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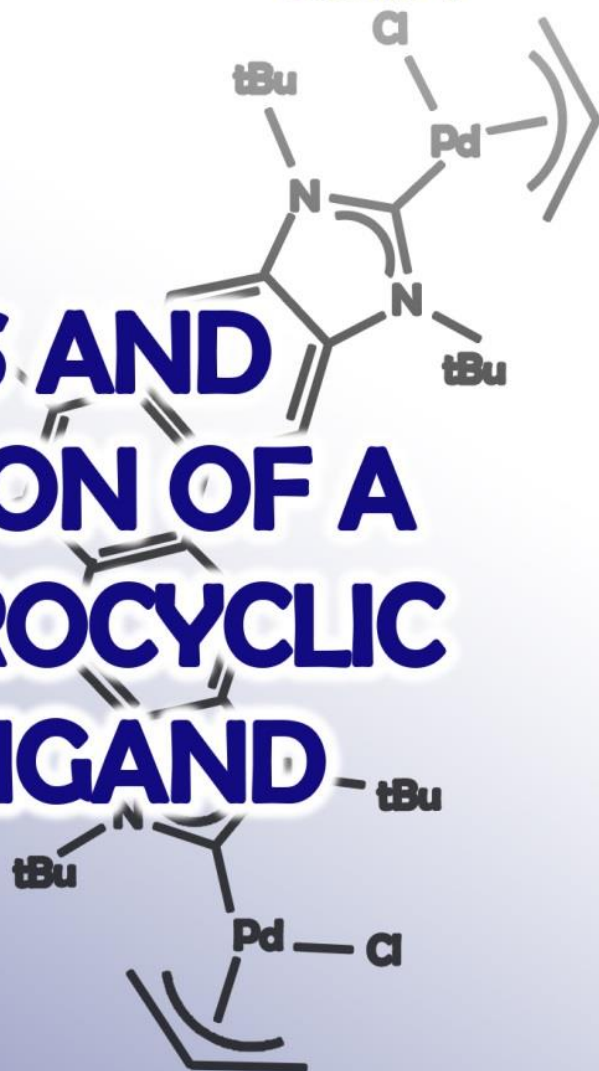
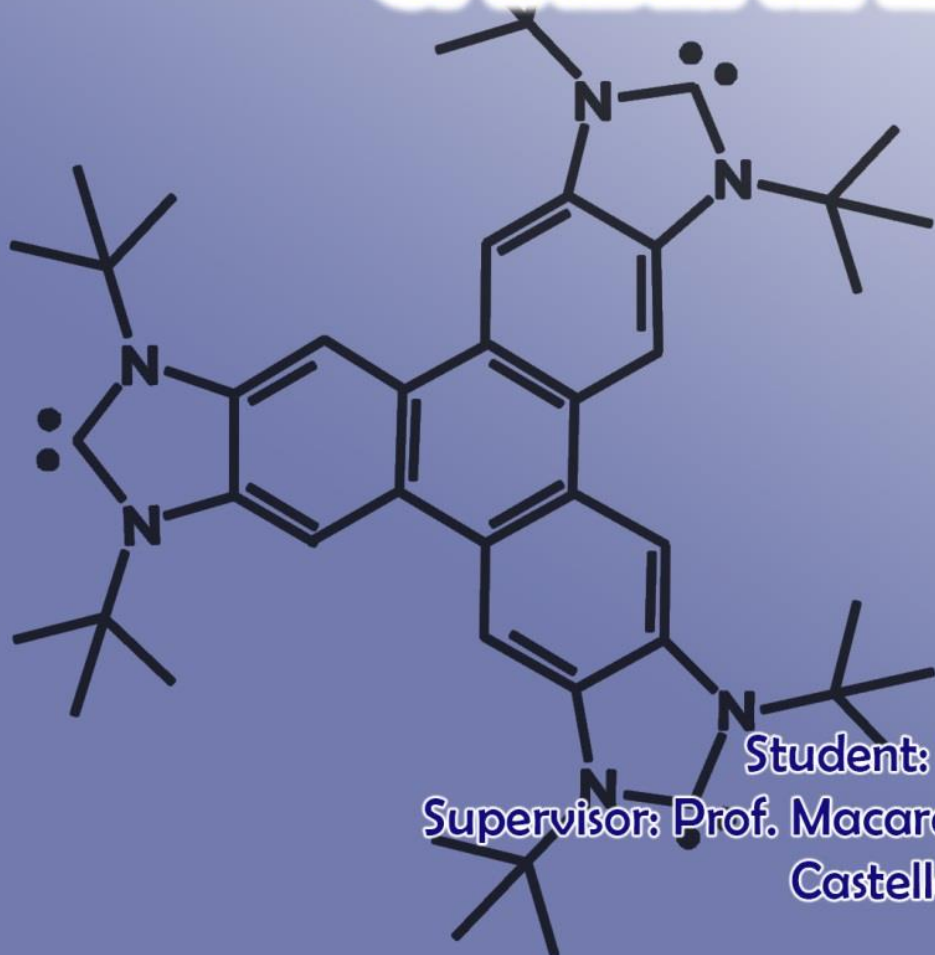
Departament de Química Inorgànica i Orgànica

Àrea de Química Inorgànica



**UNIVERSITAT
JAUME·I**

SYNTHESIS AND COORDINATION OF A TRIS-N-HETEROCYCLIC CARBENE LIGAND



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“El primer paso no es nada; el último es el difícil”.

Victor Hugo, en su novela *Los miserables*

Nomenclature

The starting material and the intermediates in the synthesis of the pursued tris-imidazolium salt are named with letters **A** to **C**. The tris-imidazolium salt $[\text{DH}_3](\text{BF}_4)_3$ is the precursor of the ligand **D** that contains three acidic protons and three tetrafluoroborates as counter-ions. The complex described in the manuscript, **1D**, contains the ligand **D** coordinated to three palladium centers.

List of abbreviations

CDCl_3	deuterated chloroform
<i>ditz</i>	1,2,4-triazolyl-3,5-diylidene
$\text{DMSO-}d_6$	deuterated dimethylsulfoxide
EtOH	ethanol
Et_2O	diethyl ether
g	gram
h	hour
HC(OEt)_3	triethylorthoformate
HSQC	Heteronuclear Single Quantum Correlation
$\text{IPr}\cdot\text{HCl}$	1,3-bis(2,6-diisopropylphenyl)imidazolium chloride
IPr	1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene ligand
KHMDS	potassium bis(trimethylsilyl)amide
M	molar
mL	milliliter
mmol	millimol
NaOAc	sodium acetate
NaOtBu	sodium <i>tert</i> -butoxide
NHC	N-heterocyclic carbene
NMR	Nuclear Magnetic Resonance
arom.	aromatic
d	doublet
(M)Hz	(Mega)Hertz
<i>J</i>	coupling constant
m	multiplet
ppm	parts per million
quat.	quaternary

s	singlet
$[\text{PdCl}(\eta^3\text{-allyl})]_2$	allylpalladium (II) chloride dimer
$[\text{Pd}(\text{OAc})_2]$	palladium (II) acetate
SPS	Solvent Purification System
THF	tetrahydrofuran
$^{\circ}\text{C}$	degree Celsius
μL	microliter
μm	micrometer

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1. GENERAL INTRODUCTION

1.1. CARBENES

The International Union of Pure and Applied Chemistry (IUPAC) defines carbenes as electrically neutral species with general formula $R_2C:$, in which the carbon is covalently bonded to two univalent groups of any kind (or a divalent group) and bears two non-bonding electrons.¹

They can present different geometry, according to the angle formed by the carbon and the two R substituents. If the geometry is linear, the carbon has a sp hybridization, with two sp orbitals and two p orbitals. If the molecule is bent, a change in the hybridization occurs from sp to sp^2 , where one of the p orbitals remains unchanged (this orbital now is called p_π and the p orbital transformed in sp^2 is called σ).²

Lennard-Jones and Pople determined the existence of two different ground state multiplicity for the simplest carbene, methylene carbene ($CH_2:$), when they studied the geometry and properties of small molecules: the singlet state (in which the spins of the non-bonding electrons are paired in the same orbital and another orbital remains empty) and the triplet state (in which the spins of the non-bonding electrons are parallel in two different orbitals).^{3,4}

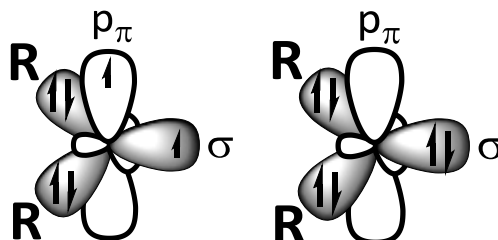


Figure 1.1 Triplet (left) and singlet (right) state

Depending on the energy difference between the orbitals σ and p_π , the ground state of the molecule will vary. Thus, the singlet state is favored when the difference is greater than 2 eV, while the triplet state is preferred when the value is lower than 1.5 eV.²

The nature of the substituents produces several effects on the ground state multiplicity of the molecule, among which are inductive and mesomeric:

In the case of σ -electron-withdrawing groups, singlet state is favored because non-bonding σ orbital is inductively stabilized (its s character is increased), so the σ - p_π gap is increased.⁵

