this work aims to obtain a tetra-imidazolium salt based on pyrene (Figure 1.13), that can be used as a precursor of a tetra-NHC ligand. Pyrene was selected as a connector between the four carbene units because it is one of the most widely studied organic materials in the field of photochemistry and photophysics.

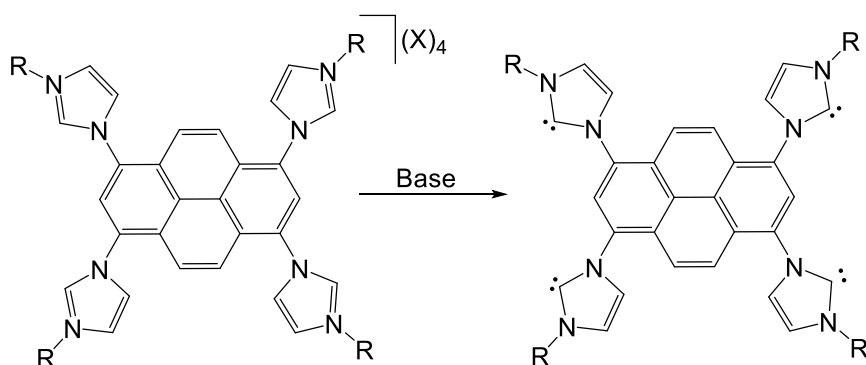


Figure 1.13. Proposed tetra-imidazolium salt and related tetra-NHC ligand

The objective is to obtain a complex in a bis-*pincer* coordination form. This compound will be able to form Janus-type complex because the two *pincer* units will be facially opposed (Figure 1.14 I). It is important to take into account that, although the ligand is designed to coordinate in a *pincer* form, there is a possibility of obtaining compounds in which each carbene unit is coordinated to a metal fragment, thus yielding tetrametallic complexes as II in Figure 1.14.

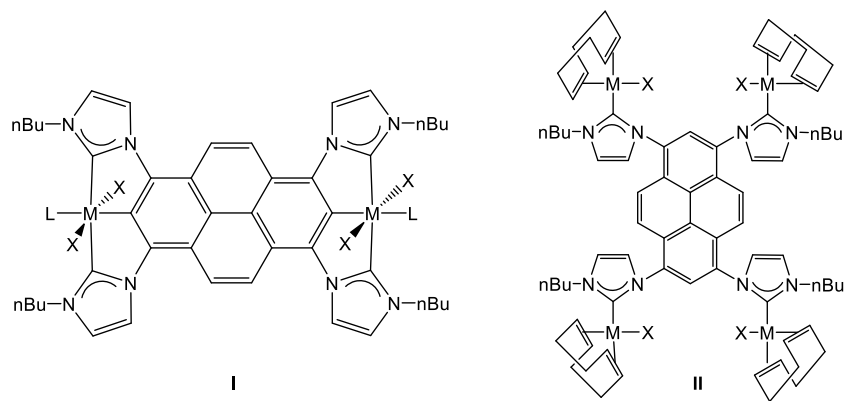


Figure 1.14. Proposed tetra-NHC ligand coordinated as tridentate (I) and monodentate (II) ligand

2.- OBJECTIVES

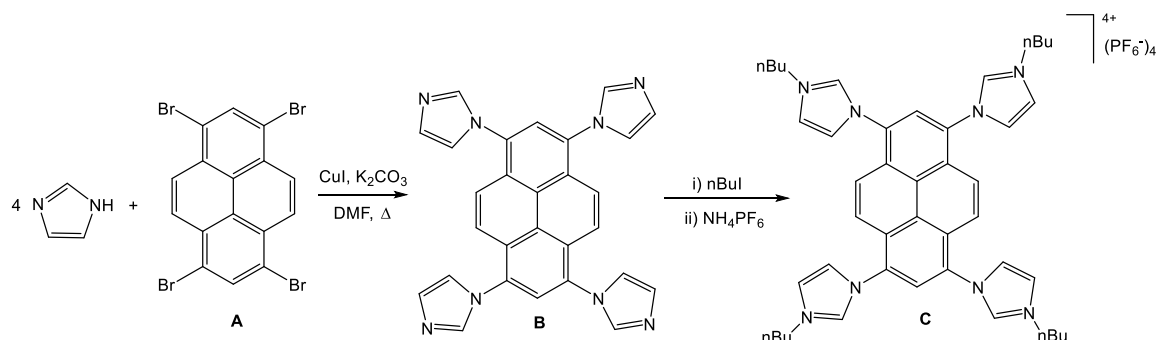
As stated in the introduction, the objective of this work is to obtain and characterize an iridium-based bis-*pincer* metallic compound. This complex is expected to feature a Janus-type topology. For this purpose, a tetra-imidazolium salt is chosen as a precursor since it is designed to coordinate in this form. The main objectives are:

- Synthesis and characterization of a pyrene-based tetra-imidazolium salt following a synthetic route designed by QOMCAT group, starting from 1,3,6,8-tetrabromopyrene.
- Synthesis and characterization of a Ir(I)-NHC complex.

3. RESULTS AND DISCUSSION

In this section, the synthesis and characterization of the precursor of a tetra-NHC ligand, a pyrene-based tetra-imidazolium salt, will be discussed. Then, the synthesis and characterization of a related tetra-NHC-based iridium complex will be described.

3.1. Synthesis of the pyrene-based tetra-imidazolium salt



Scheme 3.1. Synthesis of the pyrene-based tetra-imidazolium salt **C**

As depicted in Scheme 3.1, the pyrene-tetra-imidazolium salt **C** was prepared following a three-steps synthetic procedure starting from commercially available 1,3,6,8-tetrabromopyrene (**A**).

The first step involves a copper-catalysed nucleophilic aromatic substitution between a nucleophile (imidazole) and an aryl halide (1,3,6,8-tetrabromopyrene, **A**). This reaction is normally referred to as Ullman reaction. The reaction mixture was refluxed in DMF and in the presence of a base (K₂CO₃) for 72 h. The mixture, which was initially yellow, turned dark green after a few hours of reaction. Compound **B** was isolated as a highly insoluble dark green solid, in 96 % yield. Due to its low solubility, its characterization was only performed by means of ¹H NMR spectroscopy and mass spectrometry.

The second step involves the N-quarterisation of the imidazole rings of the so isolated tetra-imidazole compound using the corresponding alkylating agent. The alkylating agent of choice was n-butyl iodide, aiming to increase the solubility of the final compound by the introduction of four flexible n-butyl fragments.

The reaction was carried out with the compound **B** in neat nBuI at 100°C for 72 h. The resulting iodide salt was collected by filtration. In order to avoid mixture of halides when using the salt **B** as precursor of a tetra-NHC ligand, we decided to change the coordinating iodide by a non-coordinating hexafluorophosphate counterion. Hence, the third and last step consists of a counterion exchange. This reaction was carried out in methanol, using an excess of NH₄PF₆. After 24 h of reaction, compound **C** was isolated by filtration as a brown solid in 71 % yield.

Characterization of compounds **B** and **C**

Due to its low solubility, compound **B** was only characterized by ^1H NMR spectroscopy and mass spectrometry. Compound **C** was characterized by means of the most standard characterization techniques, namely ^1H and ^{13}C NMR spectroscopy and mass spectrometry. All the details regarding the synthesis and characterization of these two compounds can be found in the Experimental Section.

