STUDIES TOWARDS THE SYNTHESIS OF FUSED N-HETEROCYCLIC CARBENE PRECURSORS

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I’ve been up chasing my childhood with a pen, these are dreams old men dream.

- CWK

Don’t see how little you can do, see how much you can.

- GWG

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Contents

Abbreviations

ESMS	electrospray mass spectrometry
DCM	dichloro methane
DMF	N, N′-dimethylformamide
DMSO	dimethyl sulfoxide
equiv	molar equivalent
HRMS	high resolution mass spectrometry
I.R	infra-red
M	molar
MeCN	acetonitrile
MeOH	methanol
NMR	nuclear magnetic resonance
PPA	polyphosphoric acid
TOCSY	total correlation spectroscopy

Abstract

This thesis describes the preparation of a various NHC ligands with five and six-membered rings, different fused aromatic cores and the subsequent synthetic development of their complexation of with Ag, Ru and Pd. The investigation and preparation of these compunds was with the intention of exploring their chemical and physical properties. The synthesis of the NHC ligands proved to be difficult, but analysis and characterisation of the side products from the reactions helped to establish successful synthetic methodologies. In both the five and six-membered research conducted a common attribute was established of a pyrid-2-yl substituent at the 1 position or both the 1 and 3 positions, thus providing new NHC ligands to investigate.

The organic syntheis of the research focused on two NHC ligand functionalites, five and six membered rings. The six memerbered rings focused on 1*H*-perimidine as the core unit and the design of both bidentate and tridentate NHC ligands to mimic the structural binding relationship of 2,2′-bipyridine (bpy) and 2,2′:6′2″-terpyridine (tpy) with various metal salts. The synthesis of the bpy analogues was achieved in good overall yields with minimal synthetic challenges. However, the tpy analogue was unable to be realised due to time constraints and problems associated with its synthesis. The five membered NHC ligands synthesised were to investigate the physical effects of systematically increasing the size of its aromatic core. The main focus of the research was on the phenanthrene imidazole NHC ligands. This was investigated due to the minimal research that has been conducted on this core unit and NHC-complexes. Synthesis of the two-bidentate NHC ligands with an imidazole head group and fused phenanthrene backbone were completed, but this was with a picolyl substituent at the 1 position rather than the pyrid-2-yl substituent. This failure to isolate this product was attributed to steric influences. Pyrene-fused-imidazole NHC ligands were also investigated and pyrene offers a NHC core that hasn't been investigated previously. However, synthesis and isolation of the NHC ligands proved to be difficult and was associated with the poor solubility of the NHC ligands.

The organometallic NHC synthesis was studied extensively with the main focus on establishing appropriate conditions to give a NHC complex. The main metal investigated was ruthenium as subsequent NHC complexes were expected to have potentially interesting properties such as luminescence. The synthesis of a perimidine and phenanthrene NHC ruthenium complexes have not been isolated before, thus giving new NHC complexes. Many different synthetic routes were attempted to synthesise a perimidine NHC ruthenium complex. However, this proved difficult due to associated higher reactivity of the carbene carbon of perimidine with a new side product as a result of this research. The phenanthrene NHC complex synthesis suffered due to time constraints but potential methodology for their synthesis is stated.

Chapter 1

Introduction

1. Introduction

The term carbene refers to a neutral carbon atom with 6 valence electrons. Skell *et al*. established carbenes in the 1950s in the field of organic chemistry.[1] However, it was Fisher *et al*. who first employed them as ligands in organometallic chemistry in 1964.[2] This field of research is where carbenes have had their most significant impact, with applications in catalysis, and to a lesser degree, luminescence.[3, 4]

Carbenes can have either linear or bent geometries. The linear geometry is an extreme case, as the carbene carbon atom has an sp-hybridised orbital with two electronically degenerate p orbitals with parallel spins resulting in a triplet state. The majority of carbenes exist as an sp^2-hybridised carbon atom, resulting in a bent geometry. These bent carbenes can exist in either a triplet (unpaired electrons) or singlet state (paired electrons) as shown in figure 1.1(a) and figure 1.1(b), respectively.

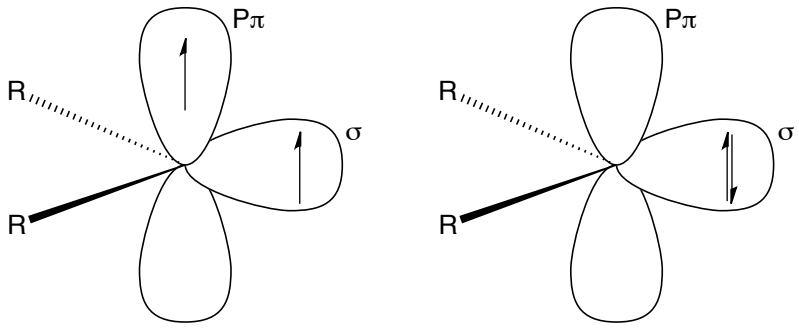


Figure 1.1: (a) Triplet carbene, and, (b) singlet carbene.

These electronic states are determined by the relative stability of the σ and P_π orbitals (P_π is the common nomenclature for a single P orbital). The electronic state of the carbene can be tuned via the substituents α to the carbene carbon atom (α-substituents) using a combination of steric and electronic effects. The triplet state is typically stabilised with σ-donating and π-withdrawing α-substituents causing the resulting σ and p_π orbitals to be close enough in energy so that both orbitals are occupied by an electron, resulting in a triplet carbene. The triplet states are typically highly reactive species, therefore large steric groups adjacent to the carbene carbon atom can be used to allow isolation of these species. In 1995 Tomioka *et al*. synthesized 2,2',4,4',6,6'-hexabromodiphenylcarbene as shown in figure 1.2. This carbene can be kept at room temperature in a crystalline state as a stable triplet carbene.[5] Evidence for the formation of the triplet carbene came from EPR spectroscopy showing the presence of unpaired electrons.

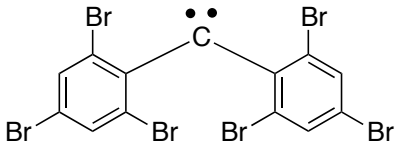


Figure 1.2: 2,2',4,4',6,6'-hexabromodiphenylcarbene, a triplet carbene that is stable at room temperature in the solid state.

Singlet carbenes are significantly more stable than their counterpart triplet carbenes. The adjacent atoms or groups to the carbene carbon are typically σ-withdrawing and π-donating heteroatoms, as shown in figure 1.3. This causes the P_π orbital to increase in energy resulting in a larger energy difference between the two σ and P_π orbitals (the HOMO and LUMO, respectively). Therefore the σ orbital is occupied allowing the singlet state carbene.[4, 6]

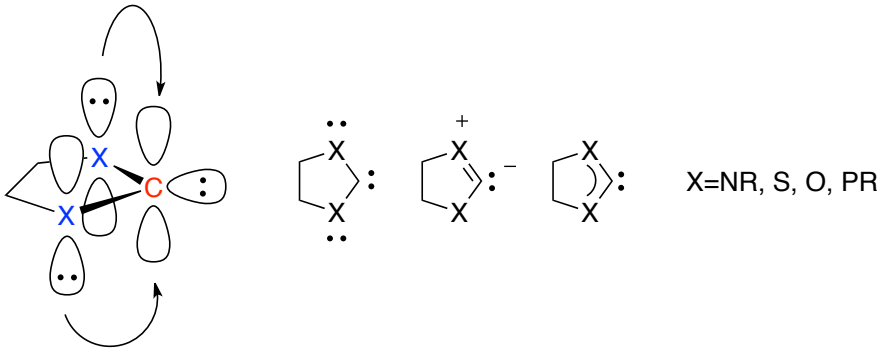
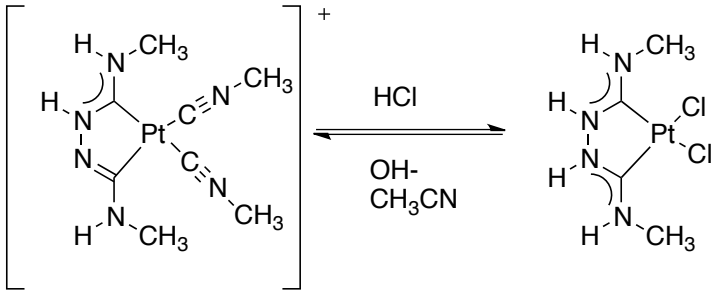


Figure 1.3: The π-donation of electron density into the carbene atom and resonance structures giving partial mulitple bond character, thus helping stabilise the singlet state of the carbene.

The low electronegativity of singlet state carbenes results in the electron pair donor ability of the carbon being quite strong. This makes singlet carbenes stronger σ-donors to metals than most tertiary phosphines due to the strong σ-character of the carbene.[7] However, the carbene carbon is also a good electron acceptor, better than that of boranes due to the empty p-orbitals of the carbene carbon.[8] Considerable research has been done into singlet carbenes, the majority of which focused on a particular sub unit, the N-Heterocyclic Carbene (NHC). These NHC's have been extensively studied due to their inherent stability and easy synthesis. Singlet carbenes don't necessarily have to be heterocycles, with an example of a heteroatom stablised carbene complex shown in figure 1.4. This heteroatom carbene complex was the first to be synthesised and was prepared in 1925 by Tschugajeff, however the analytical techniques available in 1925 could not confirm this as the first carbene complex. The red complex **1.01**, was treated with HCl forming the yellow complex, **1.02**, in a reversible reaction.[4] It wasn't until 1970 that the crystal structures of the complexes **1.01** and **1.02**

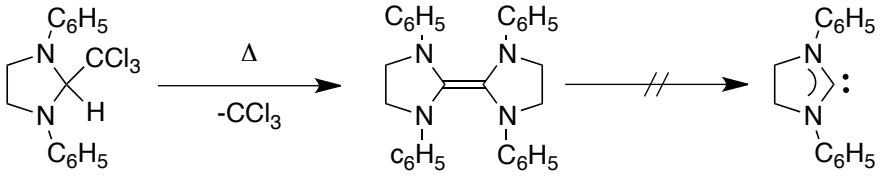
were determined, providing direct structural evidence of the first heteroatom carbene complexes.[9, 10]



1.01 **1.02**

Figure 1.4: Tschugajeff's Pt heteroatom carbene complexes **1.01** (red) and **1.02** (yellow).

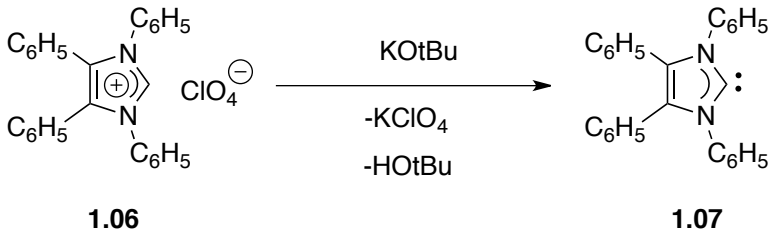
The isolation of free stable carbenes was one of the first goals in this field. A report by Wanzlick in 1960 proposed the existence of a free NHC, by suggesting the α-elimination of chloroform from **1.03** as shown in figure 1.5.[11] However, there was no supporting evidence for the NHC (**1.05**), and only the entetramine **1.04** was observed, potentially due to the lack of stability of **1.05**. The existence of **1.04** was proved by reactions with oxygen, water, nitromethane and cyclopentanone, thus confirming the nucleophilicity of **1.04**. Cross coupling experiments with the different substituents on the nitrogen atoms confirmed that the dimers are not in equlibrium with their monomers.



1.03 **1.04** **1.05**

Figure 1.5: Wanzlick's proposed mechanism to give the formation of a NHC.

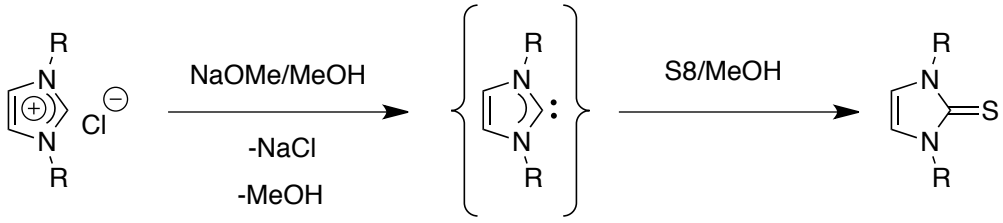
Wanzlick later recognized that the aromatic resonance of an unsaturated N-Heterocyclic five-membered ring, e.g. imidazole, would contribute to the stability of the free NHC. Investigation into tetraphenylimidazolium perchlorate, **1.06,** and deprotonation with KO^{t}Bu eventually resulted in the free NHC **1.07**, as shown in figure 1.6.



1.06 **1.07**

Figure1.6: Wanzlick's attempted synthesis of a free NHC, **1.07**.

Wanzlick was unable to isolate the product **1.07**, but there was evidence for its formation through the products that were isolated from the reactions with H_2O and $Hg(OAc)_2$.[4] In 1998 the free NHC **1.07**, was able to be isolated by Arduengo *et al*. using a modified synthetic preparation.[4, 12] Arduengo's group were the first to isolate a free NHC **1.08**, synthesising the imidazole thiones via the intermediate NHC, **1.08**, as shown in figure 1.7.[4]



1.08

Figure1.7: Arduengo's synthesis of imidazolin-2-thiones via a free NHC intermediate.

Initially this synthesis was carried out under an inert atmosphere and moisture restrictive conditions because it was assumed that the carbene intermediate was highly reactive. This reaction proceeded in a good yield, and repeated under standard conditions with a similar result. Therefore, Arduengo concluded that the carbene intermediate, **1.08**, was not as air and moisture sensitive as had originally been assumed.[13]

Arduengo then investigated the synthesis of free NHC's in detail with the deprotonation of imidazolium salts, using the sterically demanding N,N'-diadamantyl imidazolium salt, as shown in figure 1.8. Sodium hydride was used as the base with a catalytic amount of DMSO and the resulting byproducts, NaCl and hydrogen gas were easily separated. The THF solution became colorless and upon its removal colorless single crystals were formed. X-ray diffraction proved the existence of the free NHC carbene **1.09**, the first free stable NHC to be isolated.[14] The melting point of the carbene was 240°C without decomposition, supporting the theoretical thermal stability associated with NHC's, this becomes important later in the application of NHC's.

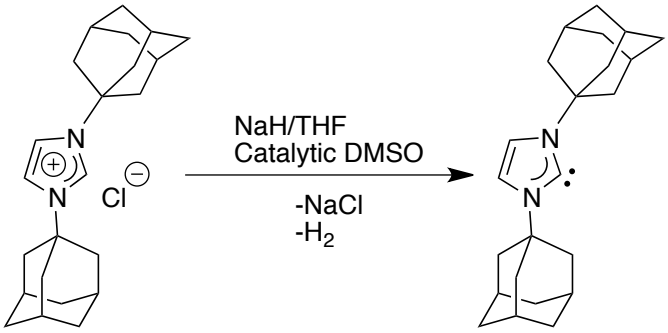


Figure1.8: Arduengo's synthesis of the first isolated NHC, **1.09**.

General NHC Synthetic Strategy

NHC molecules are an attractive area of research due to the high variability and tuneability of their molecule properties. A general synthetic strategy for the synthesis of imidazolium based NHC salts is described below in figure 1.9. Route **A** involves the stepwise addition of the R groups to the imidazole ring giving **1.11**, followed by another R group substitution, **B** resulting in the imidazolium salt **1.14**. This route allows a high degree of control and tunability due to the different nucleophilicity of the pyridine and pyrrole like nitrogen atoms. Route **C** allows for substitution of the R groups initially to give **1.12**, before the ring is closed forming the NHC salt, **1.14**. The synthesis of **1.12** is favourable when both R substituents are the same. Route **C** only requires one precursor step rather than two as described with route **A** and **B**. In order to cyclise the ring, the reaction typically involves a C1 electrophile like formic acid or $HC(OMe)_3$.

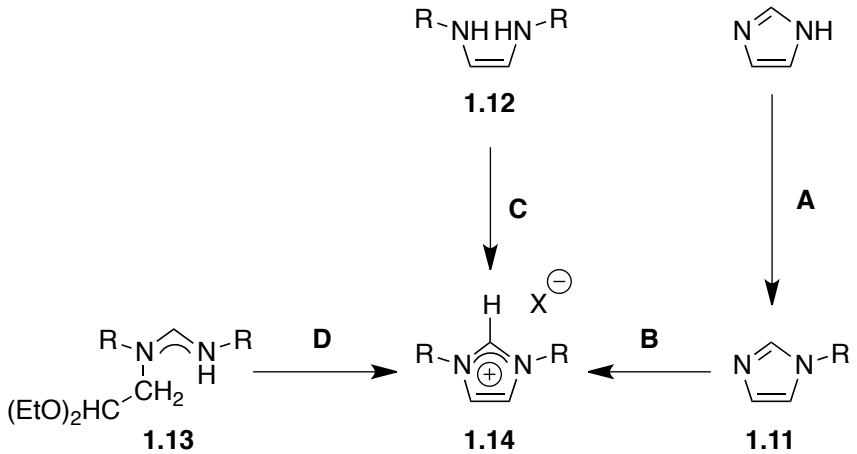
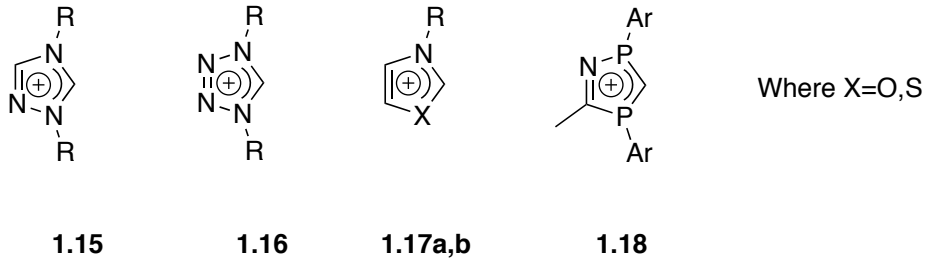


Figure 1.9: General synthetic route to achieve imidazolium based NHC salts.

The final route **D** involves the intramolecular ring annulation rather than intermolecular, as in route **C**. However, the synthesis of the precursor, **1.13** and its derivatives can be difficult due to the multiple functionality of the molecule.

Variation of NHC's

The number of nitrogen atoms in the NHC ring can also be varied, as shown in figure 1.10. Triazolium and tetrazolium salts (**1.15** and **1.16,** respectively) can be deprotonated to give their associated free NHC's. The heteratoms themselves can be modified so that oxygen, sulfur and phosphorus atoms can be incorporated into the ring α to the carbene carbon, resulting in thiozolium **1.17a**, oxazolium **1.17b,** and phosphonium **1.18** salts, respectively. The phosphonium carbene **1.18**, was first synthesized by Bertrand *et al*. and was the first stable P-heterocyclic carbene to be isolated. [15]



1.15 **1.16** **1.17a,b** **1.18**

Figure1.10: Various Heteroatomic azolium salts that can be deprotonated to give free NHC's.