Mesomeric effects are more important than inductive effects. If both R groups are π -electron-donating groups, the singlet state is preferred, since the transfer of electronic charge to the empty p_π orbital increases its energy and, consequently, the σ - p_π gap. The opposite case (π -electron-withdrawing groups) calls attention, since the interaction between an empty p orbital of the substituent interacts with a p orbital of carbon in the triplet state, changing its multiplicity and leaving a linear carbene in singlet state.⁶

Metal Carbenes

Fischer carbene complexes: The carbene (stabilized, singlet state) forms a strong bond with the metal atom (in low oxidation state), which is characterized by carbene-metal σ -donation and simultaneous metal-carbene π -back donation. The electrons are polarized towards the metal, leaving the bond with a certain double character, which decreases if the carbene substituents stabilize the carbon atom. As the carbon atom remains with a partial positive charge, it is susceptible to undergo a nucleophilic attack.⁷

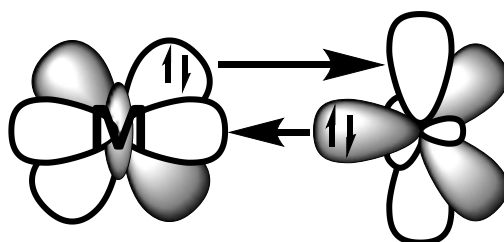


Figure 1.2 Electronic interaction in Fischer carbene complexes

Schrock carbene complexes: The carbene (poorly stabilized, triplet state) forms a covalent bond with the metal atom (in high oxidation state), where the electrons are well distributed, forming a real double bond. In this case, carbon atom is susceptible to undergo an electrophilic attack.

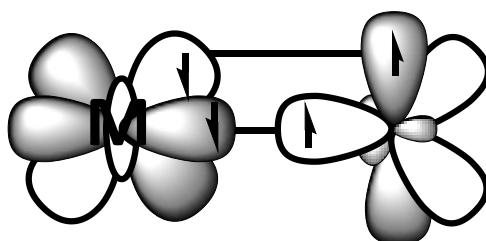


Figure 1.3 Electronic interaction in Schrock carbene complexes

1.2. N-HETEROCYCLIC CARBENES

N-heterocyclic carbenes (hereinafter, NHCs) are singlet carbenes in which the divalent carbenic center is linked to at least one nitrogen atom within the heterocycle.⁸ When they are attached to a transition metal, they form a special type of Fischer carbene complex.⁴ Its existence was postulated by Wanzlick in the 1960s,⁹ but it was not until 1991 when Arduengo *et al.* isolated the first stable NHC.¹⁰

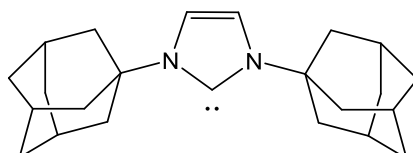


Figure 1.4 1,3-Di-1-adamantyl-imidazol-2-ylidene, first isolated stable NHC

Since then, a large number of NHC-based complexes have been synthesized, mainly because they can act as versatile catalysts of numerous reactions, as olefin metathesis.¹¹ In addition, they have certain advantages over other similar σ -donor ligands (e. g., phosphines), such as their thermal stability, superior catalytic activity, strong bond with transition metals or the easiness of synthesis of their stable precursors (such as imidazolium salts).

Applications

Due to all the features described above NHC ligands and, in particular, those coordinated to transition metals, have become useful tools in different fields of research such as:

Anti-cancer metal-drugs: NHC complexes bound to metal cations such as Pd(II), Au(I) and Cu(I) have been shown to have greater toxicity to cancer cells than cisplatin, the metal-drug mainly used for this purpose. Noteworthy, the group of Prof. Gautier has demonstrated that NHC-based Cu(I) complexes induce apoptosis (programmed cell death) in the early stages of the cell cycle.¹²

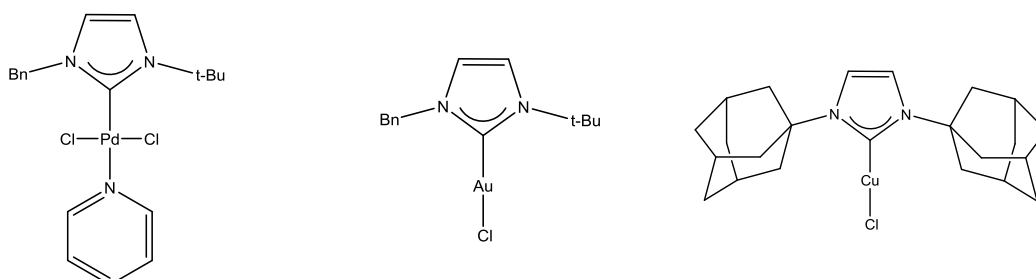


Figure 1.5 Some complexes used as anti-cancer drugs

Homogeneous catalysts: The main application of NHC-transition metal complexes is in the field of homogeneous catalysis.^{13, 14} The two most extensively studied classes of catalytic reactions are carbon-carbon cross-coupling catalyzed by palladium (although there are also heteroatom-carbon cross-coupling reactions, as Buchwald-Hartwig amination, explained in Section 3.1) and ruthenium-catalyzed olefin metathesis.

Cross-coupling reaction is the term coined to refer to those reactions in which two hydrocarbon fragments are coupled with the aid of a metal catalyst (mostly, palladium complexes). In 2010, Heck, Negishi and Suzuki were awarded the Nobel Prize in Chemistry for palladium-catalyzed cross-coupling reactions bearing their names.¹⁵

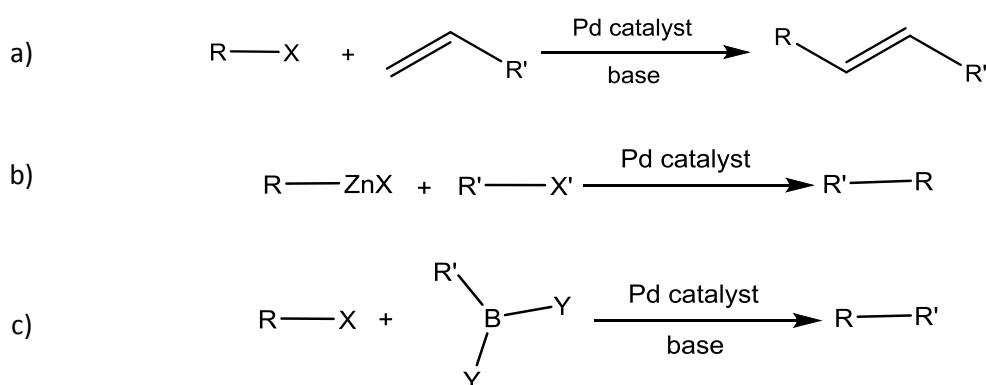


Figure 1.6 Heck (a), Negishi (b) and Suzuki (c) reactions

For these reactions, Pd-based catalysts coordinated to tertiary phosphine ligands were normally used. However, NHC-based Pd catalysts perform better, so its use has increased for this type of reactions in the last years, due to the strength of the Pd-C_{carbene} bond, which provides great stability to the active species, even at low ligand/Pd ratios and high temperatures.¹⁶

On the other hand, olefin metathesis involves those reactions that consist of the breakdown and regeneration of double bonds in olefins, which entails a redistribution of the substituents. Some examples of such reactions are ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM) and cross metathesis (CM). The Nobel Prize in Chemistry 2005 was awarded jointly to Chauvin, Grubbs and Schrock for the development of the metathesis method.

In order to carry out olefin metathesis, the presence of a catalyst is necessary. Several metal complexes (based on Mo or W) have been tested, but those that were tolerant to the presence of other functional groups in the olefin, were unstable under aerobic conditions or in the great

majority of solvents (including water), like Schrock catalyst (Figure 1.7.a). In 1995, Grubbs developed a ruthenium catalyst, tolerant of an expanded range of functional groups and highly active in RCM (known as first generation Grubbs catalyst, Grubbs I (Figure 1.7.b)).¹⁷

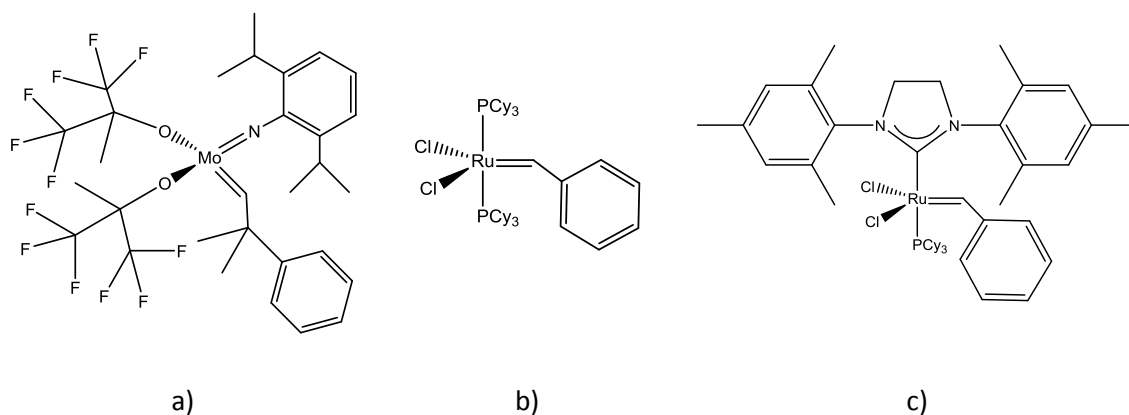


Figure 1.7 a) Schrock catalyst, b) Grubbs I and c) Grubbs II

A few years later, in 1999, the second generation Grubbs catalyst (Grubbs II in Figure 1.7.c) was obtained by replacing one of the olefins in Grubbs I by a NHC ligand, which resulted in an increase of the catalytic activity in the metathesis, attributed to the donation of electron density by the NHC ligand to the ruthenium metallic center.¹⁸