^1H NMR spectrum of **B** in $\text{DMSO-}d_6$

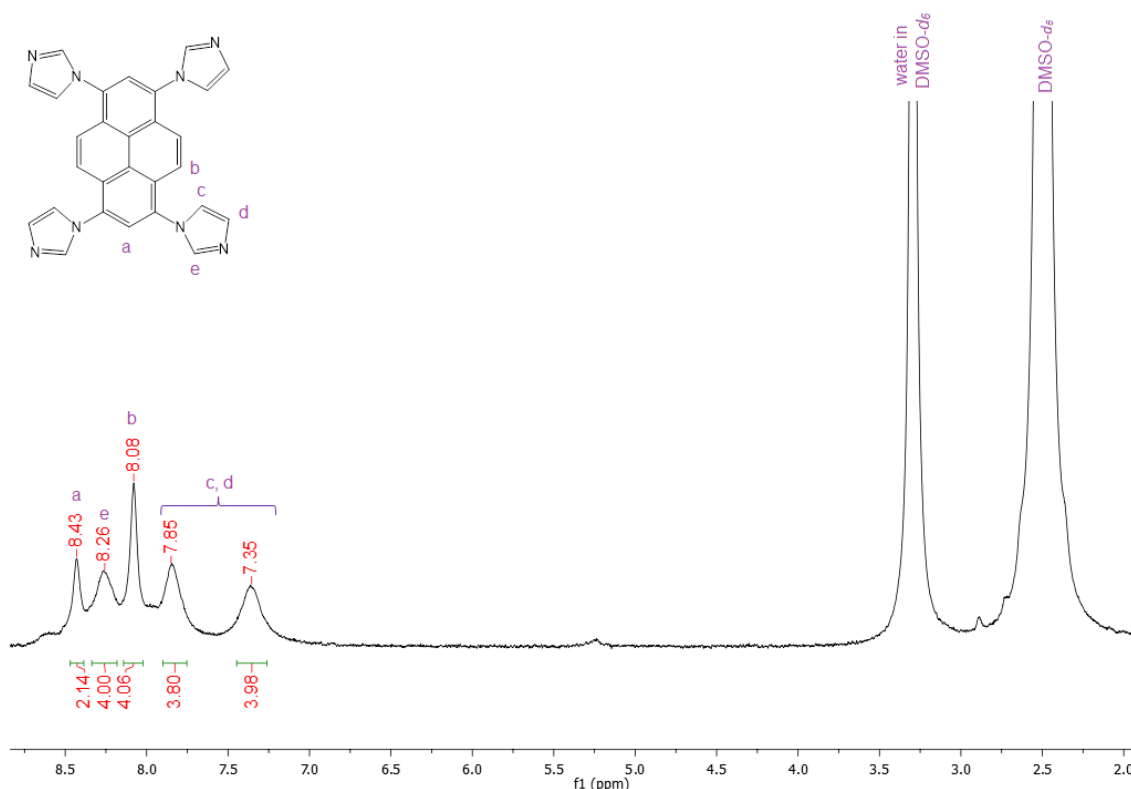


Figure 3.1. ^1H NMR spectrum of **B** in $\text{DMSO-}d_6$

Figure 3.1 shows the ^1H NMR spectrum of compound **B** in $\text{DMSO-}d_6$. The number of signals and their integration are in agreement with the proposed structure. The resonances attributed to the aromatic protons of the pyrene core are observed at 8.43 (*a*) and at 8.08 ppm (*b*). The signal due to the four equivalent protons of the NCHN groups appears at 8.26 ppm (*e*) as a singlet. Finally, the protons corresponding to the imidazole are displayed at 7.85 and 7.35 ppm (*c* and *d*).

The ESI-MS spectrum of **B** (Figure 5.1 in the Experimental Section) shows several peaks. One of these peaks, at m/z 467.2, could be tentatively assigned to $[\text{M}+\text{H}]^+$.

^1H NMR spectrum of **C** in acetone- d_6

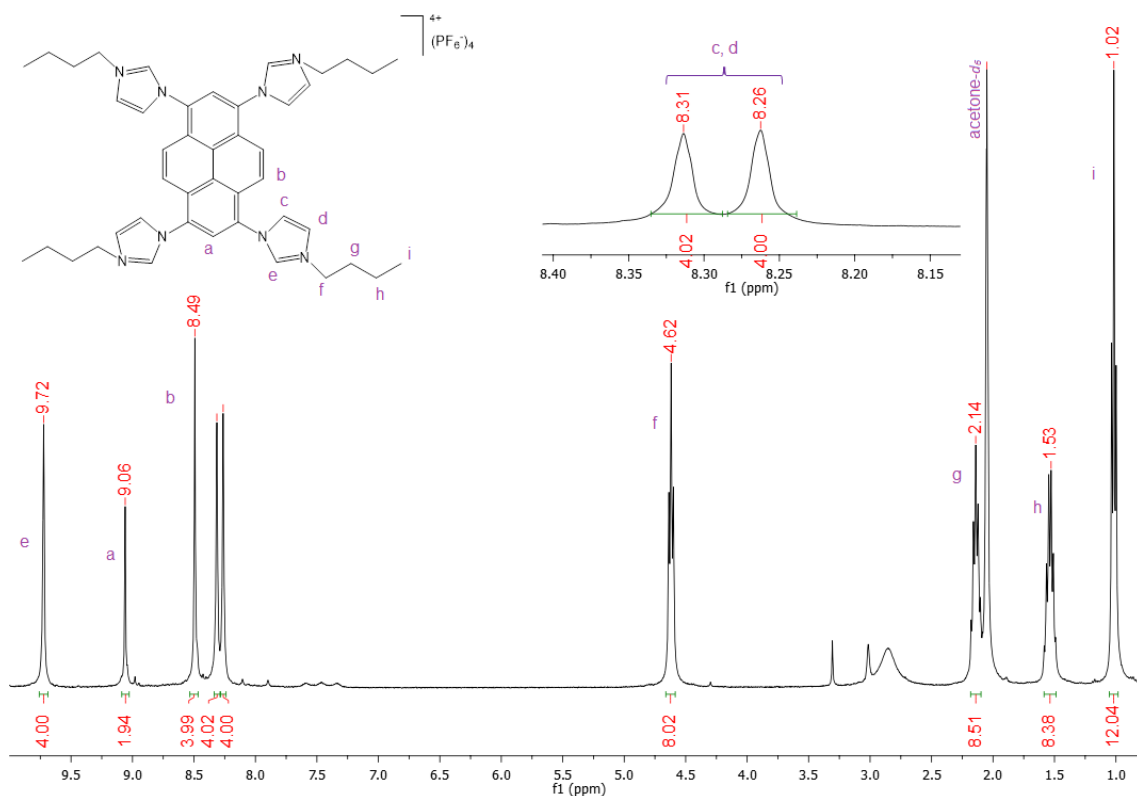


Figure 3.2. ^1H NMR spectrum of **C** in acetone- d_6 . In the inset, expansion of the aromatic region of the spectrum

Figure 3.2 shows the ^1H NMR spectrum of the tetra-imidazolium salt **C** in acetone- d_6 . The number of signals and their integration are in agreement with the two-fold symmetry of the compound.

The singlet at 9.72 ppm corresponds to the acidic protons of the NCHN groups (*e*). The next two signals (at 9.06 and 8.49 ppm) correspond to the aromatics protons of the pyrene core; the first of them corresponds to protons *a* and the second is due to protons *b*. The protons corresponding to the imidazole ring are displayed at 8.31 and 8.26 ppm (*c* and *d*, respectively).