The R groups that are attached at the N1 and N3 position play an important role in the formation of the NHC complexes and can have drastic effects on the physical and chemical properties of the complexes (these properties shall be discussed later). This can include acting as a donating group, such as 2-pyridyl, or sterically demanding with large alkyl chains that will improve the solubility of the compound or help block an active site of the NHC-metal complex. Bridging R groups play an important role in the synthesis of bis-NHC ligands known as pincer ligands. Two examples are shown below in figure 1.11. [16]

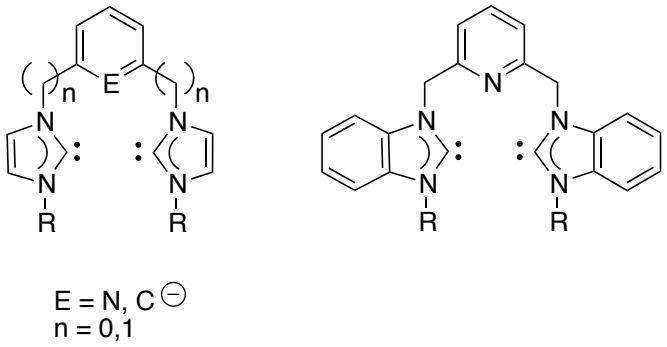


Figure 1.11: Pincer ligands with a bis-NHC moiety.

The electronic nature of the R groups also contributes to the stability of the carbene by their ability to donate or withdraw electons into or from the α-substituents of the carbene carbon, therefore electron donating groups would help stabilise the carbene.[3, 4] The large variability of the R groups allows great scope for the design and modification of NHC's.

The five-membered NHC's have only been described to this point because of their high impact in this field. However, NHC's are not limited to five-membered heterocycles. The ring size of NHC molecules can be decreased to either, three or four membered rings or, increased to six and seven membered rings. [3, 4]

The first four membered heterocyclic carbene **1.20** was synthesised in 2004 and is shown in figure 1.12.[17] Deprotonation of the heterocyclic carbene salt **1.19** proved to be more difficult, as the use of KO^{t}Bu caused ring opening through nucleophilic attack at the phosphorus atom. More sterically hindered bases were employed, such as LiMes (Mes = mesitylene) and K[N(SiMe$_3$)$_2$]. However, this caused the formation of the dimmer, entetramnine species **1.21**. Therefore more sterically imposing substituents such as 2,6-*i*Pr$_2$C$_6$H$_3$ were employed, allowing the isolation of the free NHC species **1.20**.

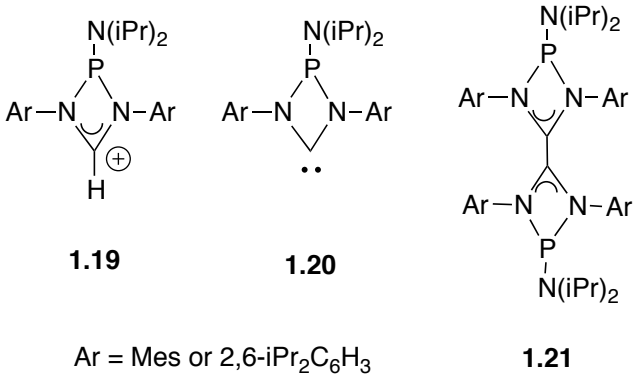


Figure 1.12: The first four membered heterocyclic carbene to be isolated, **1.20**.

The first stable six-membered NHC **1.22** was prepared by Alder *et al*. and is shown in figure 1.13. The annulation of the six-membered ring was performed with triethyl orthoformate and subsequent deprotonation with sodium hexamethyldisilazide gave the desired free NHC, **1.22**. Strong bases have typically been required to deprotonate six-membered NHC salts, due to the high pKa of the H2 proton. Therefore six-membered NHC salts are stonger bases than the five-membered based NHC's. The six-membered NHC's are also more susceptible to nucleophilic attack than their counterpart five-membered NHCs. Hence the use of sterically demanding bases such as sodium or lithium hexamethyldisilazide.[4]

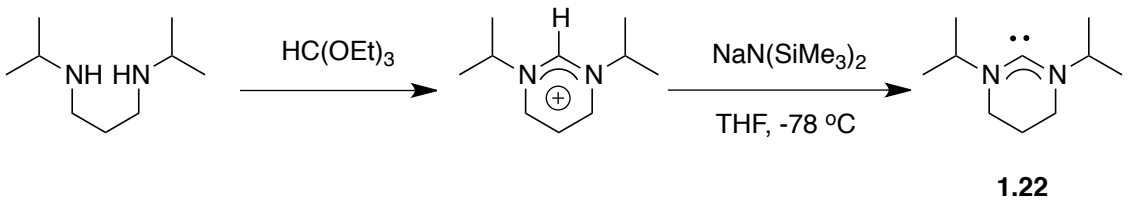


Figure 1.13: Synthesis of the first 6-membered stable NHC.

The NHC, **1.22** proved not to dimerise to the entetramine under standard conditions. However, a derivative of **1.22** with an extended backbone, **1.23**, has been shown to dimerise giving the entetramine **1.24** as shown in figure 1.14. Richeson *et al*. showed that dimerisation mostly occurred upon the deprotonation of the symmetrical N,N'-bis substituted perimidinium salts. Whereas the unsymmetrical species, **1.25,** deprotonates to the free NHC **1.26**.[18] This was attributed to the presence of an alkyl group as one of the substituents on the nitrogen atoms. From X-ray crystallography analysis the carbene carbon of **1.26** was in the backbone plane of the molecule, but the carbene carbon of **1.24** was out of the backbone plane. There was also a torsional twist of each of the perimidine scaffolds of **1.24** due to the sterically demanding R groups in competition with the p-conjugation of the compound. The NHC, **1.26** had a similar shift in the carbene resonance in the ^{13}C-NMR compared to a saturated five-membered NHC, rather than an unsaturated five-membered NHC. This indicates that perimidine carbenes are more reactive as they are not stabilised by electronic delocalisation of the entire molecule. [18]

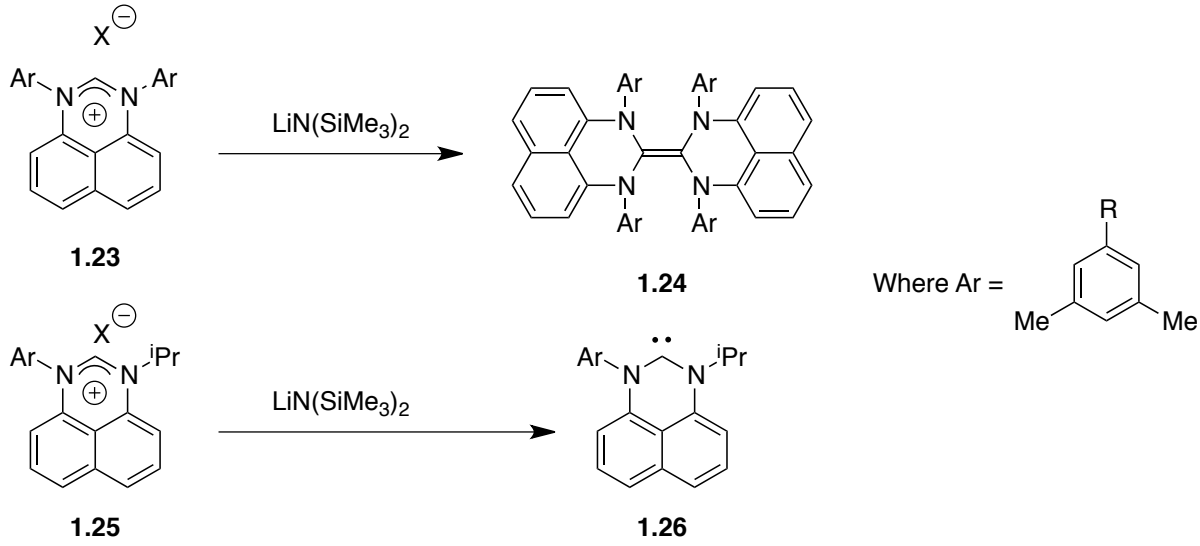


Figure 1.14: Differences in dimerisation of symmetrical and unsymmetrical perimidine NHC's.

The synthesis of a seven-membered NHC, **1.27**, was achieved by condensation of 2,2'-diaminobiphenyl with 2-adamantanone completed by Stahl *et al*. This was then reduced with $LiAlH_4$, followed by ring annulation with triethyl orthoformate resulting in the diazepinium salt **1.27**, as shown in figure 1.15. Single crystal X-ray diffraction showed the existence of **1.27**.

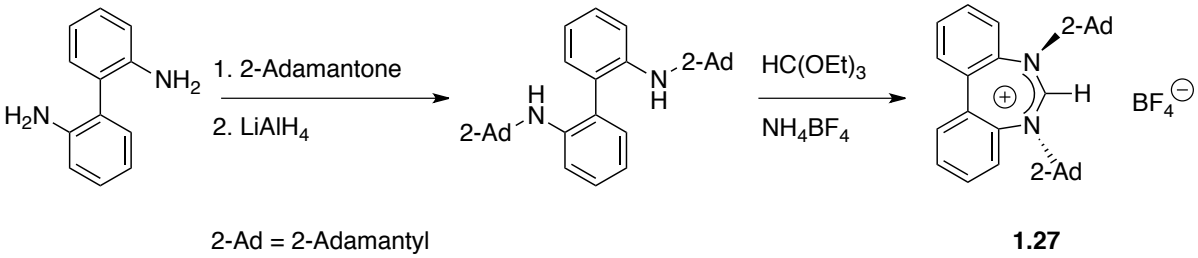


Figure 1.15: Synthesis of the diazepinium salt via ring closing the diaminobiphenyl precursor.

The synthesis of another seven-membered NHC salt was attempted where R = mesitylene. However, the annulation reaction was unsuccessful. This was attributed to the weak basicity of the N-aryl groups, hence the use of the N-alkyl group, adamantyl. The diazepinium salt was obtained in almost quantitative yields. However, subsequent deprotonation was only achieved *in situ* with $[PdCl\{(allyl)\}]_2$ and the free NHC could not be isolated. The Pd-complex was air stable and single crystal X-ray analysis could be completed providing direct structural evidence the formation of the NHC-complex.[19]

Modification of steric and physical properties can be achieved by extending the backbone of NHC's through various aromatic. In 2008 Tapu *et al*. synthesized the first phenanthrene-imidazole fused NHC ligand, **1.31** and various metal complexes, **1.33** and **1.34**, as shown in figure 1.16.[20]

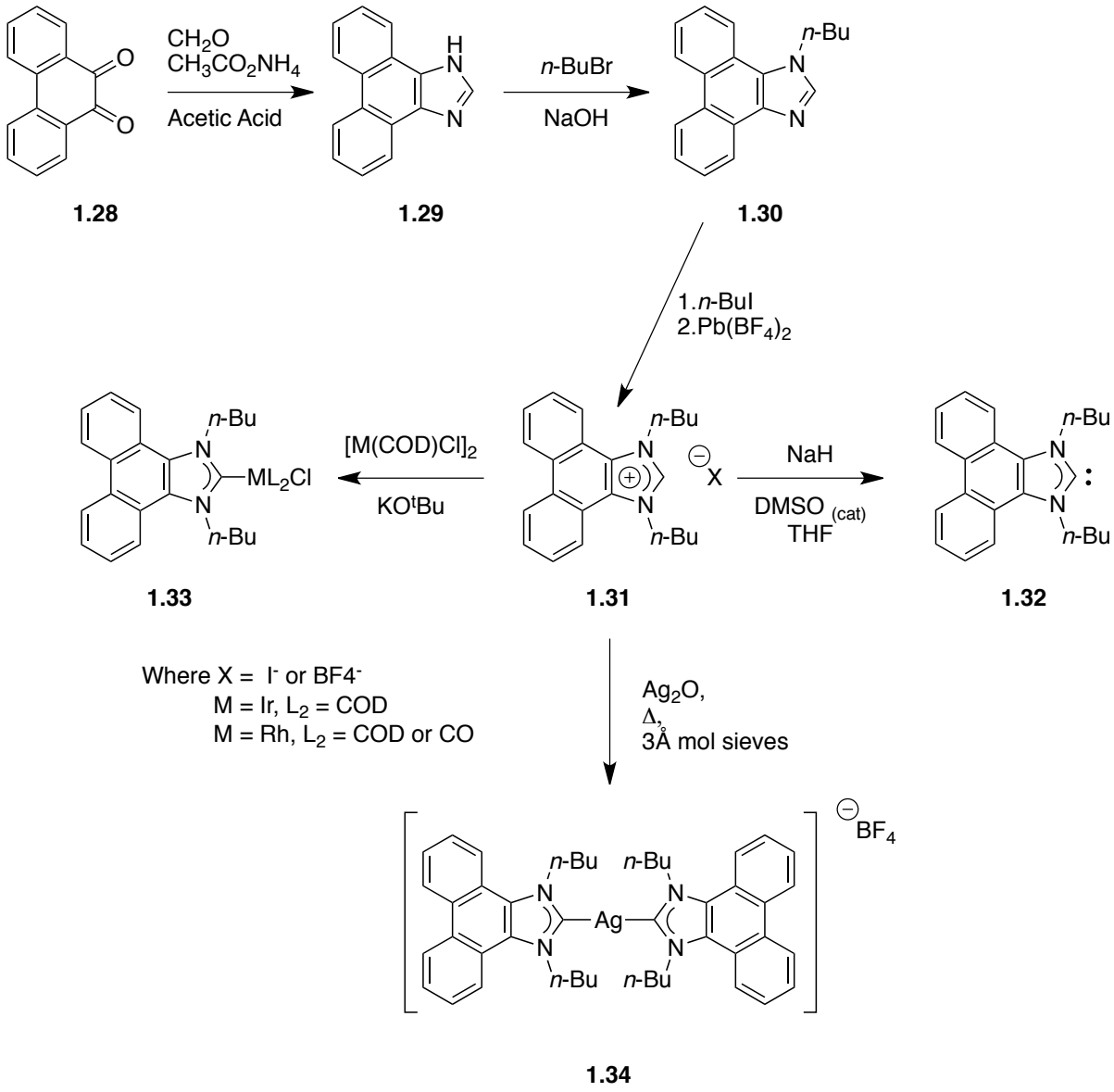


Figure 1.16: Synthesis of a phenanthrene imidazole based NHC, **1.28** and its metal complexes, **1.33** and **1.34**

The backbone extended NHC salt **1.31** was prepared from starting material **1.28**. Imine condensation and ring closing of **1.28** was completed in one step forming **1.29**. The *n*-Butyl groups were then substituted onto the pyrrole and pyridine like nitrogen atoms giving **1.30** and **1.31** in two steps. The free NHC, **1.32**, was isolated by deprotonation with sodium hydride. A variety of complexes were prepared with silver, iridium and rhodium salts, **1.33** and **1.34**. The structural characteristics were subsequently studied using single crystal X-ray crystallography. Luminescent studies of the NHC salt **1.31** and its associated iridium and rhodium COD complexes, **1.33**, showed fluorescent emission in the 330-430 nm range at 256 nm excitation.[20] Heinicke *et al*. also synthesised a phenanthrene imidazole NHC with ortho- and para-toluene substituents at the N1 and N3 positions in 2009.[21] These NHC ligands were complexed with various silver, palladium and rhodium salts, and their

structural characteristics have been studied via single crystal X-ray crystallography with similar binding to Tapu *et al*. reported complexes

Abnormal NHC's

The tuneability of imidazole NHC molecules can be further extended, as they are not limited to form through the C2 carbon, but can also at the C4 or C5 carbon as shown in figure 1.17(a) and figure 1.17(b), repectively. This occurs due to proton migration from the C4 or C5 position to the C2 carbon. This type of carbne is commonly referred to as an "abnormal" NHC. [21-23]

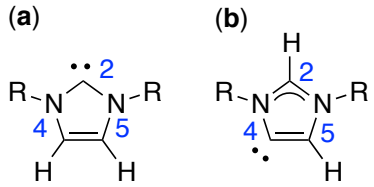


Figure 1.17: (**a**) Generic imidazolium NHC's with the standard carbene, (**b**) and abnormal cabene, highlighting the different sites the carbene can exist at.

This unique binding was discovered via the typical synthesis of a metal-NHC complex and can be achieved a number of different ways (these various routes to metal-NHC complex formation shall be discussed later).[22] There is not a significant amount of NHC complexes that show abnormal binding. However, there is a growing interest in this sub field of NHC's. This is due to the increasing use of *in situ* carbene generation in catalytic systems that are not fully characterised and abnormal carbenes may be a contributing factor to these systems.[22] Abnormal NHC's can exist due to the acidity of the protons at the C4 and C5 position of imidazole-2-ylidene, as shown in figure 1.17(b). The replacement of the protons with either halogen or deuterium atoms can be achieved with the chlorination of 1,3 dimesitylimidazole-2-ylidene using carbon tetrachloride to form **1.35**, as shown in figure 1.18.[22] The chlorinated product **1.35** is more stable than its precursor and does not react with the chloroform that is produced in the reaction. The NHC **1.35** is stable in the solid state and can be exposed to an oxygen atmosphere for two days, or overnight in a benzene solution.

Figure 1.18: Chlorination of 1,3 dimesitylimidazole-2-ylidene to form **1.35**.

Abnormally bound NHC complexes can be synthesized with a variety of metals Fe, Os,[23] Co, Rh, Ir, Ni, Pd, Cu, Au and Ag.[22] Iridium is the most commonly studied abnormally bound NHC complex

species due to the high reactivity of Ir in homogeneous catalytic transformations with many examples of C-C and C-H activation of alkanes.[22] The formation of the abnormal NHC complex, **1.36**, is in competition with the classical NHC complex **1.37** at the C2 position and can be dictated by the R groups as depicted in figure 1.19.

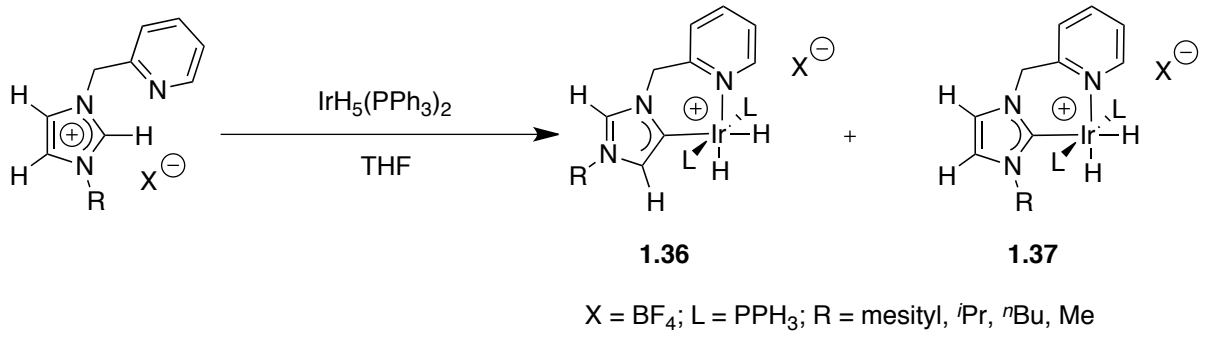


Figure 1.19: The abnormal, **1.36**, or classically, **1.37**, bound NHC-Ir complex can be obtained separately or in a mixture.