Addressable NHC anchors for gold surfaces: Chemisorption of some functional groups, such as thiols, on gold surfaces has enabled countless technological advances in the fields of electronics, sensing, microfabrication, and nanotechnology. NHCs are outlined as a potentially useful class of reagents for binding to inorganic surfaces, due to their exceptional σ -donating and moderate π -backbonding ability, which has made them ligands of choice for late transition metals like Ru(II) and Au(I). It is envisioned that these same characteristics could lead to strong, partially conjugated, surface bonds.¹⁹

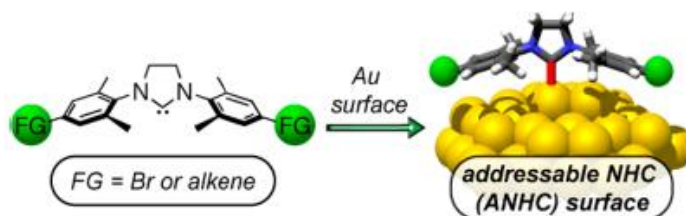


Figure 1.8 Functionalization of gold with ANHCs

Conjugated organometallic polymers (COMPs): The incorporation of transition metals into aromatic organic chains generates COMPs, materials with interesting electromechanical properties. However, the synthesis of this type of material entails serious difficulties, since working in an inert atmosphere or under anhydrous conditions can affect the stability of these compounds. Recently, the use of poly-NHCs (*vide infra*) as building blocks of these COMPs has increased because of the wide variety and high affinity of the NHCs for a wide range of transition metals.²⁰

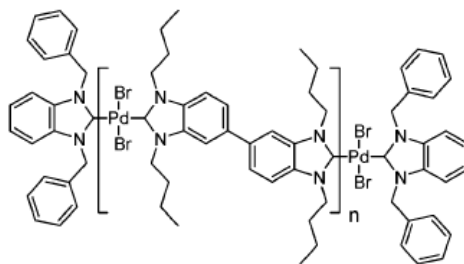


Figure 1.9 Bis-NHC-palladium polymer

Luminescent M-NHC complexes: Luminescent complexes can be designed by combining cyclometallated species and strongly σ -donating carbon ligands such as NHCs, ensuring strong ligand fields with high lying d–d excited states. The great versatility of these ligands opens a huge range of possibilities in the synthesis of phosphorescent materials with emission colors over the entire visible spectrum. These materials are of great interest in the preparation of OLEDs, as well as other applications, such as antitumoral agents, phosphorescent sensors, and photochemical water splitting. An excellent review gives a detailed account on the photophysical properties of NHC-based metal complexes.²¹

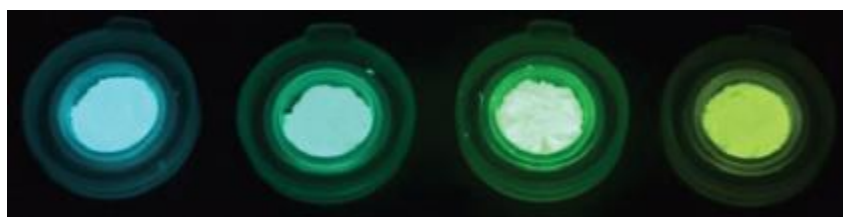


Figure 1.10 Some Au(I)-NHC complexes under UV light at 350 nm

1.3. POLY-NHCs

Their great topological versatility, their electronic properties and their ability to form stable complexes with a large variety of transition metals have raised NHCs to a privileged position in the design of all kinds of homogeneous catalysts, including those having more than one metal.²²

Bis-NHC: These are ligands with two carbene units. Among them, Janus-type ligands, that own their two units NHC arranged in opposite faces, in analogy to the representations of the Roman god Janus, stand out.²³

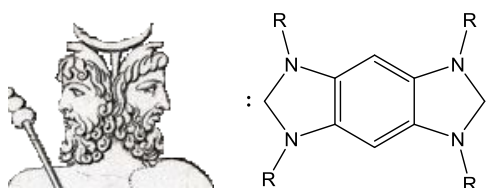


Figure 1.10 Representation of Roman god Janus and a Janus-bis-NHC ligand:
benzobis(imidazolylidene)

In addition to the formation of homo-bimetallic compounds (e.g., Au (I)),²⁴ more interesting is the synthesis of hetero-bimetallic species that allow to carry out tandem catalytic reactions, in which each metallic center facilitates a mechanistically different reaction.

An example developed by the Group of Organometallic Chemistry and Homogeneous Catalysis (QOMCAT) of Universitat Jaume I is the Ir(III)-Pd(II) hetero-bimetallic complex depicted in Figure 1.11. The two metal fragments are connected by the so-called *ditz* ligand. This complex is able to catalyze the sequential dehalogenation (performed by palladium center) and transfer hydrogenation (performed by iridium center) of haloacetophenones.²⁵

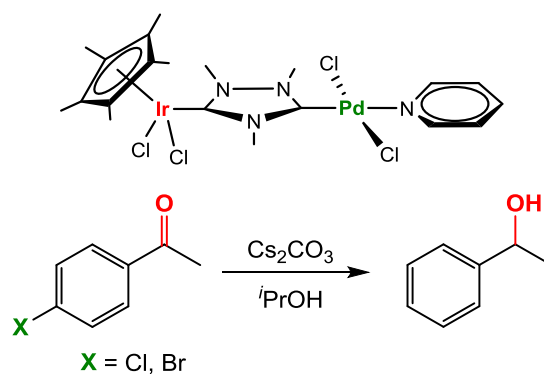


Figure 1.11 Ir(III)-Pd(II) heterodimetallic complex and the tandem dehalogenation/transfer hydrogenation of haloacetophenones

Tris-NHC: The first tris-NHC with D_3h -symmetry was reported in 2010 by Bielawski and co-workers. This ligand contains three NHC centers connected by a triptycene core. Despite being a very interesting example of a tris-NHC ligand, its coordination ability was not studied by the authors.²⁶

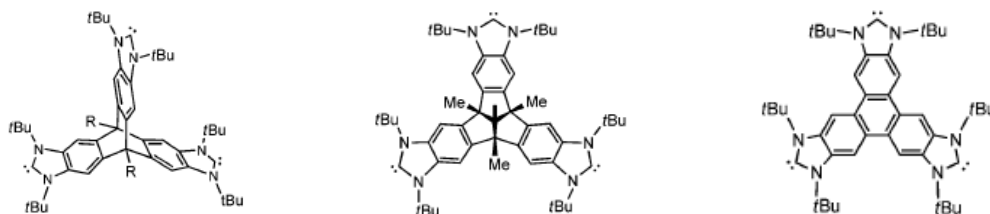


Figure 1.12 Triptycene, tribenzotriquinacene and triphenylene-based tris-imidazolyliidene ligands

Since then, the QOMCAT group has developed other rigid trimetallic complexes with three-fold symmetry based on tris-NHC ligands, such as tribenzotriquinacene-tris-imidazolyliidene²⁷ or triphenylene-tris-imidazolyliidene (ligand studied in this work).²⁸

2. OBJECTIVES

Based on the research activity developed by the QOMCAT group, focused on the coordination chemistry of NHC ligands and the evaluation of the properties of the resulting metal complexes, the main objectives of the work presented here are:

- Synthesis and characterization of a triphenylene-based tris-azolium salt, which is the precursor of a tris-NHC ligand with a rigid structure.
- Coordination of the obtained tris-NHC ligand to Pd(II) and characterization of the resulting trimetallic complex.

Other objectives, more related with the training of the candidate, were pursued:

- Acquire skills in the most commonly employed techniques in an Organometallic Chemistry laboratory such as the use of glass manifold and standard Schlenk tube techniques.
- Acquire skills in the standard characterization techniques employed in an Organometallic Chemistry laboratory such as NMR spectroscopy.

3. RESULTS AND DISCUSSION

In this section, the synthesis and characterization of the precursor of a tris-NHC ligand, a triphenylene tris-imidazolium salt, will be discussed. Then, the synthesis and characterization of a related tris-NHC-based complex will be described. As described in detail in this part, the bromination of triphenylene to 2,3,6,7,10,11-hexabromotriphenylene was carried out as described in the literature²⁹ and the following steps of the synthetic route were performed as described earlier by the QOMCAT group.²⁸

3.1. SYNTHESIS OF THE TRIPHENYLENE-BASED TRIS-IMIDAZOLIUM SALT

As depicted in Scheme 3.1, the pursued triphenylene-based tris-imidazolium salt $[\text{DH}_3](\text{BF}_4)_3$ was prepared following a three-steps synthetic methodology starting from commercially available triphenylene (**A**).