Finally, the signals due to the protons of aliphatic chain appear at 4.62, 2.14, 1.53 and 1.02 ppm as a triplet, a multiplet, a multiplet and a triplet, respectively (protons labelled as *f*, *g*, *h* and *i* in Figure 3.2).

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

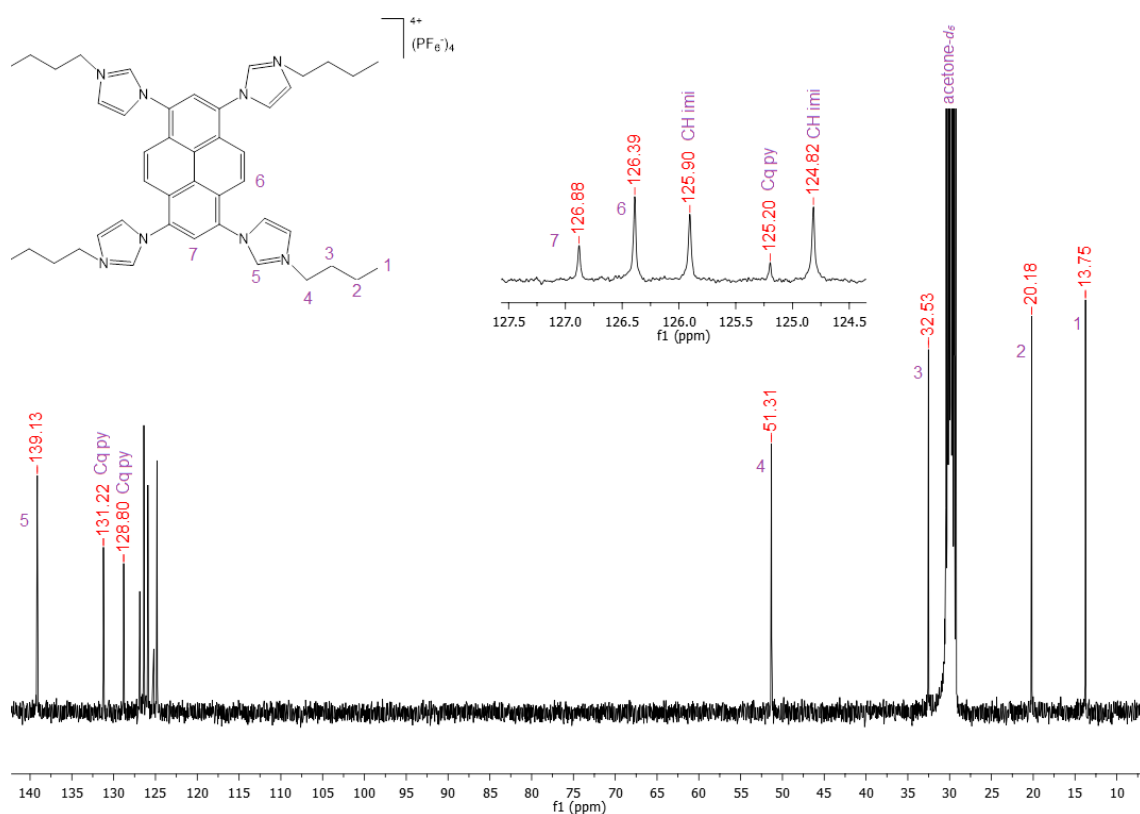


Figure 3.3. ^{13}C NMR spectrum of **C** in acetone- d_6 . In the inset, expansion of the aromatic region of the spectrum.

Figure 3.3 shows the ^{13}C NMR spectrum of compound **C** in acetone- d_6 . Again, the number of signals is in agreement with the two-fold symmetry of the compound. The signal attributed to the NCHN carbons (5) is displayed at 139.13 ppm. The resonance due to the aromatic CH groups of the pyrene core are shown at 126.88 and 126.39 ppm (7 and 6, respectively). The signal attributed to the carbons of the n-butyl substituents are observed at 51.31, 32.53, 20.18 and 13.75 ppm (4, 3, 2 and 1, respectively). The rest of signals corresponding to the quaternary carbons of the pyrene core are conveniently displayed on the spectrum, labelled as Cq py. The carbons attributed to the CH groups of the imidazole rings (CH imi) are displayed at 125.90 and 124.82 ppm.

The ESI-MS spectrum of **C** (Figure 5.2 in the Experimental Section) exhibits the most intense peak at m/z 279.9 assigned to $[\text{M}+\text{PF}_6]^{3+}$. We observed less intense peaks at m/z 173.7 and 492.2, assigned to $[\text{M}]^{4+}$ and $[\text{M}+2\text{PF}_6]^{2+}$, respectively.

3.2. Synthesis of the tetra-NHC-based iridium complexes

Once the pyrene-based tetra-imidazolium salt **C** was prepared and conveniently characterized, we decided to explore its coordination capability as a tetra-NHC ligand precursor. Unlike P- or

N- donor ligands, the coordination of an NHC ligand to a metal fragment requires the activation of its azolium precursor. The use of a weak base has become one of the most widely used routes to NHC-metal complexes. NaOAc, Cs₂CO₃ or trimethylamine are among the most commonly employed.

In our case, the tetra-imidazolium salt **C** was reacted with [IrCl(COD)]₂ in the presence of a weak base such as trimethylamine. The reaction was carried out in refluxing acetonitrile for 5 h. After this time, the mixture was allowed to reach room temperature. The mixture was filtered and the resulting crude solid was dissolved in dichloromethane and purified by a column chromatography on silica gel eluting with a 9:1 mixture of CH₂Cl₂/acetone. Upon purification, an orange solid was isolated in a 40 % yield. In principle, as stated in the introduction, we were expecting to isolate the di-iridium complex depicted in Figure 3.4 in which the two bis-NHC units are coordinating in a *pincer* fashion to one of the two iridium(I) centres.

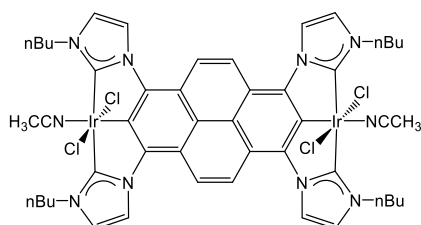
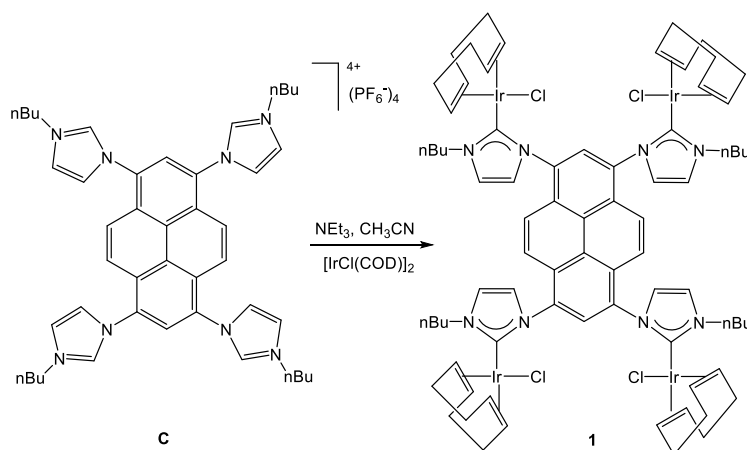


Figure 3.4. Expected *bis*-pincer iridium complex

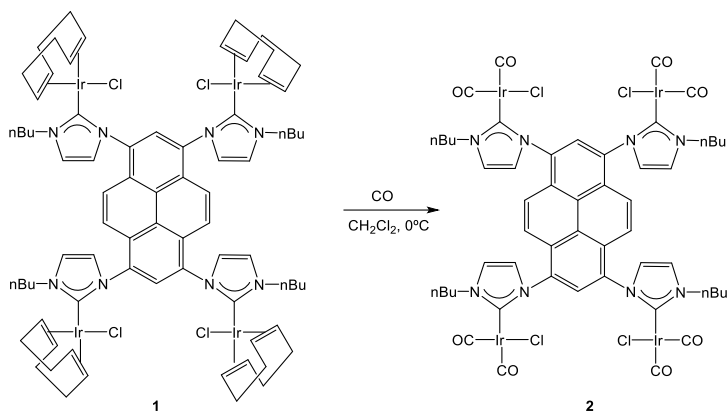
However, after a careful characterization of the isolated solid using NMR spectroscopy and mass spectrometry, we concluded that the solid was the tetra-iridium complex **1** (Scheme 3.2).