If the R groups are mesityl, ^{i}Pr or ^{n}Bu the formation of the C4 abnormally bound NHC complex is observed in almost quantitative yields, without the necessity for schlenk techniques. However, when the methyl adduct is used, both of the isomers are obtained in a ratio of ca. 1:1 abnormal:normal. This ratio was determined by the integrals of the ^{1}H-NMR spectra, as **1.36** and **1.37** from one another. This shows that steric influences are an important factor in designing NHC ligands. [22]

Synthesis of NHC Complexes

NHC complexes are not the first example of carbenes employed as ligands. Initially organometallic carbene complexes were investigated. In 1964 Fischer *et al*. unknowingly reported the synthesis of the first metal carbene complex **1.38** to be characterised, as shown in figure 1.20.[2]

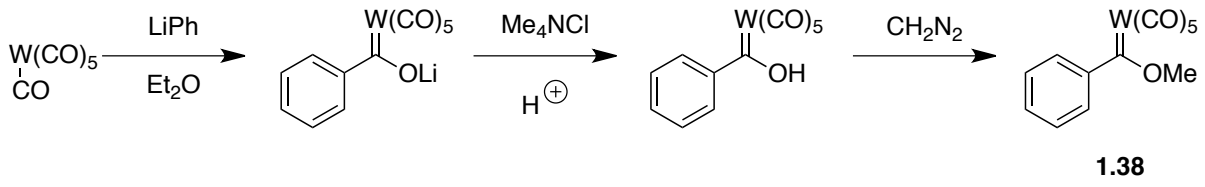


Figure 1.20: The first organometallic carbene complex, **1.38**.

This lead to more complexes with different metals such as Cr(0), Fe(0) and Mn(0) species with different alkyl and alkoxy groups on the carbene.[24] These carbenes became known as Fischer carbenes, and like NHC's, exist in a singlet spin state due to the stabilisation of the α-heteroatom to

the carbene carbon. In 1968 Öfele[25, 26] and Wanzlick *et al*.[27] on separate occasions in the same year synthesised the first NHC-complexes as shown in figure 1.21(a) and figure 1.21(b), respectively.

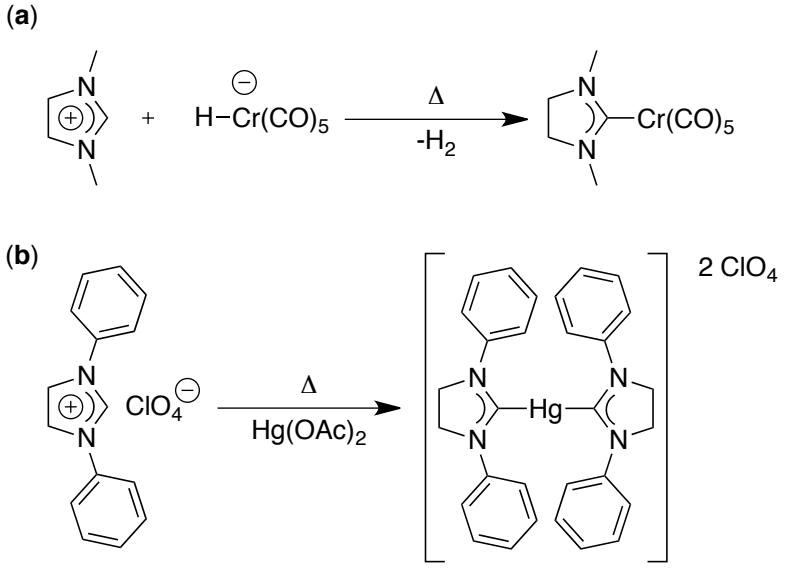


Figure 1.21: (a), Öfele's NHC complex, (b) Wanzlick's NHC complex, the first NHC complexes to be synthesised.

Both of the reactions involved a saturated imidazolium NHC salt where Öfele. prepared the chromium complex (figure 1.21(**a**)) with the loss of hydrogen gas and Wanzlick *et al*. synthesised a mercury complex (figure 1.21(**b**)) with a perchlorate counter anion. In 1968 Öfele also reported the synthesis of the first carbene complex without any α-heteroatoms, thus giving a non-stabilised carbene complex **1.39**, as shown in figure 1.22.[28]

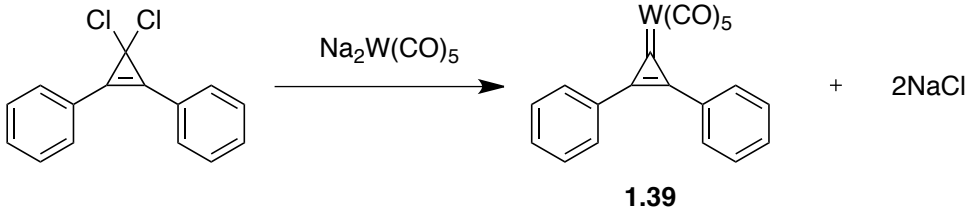
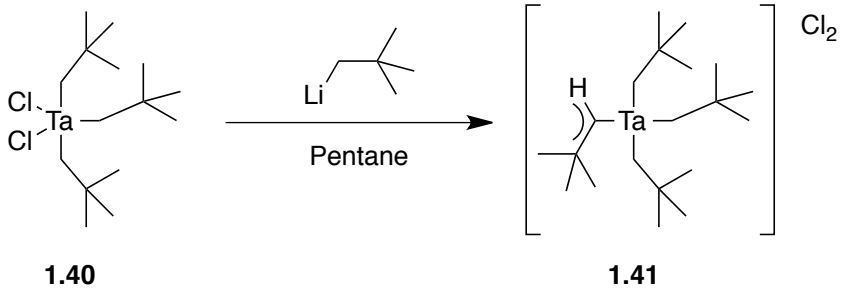


Figure 1.22: The first non-stabilised carbene complex, **1.39**.

In 1974 Schrock reported the first synthesis of a high oxidation state metal-alkylidene complex **1.41**, as shown in figure 1.23. This complex **1.41** was obtained via an α-hydrogen abstraction from the precursor complex **1.40**.[29]



1.40 **1.41**

Figure 1.23: Schrock carbene complex with a d^0 metal

The Schrock carbene ligand in complex **1.41** was a triplet spin state carbene complex. This is due to the lack of stabilisation by no electron rich α-substituents to the carbene carbon.

The Fischer or stabilized singlet carbenes have strong metal-carbon bonds because of the bent geometry of the carbenes due to the electron donating α-substituents, for example amino or alkoxy groups.[26, 30, 31] The bent geometry results in a small bond angle at the central carbene carbon, thus giving the required geometry to bind strongly and easily to metals. Triplet carbenes have a wider valance angle, therefore giving a much weaker metal-carbon bond.[30, 31] The electronic factors of the carbene also play a major role in the strength of the metal-carbon bond. The metal-carbon bond of a singlet Fischer carbene or similarily a NHC ligand arises from the carbene-metal σ-donation and simultaneously the metal-carbon π-back donation.[32] The π-back donation is negligible due to the π-donation from the α-substituents on the Fischer or NHC ligand. The strong carbon-metal bond also has partial double bond characteristics polarising the carbon atom, making the carbon electrophilic and sucseptable to nucleophilic attack. Schrock complexes have the opposite properties due to the triplet nature of the carbene. A covalent bond is made with the s orbital's of the carbene and metal rather than an ionic like bond of the singlet carbene-metal complexes. The π-bonding is shared equally in the Schrock carbene between the metal and carbon.[32, 33] This makes the carbene-metal bond nucleophilic and the carbene centre is susceptible to react with electrophiles.[26]

It was Wanzlick *et al*. that established as early as 1968 metal complexes with NHC ligands.[27] The majority of metal-NHC complexes are formed with imidazolium based NHC ligands. This could be associated with the ease of synthesis, availability and complexation compared to that of six or greater membered NHC ligands. A wide synthetic scope is available to prepare metal-NHC complexes. The simplest method for obtaining a metal-NHC complex is reaction of the desired metal and the free NHC. Deprotonation of the NHC ligand is dependant on the relative pKa of the C-H proton at the C2 carbon, allowing a range of different bases to be employed to give the free NHC ligand. The use of strong bases however has limitations, as it may result in undesirable deprotonation at sites other than the C2 carbon whereas a weak base may be nucleophilic enough to react with the electrophilic C2 carbon of an NHC salt.

The majority of complexes are prepared by the reaction with Ag_2O followed by transmetallation to a different transition metal or lanthanide. There are three typical routes (**A**,**B** and **C**) to obtain a Ag-NHC complex as depicted in figure 1.24. The figure uses a general imidazloium based NHC ligand, but can be interchanged with a variety of different NHC ligands.

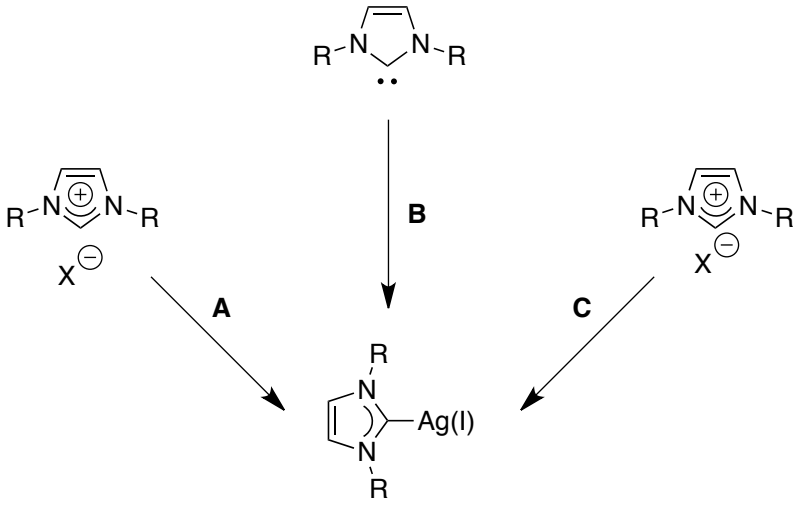


Figure 1.24: Various routes to establish an NHC-Ag(I) complex.

Route **A** describes the use of a silver with basic anions to act as a mild base, i.e. Ag_2O, Ag_2CO_3 $Ag(OAc)/Na_2CO_3$ including other mild bases depending on the NHC ligand. The second route **B** is reacting the free NHC ligand with a variety of silver salts (AgOTf, AgCl, AgBr, $AgBF_4$, $AgPF_6$ etc), where the NHC salt is firstly deprotonated with NaH, NaOAc, KO^{t}Bu $LiN(SiMe_3)_2$ etc. Finally route **C** uses a phase transfer catalyst (PTC) under basic conditions to react with the NHC salt in the presence of a silver salt. This can help solubility issues with the NHC salt in organic solvents. All of these routes result in a Ag-NHC complex, a relatively labile metal complex[34] that can be exchanged with another metal. The Ag-NHC complexes are typically air stable and do not require purified solvents or the use of external base. The C2 carbon is normally deprotonated whilst the other acidic protons such as the C4 and C5 protons of imidazole based NHCs do not react.[4]

Oxidative addition to the C2-X bond with d^8 or d^{10} metals can be achieved. Complexes with Pd, Pt, Ni, Ir and Rh have been isolated via this methodology.[35] This offers another synthetic route to obtain a metal complex if the silver methodology is unsuccessful. This method has a high degree of flexibility in the synthesis with a large variety of metal salts, the temperature of the reaction is run and the time can be modified. A general scheme shows the oxidative addition of Pt^0 into the 1,3-dimethylimidazolium salt, as shown in figure 1.25.

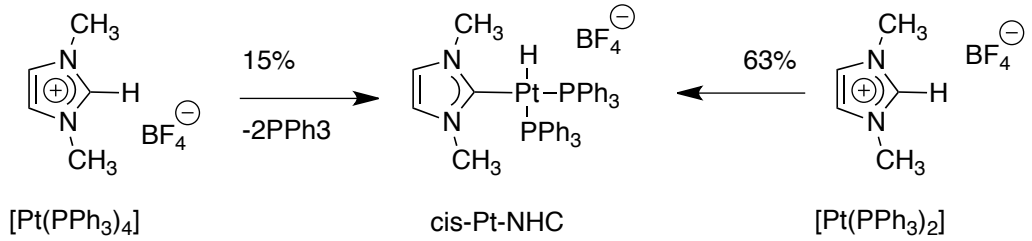


Figure 1.25: Oxidative addition of an imidazole based NHC salt by Pt^0

Another method of NHC ligand complexation is effectively creating a leaving group at the C2 position. Crabtree *et al*. reported that N,N'-dimethylimidazolium-2-carboxylate, **1.42**, can act as a carbene transfer reagent for various metals such as Ru, Rh, Ir and Pd resulting in **1.43** as shown in figure 1.26(a) with CO_2 being generated in the reaction process.[36, 37] These reactions proceed in good yields and the exclusion of air and moisture is not required, providing the metal precursor is not sensitive to these conditions. However, this method of complexation is limited by the synthesis of the NHC carboxylate salt. This carboxylate moiety can be interchanged with an isobutylester group, **1.44** giving a similar complex **1.45** as shown in figure 1.26(b). This method of decarboxylation usually proceeds in high yields given the mild conditions.

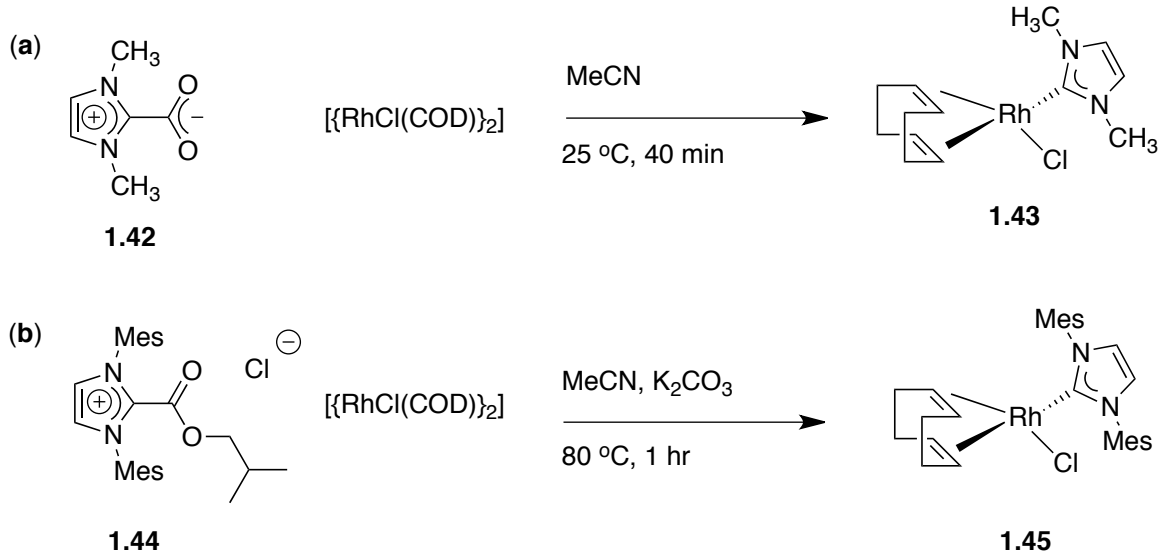


Figure 1.26: (a), Imidazolium carboxylate salt, **1.42** and it Rh complex **1.43**, (b), Isobutylester imidazolium salt, **1.44** and its Rh complex **1.45**.

A rare technique that has been used in the synthesis of metal-NHC complexes is metal vapor synthesis by reacting a M^0 (atomic) with the free NHC ligand. This technique requires a metal pellet to be evaporated with an electron beam and the sublimed free NHC ligand to be co-condensed over 90 mins.[38] Cloke *et al*. developed this technique and used an NHC ligand with a high vapour pressure and the NHC salt was deprontated with potassium tert-butoxide in a similar manner to Arduengo *et al*. in 1994.[6] The general reaction conditions are shown in figure 1.27.

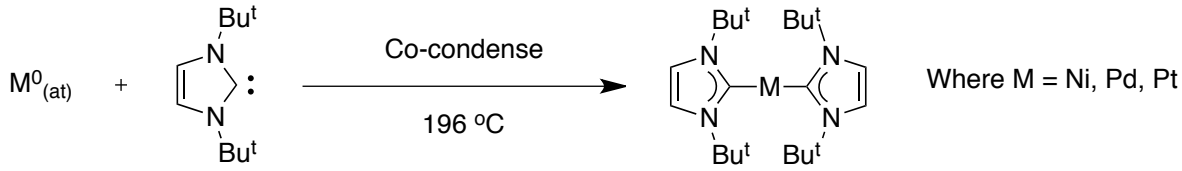
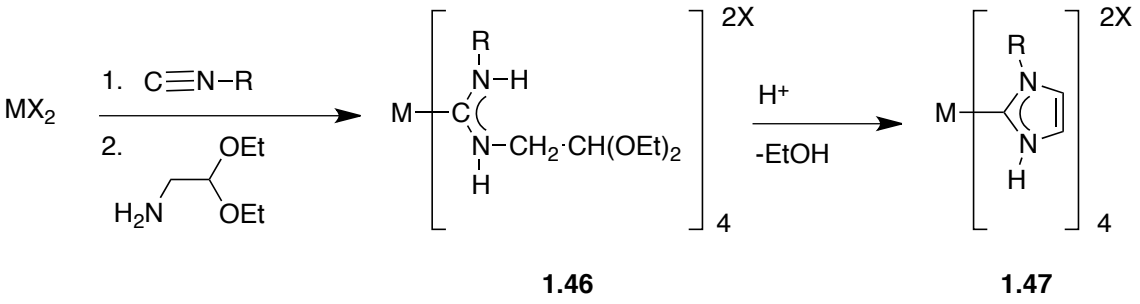


Figure 1.27: The metal vapour synthesis technique developed by Cloke *et al*.

Finally, utilising the metal as a template can give metal bound NHC complexes. The cyclisation to give the NHC ligand is the last step of synthesis. This is common for the synthesis of heteroatom carbenes including cyclic and acyclic. One of the synthetic routes is shown below in figure 1.28.



1.46 **1.47**

Figure 1.28: Template synthesis to achieve heteroatom acyclic complex, **1.46** and cyclic carbene complexe, **1.47**.