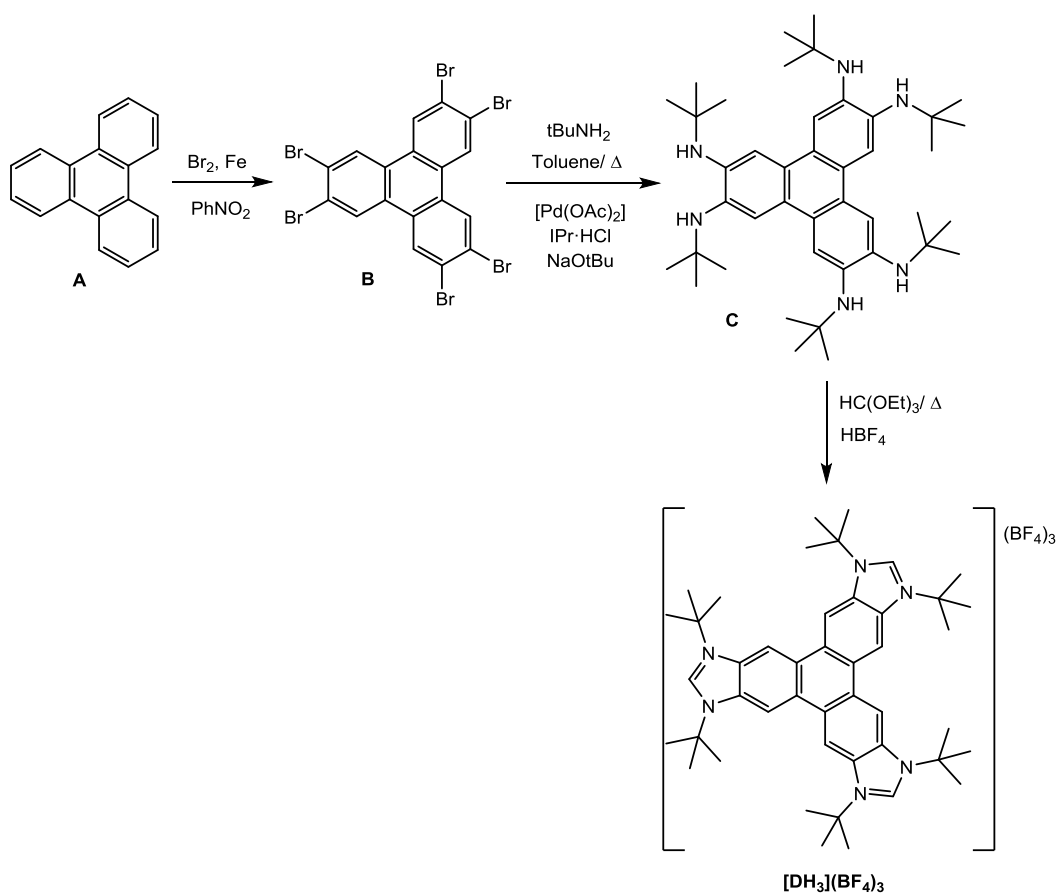
The first step involves the Lewis-acid-catalyzed bromination of triphenylene to yield 2,3,6,7,10,11-hexabromotriphenylene (**B**). The addition of iron is necessary in order to form FeBr_3 , that acts as catalyst in the electrophilic aromatic substitution of **A**. Compound **B** was recrystallized with 1,2-dichlorobenzene as an highly insoluble white solid in almost quantitative yield. Attempts to characterize **B** by means of NMR spectroscopy were unsuccessful due to its high insolubility.

The second step involves a Buchwald-Hartwig amination, where compound aryl halide **B** suffers a cross-coupling with an amine (*tert*-butylamine), in the presence of a palladium catalyst (formed *in situ* from $[\text{Pd}(\text{OAc})_2]$, $\text{IPr}\cdot\text{HCl}$ and NaOtBu) in refluxing dry toluene. After 12h of reaction, the mixture was filtered over Celite and the filtrate was dried under vacuum. The reaction afforded the corresponding hexa-aminotriphenylene compound **C** as a dark red crystalline solid in almost quantitatively yield. Compound **C** was directly used in the next step without further purification, due to its instability in aerobic atmosphere and its photosensitivity.

It is worth mentioning that this reaction is an example of a C-N cross-coupling reaction catalyzed by a Pd(II)-NHC complex, as discussed in the introduction. In this regard, Hillier *et al.* found that, using the bulky nucleophilic carbene IPr as supporting ligation, the catalytic C-N coupling of aryl bromides can undergo at room temperature. The base (NaOtBu) plays a double role, namely to deprotonate the imidazolium salt to liberate the free carbene ligand and to act as a strong base to neutralize the HBr formed in the course of the coupling reaction.³⁰

The last step involves a formylative cyclization of compound **C** using $\text{HC}(\text{OEt})_3$ as solvent under acidic conditions (HBF_4 in Et_2O). In this formylative cyclization, EtOH is eliminated as a byproduct. The mixture was refluxed overnight under aerobic conditions. The tris-imidazolium salt $[\text{DH}_3](\text{BF}_4)_3$ was precipitated from a $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ mixture and was collected by filtration. The desired salt was isolated as an off-white solid.

All the already known compounds (**C** and $[\text{DH}_3](\text{BF}_4)_3$, Scheme 3.1) were identified according to previously reported spectroscopic data. All the details regarding the synthesis and characterization of all the compounds can be found in the Experimental Section.



Scheme 3.1 Synthetic route to tris-imidazolium salt $[\text{DH}_3](\text{BF}_4)_3$

Characterization of compounds **C** and $[\text{DH}_3](\text{BF}_4)_3$

^1H NMR spectrum of **C** in CDCl_3

Figure 3.1 shows the ^1H NMR spectrum of 2,3,6,7,10,11-hexa(*tert*-butylamino)triphenylene (**C**) in CDCl_3 . The number of signals and their integration is in agreement with the three-fold symmetry of the compound.

The singlet at 7.85 ppm corresponds to the aromatic protons of the triphenylene core (*c*). The resonance attributed to the NH group (*b*) appears at 3.81 ppm as a singlet. Finally, the signal due to the *tert*-butyl N-substituents appears as a singlet at 1.39 ppm (*a*).