Scheme 3.2. Synthesis of tetra-iridium complex **1**

The ¹H and the ¹³C NMR spectra of complex **1** were found complicated to assign, due to the high number of overlapped signals (Figures 5.3 and 5.4 in the Experimental Section). In order to simplify the assignation of signals in the aliphatic region, we decided to exchange the 1,5-cyclooctadiene (COD) ligands by less sterically demanding carbonyl ligands.

Complex **1** was transformed into its corresponding carbonylated derivative by bubbling CO through a solution of the complex in dichloromethane at 0°C (Scheme 3.3). The evolution of the reaction can be easily followed because the bright yellow solution of **1** changes to pale yellow once the COD is displaced by the carbonyl ligands. The addition of n-hexanes allowed the precipitation of **2** as a pale yellow, air and moisture-stable solid in almost quantitative yield.



Scheme 3.3. Synthesis of tetra-iridium complex **2**

Characterization of tetra-iridium complex **2**

*¹H NMR spectrum of complex **2** in CDCl₃*

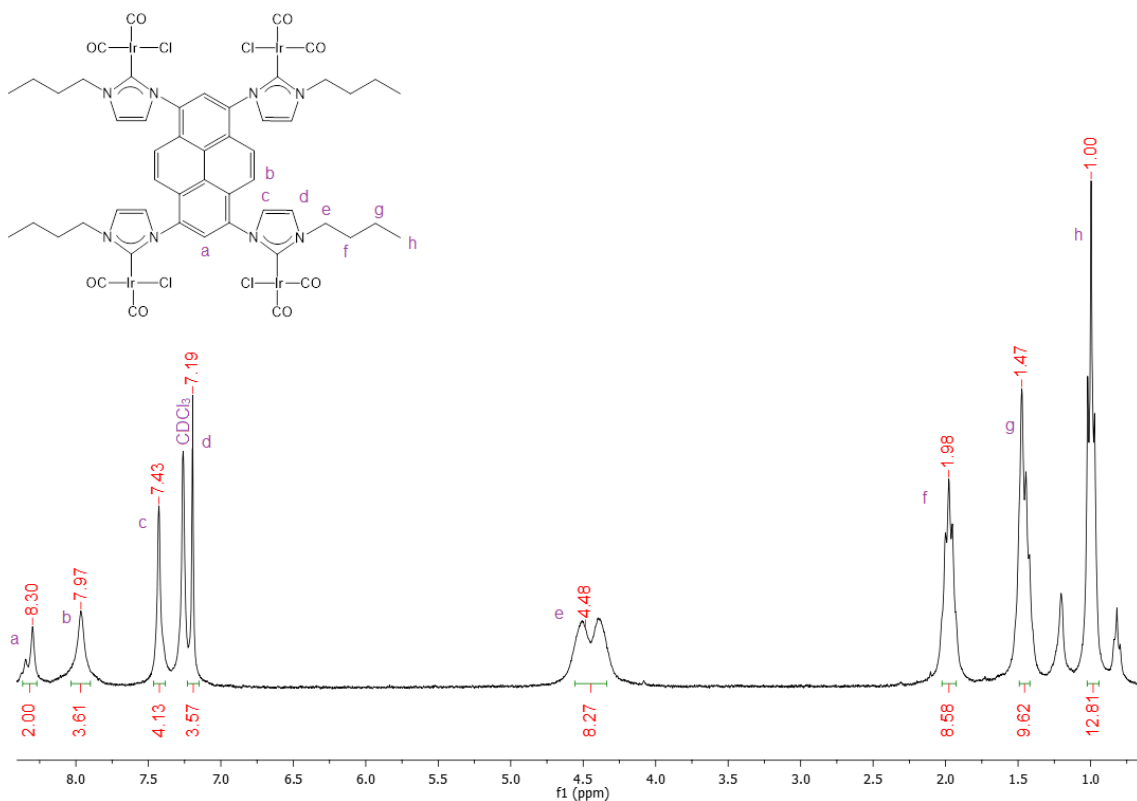


Figure 3.5. ¹H NMR spectrum of **2** in CDCl₃

Figure 3.5 shows the ^1H NMR spectrum of complex **2** in CDCl_3 . The number of signals and their integration are in agreement with the two-fold symmetry of the compound. The resonance attributed to the aromatic protons of the pyrene core are observed as a two singlets at 8.30 and 7.96 ppm (*a* and *b*, respectively). The protons corresponding to the imidazole rings appear at 7.43 and 7.19 ppm (*c* and *d*). Finally, the signals due to aliphatic chain appear at 4.52, 1.98, 1.47 and 1.00 ppm (*e*, *f*, *g* and *h*, respectively).