The tetraiso-cyanide group is firstly coordinated to the metal making the carbon susceptible to nucleophilic attack by the amino acetylaldhyde. The acyclic carbene complex, **1.46** can then undergo an acid catalyzed cyclisation reaction giving the N-heterocyclic carbene complex, **1.47**.[39] In order to obtain a heterocyclic carbene complex the cyanide group can be interchanged for a carbonyl functionality, thus giving an oxygen and nitrogen contain heterocycle carbene complex.[40] Imidazole and oxazole fuzed systems can be obtained by using phenyl based cyano and carbonyl groups respectively.

Applications of NHC complexes

The most prolific application of NHC complexes is in catalysis, where they are often preferred over tertiary phosphine ligands in some cases. This is largely attributed to the stronger σ-donor ability of the NHC ligand and the small π-back bonding nature of NHC ligand.[41] This allows for a strong metal to NHC ligand bond that can prevent decomposition of the complex during the catalysis process. The high variability of NHC ligands results in easy tunability so the catalytically active site at the metal centre is not hindered. Catalytic properties of NHC complexes have been studied with a variety of metals, including Pd, Ru, Os, Co, Rh, Ir, Au, Ni, Cu.[42] However, ruthenium and palladium complexes shall only be discussed due to their large influence in this area.

Pd based NHC complexes have proven to be extremely good catalysts for cross coupling reactions, playing an important role in synthetic organic chemistry. Herrmann *et al*. reported the use of 1,3-dimethylimidazolium iodide as the NHC ligand reacting with $Pd(OAc)_2$ to give the precatalyst, **1.48**. The Heck reaction can be performed after the reductive elimination of **1.48**, giving the catalytically active Pd(0) species **1.49**.[43] The catalysis proved to be successful and NHC ligands are the only ligand to challenge the use of tertiary phosphine ligands. A general scheme of what Herrmann *et al*. conducted is shown below in figure 1.26.

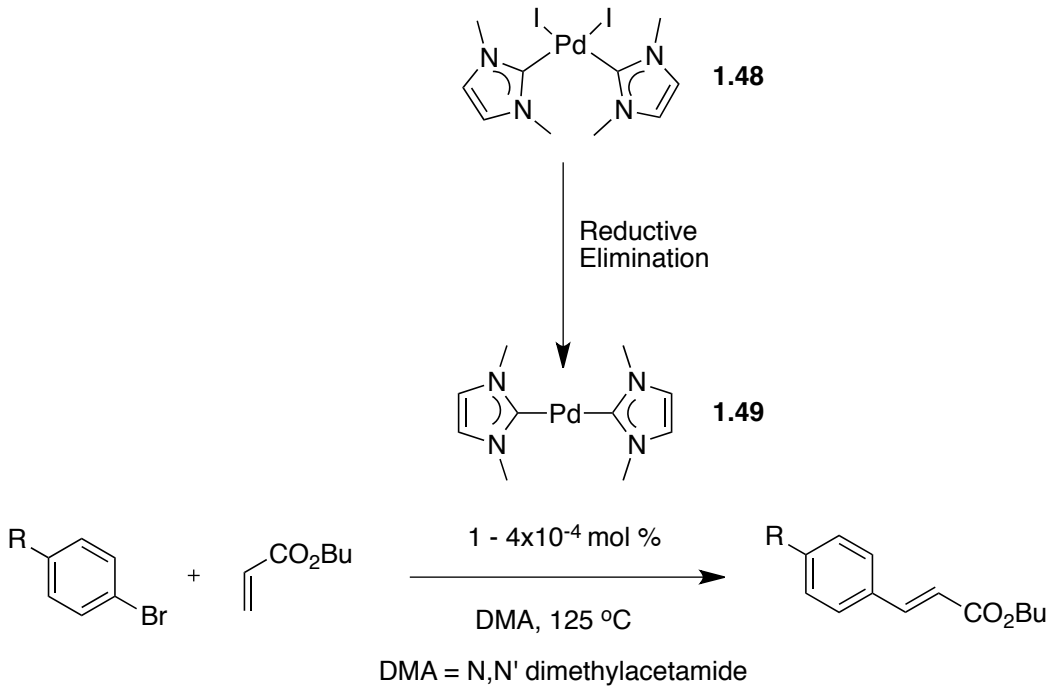
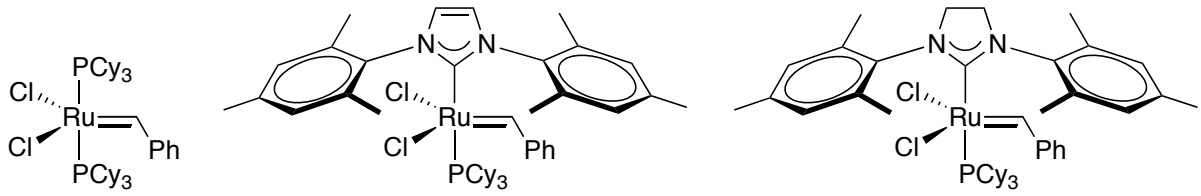


Figure 1.26: The heck reaction performed with a NHC-Pd complex by Herrmann in 1995

The precatalyst, **1.48** exhibits high stability in the solid and solution states, resulting in easy handling and storage. The use of NHC-Pd complexes also eliminates the 'black box' character that is often associated with cross-coupling reactions and catalysis, due to the well defined binding of the NHC ligand to the Pd metal.[44] The use of well-defined catalysts also means that the ligand to metal ratio can be controlled (ideally 1:1).[44, 45] This is important due to degradation of the phosphine catalyts therefore requiring an excess of the ligand often 100 times more than the metal in order to control the equilibrium in the activation and propogation steps of the homogeneous catalysis.

Prof. Robert H. Grubbs made a significant advancement in olefin metathesis through the use of ruthenium catalysis.[46-49] The catalysts became known as 'Grubbs Catalyst' and the first generation **1.50**, is shown in figure 1.27. This utilises two phosphine ligands and acts as a pre-catalyst with an array of different substituents. As mentioned earlier, the degradation of P-C bonds at elevated temperatures gives justification into investigations of similar yet more stable ligands in order to obtain a better catalyst. This is where Grubbs used imidazole based NHC ligands to form the 2nd

generation catalysts **1.51**. The NHC ligand is able to stabilize the catalytic intermediate and the R groups can be varied to optimise the efficiency of the reaction. The stabilization of the catalyst **1.51** is achieved through electronic and steric means and prevents mono-, as well as bimolecular, decomposition pathways.[50] The Grubb's group have prepared numerous NHC-ruthenium complexes where the NHC ligands have different ring sizes and unsaturated or saturated heterocycles. Showing that the saturated NHC ligand gave an even high activity to the metal center. [51, 52]

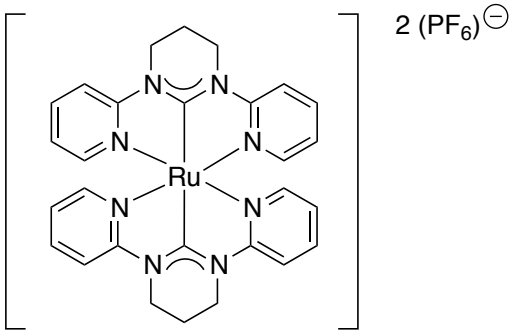


1.50 **1.51** **1.52**

Figure 1.27: Grubb's various ruthenium olefin metathesis catalysts.

However, one limitation that was observed was the formation of a hydridic by-product. This by-product was formed with a catalyst similar to **1.52**, but with the N-R substituents being 2,6-diisopropylphenyl rather than the mesitylene groups. The by-product was $(PCy_3)_2Ru(H)_2Cl_2$ and with the use of IR analysis the characteristic peak of the Ru-H was apparent and ^{1}H-NMR proved the existence of the hydride ligands. These 2nd generation catalysts proved to be far superior to the first, but no single catalyst was better than the others at any one particular reaction as different NHC ligands turned out to be optimal for different applications.[49]

In addition to catalysis NHC ligands can be used to promote the luminescent properties of a complex. Once again this is attributed to the strong σ-donor abilities of the carbene resulting in a strong metal-carbon bond.[53-55] This causes an increase in the energy gap between the metal-ligand charge transfer (MLCT) state and the non emissive metal centered (^{3}MC) triplet state,[56] resulting in a longer excited state life-time of the complex. $Ru(tpy)_2$ has a life time of 0.25ns at room temperature,[57, 58] hindering its use for photosensitizer applications. In 2011 Schaper *et al*.[59] synthesised the ruthenium complex **1.53**, as shown in figure 1.28. This complex showed an emission in the red at 753 nm in the solid state at room temperature.

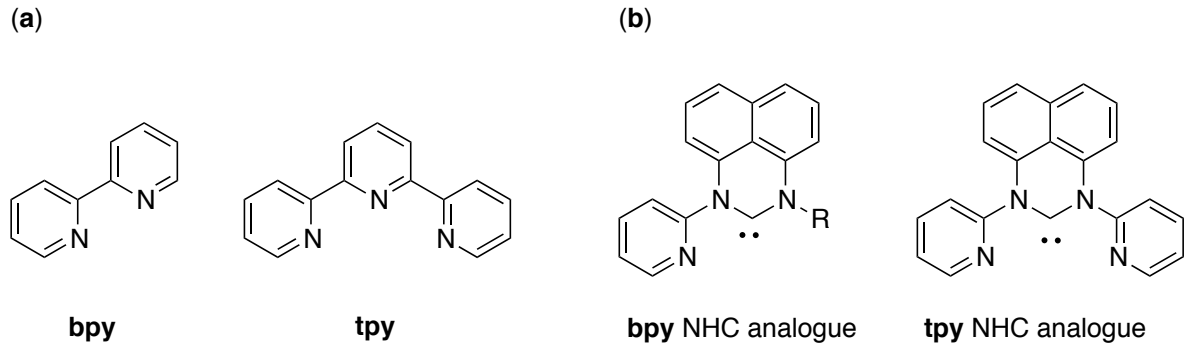


1.53

Figure 1.28: Bis-pyridinium NHC ruthenium complex, **1.53** with two hexafluorophosphate anions.

General Aim of this Research

This masters project has conducted reseach with six-membered (Chapter Two) and five-membered (Chapter Three) NHC ligands. The 6-membered ring was chosen as the goal was to synthesize NHC analogues of 2,2′-bipyridine, **bpy** and 2,2′:6′2″-terpyridine, **tpy** as shown in figure 1.29(a) due to the structural similarities. Upon synthesis the NHC ligand analogues (figure 1.29(b)) would be complexed to ruthenium and other metal salts. The ruthenium complexes $[Ru(bpy)_3]^{2+}$ and $[Ru(tpy)_2]^{2+}$ have been widely studied for their unique electrochemical and photochemical properties, hence the investigation with NHC mimics of these **bpy** and **tpy** ligands. Due to the difficulties that are known to exist with the deprotonation of six-membered NHC salts a variety of different methods have been explored in order to justify the use of strong sterically hindering bases.



bpy **tpy** **bpy** NHC analogue **tpy** NHC analogue

Figure 1.29: (a) Heterocyclic ligands **bpy** and **tpy**, (b), Perimidine-NHC analogues of **bpy** and **tpy**

The imidazole NHC ligand is more widely studied, but little research has been conducted that focus on the extension of the backbone by fusing various aromatic groups to the imidazole NHC head group. The synthetic targets of this chapter follow the progression of the larger fused systems onto an imidiazole head group as shown in figure 1.30. The properties of the NHC salts synthesised have been explored and characterised. The pyrene NHC salt also offers a new NHC core unit that has not

been synthesised before. Therefore with the backbone of the imidazole based NHC ligands being extended, studies have been carried out to determine if larger π-delocalized systems are employed, does this have a favorable affect on the luminescent properties of the associated complexes as this should produce a greater observed luminescent excitation.[60-62] Figure 1.30 shows a general ligand design and the increase in aromaticity in the backbone of the ligand core.

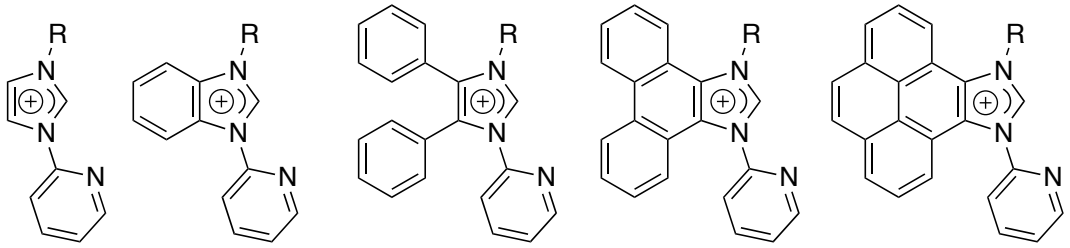


Figure 1.30: Imidazole based NHC ligands and their extension of an aromatic core unit.

Chapter 2

Perimidine based NHC ligands

2. Perimidine based NHC ligands

Introduction

The most extensive research concerning NHC ligands and their various metal complexes has focused on imidazole based ring systems, as outlined in chapter one. However, as mentioned in chapter one, NHC's are not restricted to five-membered rings. NHC's can be extended into six-membered rings such as the NHC pyrimidine salt (figure 2.1(a)) and extension of the carbene heterocycle with various aromatic cores can lead to the NHC perimidine salt, as shown in figure 2.1(b). This chapter describes the synthesis of a variety of perimidine-based molecules that have the potential to act as NHC ligands and preliminary investigations to determine a methodology for the synthesis of their transition metal based complexes.

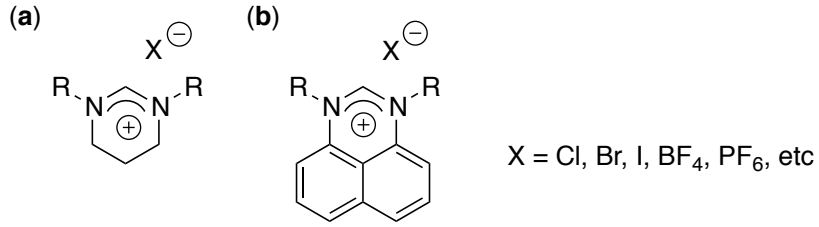


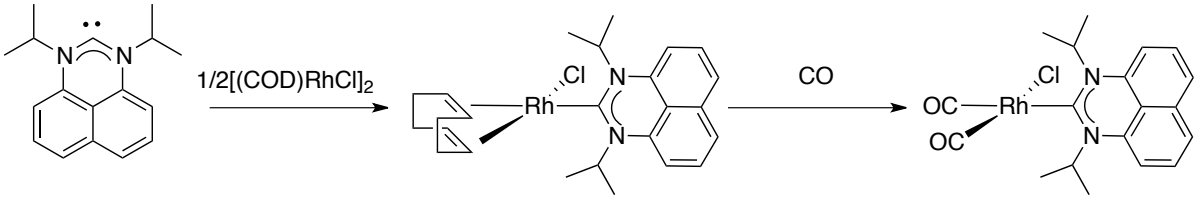
Figure 2.1: (a), NHC pyrimidinium salt, (b), perimidinium NHC salt, both six-membered NHC ligands with various R groups and anions

The chemistry of perimidine however was not initially studied for its ability to act as a NHC ligand. Denny *et al*. described the use of the perimidine moiety to synthesize a range of molecules that were investigated for their DNA intercalation properties as potential antitumor agents.[63] Perimidine is one of the few unique azines where the lone pair of the pyrrole-like nitrogen participates in the π system of the molecule. This gives the perimidine unusual electronic properties due to the delocalisation of electrons between the heterocyclic ring and fused naphthalene. This gives perimidine both π-excessive and π-deficient characteristics.[63]

The synthesis of perimidine NHC salts is possible through a variety of different routes. These are typically the same as imidazole based NHC salts, with a general synthetic approach described in detail in chapter one.

In 2003 Richeson *et al*. published a communication where they described the synthesis of the first perimidine NHC metal complex, as shown in scheme 2.1.[64] The free NHC, **2.01**, has isopropyl substituents at the N1 and N3 positions. The complexation of **2.01** was achieved by its reaction with $[Rh(COD)Cl]_2$ (COD = 1,4 cycloocatadiene) at room temperature where a yellow NHC-metal

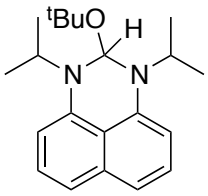
complex was obtained. Evidence for formation of **2.02** came from single crystal X-ray analysis and subsequent ^{1}H-NMR and ^{13}C-NMR studies. The Rh-carbene carbon had shifted significantly upfield to 213.3 ppm compared to the free carbene at 241.7 ppm.



2.01 **2.02** **2.03**

Scheme 2.1: The first perimidine NHC complex

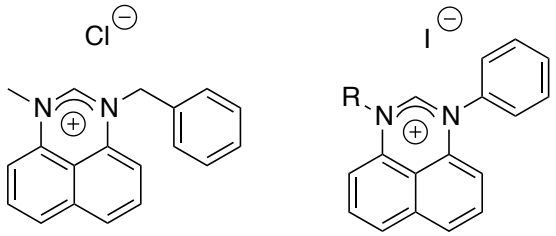
The complex **2.03** was obtained by reaction of complex **2.02** with CO giving the exchange between the COD and CO auxiliary ligands. The complex **2.03** can also be obtained via the reaction of the free carbene **2.01** with ½[Rh(CO)$_2$Cl]$_2$. The formation of **2.01** was achieved by use of a strong sterically hindered base, LiN(SiMe$_3$)$_2$. Attempted deprotonation of the precursor NHC salt did not work with NaO^{t}Bu and only the nucleophilic additon of the alkoxide anion to the electrophilic C2 carbon **2.04** was observed, as shown in figure 2.2. However, successful deprotonation with NaO^{t}Bu has been achieved with other perimidine NHC salts. The common feature was the sterically demanding different R groups that resulted in the free NHC that may help hinder the nucleophilic alkoxide to attack the C2 atom.