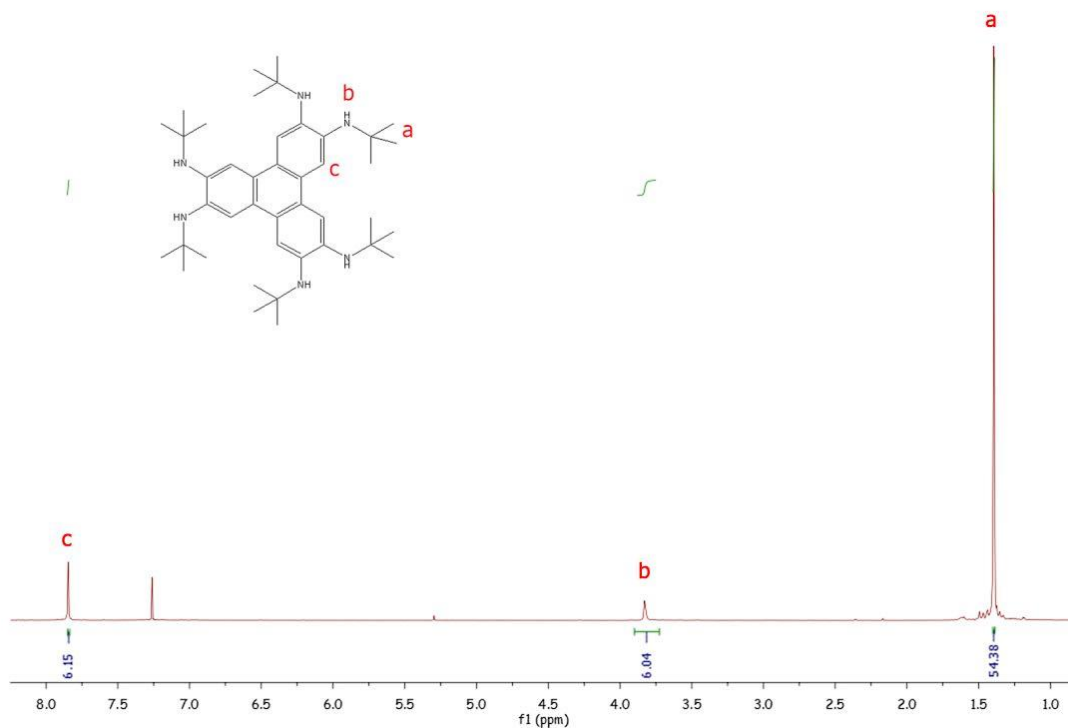


Figure 3.1 ^1H NMR spectrum of **C** in CDCl_3

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

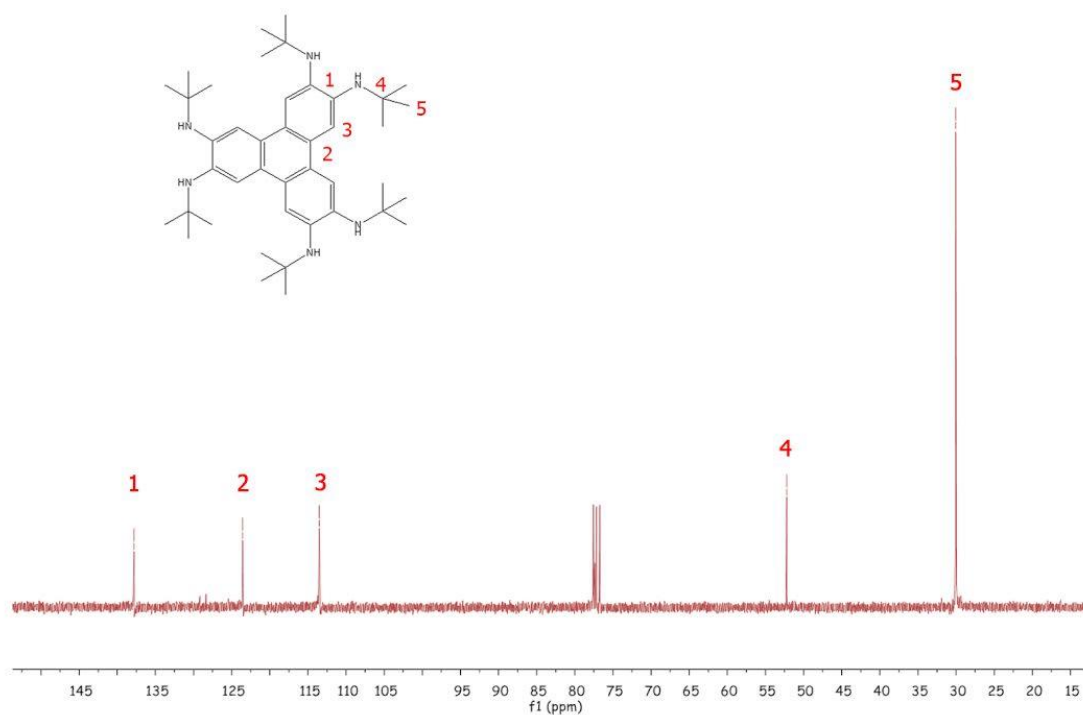


Figure 3.2 ^{13}C NMR spectrum of **C** in CDCl_3

Figure 3.2 shows the ^{13}C NMR spectrum of 2,3,6,7,10,11-hexa(*tert*-butylamino)triphenylene (**C**) in CDCl_3 . The first three signals (137.8, 123.6 and 113.5 ppm) correspond to those carbons that constitute the triphenylene core, where quaternary carbons (1 and 2) produce the first two signals and tertiary carbons (3), the last one. The signals attributed to the carbons of the *tert*-butyl substituents are observed at 52.2 and 30.0 ppm (4 and 5, respectively).

^1H NMR spectrum of $[\text{DH}_3](\text{BF}_4)_3$ in $\text{DMSO-}d_6$

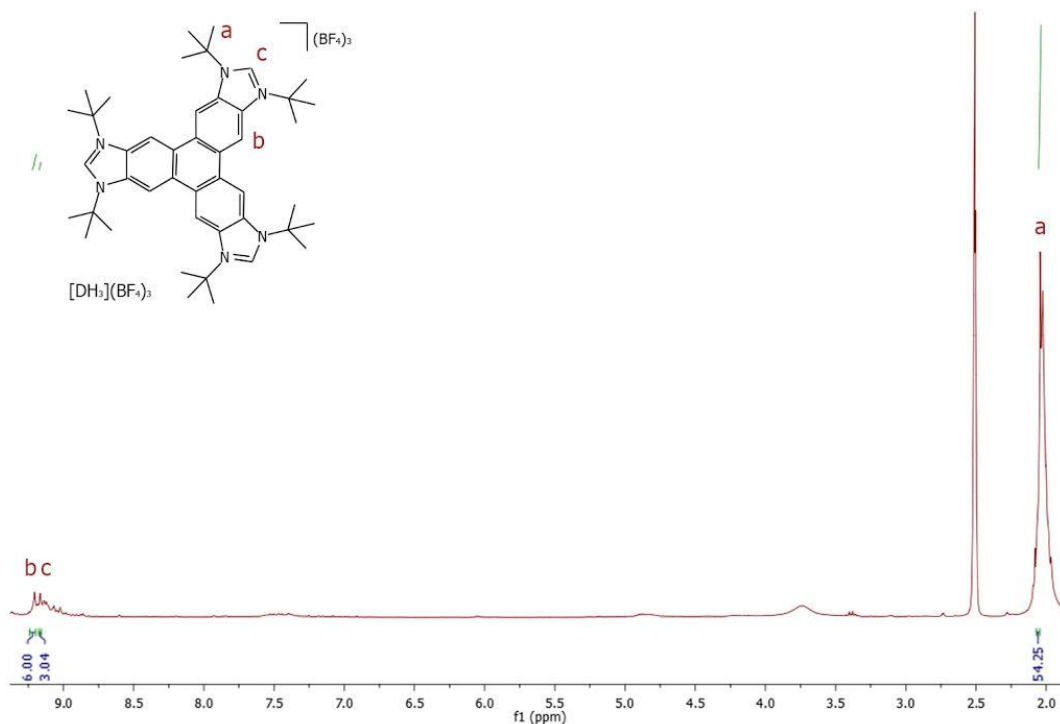


Figure 3.3 ^1H NMR spectrum of $[\text{DH}_3](\text{BF}_4)_3$ in $\text{DMSO-}d_6$

Figure 3.3 shows the ^1H NMR spectrum of the obtained tris-imidazolium salt in $\text{DMSO-}d_6$. Again, the number of signals and their integration is in agreement with the three-fold symmetry of the compound.

Protons shaping the triphenylene core (*b*) generate a singlet at 9.21 ppm. Very close to that peak, there is another singlet (at 9.17 ppm), whose resonance is attributed to the acidic protons linked to the carbon atom that lies between the nitrogen atoms (NCHN, *c*). Upon coordination to a metal fragment, the disappearance of this signal would be the first evidence that the coordination has taken place. For the assignment of these two very close peaks, a HSQC experiment was carried out (*vide infra*). Finally, the signal due to the protons of the *tert*-butyl groups (*a*) appears as a singlet at 2.05 ppm.

^{13}C NMR spectrum of $[\text{DH}_3](\text{BF}_4)_3$ in $\text{DMSO-}d_6$

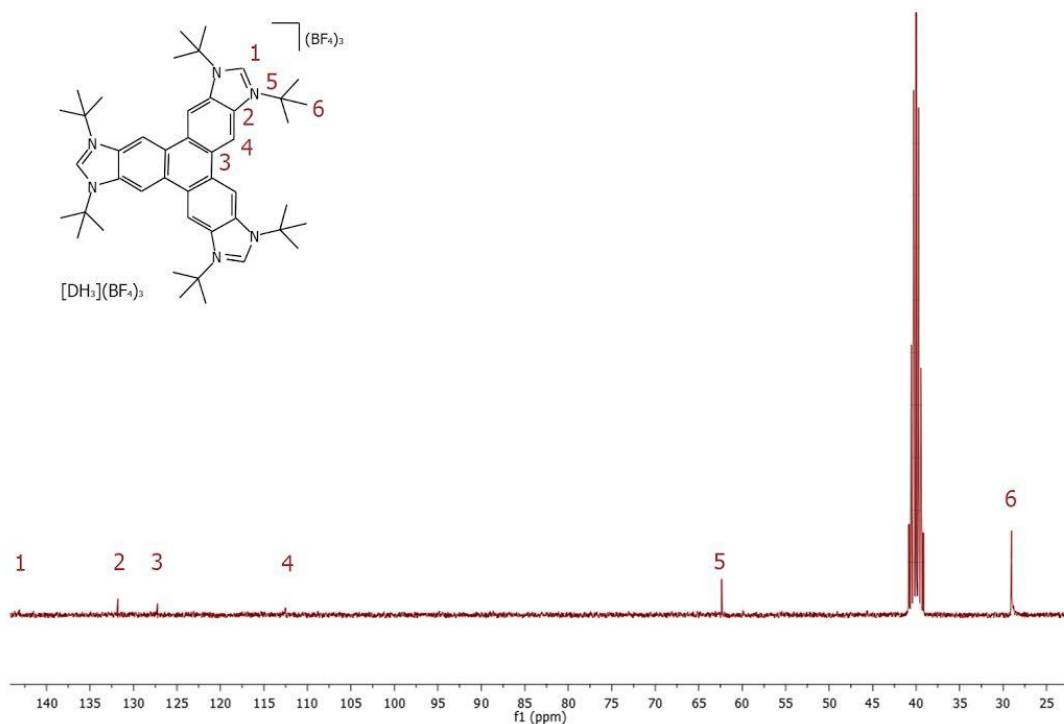


Figure 3.4 ^{13}C NMR spectrum of $[\text{DH}_3](\text{BF}_4)_3$ in $\text{DMSO-}d_6$

The ^{13}C NMR spectrum of the obtained tris-imidazolium salt in $\text{DMSO-}d_6$ is shown in Figure 3.4. The number of signals is in agreement with the three-fold symmetry of the compound. The first signal, at 143.2 ppm, corresponds to the carbon atom located inter nitrogen atoms (NCHN, 1). The three following signals (131.8, 127.2 and 112.5 ppm) are due to carbons constituting triphenylene core: Quaternary carbons (2 and 3) generate the first two peaks and tertiary carbons (4), the last one. Another two peaks at 62.4 and 29.0 ppm are produced, respectively, by carbon atoms which forms t-butyl substituents of amines (5 and 6).