^{13}C NMR spectrum of complex **2** in CDCl_3

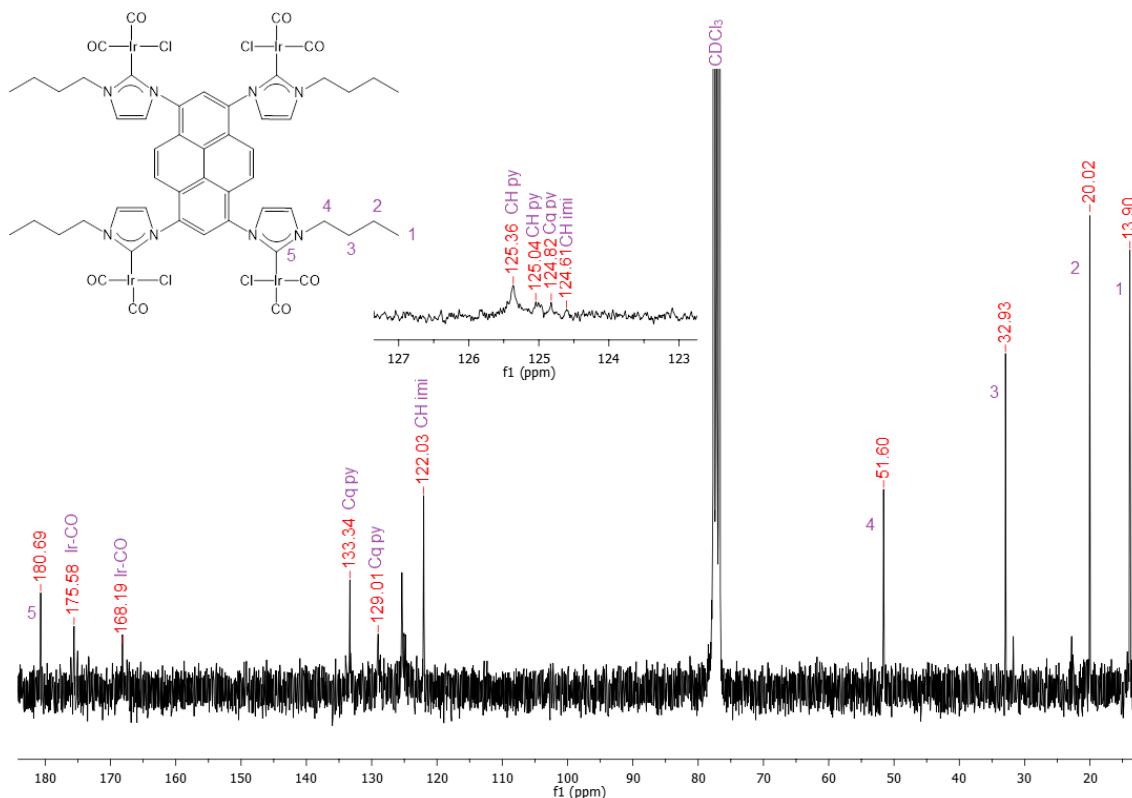


Figure 3.6. ^{13}C NMR spectrum of **2** in CDCl_3 . In the inset, expansion of the aromatic region of the spectrum

Figure 3.6 shows the ^{13}C NMR spectrum of complex **2** in CDCl_3 . The signal attributed to the metallated carbene-carbons atoms (5) appear at 180.69 ppm and the other metallated carbons atoms are displayed at 175.58 and 168.19 ppm (*Ir-CO*). The carbon atoms corresponding to aliphatic chain appear at 51.60, 32.93, 20.02 and 13.90 ppm (4, 3, 2 and 1, respectively). Signals at 133.34, 129.01, 125.36, 125.04 and 124.82 ppm are due to pyrene carbons; the first two correspond to the quaternary carbons (*Cq py*) and the other three correspond to tertiary carbons (*CH py*). The resonances at 124.61 and 122.03 ppm correspond to the carbon atoms of the imidazole rings.

The ESI-MS spectrum (positive ions) of **2** shows at 1791.3 m/z the peak assigned to $[M-Cl]^+$. And the IR spectroscopy displays two strong bands in the carbonyl region (2068, 1984 cm^{-1}) indicating a *cis* configuration.

4.- CONCLUSIONS

In this work, firstly, we have synthesized a tetra-imidazolium salt as a precursor from 1,3,6,8-tetrabromopyrene following the route designed by the group that involves an Ullman reaction between the starting compound and imidazole and, subsequent N-quaternization of the imidazole rings with n-butyl iodide that it was used as alkylating agent.

Following a metallation method widely employed in the group, we explore the coordination capabilities of the new tetra-NHC ligand towards iridium, using $[\text{IrCl}(\text{COD})]_2$ as metal precursor. After a careful characterization of the isolated complex by means of NMR spectroscopy and mass spectrometry, which are described in the discussion section, we confirmed its tetranuclear nature, so each carbene unit is coordinated to a different metal fragment.

5. EXPERIMENTAL SECTION

5.1. General methods

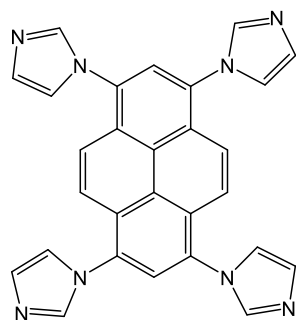
The synthesis of compounds **B** and **C** was carried out in a thick-walled Schlenk tube fitted with a Teflon cap. The synthesis of compound **B** was performed under nitrogen atmosphere. Complexes **1** and **2** were prepared using standard Schlenk tube techniques under nitrogen atmosphere.

Anhydrous solvents used were dried using a Solvent Purification System (SPS MBRAUN). All other reagents were used as received from different commercial suppliers.

NMR spectrum were recorded on a Bruker 300 or 400 MHz using CDCl₃, DMSO-*d*₆ or acetone-*d*₆ as solvents. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument, infrared spectra (FIT-IR) were performed on a Bruker EQUINOX 55 spectrometer with a spectral window of 4000-600 cm⁻¹.

5.2. Synthesis and characterization of the tetra-imidazolium salt

Synthesis of compound B



1,3,6,8-Tetrabromopyrene (**A**, 0.50 g, 0.97 mmol, 1 eq.), imidazole (0.26 g, 3.86 mmol, 4 eq.), K₂CO₃ (1.08 g, 7.77 mmol, 8 eq.) and CuI (0.07 g, 0.39 mmol, 0.4 eq.) were placed together in a high pressure Schlenk tube fitted with a Teflon cap. The Schlenk tube was evacuated and filled with nitrogen three times. N,N'-Dimethylformamide (12 mL) was added under nitrogen atmosphere and the resulting mixture was heated at 170°C for 72 h.

The reaction mixture was initially yellow and turned to dark green after a few hours of reaction.

After 72 h of reaction, the mixture was allowed to reach room temperature. Water was added to the resulting solution. The solid formed was collected by filtration and washed with water. Compound **B** was isolated as a dark green solid. Compound **B** was obtained as a highly insoluble solid, so its characterization was only performed by means of ¹H NMR spectroscopy and electrospray mass spectrometry. Yield: 0.43 g, 96 %.

¹H NMR (500 MHz, DMSO-*d*₆): δ 8.43 (s, 2H, CH_{py}), 8.26 (s, 4H, NCHN), 8.08 (s, 4H, CH_{py}), 7.85 (s, 4H, CH_{imid}), 7.35 (s, 4H, CH_{imid}). Electrospray MS (20 V, *m/z*): 467.2 [M+H]⁺.