2.04

Figure 2.2: The α-diamino ether by-product, **2.04**, from the nucleophilic addition of the alkoxide anion

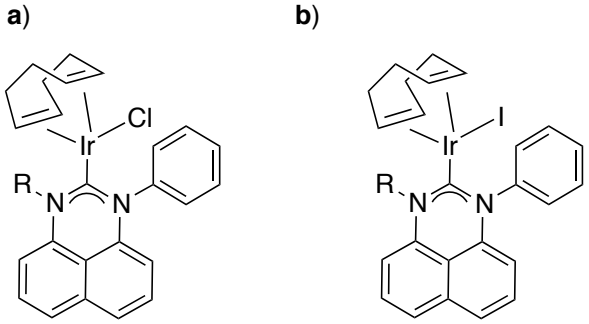
Mashima *et al*. investigated iridium-based complexes with perimidine NHC ligands **2.05** - **2.07** in 2010, as shown in figure 2.3. The NHC ligands were used to initially bind a complex then cyclometalate at the C2 carbon of the phenyl substituents. It was anticipated that the NHC ligand would affect the C-H bond activation of these iridium complexes and the phosphorescent properties of their cyclometallated NHC-iridium complexes. [65]



2.05 **2.06** : R = Me
2.07 : R = iPr

Figure 2.3: Permidine NHC salts with aryl R groups at the N1 position

The ligands **2.06** and **2.07** were complexed with $[IrCl(COD)]_2$ by carbene transfer with Ag_2O. The reaction was performed at reflux in toluene for 24 hours using standard Schlenk techniques giving the complexes **2.08** and **2.09,** as shown in figure 2.4(a). The similar NHC iridium complexes **2.10** and **2.11** (figure 2.4(b)) were synthesised from a different synthetic route. The deprotonation was conducted with $LiN(SiMe_3)_2$ in THF at room temperature again with standard Schlenk techniques. The different halogens on the complexes were attributed to the different solubility of the LiI and AgI that formed during the reaction.



2.08 : R = Me
2.09 : R = iPr

2.10 : R = Me
2.11 : R = iPr

Figure 2.4: (a), transmetallation with Ag_2O to give the iridium complexes, **2.08** and **2.09**, (b), deprotonation of the NHC salts, **2.06** and **2.07**, with $LiN(SiMe_3)_2$ to give NHC-iridium complexes, **2.10** and **2.11**. Two different synthetic routes to obtain similar NHC-iridium complexes.

The synthesis of an iridium complex with the NHC ligand, **2.05,** was also achieved giving a similar complex structure compared to **2.08**. The phenyl substituent of **2.08** was also able to be cyclometallated to the iridium metal center, resulting with mono, and bis, NHC iridium complexes. The C-H activation of the phenyl substituent and other derivatives is dependent on the ring size of the hetero-aromatics.[66] They also showed that the transfer of a silver NHC complex with a perimidine based NHC ligand could aid iridium complex formation.

This chapter will describe 1*H*-perimidine NHC ligands that share a common feature by having a 2-pyridyl group at the N1 position. This motif at N1 position has not been synthesized before. Therefore any substituent at N3 position will give a new NHC salt and giving the synthesis of bidentate and tridentate NHC ligands shown in figure 2.5. There has been little attention placed on perimidine based NHC complexes and there has been no reported ruthenium or silver complex with a perimidine NHC ligand.

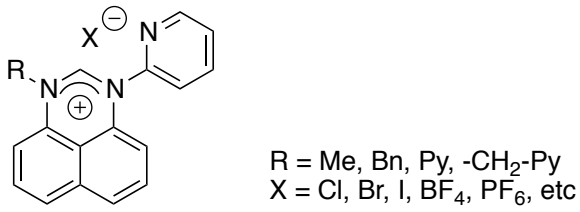
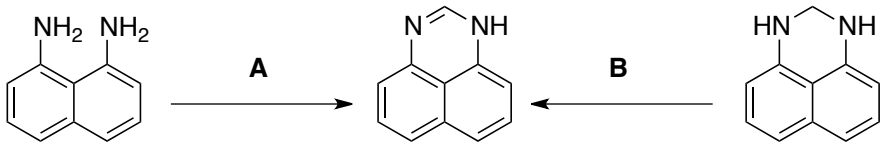


Figure 2.5: The general perimidine NHC salt design to be utilised in this investigation.

Ligand Synthesis.

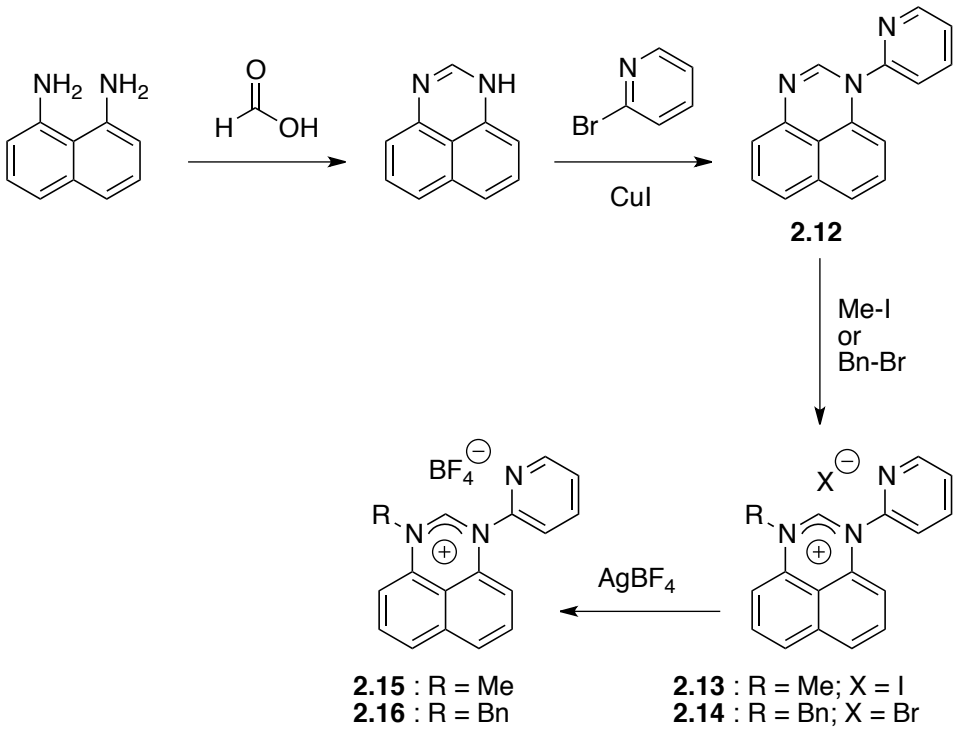
The synthetic procedure to achieve 1*H*-perimidine utilises 1,8-diaminonaphthalene and a subsequent ring annulation reaction. There are two potential different synthetic routes to achieve this shown below in scheme 2.2.



Scheme 2.2: Three routes to obtain 1*H*-perimidine. (A), formic acid, reflux, Ar atmosphere; (B), pyrosulfate.

The synthetic route **A** typically uses formic acid as the C1 electrophile to complete the annulation reaction with almost quantitative yields. However, $CH(OMe)_3$ and its ethyl derivative have also been used with success giving excellent yields (~80%).[67] The solvent used in this route has also varied with DMF, acetone and ethanol all being used at reflux under an inert atmosphere. Route **B** involves the mild dehydrogenating agent pyrosulfate to obtain 1*H*-perimidine in an excellent yield (95%).[68] However, this route requires the synthesis of the precursor, 2,3-dihydro-1*H*-perimidine. The synthetic route chosen was **A** due to the availability of the starting material 1,8-diaminonaphthalene, and gave 1H-perimidine in one step.

Therefore the reaction was performed with formic acid in an inert argon atmosphere at reflux for 18 hours to give 1*H*-perimidine in a good yield (85%) following a modified literature procedure described by Denny *et al*.[63], as shown in scheme 2.3. This was then recrystallised from ethanol to give 1*H*-perimidine as pale orange crystals. The 1*H*-perimidine was further purified by column chromatography on silica with EtOAc as the eluent in order to obtain a pure product. ^{1}H-NMR and mass spectrometry analysis confirmed the synthesis of 1*H*-perimidine. The m.p. was 212-215 °C which compared to 225-226 °C.[68] The characteristic singlet proton peak from the ^{1}H-NMR at H2 was 7.41 ppm.



Scheme 2.3: Synthetic route to obtain bpy NHC salts.

The synthesis of **2.12** was completed via an Ullmann type C-N coupling reaction. This step was initially performed with Cu_2O as the catalyst from a preparation described by Jha *et al*. in 2007.[69] However, the preparation was modified, as the solvent used was DMSO rather than DMF due to the potential decomposition of DMF at higher temperatures. The reaction was performed in an inert atmosphere of argon and stirred at 100 °C for 18hrs. The isolated yield of the product was quite low (27%). This hindered the amount of progress, as large quantities of 1*H*-perimidine were needed in order to continue with the reaction scheme. Therefore a different source of copper catalyst was utilised to obtain a better yielding reaction. Chen *et al*. showed the N-arylation of 1*H*-perimidine with bromobenzene and 2,6-dibromopyridine in 53% and 62% yields, respectively, with CuI as the catalyst rather than Cu_2O.[70] Therefore CuI was used and the temperature of the reaction was also increased from 100 °C to 150 °C. The percentage yield improved to 79%. Washing with Et_2O was a crude procedure to purify **2.12**. Column chromatography was performed on silica with EtOAc: MeOH, 90:10, respectively to give **2.12** as a pure product. Full characterisation of **2.12** was completed with the ^{1}H-NMR shown in figure 2.6, The characteristic H2 singlet proton was at 7.60 ppm and the C2 atom was measured at 146.89 ppm in DMSO-d_6. HRMS also supported the synthesis of **2.12** with [M+H$^+$]; found: 246.1026, calculated: 246.1026.

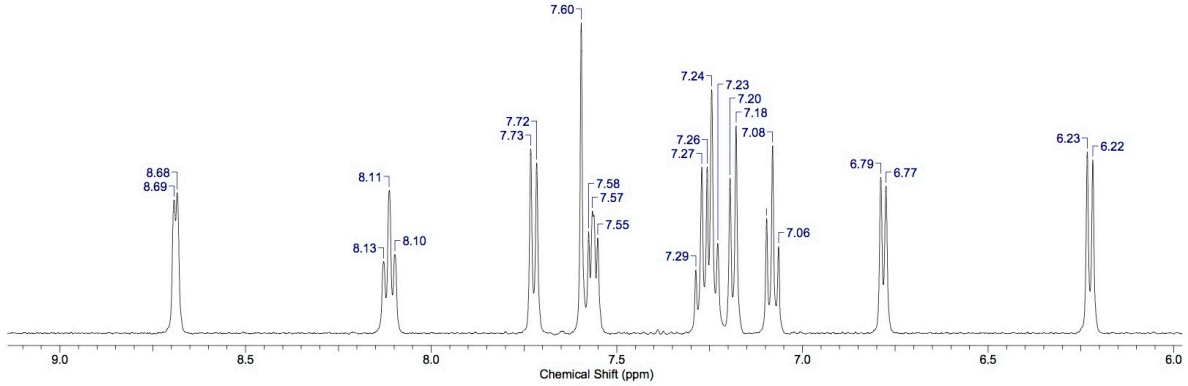


Figure 2.6: Enlarged aromatic region of the ^{1}H-NMR of compound **2.12**, in DMSO-d_6.

The formation of the perimidine NHC salts with methyl (**2.13**) and benzyl (**2.14**) derivatives at the N3 position were obtained initially in poor yields (35% and 42%, respectively) by performing the reaction at reflux with **2.12** in a solution of EtOAc with an excess (2.5 times) of the specific alkyl halide for 18 hours. The poor yields were attributed to the open atmosphere and the one pot synthesis nature of the reaction. Therefore, the method was improved by refluxing **2.12** in a solution of EtOAc with a volume sufficient to dissolve all of the starting material at reflux. To this hot solution a two and a half fold excess of the specific alkyl halide was added. The reaction was run under an inert argon atmosphere for 18 hours. The yields obtained under these new conditions improved drastically, giving 81% of **2.13** and 74% of **2.14**. EtOAc was chosen as the solvent because it was known that the subsequent NHC salt is a charged species and would precipitate out of solution. The precipitate that was isolated required no further purification, with ^{1}H-NMR and mass spectrometry confirming the synthesis of the two NHC salts, **2.13** and **2.14**. The ^{1}H-NMR of the NHC salt **2.13**, as the iodide salt is shown in figure 2.7.

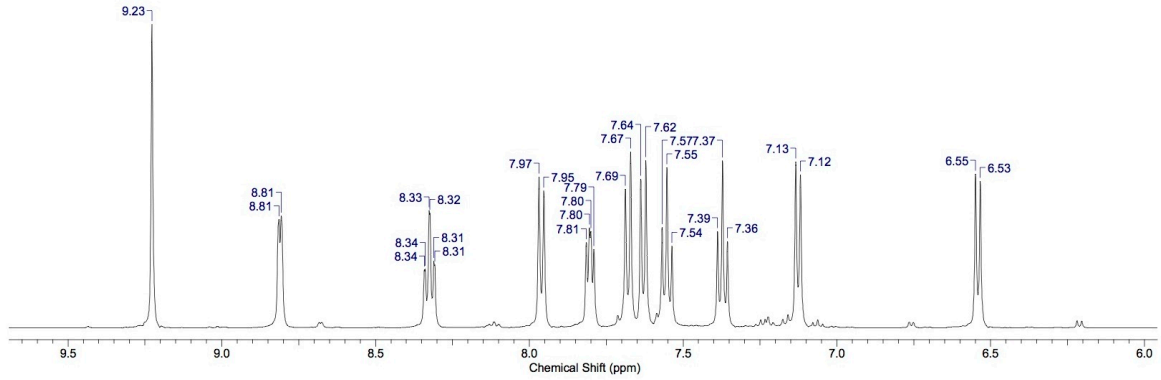


Figure 2.7: The enlarged aromatic region of the ^{1}H-NMR of the NHC salt, **2.13** in DMSO-d_6.

The H2 proton peak of the NHC salt, **2.13** was measured to be 9.23 ppm and the C2 carbon was measured at 153.20 ppm, with both the ^{1}H-NMR and ^{13}C-NMR carried out in DMSO-d_6. The proton

peak has shifted significantly downfield compared to, **2.12**, as **2.13** is now a charged species. This shift of approximately 2 ppm is apparent in both of the NHC salts, **2.13** and **2.14**. The ^{1}H-NMR of **2.14** is shown below in figure 2.8. The difference between the H2 proton of the NHC salts **2.13** and **2.14** is small but still apparent with a difference of 0.32 ppm as the H2 proton of **2.14** was measured to be 9.62 ppm and the ^{13}C-NMR showed the C2 carbon at 154.0 ppm.

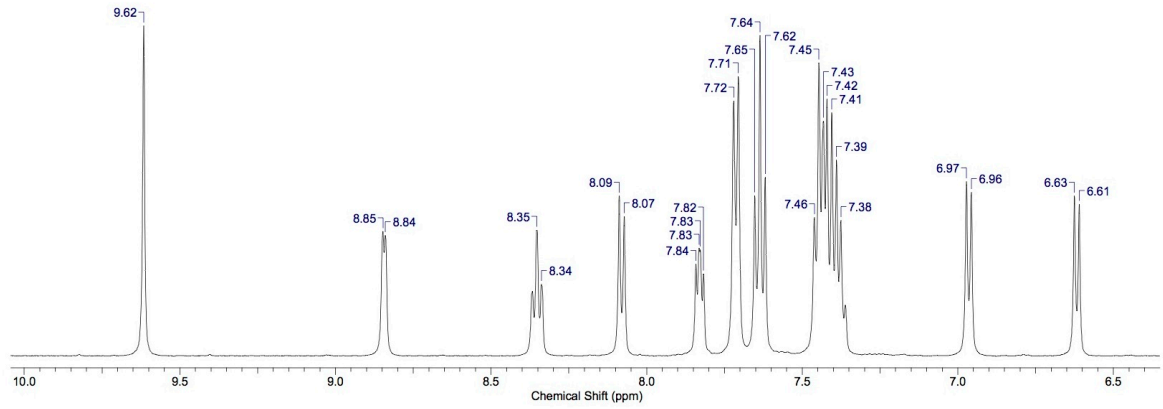
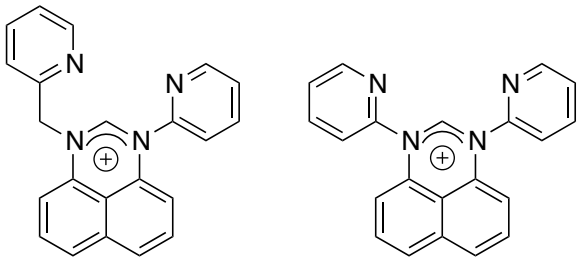


Figure 2.8: The aromatic region of the NHC salt, **2.14**.

The two NHC salts **2.13** and **2.14** underwent halide metathesis to give a tetrafluoroboarate anion. The reaction proceeded by reacting the specifc NHC salt in a MeOH solution with $AgBF_4$, in a 1:1 ratio at room temperature for 15 hours resulting in **2.15** and **2.16,** respectively. The reactions proceeded in quantitative yields and the halide was exchanged as it was suspected to be potentially interfering in the formation of a complex species.

The tridentate perimidine NHC salts, **2.17** and **2.18**, were of particular interest as they offered structural similarities to the N-hetrocycle, terpyridine, with the two NHC salts, **2.17** and **2.18** depicted in figure 2.9. The synthesis of the 2-picolyl derivative, **2.17** was attempted under the same conditions that gave the products **2.13** and **2.14**. The reaction did not proceed with any evidence of the salt formation via mass spectrometry analysis. Mass spectrometry analysis typically gives strong evidence that the desired NHC salt had been synthesised due to the charged nature of the species. The failed synthesis of the NHC salt **2.17** was attributed to the reactant, 2-picolyl hydrochloride as it exists as an acid salt. This may cause protonation of the N3 atom, thus hindering its ability to perform the S_N2 reaction to give the NHC salt, **2.17**. Therefore the reaction was carried out in toluene at reflux for 48 hours with an excess of Et_3N present to neutralize any acid present. This reaction showed promise via mass spectrometry. However, the product was unable to be isolated. The harsher reaction conditions may have resulted in side reactions, giving the potential dimerisation and polymerization of the 2-picolyl chloride hydrochloride. There is little to dictate the chemoselectivity of the reaction due to the presence of two pyridine nitrogen atoms in the starting material **2.12**.

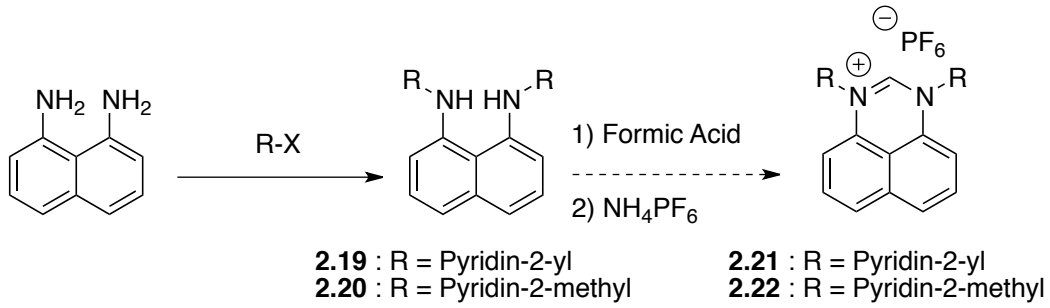


2.17 **2.18**

Figure 2.9: The tridentate perimidine NHC salts **2.17** and **2.18**.