HSQC spectrum of $[\text{DH}_3](\text{BF}_4)_3$ in $\text{DMSO-}d_6$

As mentioned above, in the ^1H RMN spectrum of product **C** (Figure 3.3), two peaks appear around 9.20 ppm. In order to elucidate which proton corresponds to each peak, a HSQC experiment was carried out.

This technique consists in the generation of a two-dimensional spectrum, where one axis corresponds to the proton spectrum (^1H NMR) and the other to another nucleus different from proton spectrum (in this case, ^{13}C NMR). Thus, it is shown what type of specific proton is attached to each carbon atom.

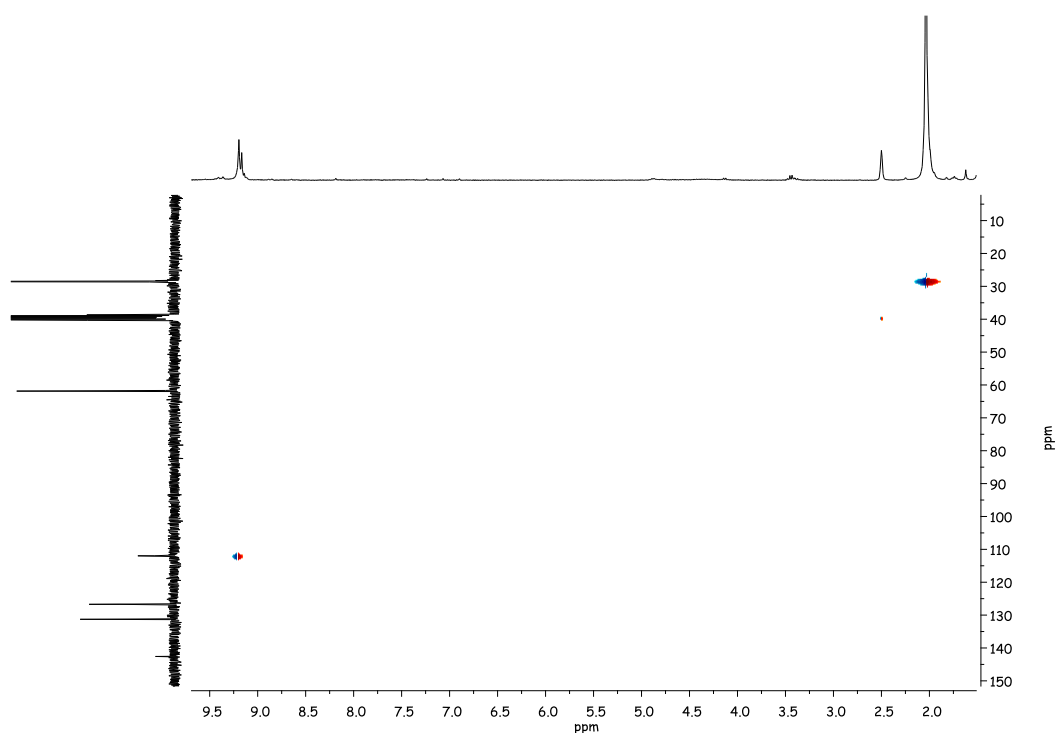


Figure 3.5 HSQC spectrum of $[\text{DH}_3](\text{BF}_4)_3$ in $\text{DMSO-}d_6$

If we focus in the area of interest, we can see that the signal corresponding to the acidic protons at 9.17 ppm (NCHN, *c*, Scheme 3.3) in the ^1H NMR spectrum is coupled to the signal at 143.2 ppm (NCHN, *1*, Scheme 3.4) in the ^{13}C NMR spectrum. Furthermore, we can observe that the peak corresponding to the six equivalent proton atoms of the triphenylene core that appears at 9.21 ppm (*b*, Scheme 3.3) in the ^1H NMR spectrum couples with that at 112.5 ppm (*4*, Scheme 3.4) in the ^{13}C NMR spectrum.

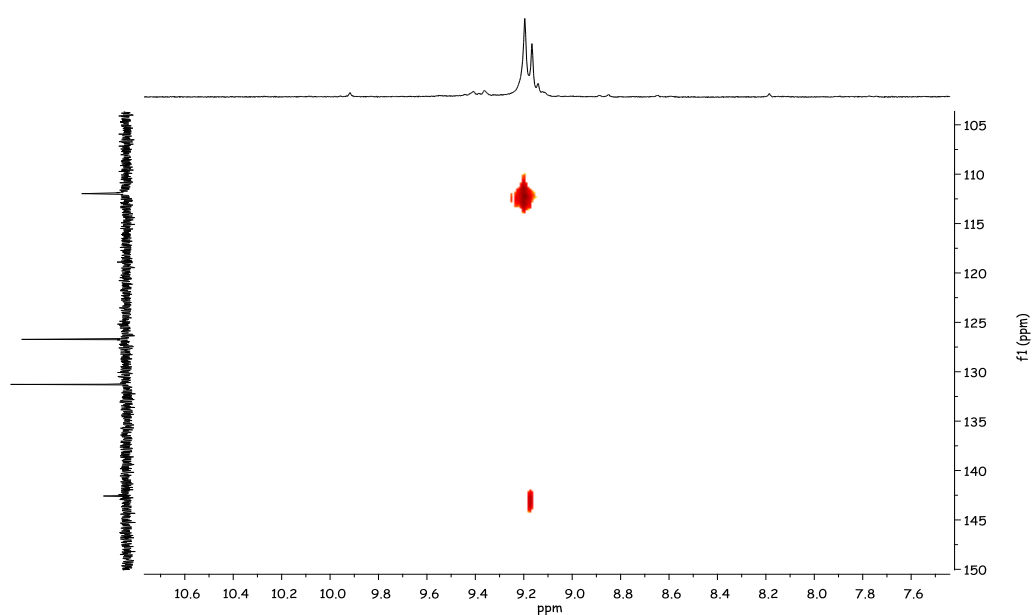
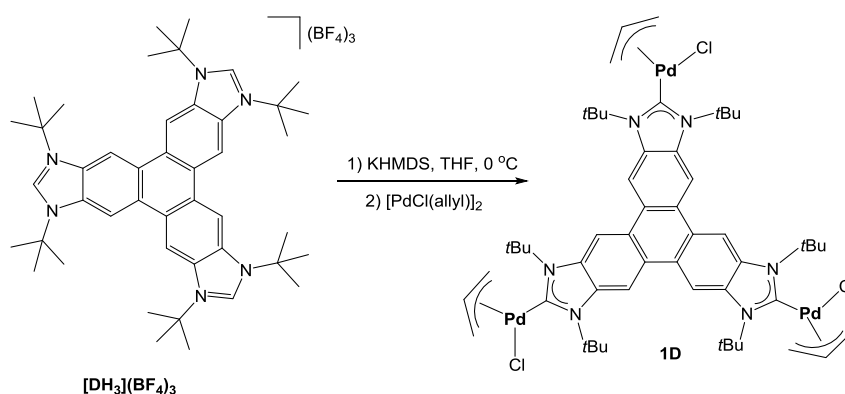


Figure 3.6 Area of interest in HSQC spectrum of $[\text{DH}_3](\text{BF}_4)_3$ in $\text{DMSO-}d_6$

3.2. SYNTHESIS OF THE TRIMETALLIC COMPLEX

Once the triphenylene-based tris-imidazolium salt $[\text{DH}_3](\text{BF}_4)_3$ was prepared and conveniently characterized, we decided to explore its coordination capability as tris-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, since it does not require working in an extremely inert atmosphere. NaOAc, Cs_2CO_3 or trimethylamine are among the most commonly employed. However, the activation of salt $[\text{DH}_3](\text{BF}_4)_3$ was not successful using any of the weak bases normally employed. Therefore, the activation of the salt was carried out using a strong base such as potassium bis(trimethylsilyl)amide (KHMDS).



Scheme 3.2 Synthesis of trimetallic complex **1D**

Scheme 3.2 depicts the methodology employed to obtain the trimetallic complex **1D**. In the first step of the reaction, $[\text{DH}_3](\text{BF}_4)_3$ was treated with KHMDS at $0\text{ }^\circ\text{C}$ in dry THF, in order to activate the tris-imidazolium salt to form the corresponding tris-NHC ligand. Then, a solution of $[\text{PdCl}(\eta^3\text{-allyl})]_2$ in dry THF was added to the first reaction vessel. The resulting reaction mixture was stirred for 10 min on the ice bath and for 2 h at room temperature. After removal of the volatiles, the resulting crude solid was purified by column chromatography on silica gel eluting with CH_2Cl_2 :acetone mixtures. Complex **1D** was isolated as a yellow solid in moderate yield.