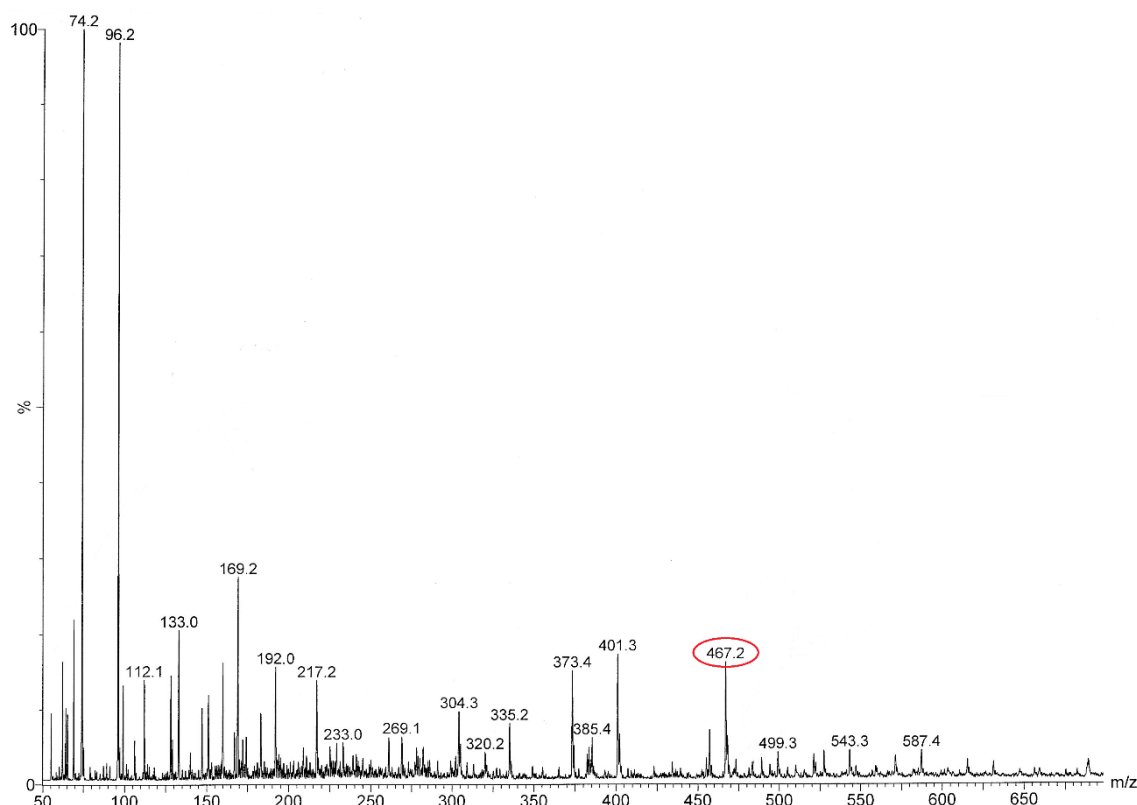
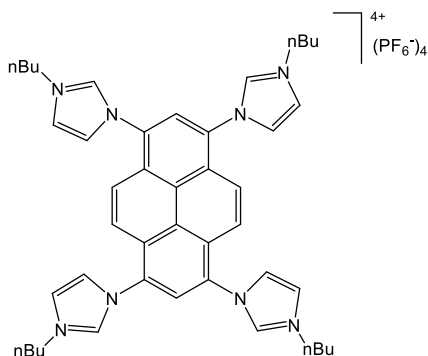


Figure 5.1. ESI-MS spectrum of **B**

Synthesis of compound **C**



A mixture of compound **C** (0.52 g, 1.11 mmol, 1 eq.) with *n*BuI (16 mL, 88.8 mmol, 80 eq.) was heated at 100°C for 72 h in a high pressure Schlenk tube fitted with a Teflon cap. Once at room temperature, the solvent was distilled under vacuum.

The solid residue so obtained (1.17 mg, 0.98 mmol, 1 eq.) was dissolved in methanol (15 mL) and treated with NH_4PF_6 (800 mg, 4.91 mmol, 5 eq.). The mixture was heated overnight. The next day, the cooled reaction mixture was filtered. Compound **C** was isolated by filtration as a dark green solid. Yield: 0.88 g, 71 %.

^1H NMR (400 MHz, acetone- d_6): δ 9.72 (s, 4H, NCHN), 9.06 (s, 2H, CH_{py}), 8.49 (s, 4H, CH_{py}), 8.31 (s, 4H, CH_{imid}), 8.26 (s, 4H, CH_{imid}), 4.62 (t, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.14 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.53 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.02 (m, 12H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (400 MHz, acetone- d_6): δ 139.13 (NCHN), 131.22 ($\text{C}_{\text{q py}}$), 128.80 ($\text{C}_{\text{q py}}$), 126.88 (CH_{py}), 126.39 (CH_{py}), 125.90 (CH_{imid}), 125.20 ($\text{C}_{\text{q py}}$), 124.82 (CH_{imid}), 51.31 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 32.53 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 20.18

(NCH₂CH₂CH₂CH₃), 13.75 (NCH₂CH₂CH₂CH₃). Electrospray MS (20 V, *m/z*): 173.7 [M]⁴⁺, 279.9 [M+PF₆]³⁺, 492.2 [M+2PF₆]²⁺.

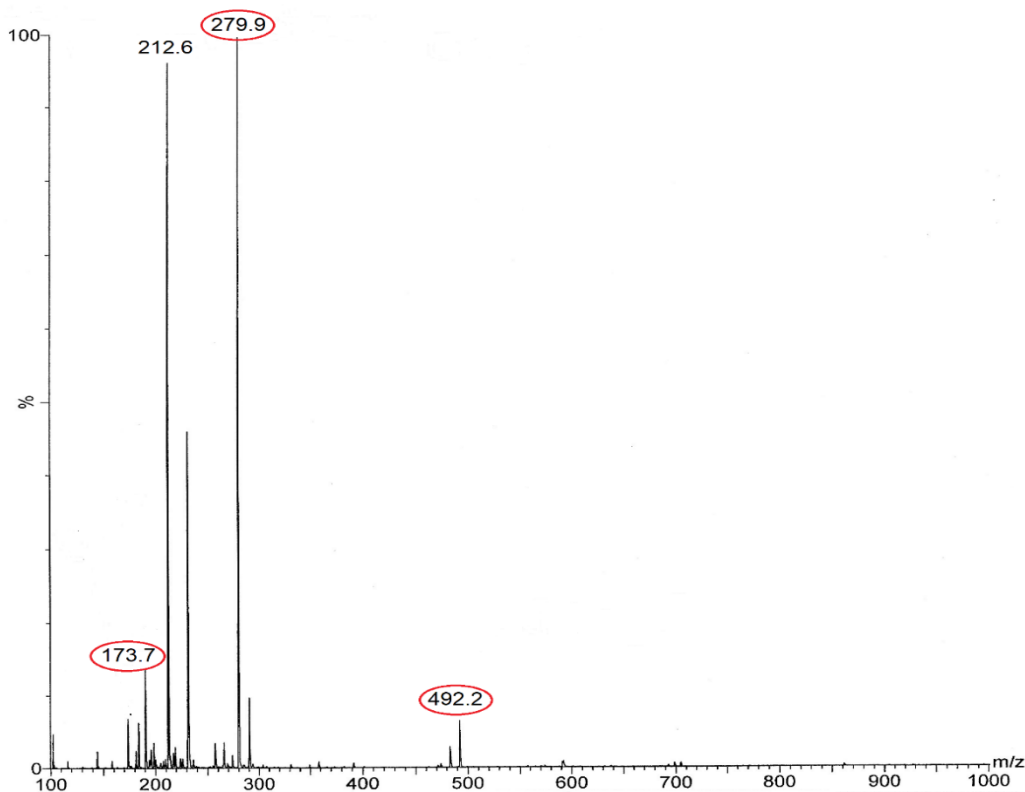
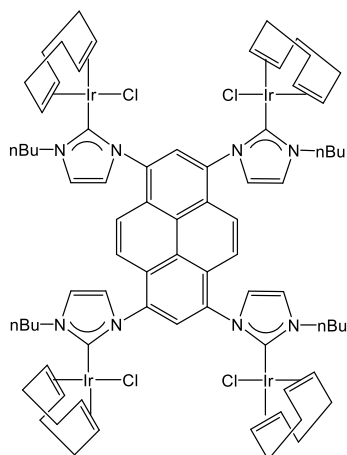


Figure 5.2. ESI-MS spectrum of **C**.

5.3. Synthesis and characterization of the metal complex

Synthesis of the tetrametallic complex **1**



To carry out the synthesis of the tetrametallic compound **1**, three Schlenk tubes were required.

The tetra-imidazolium salt **C** (0.1 g, 0.08 mmol, 1eq.) was placed in the first Schlenk tube (1). The metal precursor, [IrCl(COD)]₂, (0.14 g, 0.17 mmol, 2.2 eq.) was introduced in the second Schlenk tube (2). Tubes 1 and 2 were evacuated and filled with nitrogen three times too. The third Schlenk tube (3) was employed to collect dry acetonitrile (25 mL) from the Solvent Purification System (SPS).