The synthesis of the NHC salt, **2.18** was attempted under numerous different conditions. The first being the same synthetic method as described before, via EtOAc reflux with a further equivalent of 2-bromo pyridine and **2.12**. However, there was no evidence of the formation of the product according to ^{1}H-NMR and mass spectrometry analysis. Therefore the reaction was refluxed in a solution of toluene for 48 hours in order to force the reaction to completion. However, the elevated temperatures of refluxing toluene did not result in the desired NHC salt, **2.18**. This unsuccessful reaction was assigned to the difference in the substitution reactions. Whereas before S_N2 type reactions were being carried out, in order to form the NHC salts, **2.13** and **2.14**, the formation of **2.18** requires an S_NAr reaction. A one step reaction was conducted in an attempt to synthesise **2.18**. 1*H*-perimidine and 2-bromo pyridine (2.5 times excess) were combined in a schlenk tube. The reaction was performed under an inert atmosphere and moisture restrictive conditions for 18 hours in dry DMSO at 100 °C. The product **2.18** was not isolated and an insoluble black precpitate was all that resulted from the reaction. Therefore the last option attempted was using a sealed tube as the reaction vessel. The starting material, **2.12** was added to the sealed tube and 2-bromo pyridine was used as the solvent in 10-fold excess. The reaction ran for 24 hours at 180 °C and upon removal of the solvent under vacuum the analysis by ^{1}H-NMR and mass spectrometry showed no sign of product.

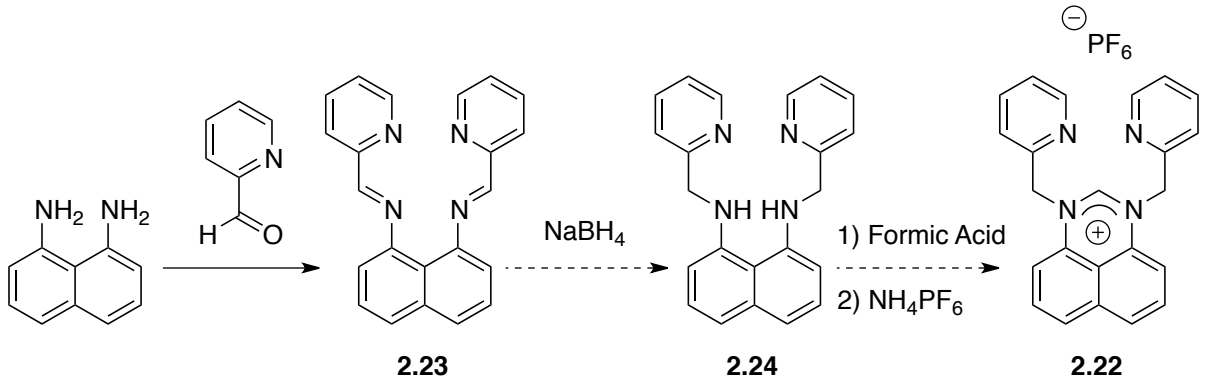
Due to the failure of the synthetic route to give the NHC salts **2.17** and **2.18** via the attachment at the N3 nitrogen of **2.12**, a different method was investigated. The R substituents would be substituted at the nitrogen atoms before the annulation reaction. The difficulty previously was the unreactive pyridine like nitrogen (N3) of 1*H*-perimidine, whereas substitution at the pyrrole like nitogen (N1) was obtained in a good yield to give **2.12**. The new synthetic scheme is shown below in scheme 2.4



Scheme 2.4: The attempted synthesis of the **2.19** and **2.20** via R group substitution followed by the ring annulation reaction to give the NHC salts, **2.21** and **2.22**.

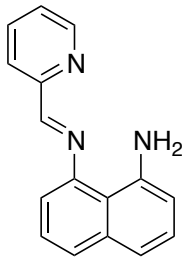
Two reactions were completed under the same conditions with the same starting material, 1,8-diaminonaphthalene. The reactants were varied with a three-fold excess of 2-bromo pyridine and a two and a half fold excess of picolyl hydrochloride. Both reactions to give the products **2.19** and **2.20** were carried out in DMF at reflux with K_2CO_3 as the base in a two-fold and six-fold excess of K_2CO_3, respectively in order to neutralise any acid produced. Both reactions were run for 48 hours under an inert argon atmosphere. The crude reaction mixture was washed with water and DCM and the organic fraction was isolated and dried upon $MgSO_4$. Upon removal of the DCM a significant amount of impurities were present via Thin Layer Chromatography analysis on silica. Purification was attempted via column chromatography. However, this was unsuccessful and the products could not be isolated or characterised. Therefore the subsequent ring annulation with formic acid was not completed.

The synthesis of **2.22** was attempted via the synthetic scheme 2.5 shown below. This could be achieved with the reactant 2-pyridine carboxaldehye and 1,8-diaminonaphthalene and the resulting diimine formation to give **2.23**. The reduction of **2.23** with $NaBH_4$ would result in **2.24**. Finally the formation of the NHC salt, **2.22** could then be obtained with formic acid to complete the annulation reaction.



Scheme 2.5

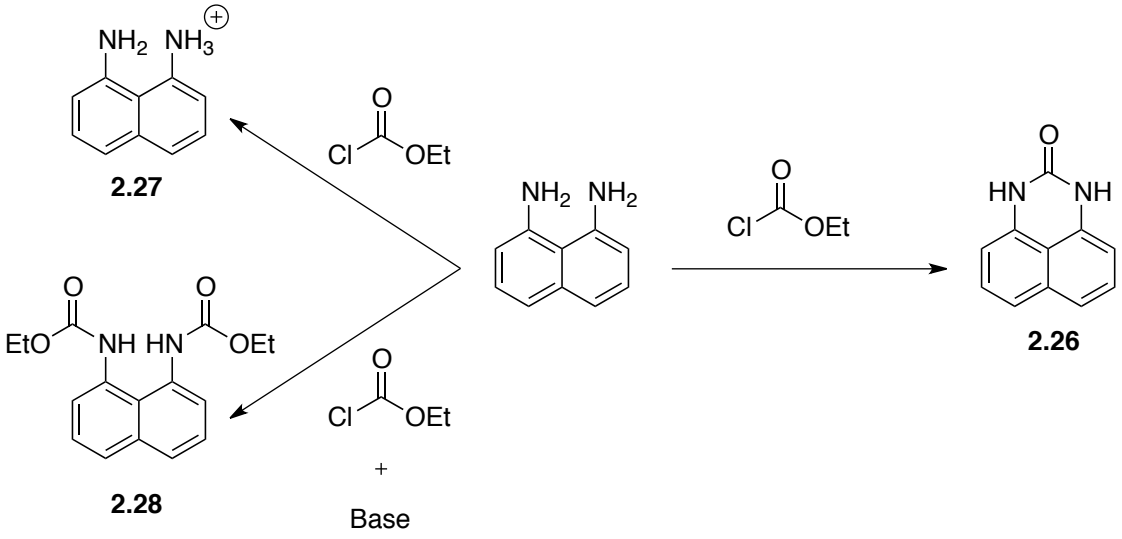
The imine condensation reaction was carried out in methanol at reflux for five hours according to Shakir *et al*.[71] The reaction mixture was then purified by column chromatography on silica with a gradient EtOAc: Hexane solution. The fraction isolated was however primarily the mono substituted imine, **2.25** as shown in figure 2.10. A reason for the impure isolation of products from this reaction could be due to the different E/Z isomers that are possible for the diimine, **2.23** and the imposed steric hinderance resulting in the isolation of **2.25**. The reaction was not repeated, but full characterisation was performed on the mono imine product **2.25**. The reduction of **2.25** was not completed nor the annulation reaction with formic acid due to time constraints.



2.25

Figure 2.10: The mono-imine side product, **2.25** in the attempted synthesis of **2.23**

The success of the Ullmann coupling reaction to give, **2.12** indicated a reaction pathway that could lead to the NHC salt, **2.18**. Therefore the synthesis of perimidin-2-one, **2.26** provided a synthetic route to achieve this as shown in scheme 2.6. However, significant method development was required in order to obtain a substantial amount of **2.26**. The first synthetic route attempted came from the same paper where Denny *et al*. described the synthesis of 1*H*-Perimidine.[63] The 1,8-diaminonaphthalene was added to a hot solution of 2M HCl containing one equivalent of NaOCN. The reaction stirred at 100 °C for an hour followed by cooling to 0 °C. The reaction could not be repeated as reported (91% yield), as the conditions the reaction was performed under did not specify duration of heating and cooling or the temperature of the reaction mixture. Therefore this method was abandoned. Sturla *et al.* utilised chloro ethylformate as the carbonyl source in order to obtain **2.26**.[72]

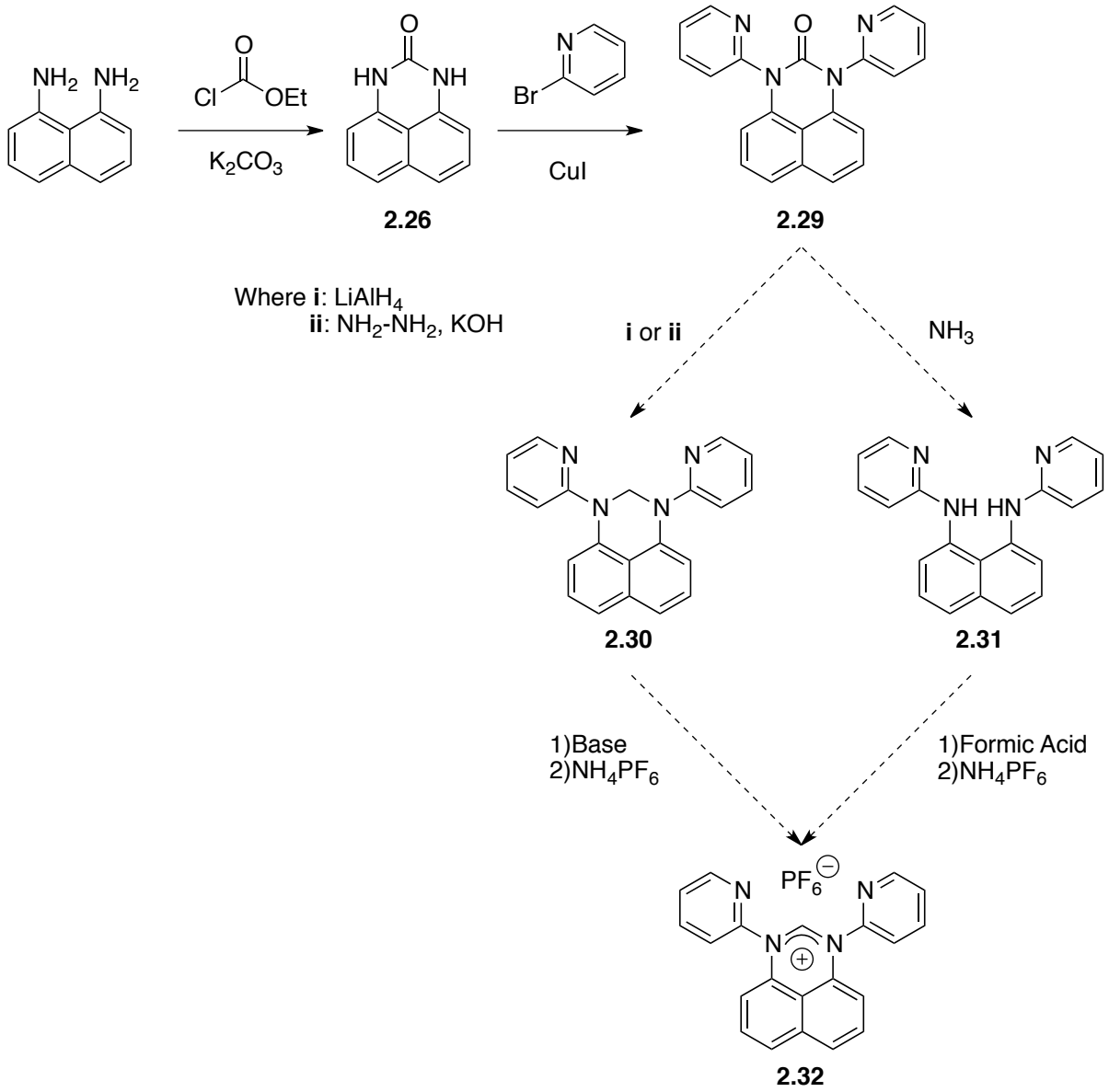


Scheme 2.6

This synthetic route gave the product **2.26**. The initial yield obtained was between 10-15% which was to low considering further synthetic steps were required. This therefore required some method development through the variation of the concentration, addition of heat and treatment with base. The concentration of 1,8-diaminonaphthalene played an important role as having a dilute concentration lead to the synthesis of the protonated starting material, **2.27** due to the formation of HCl and the strong basicity of 1,8-diaminonaphthalene. The rate of addition of chloro ethylformate played an important role as well, as if it was added to slowly this lead to protonating 1,8-diaminonaphthalene (**2.27**), whereas if it was added too fast the diethyl carbamate, **2.28** was made due to the high reactivity of the chloro ethylformate. The addition of base was introduced into the reaction scheme to combat the prontonation of 1,8-diaminonaphthalene. The final reaction conditions required 1.3 equivalents of chloro ethylformate and 1 equivalent of K_2CO_3 to act as the base. The addition of the chloro ethylformate was done drop wise over 30 mins at 0 °C. The reaction mixture was subsequently allowed to reach room temperature and set to reflux for 18 hours. Upon cooling to room temperature the cream pink precipitate from the reaction mixture was isolated via filtration and washed with DCM in a good yield (48%). ^{1}H-NMR confirmed the precipitate as the pure product **2.26**.

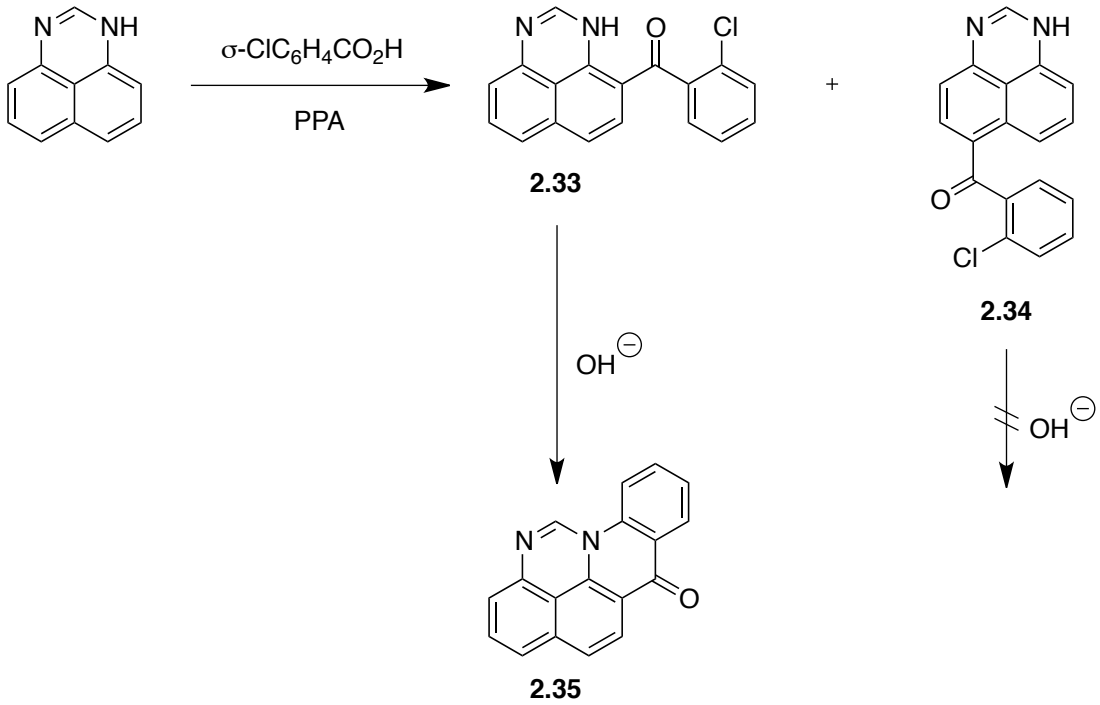
Upon synthesis of **2.26**, the Ullmann coupling reaction was performed to give **2.29**. The conditions the reaction was run under required 20% mol of CuI due to the two coupling reactions and ran for two days at 150 °C under an inert argon atmosphere and moisture restrictive conditions. The isolation of the product, **2.29** as a pale pink precipitate was achieved in a good yield (74%). The synthetic route is shown in scheme 2.7. The removal of the carbonyl functionality was not attempted as complex formation with the bpy NHC perimidinium salts was to be first established. However, three different routes could have been taken in order to isolate **2.32**. The first method could use ammonia to remove the carbonyl functionality by the loss of urea to give, **2.31**. This could then be reacted with formic acid and precipitated with ammonium or potassium hexafluorophosphate. The other synthetic route, i, is

the reduction of the carbonyl with $LiAlH_4$ or via a Wolf-Kishner reduction, ii. The urea functionality can be reduced by $LiAlH_4$ as Starikova *et al*. demonstrated in 2005 with similar di-substituted perimidin-2-one species.[73] They reported the formation of an sp^3 hybridised carbon at the C2 position. They were able to obtain the NHC perimidium salt by deprotonation of the CH_2 group at C2. The Wolf-Kishner reduction is also mentioned due to the unreactivity of the amide functional group. This method employs the use of hydrazine and a base such as KOH, resulting in the sp^3 hybridised carbon at C2 (**2.30**). However once again, this may be further deprotonated by the use of base *in situ* and the NHC perimidine salt, **2.32** may be realised due to the inherent stability of the conjugated aromatic system.



Scheme 2.7: The synthetic route to achieve the terpyridine perimidine NHC analogue, **2.32**.