Characterization of the trimetallic complex **1D**

^1H NMR spectrum of **1D** in CDCl_3

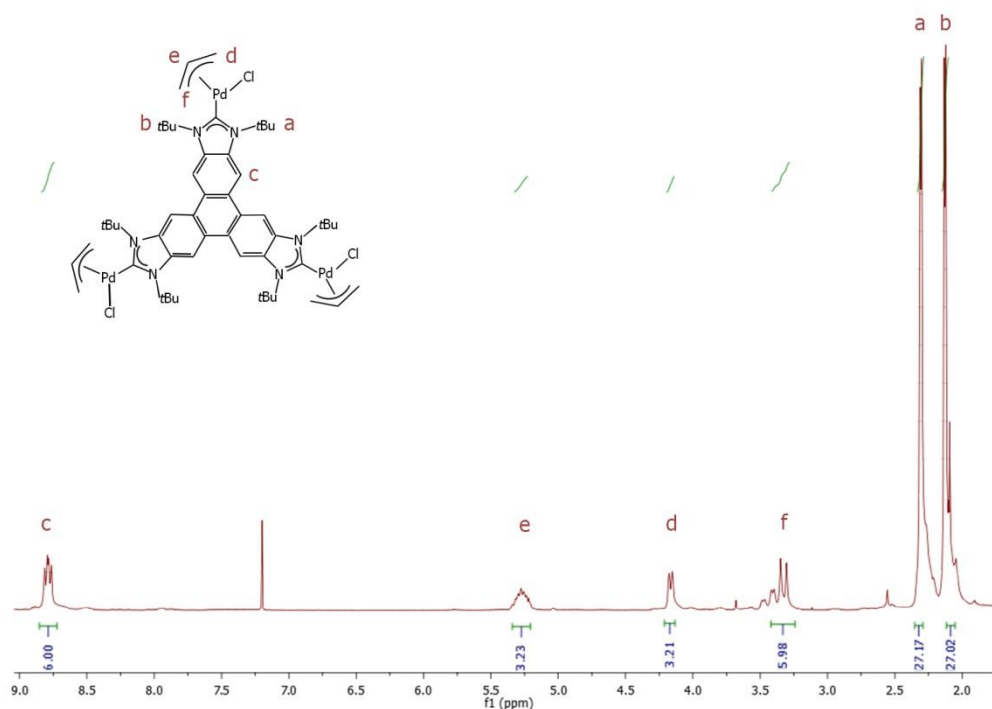


Figure 3.7 ^1H NMR spectrum of **1D** in CDCl_3

Figure 3.7 shows the ^1H NMR spectrum of the trimetallic complex **1D** in CDCl_3 . As can be seen in Figure 3.7, the ^1H NMR of **1D** is complicated because, apart from the two possible atropisomers depicted in Figure 3.8, the three η^3 -allyl ligands can present η^3 - η^1 - η^3 isomerization, breaking the symmetry of the compound.

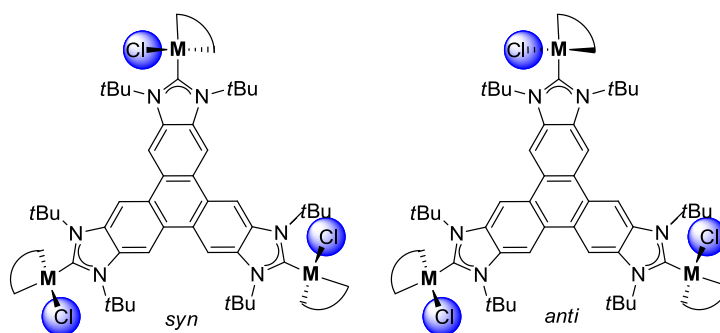


Figure 3.8 Possible *syn* and *anti* atropisomers of complex **1D** ($\text{M} = \text{Pd}(\eta^3\text{-allyl})$)

The six protons corresponding to the triphenylene core (**c**) appear as a multiplet at 8.79 ppm, suggesting that they are not equivalent, as in the case of the salt and the hexa-aminotriphenylene compound **C** (see Figures 3.1 and 3.3).

The ^1H NMR spectrum shows five distinct and defined resonances for the allylic groups, which is in agreement with other Pd(II)-allyl complexes bearing NHC ligands.³¹ The strong σ -donor properties and greater *trans* influence of the carbene ligand, compared with the chloride ligand, causes the allylic carbon atom *trans* to carbene to be weakly bonded, consequently causing the asymmetry in the allylic bonding. The central allylic CH proton appears as a complex multiplet at 5.28 ppm (*e*). The allylic CH₂ protons *pseudo-trans* to the carbene units appear as rather complicated multiplets at 4.17 and 3.35 ppm (*d* and *f*). Only one of the two signals, corresponding to the allylic CH₂ protons *pseudo-trans* to the chloride ligands, can be observed in the ^1H NMR spectrum at 3.35 ppm (*f*). The missing signal may be underneath a more intense signal corresponding to the protons of the *tert*-butyl groups. The ^1H NMR also shows two resonances for the *tert*-butyl groups at 2.31 and 2.13 ppm (*a* and *b*, respectively), suggesting that the *tert*-butyl CH₃ protons are in a slightly different chemical environment.

^{13}C NMR spectrum of **1D** in CDCl₃

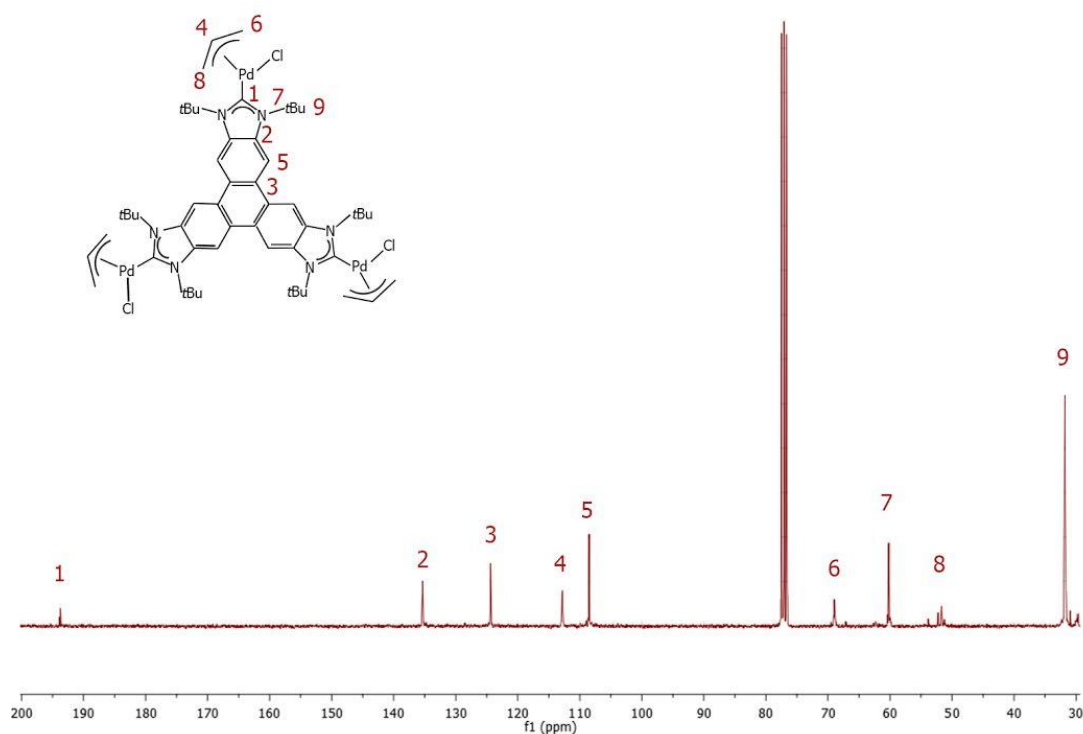


Figure 3.9 ^{13}C NMR spectrum of **1D** in CDCl₃

The most characteristic signal in the ^{13}C NMR spectrum of **1D** is the singlet attributed to the magnetically equivalent metallated carbene-carbons at 193.7 ppm (**1**). Signals at 135.3, 124.4 and 108.5 ppm are due to those carbons constituting triphenylene core: Quaternary carbons (**2** and **3**) generate the first two peaks and tertiary carbons (**5**), the last one. Moreover, allylic

substituent attached to palladium atom generates another three peaks at 112.8 (due to central carbon, 4), 69.0 (terminal carbon closer chloride substituent, 6) and 51.7 ppm (terminal carbon closer *tert*-butyl linked to nitrogen atoms, 8). Finally, two peaks at 60.2 and 31.8 ppm correspond to the *tert*-butyl substituents (7 and 9, respectively).

4. CONCLUSIONS

First, in this work we have synthesized a triphenylene-based tris-imidazolium salt as precursor of a star shaped tris-NHC ligand, following a synthetic route previously designed in the QOMCAT group, starting from commercially available triphenylene.

The synthetic route to the tris-imidazolium salt implies the Buchwald-Hartwig multifold amination of the hexa-bromotriphenylene compound **B**, and subsequent trisannulation of the resulting hexa-amine **C** with a trisalkyl orthoformate, yielding the pursued salt **[DH₃](BF₄)₃**.

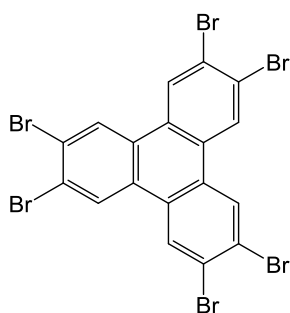
The tris-imidazolium salt **[DH₃](BF₄)₃** was reacted with $[\text{PdCl}(\eta^3\text{-allyl})]_2$ under inert conditions in the presence of KHMDS, affording the preparation of the trimetallic complex **1D**.