When the three Schlenk tubes were under nitrogen atmosphere, 20 and 5 mL of acetonitrile were introduced in tubes 1 and 2, respectively, *via* syringe. Trimethylamine (0.55 mL, 3.39 mmol, 50 eq.) was also added to tube 1. The two resulting mixtures were stirred. After 30 min, the solution in tube 2 was transferred *via* oven dried cannula to the solution in tube 1. The resulting

mixture was heated at 90°C for 5 h. Once the orange solution was at room temperature, it was filtered.

The orange solid was dissolved in dichloromethane and poured over a chromatographic column (packed with silica gel and dichloromethane). Column chromatography using a 90:10 mixture of CH₂Cl₂/acetone afforded the separation of an orange band that contained complex **1**

The ¹H (Figure 5.3) and the ¹³C NMR (Figure 5.4) spectra of complex **1** were found complicated, due to the high number of overlapped signals. This is why we decided to exchange the 1,5-cyclooctadiene ligands by less sterically demanding carbonyl ligands.

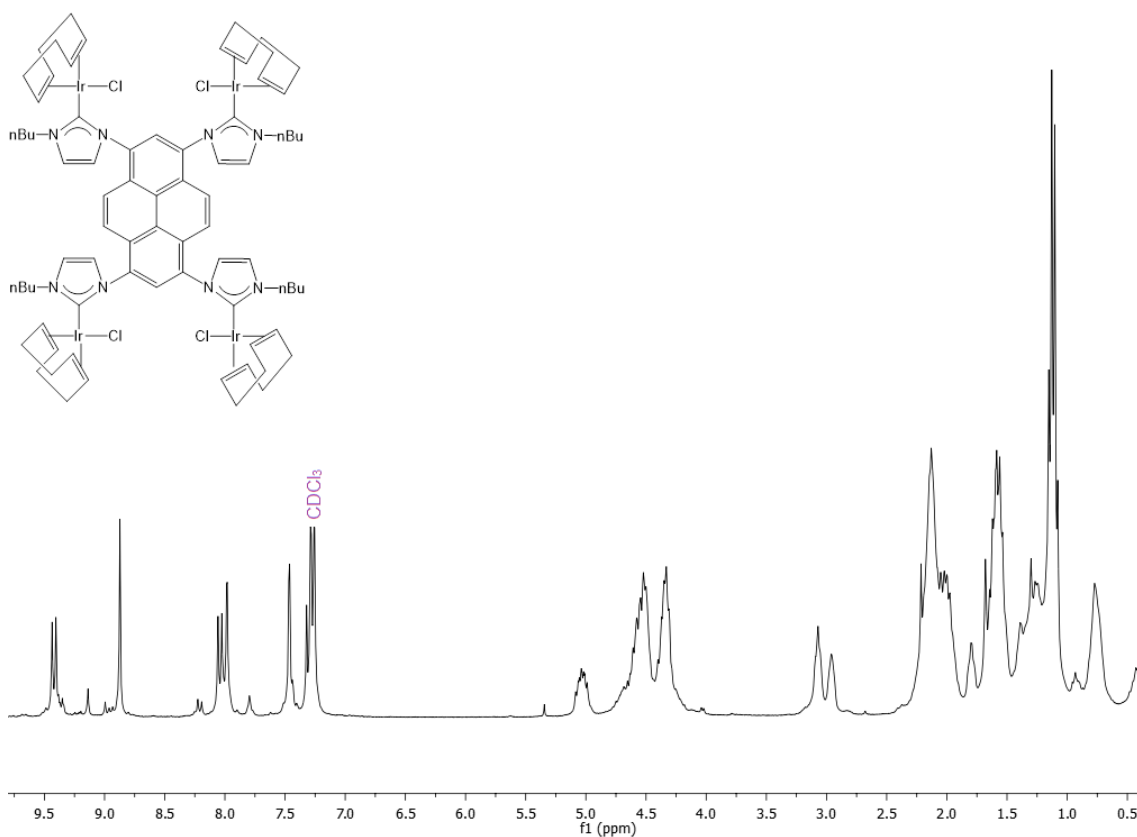


Figure 5.3. ¹H NMR spectrum of **1** in CDCl₃

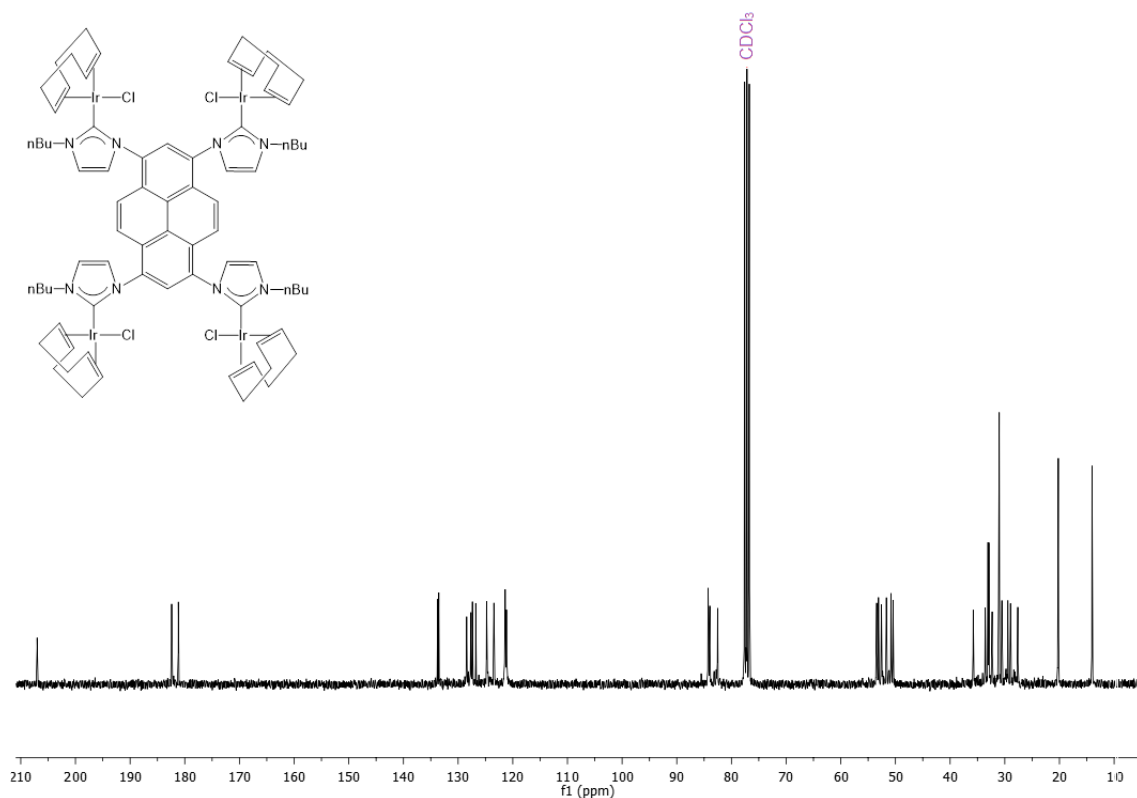
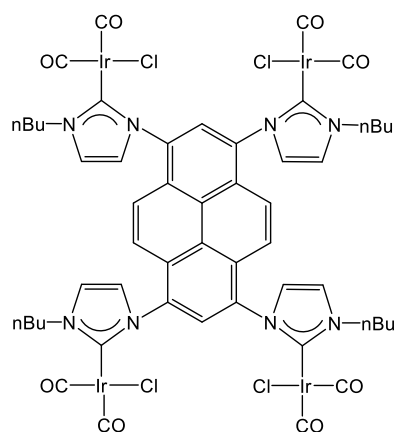


Figure 5.4. ^{13}C NMR spectrum of **1** in CDCl_3

Synthesis of the tetrametallic complex **2**



CO gas (1 atm, 10 mL/min) was passed through a solution of complex **1** (50 mg) in dichloromethane (15 mL) for 20 minutes at 0°C . After this time, the solution was concentrated under reduced pressure. After the addition of hexanes, a light yellow solid precipitated, which was separated by filtration. Complex **2** was obtained almost quantitatively.