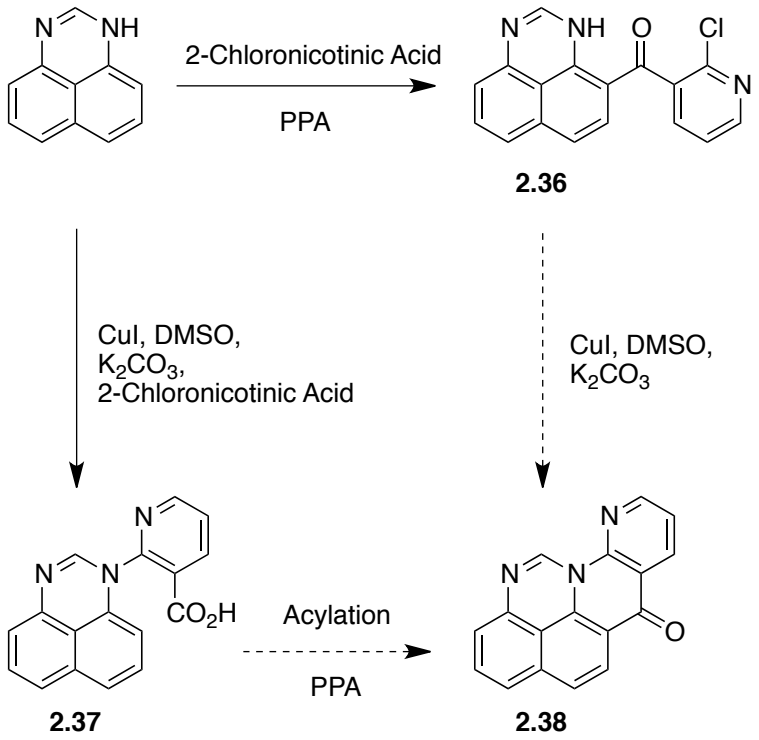
The synthetic route described in scheme 2.7 offers a feasible pathway to achieve the terpyridine NHC analogue **2.32**. This was the only example that resulted in the di-pyridine substition of 1*H*-perimidine. In the attempt to explore greater fused perimidine system that could potentially act as NHC's a unique strategy was found. In 2002 Pozharskii *et al*. completed the first synthesis of **2.35**, a fused perimidine moiety similar to that of **2.12**, as shown in scheme 2.8.[74] The reaction to form the precursor **2.33** proceeded with a yield of 49% and the subsequent formation of **2.36** resulted in a 60% yield. The acylation of perimidine with σ-chlorobenzoic acid was attempted under the same conditions that Pozharskii *et al*. desbribed, where 1*H*-perimidine, σ-chlorobenzoic (1.5 times excess) and freshly prepared PPA (PolyPhosphoric Acid) were stirred at 130 °C for two hours. The reaction was quenched with water and basified with ammonia. The organic phase was then extracted with Et_2O and dried upon MgSO4 to give a crude residue. Column chromatography on silica was attempted in order to purify the crude residue. However, the product **2.33** could not be isolated from the column as too many side products were present. The fractions that were isolated showed no direct evidence of the product **2.33** via ^{1}H-NMR.



Scheme 2.8

The product **2.34** was not observed as a bi-product of the reaction despite the observation by Pozharskii *et al*. who were able to synthesise **2.34** in a good yield (67%) perhaps due to running the reaction at 80 °C rather than 130 °C.[74] Thus highlighting the thermodynamic vs. kinetic control of the reaction. The formation of **2.34** is due to the ortho/para directing ability of the nitrogen atoms on the naphthalene system.

The acylation reaction was repeated one more time under the same conditions however the reagent σ-chlorobenzoic was exchanged for 2-chloronicotinic acid, thus giving a pyridine heterocycle **2.36** in place of the phenyl as shown in scheme 2.9. This gives a similar motif to the other ligands previously described. The compound **2.38**, also offers a larger fused aromatic ring system compared to **2.12** and the potential for further reactions to be attempted due to the carbonyl functionality at the C3 position of the pyridine group.



Scheme 2.9: The attempted synthesis of larger fused perimidine systems to act as potential bpy NHC analogues, **2.38**.

The synthesis of **2.37** was not accomplished, as no evidence of **2.37** could be seen from mass spectrometry or ^{1}H-NMR as only 1H-perimidine was present. In order to realize the product **2.39** an Ullmann coupling reaction would have been used due to its success established with the synthesis of **2.12** as previously mentioned. A different route was attempted due to the failure of the acylation step, where the Ullmann coupling reaction was performed first giving **2.38**. This reaction ran overnight in an inert argon atmosphere and dry DMSO at 150 °C with an one and a half fold excess of potassium carbonate to act as the base and two times excess of 2-chloronicotinic acid with 10mol% of CuI. The reaction resulted in an unknown product via ^{1}H-NMR and therefore the acylation step with PPA was not completed and the synthesis of **2.39** was abandoned.

The Crystal Structures of NHC salts.

The conformations of perimidine NHC salts have had little attention, but crystal structures of similar free perimidine NHC's are reported by Richeson *et al*.[18] The proposed conformation of the NHC salts is determined by through space interactions of the ring systems of the NHC salt. Similar to that of N-Heterocycle systems[75] The intramolecular interactions can be attractive via hydrogen-bonding (figure 2.11(a)) or repulsive due to steric and/or electrostatic interactions as shown in figure 2.11(b) and figure 2.11(c), respectively.

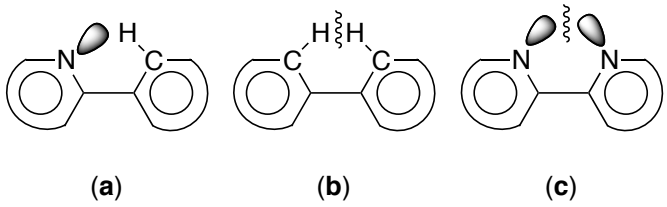


Figure 2.11: Intramolecular interactions in biheterocycles.

Attractive interactions promote coplanarity due to the overalp of orbitals required, whereas repulsive interactions will disfavour coplanarity. Intermolecular interactions via π-π stacking are a favourable interaction between conjugated aromatic systems. These π-π interactions have an offset distance associated with them that is described as a plane shift distance. The stacking can either interact face-to-face or edge-to-face, as shown in figure 2.12(a) and figure 2.12(b), respectively.

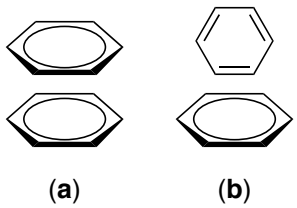


Figure 2.12: (a), face-to-face, (b), edge-to-face, π-π stacking interactions.

The crystal structures of two of the bpy NHC analogues were obtained in order to investigate the inter- and intra- molecular interactions described earlier. Crystals of the NHC ligand, **2.14**, were grown by diffusion of hexanes into a DCM and were suitable for X-ray crystallography. Compound **2.14** crystallised in the monoclinic space group $P2_1/c$, with one molecule of **2.14**, its associated bromide anion and a DCM molecule disordered over 2 positions in the asymmetric unit which has been omitted out for clarity, as shown in figure 2.13(a).

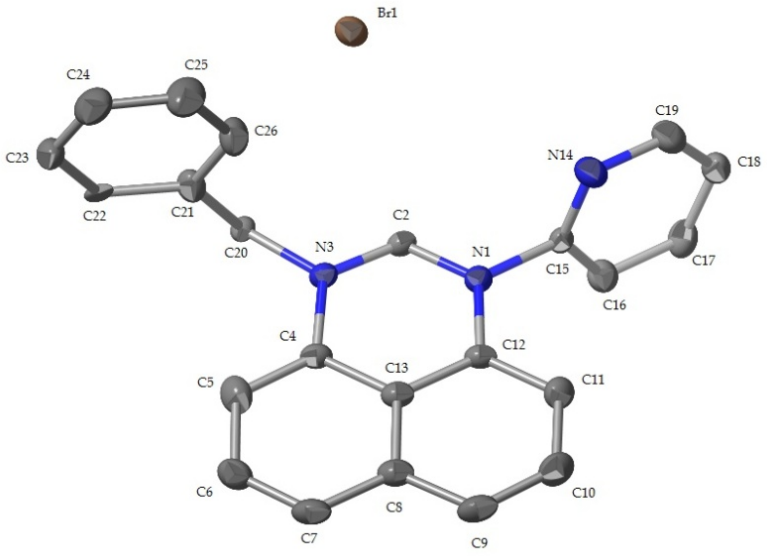


Figure 2.13: The asymmetric unit of the NHC salt **2.14**, with the protons omitted for clarity and the numerical assignment.

The bond distances between of the two nitrogen atoms to the C2 atom are 1.327(1) Å and 1.314(1) Å for N1 and N3, respectively. The angle of the pyridine ring to the central perimidine ring was 82.636(3)° and the phenyl ring to the same perimidine central ring was 90.422(3)°. Richeson *et al*. synthesised a similar free NHC perimidine ligand with comparative plane-plane angles.[18] The crystal packing of **2.14** is dominated by face-to-face π-π interactions between the naphthalene rings of the perimidine unit with an adjacent molecule (plane-centroid distance 3.413(1) Å with a plane-plane shift distance of 1.723(1) Å), as shown in figure 2.14.

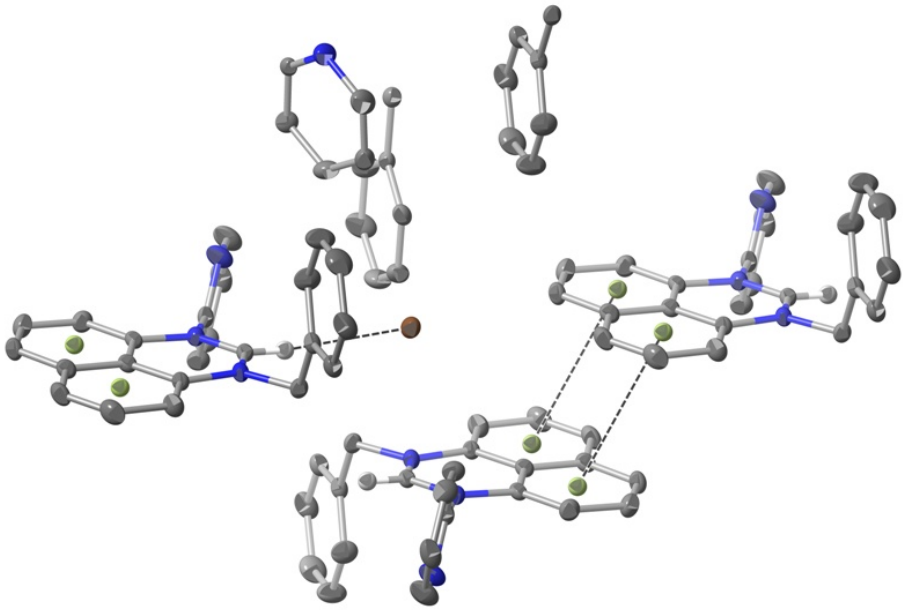


Figure 2.14: The pocket surrounding the bromine anion, influencing the shift of the π-π interactions.

There is a weak hydrogen bonding interaction between the H2 proton and the bromine anion with a distance of 2.726(1) Å. The hydrogen bonding and steric effects induced by adjacent molecules (only significant parts of these adjacent molecules are shown for clarity) has influenced the π-π interactions of the naphthalene rings resulting in a larger shift distance than usual.

The NHC ligand **2.15** was also grown into single crystals that allowed their structure to be determined via X-ray crystallography, with **2.15** crystallising in the monoclinic space group $P2_1/c$. The asymmetric unit contained **2.15** and its associated tetrafluoroborate anion, as shown in figure 2.15(a). The bond distances are as follows for the NHC ligand, **2.15**. The carbon-nitrogen bonds for the perimidine ring, N1-C2 and N3-C2 are 1.329(1) Å and 1.315(1) Å, respectively. The plane angle of the pyridine ring and the perimidine central ring was 54.81(4)°. This angle is significantly more co-planer with the central perimidine ring compared to the same angle in the NHC salt, **2.14** with a difference of ~30°. This can be attributed to a weak hydrogen bonding interaction between the H2 proton and N14 atom with a bond distance of 2.559(1) Å. This hydrogen bonding interaction attempts to make the two rings co-planar, but steric repulsion between H11 and H16 prevents this with a bond distance of 2.315(1) Å. Thus resulting in an angle to appease both the repulsion and attractive interactions. The hydrogen bond distances may not be accurate as the position of the proton is fixed rather than measured. Once again the crystal packing is dominanted by face-to-face, π-π interactions between the backbone naphthalene rings of the perimidine core and an adjacent molecule (plane-centroid distance of 3.340(1) Å and a plane-plane shift of 1.427(2) Å), as shown in figure 2.15(b).

(**a**) (**b**)

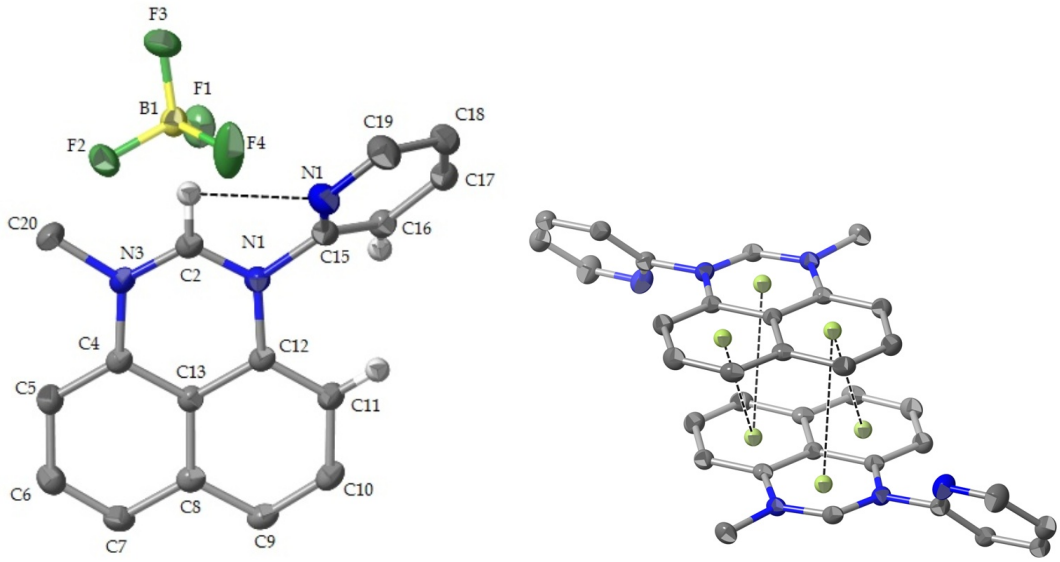
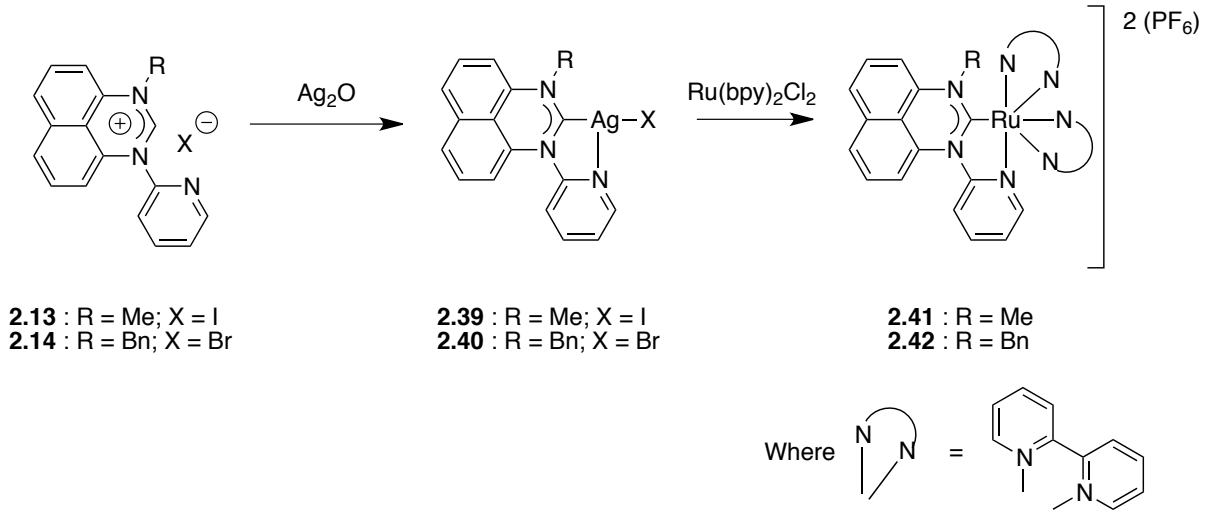


Figure 2.15: (**a**), The asymmetric unit with numerical assignment and, (**b**), The inter-molecular interactions, of the NHC salt, **2.15**, protons have been omitted for clarity.

There are also π-π interactions between the phenyl ring (C4, C5, C6, C7, C8, C13) and the central perimidine ring (plane-centroid distance of 3.301(2) Å and a plane shift distance of 1.128(3) Å) again shown in figure 2.15(b). There were no intermolecular hydrogen bonding interactions that could be observed or any sign of solvent. The tetrafluoroborate anion did show some disorder in the occupancy of the fluorine atoms. The atom F2 showed an occupancy of one, whereas the other fluorine atoms (F1, F3, F4) where split with an 83% occupancy and a different position with 17% occupancy. In figure 2.15(a) the positions with occupancy of 83% are only shown for clarity.

Synthesis of NHC complexes

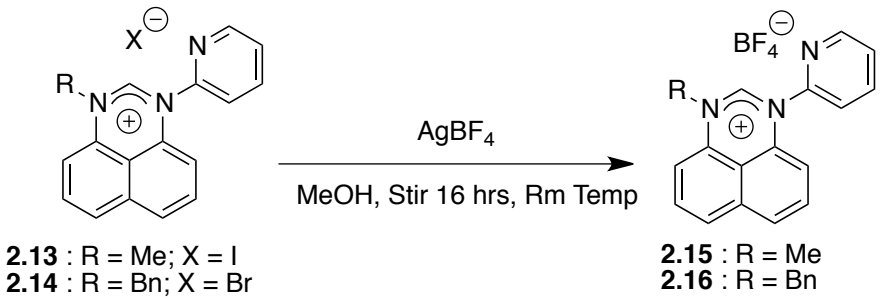
The majority of complex synthesis was completed with the goal of forming the first silver or ruthenium complex with a perimidine based NHC ligand. It has been established that the deprotonation of perimidine NHC salts are more difficult than their imidazolium counterparts.[4] The perimidine NHC salts **2.13** and **2.14** and the tetrafluoroborate counterparts, **2.15** and **2.16** were the only NHC salts attempted to be complexed due to the difficulty associated with the ligand synthesis. Silver complexes of **2.13** and **2.14** were attempted first, as the silver could be exchanged to give a ruthenium complex as shown below in the general scheme 2.10.



Scheme 2.10: The attempted synthesis of the silver (**2.39** and **2.40**) and ruthenium (**2.41** and **2.42**) NHC-complexes.