5. EXPERIMENTAL SECTION

5.1. GENERAL PROCEDURES

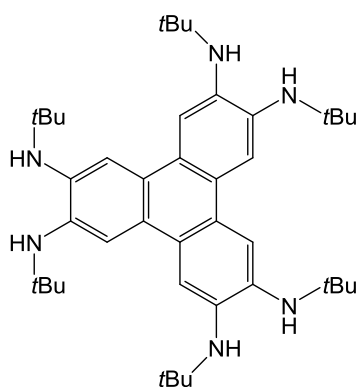
Whereas the synthesis of compounds **B** and $[\text{DH}_3](\text{BF}_4)_3$ was carried out under aerobic conditions, the preparation of **C** and **1D** required the use of standard Schlenk tube techniques under nitrogen atmosphere. Triphenylene (**A**) was used as received from the commercial supplier. 2,3,6,7,10,11-Hexabromotriphenylene (**B**) was synthesized according to literature methods.²⁹ 2,3,6,7,10,11-Hexa-*tert*-butylamine-triphenylene (**C**), the tris-imidazolium salt $[\text{DH}_3](\text{BF}_4)_3$ and the trimetallic complex **1D** were prepared following synthetic routes developed by QOMCAT group.²⁸ Anhydrous solvents used were dispensed by a MBRAUN SPS and required reagents were used as purchased from different commercial suppliers. Chromatographic column was performed in silica gel Merck 60, 62-200 μm , using the mixture of solvents indicated *ut infra*. NMR spectra were recorded on a Bruker 300 MHz, using CDCl_3 or $\text{DMSO}-d_6$ as solvents.

5.2. SYNTHESIS AND CHARACTERIZATION THE TRIS-IMIDAZOLIUM SALT



Synthesis of 2,3,6,7,10,11-hexabromotriphenylene (B)

To a solution of triphenylene (1.92 g, 8.56 mmol, needle-shape white solid) in nitrobenzene (82 mL, yellow liquid) with iron powder (0.19 g, 3.40 mmol) was added bromine (4 mL, 77.7 mmol, red liquid) dropwise. Then, the solution was allowed to stand for 24 h. The mixture was heated at 210 °C for 2 h and allowed to reach room temperature. Diethyl ether (150 mL) was added to the resulting solution. The solid so formed was collected by filtration and it was washed several times with diethyl ether. The crude solid was recrystallized from 1,2-dichlorobenzene to yield compound **B** (5.27 g, 90 %) as a white solid. The high insolubility of compound **B** prevented its characterization by means of NMR spectroscopy.

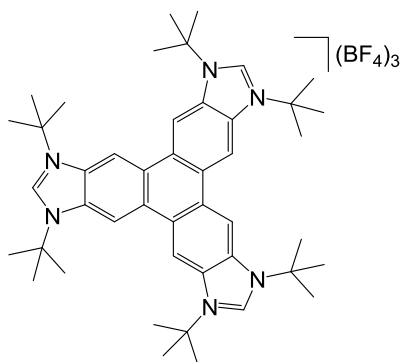


Synthesis of 2,3,6,7,10,11-hexa-tert-butylamine-triphenylene (C)

$[\text{Pd}(\text{OAc})_2]$ (12.7 mg, 0.06 mmol) and $\text{IPr}\cdot\text{HCl}$ (48.3 mg, 0.11 mmol) were placed together in a Schlenk tube. Compound **B** (503.6 mg, 0.72 mmol) was placed in another Schlenk tube. The two Schlenk tubes were evacuated and filled with

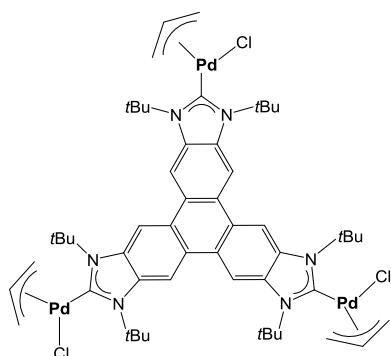
nitrogen three times. Dry toluene was added to the two Schlenk tubes (10 and 20 mL, respectively) via syringe. Sodium *tert*-butoxide (2M in toluene, 80 μ L, 0.16 mmol, and 2.6 mL, 5.2 mmol) was added to Schlenks 1 and 2, respectively. *Via* oven dried cannula, the solution in Schlenk 1 was transferred over Schlenk 2. Then, *tert*-butyl amine (0.8 mL, 7.6 mmol) were added to Schlenk 2 (a white suspension was in the reaction Schlenk). The resulting mixture was heated under reflux for 16 h. The dark red solution formed was cooled and filtered over Celite. After removal of the volatiles, the desired product **C** was isolated as a dark red solid in a quantitative yield. ^1H NMR (300 MHz, CDCl_3): δ 7.85 (s, 6H, $\text{CH}_{\text{arom.}}$), 3.81 (s, 6H, NH), 1.39 (s, 54H, $\text{C}(\text{CH}_3)_3$) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 137.8 ($\text{C}_{\text{quat. arom.}}$), 123.6 ($\text{C}_{\text{quat. arom.}}$), 113.5 ($\text{CH}_{\text{arom.}}$), 52.2 ($\text{C}(\text{CH}_3)_3$) and 30.0 ($\text{C}(\text{CH}_3)_3$) ppm.

Synthesis of $[\text{DH}_3](\text{BF}_4)_3$



A mixture of compound **C** (572 mg, 0.87 mmol) in triethylorthoformate (60 mL) was placed on an ice bath. Then, $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (0.4 mL, 2.91 mmol) was added dropwise. The black suspension mixture was heated at 150 $^\circ\text{C}$ for 16 h under aerobic conditions. A light brown suspension was obtained. After cooling to room temperature, diethyl ether was added and the precipitated solid was collected by filtration. The light brown product was precipitated in a acetonitrile/diethyl ether mixture. Compound $[\text{DH}_3](\text{BF}_4)_3$ (348.7 mg, 42 %) was isolated as an off-white solid. ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 9.21 (s, 6H, $\text{CH}_{\text{arom.}}$), 9.17 (s, 3H, NCHN) and 2.05 (s, 54H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$): δ 143.2 (NCHN), 131.8 ($\text{C}_{\text{quat. arom.}}$), 127.2 ($\text{C}_{\text{quat. arom.}}$), 112.5 ($\text{CH}_{\text{arom.}}$), 62.4 ($\text{C}(\text{CH}_3)_3$) and 29.0 ($\text{C}(\text{CH}_3)_3$).

5.3. SYNTHESIS AND CHARACTERIZATION OF THE TRIMETALLIC COMPLEX



$[\text{DH}_3](\text{BF}_4)_3$ (152.7 mg, 0.16 mmol) was placed in a Schlenk tube. In another Schlenk tube, $[\text{PdCl}(\eta^3\text{-allyl})]_2$ (90.1 mg, 0.25 mmol) was placed. The two tubes were evacuated and filled with nitrogen three times. 10 mL of dried THF were added to the first Schlenk tube (a light brown suspension) and 5 mL to the second one (orange solution) *via* syringe. The first Schlenk tube was placed on an ice bath and KHMDS (1.1 mL, 0.55 mmol) were added (the solution turned caramel). The solution in the second Schlenk tube was transferred *via* oven dried cannula to the first one and the mixture was stirred for 10 min on the ice bath and for 2 h at room temperature. The black solution was dried under vacuum in order to eliminate volatile components. The rest was dissolved with dichloromethane and filtered over Celite. The filtrate was evaporated and the product was dried under vacuum. The dried product was dissolved in CH_2Cl_2 and it was poured over chromatographic column (packed with silica gel and CH_2Cl_2). Column chromatography using mixtures of CH_2Cl_2 /acetone (from 9:1 to 1:1) afforded the separation of a yellow band that contained compound **1D**. Compound **1D** was isolated as a pale yellow solid after precipitation in a mixture CH_2Cl_2 /hexane. ^1H NMR (300 MHz, CDCl_3): δ 8.79 (m, 6H, $\text{CH}_{\text{arom.}}$), 5.28 (m, 3H, CH_{allyl}), 4.17 (d, 3H, $\text{CH}_{2\text{allyl}}$), 3.35 (m, 6H, $\text{CH}_{2\text{allyl}}$), 2.31 (d, $^4J_{\text{H-H}}=2.31$ Hz, 27H, $\text{C}(\text{CH}_3)_3$), 2.13 (d, $^4J_{\text{H-H}}=2.13$ Hz, 27H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (300 MHz, CDCl_3): δ 193.7 (Pd- $\text{C}_{\text{carbene}}$), 135.3 ($\text{C}_{\text{quat. arom.}}$), 124.4 ($\text{C}_{\text{quat. arom.}}$), 112.8 (CH_{allyl}), 108.5 ($\text{CH}_{\text{arom.}}$), 69.0 ($\text{CH}_{2\text{allyl}}$), 60.2 ($\text{C}(\text{CH}_3)_3$), 51.7 ($\text{CH}_{2\text{allyl}}$), 31.8 ($\text{C}(\text{CH}_3)_3$).

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