^1H NMR (300 MHz, CDCl_3): δ 8.30 (s, 2H, CH_{py}), 7.97 (s, 4H, CH_{py}), 7.43 (s, 4H, CH_{imid}), 7.19 (s, 4H, CH_{imid}), 4.48 (d, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.98 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.47 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.00 (t, 12H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C NMR (300 MHz, CDCl_3): δ 180.69 (Ir-Carbene), 175.58 (Ir-CO), 168.19 (Ir-CO), 133.34 ($\text{C}_{\text{q py}}$), 129.01 ($\text{C}_{\text{q py}}$), 125.36 (CH_{py}), 125.04 (CH_{py}), 124.82 ($\text{C}_{\text{q py}}$), 124.61 (CH_{imid}), 122.03 (CH_{imid}), 51.60 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 32.93 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 20.02 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 13.90 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). Electrospray MS (20V, m/z): 1791.3 $[\text{M}-\text{Cl}]^+$. IR (KBr): 2068 ($\nu_{\text{C}=\text{O}}$) cm^{-1} , 1984 ($\nu_{\text{C}=\text{O}}$) cm^{-1} .

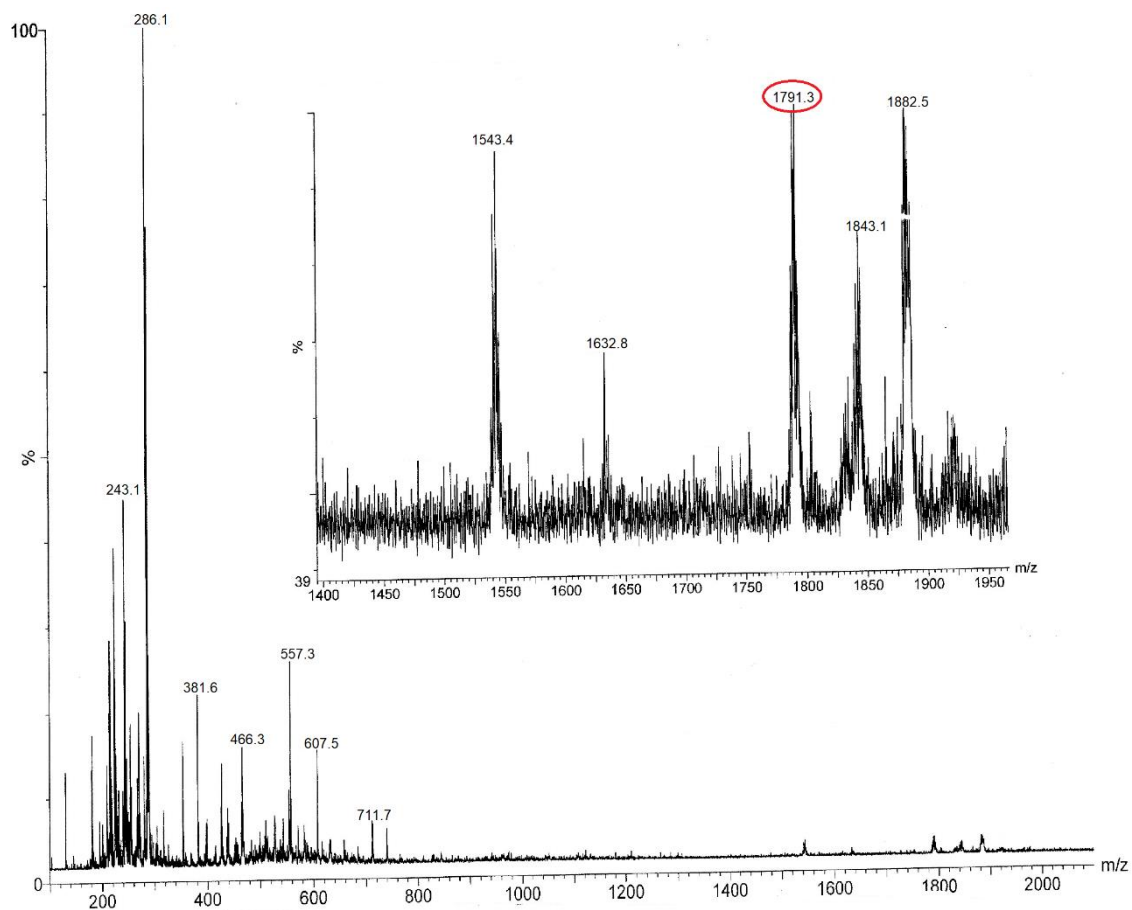


Figure 5.5. ESI-MS spectrum of 2

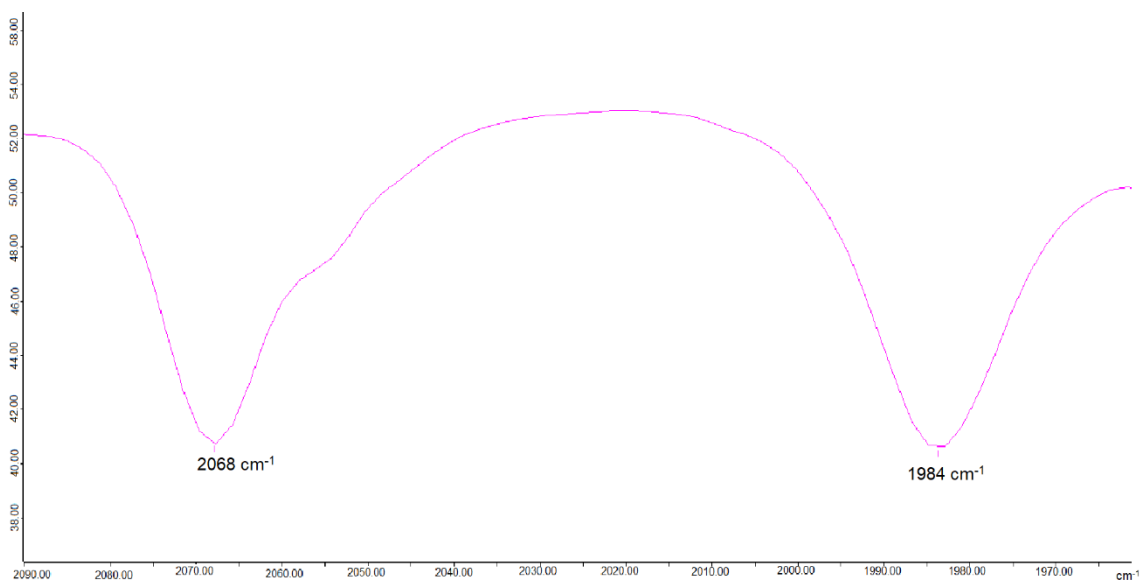


Figure 5.6. IR spectrum of complex 2 recorded in solution

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