The NHC ligands, **2.13** and **2.14** were refluxed in MeCN with Ag_2O for 72 hours, following a modified procedure described by Kunz *et al*.[76] although their method utilised imidazolium NHC ligands. This procedure was chosen due to the similarity of R groups on the nitrogen atoms and it used MeCN as the solvent rather than the majority of researchers that use DCM. The reason to avoid DCM was due to the partial insolubility of the NHC salts. The reaction was worked up by removing the precipitate that formed and subsequent analysis of the filtrate showed no sign of product **2.39** or **2.40** via mass

spectrometry with only undefined peaks. The lack of evidence for the formation of a silver complex resulted in the attempted one-pot synthesis of **2.41**. Using a preparation established previously in the group, the NHC salt **2.13** was combined with Ag_2O and refluxed in ethylene glycol for one hour.[77] To this hot solution $Ru(bpy)_2Cl_2$ was added and allowed to reflux for a further 18 hours. The workup involved precipitating the ruthenium complex with NH_4PF_6. However, analysis of the precipitate via mass spectrometry showed the presence of ruthenium salts due to the isotope distribution, but the desired product **2.42** was not in the sample mixture. The other ruthenium peaks could not be determined to be a specific complex and ^{1}H-NMR data did not give clear evidence to the structural characteristics of the ruthenium species The failure to synthesise **2.41** from the method described previously lead to a different approach as the silver complex **2.39** was not forming in the reaction mixture. The halogen anion associated with the NHC ligands **2.13** and **2.14** may have been competitively binding with the silver in the reaction mixture hindering the formation of the complexes **2.40** and **2.41**. Therefore the halogen was exchanged with a tetrafluoroborate anion as shown below in scheme 2.11.

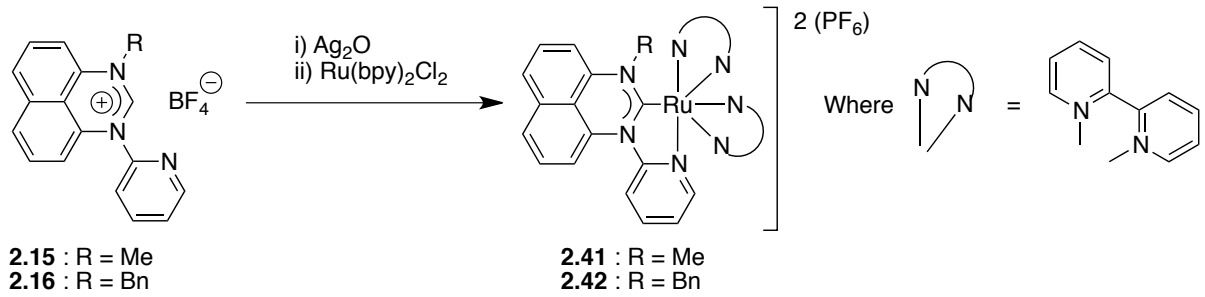


Scheme 2.11: Synthesis of tetrafluoroborate NHC salts.

The reaction was performed on a 1:1 ratio of $AgBF_4$ and the ligand **2.13** or **2.14** to allow all of the halogen to react with the silver and exchange the anion for a tetrafluoroborate anion. The silver salt was filtered over Celite and the filtrate dried giving the desired product **2.15** and **2.16** in a quantitative yield. Catelano *et al* described a preparation of a silver NHC imidazolium complex and the use of a phase transfer catalyst to aid in the reaction.[78] The reaction to give the proposed complexes **2.43** and **2.44** was modified slightly by using a different phase transfer catalyst than described and using silver oxide as the silver source rather than $AgBF_4$, as shown in scheme 2.12.

Scheme 2.12: The attempted synthesis of a di-NHC silver complex.

The reaction did not give any clear indication of a silver complex via mass spectrometry and ^{1}H-NMR analysis, as there was predominantly starting material present. Indicating the free NHC's were still not being formed in the reaction, or the silver complexes were labile and/or decomposing over time. The attempted synthesis of a ruthenium complex was performed again under the same reaction conditions as previously described, as shown in scheme 2.13. However, the tetrafluoroborate NHC salts (**2.15** and **2.16**) were used in place of **2.13** and **2.14**.



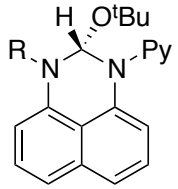
Scheme 2.13: The attempted synthesis of ruthenium NHC complexes, **2.41** and **2.42**.

Initial observations showed the presence of both **2.41** and **2.42** upon work up of the reaction mixture via mass spectrometry. In each reaction there were at least three other major peaks that could be seen from the mass spectrometry analysis. Two out of the four peaks could be identified, with one as either **2.41** or **2.42**. The other peak had m/z of 285.0551 and upon analysis could have been $[Ru(bpy)_3]^{2+}$. The formation of $[Ru(bpy)_3]^{2+}$ is not surprising due to the elevated temperatures (~200 °C) and time (18 hours) the reaction and was conducted for. The two other major peaks could not be assigned to a particular compound and the ^{1}H-NMR was inconclusive due to the impurities present in the sample. Recrystallisations of the crude mixtures for both reactions were attempted. However, this did not yield the desired product either. Therefore reaction conditions were modified to ideally give the desired products in good yields with minimum side products.

In order to establish that the silver oxide was aiding the formation of a NHC complex, **2.15** and excess silver oxide were combined in ethylene glycol and irradiated in a microwave reactor for 3x1 minutes. The reaction mixture was analysed by mass spectrometry for the existence of a silver NHC complex.

However, the analysis only showed the ligand was present. This gave an indication that the silver-NHC complex was not produced and observation of the ruthenium complex described previously was primarily due to the ruthenium and the high temperatures that it was run under. A precipitate also formed from the reaction, it appeared to be Ag^0 from the metallic complexion but could broken up with a pale brown precipitate incapsulated inside the proposed metallic silver precipitate. No analysis was carried out to determine if Ag^0 was made and its formation was unclear at this time.

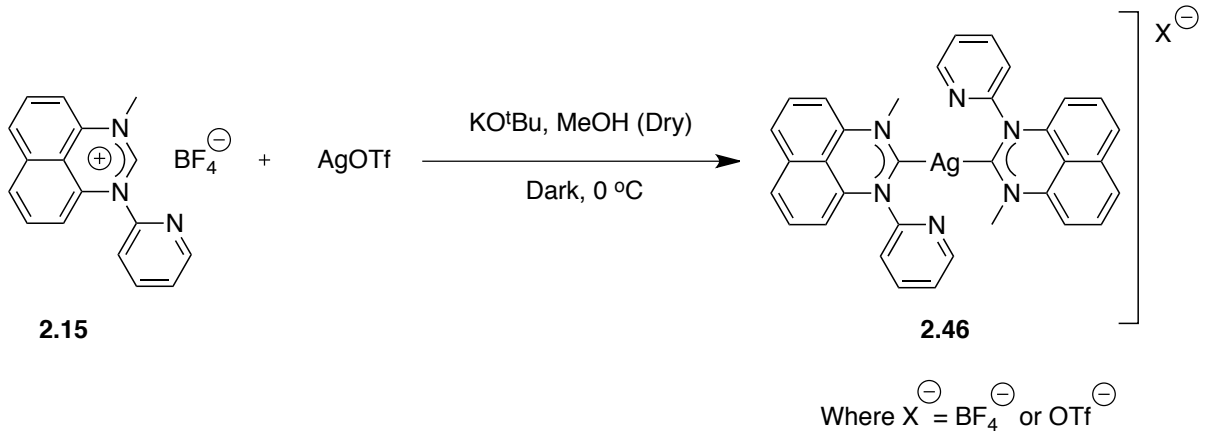
A different deprotonation method was required in order to form a NHC complex with the ligands **2.15** and **2.16**. Therefore the use of a base *in situ* with a silver salt was attempted. Richeson *et al*. described the nucleophilic attack of NaO^tBu to one of their perimidine salts giving the diamino ether **2.04**.[18] The diamino ethers, **2.46** and **2.47** (as shown in figure 2.16) were not observed at any point via analysis with mass spectrometry from the resulting deprotonation reactions carried out. The steric hindrance imposed by the N1 pyridyl substituent may have prevented the nucleophilic attack of the butoxide anion at C2 explaining why **2.46** and **2.47** were not observed.



2.46 : R = Me, Py = 2-pyridyl
2.47 : R = Bn, Py = 2-pyridyl

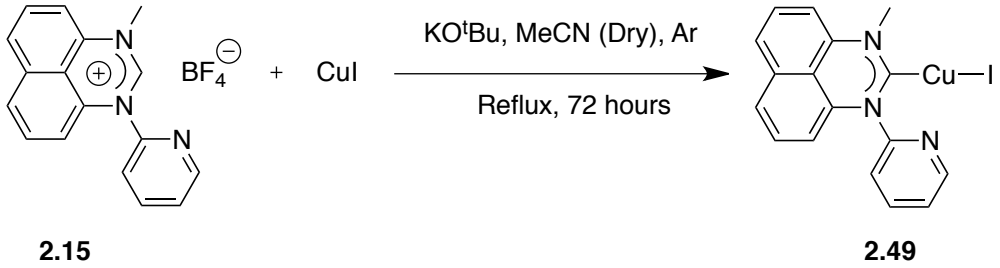
Figure 2.16: The resulting products of nucleophilic attack by butoxide with **2.15** and **2.16**.

Therefore the NHC ligand **2.15** was reacted with AgOTf in a MeOH solution with KO^tBu to deprotonate the NHC salt, **2.15** in order to give the free NHC *in situ* and the subsequent silver complex **2.48**. The reaction was performed under dark conditions at 0 °C as shown in scheme 2.14.



Scheme 2.14: The attempted synthesis of the di-NHC silver complex, **2.48**.

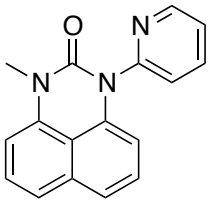
Mass spectrometry analysis showed that the NHC salt **2.15** still remained in the crude sample isolated and no sign of the proposed silver complex **2.48** was observed giving an indication that the KO^{t}Bu may not be a strong enough base to deprotonate **2.15**. Therefore due to the lack of success with Ag-NHC complexes a different d^{10} metal was chosen to highlight if these d^{10} NHC complexes could be formed. The reaction was performed with **2.15** and CuI as the metal source as shown in scheme 2.15.



2.15 **2.49**

Scheme 2.15: The attempted synthesis of a coppe(I)-NHC complex, **2.49**.

The proposed structure of the Cu-NHC complex, **2.49**, was not realised and mass spectrometry analysis showed the presence of the NHC ligand, **2.15**, still remaining in solution after refluxing in MeCN for 72 hours. However, other compounds were present from mass spectrometry analysis that could not be determined via their mass alone. Therefore column chromatography was performed on silica in order to isolate these products and determine why the reaction with the NHC ligand, **2.15**, was not progressing with d^{10} metals and ruthenium. From the column only one fraction was isolated to be pure, giving **2.50**, as shown in figure 2.17.



2.50

Figure 2.17: The perimid-2-one compound, **2.50**, isolated from the reaction intended to give **2.49**.

The mass spectrometry analysis showed m/z of 276.1133, 16 mass units greater than the NHC salt **2.15**, therefore in conjunction showing the presence of a urea like functional group. In order to prove that **2.50** had carbonyl functional group at C2 an IR spectrum was obtained with a definitive peak at 1677 cm^{-1} supporting a carbonyl bond stretching due to the similarity exhibited in similar compounds **2.26** (1666 cm^{-1}) and **2.29** (1668 cm^{-1}). The isolated product **2.50** was also grown as single crystals via slow evaporation of MeCN. The compond **2.50** crystallised in the orthorhombic space group *Pnma*. The asymmetric unit shown in figure 2.18 contains half the perimidine ring and methyl group and the pyridine ring, which is disordered over two positions about the mirror plane.

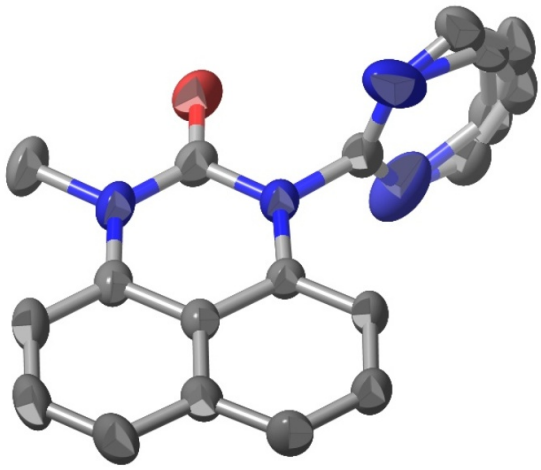


Figure 2.18: Compound **2.50** with a disordered pyridine ring shown, hydrogen atoms have been omitted for clarity.

The pyridine ring was found over the two positions it occupies with an angle of it to the central perimidine ring of 90.0°. The bond distance of the of the between the C2 carbon and the oxygen atom was measured to be 1.223(1) Å. The carbon-nitrogen bond distances for N1-C2 and C2-N3 are 1.388(1) Å and 1.367(1) Å, respectively. The angle of N1-C2-N3 was measured to be 116.77(1)°. The crystal packing of compond, **2.50** is primarily made up of face-face, π-π interactions of the perimidine core unit as shown in figure 2.19.

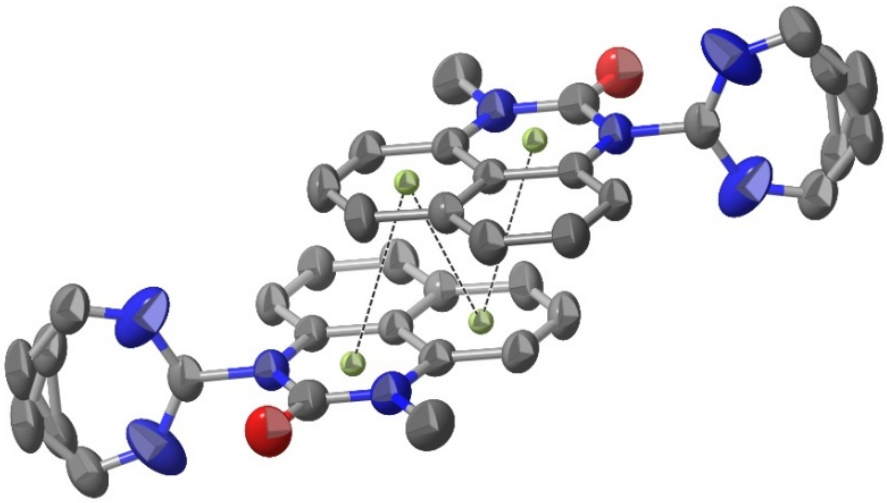
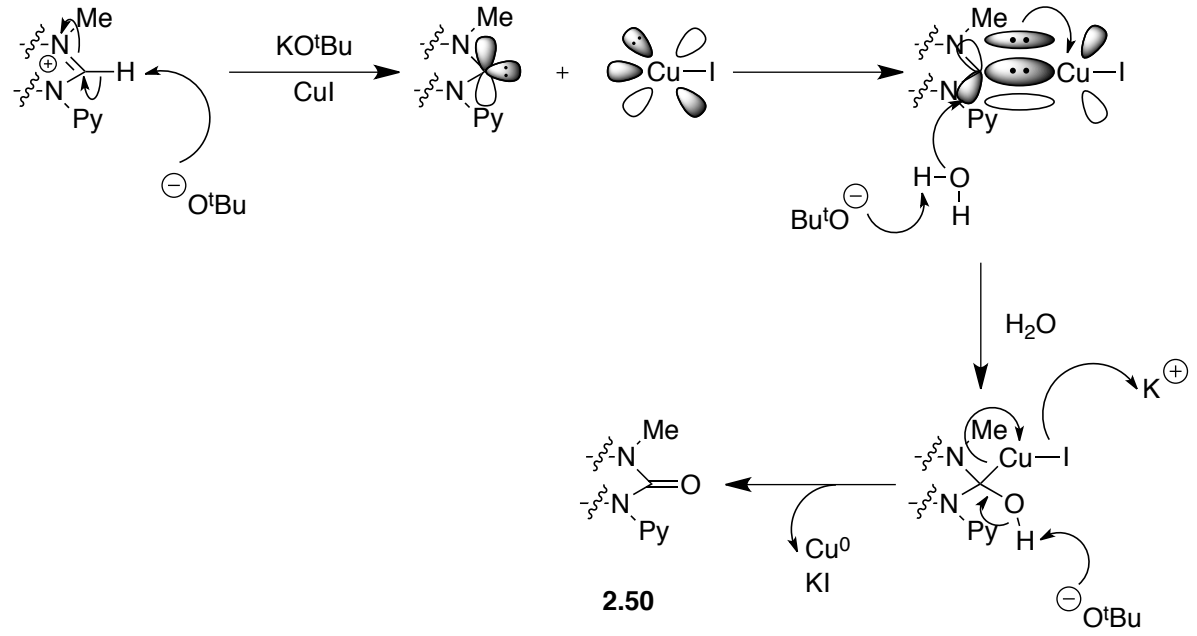


Figure 2.19: The intermolecular π-π interactions of **2.50**.

The phenyl ring of exhibts π-π interactions with the same phenyl ring of an adjacent molecule (plane-centroid distance 3.408(1) Å and plane-plane shift distance of 1.689(1) Å). This phenyl ring also has π-π interactions with the central perimidine ring (plane to centroid distance of 3.408(1) Å and plane-plane shift distance of 1.256(1) Å). These were the only observable intermolecular interactions of **2.50**.

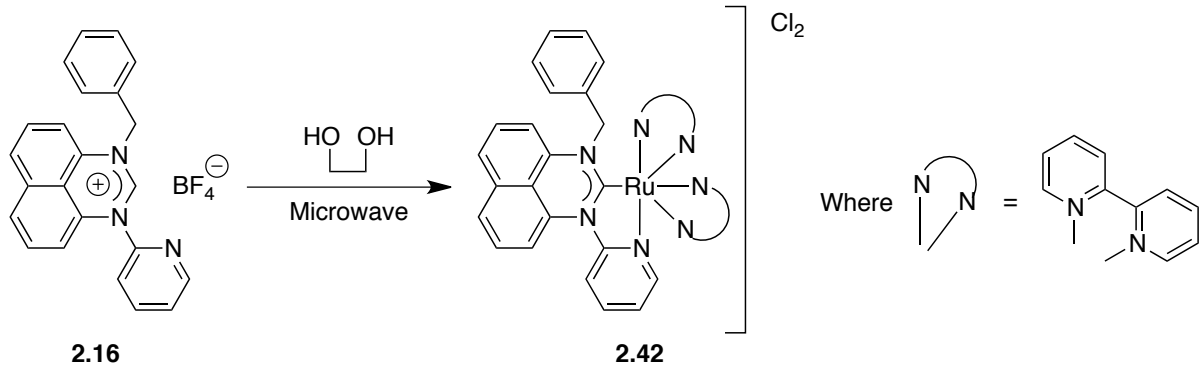
Product **2.50** has not been synthesised before and nor has a similar urea like product been isolated from other perimidine NHC research. The formation of **2.50** is suspected to go via the NHC-Metal complex and the nucleophilic attack of water in the reaction mixture to eliminate Cu^0 and KI giving the product **2.50**. A postulated mechanism is shown in scheme 2.16.



Scheme 2.16: The proposed mechanism for the formation of **2.50**.

The proposed formation of Cu^0 is due to observation of Ag^0 in previous reactions even though no Cu^0 precipitate was observed. No further studies were carried out in order to fully characterise this proposed mechanism.

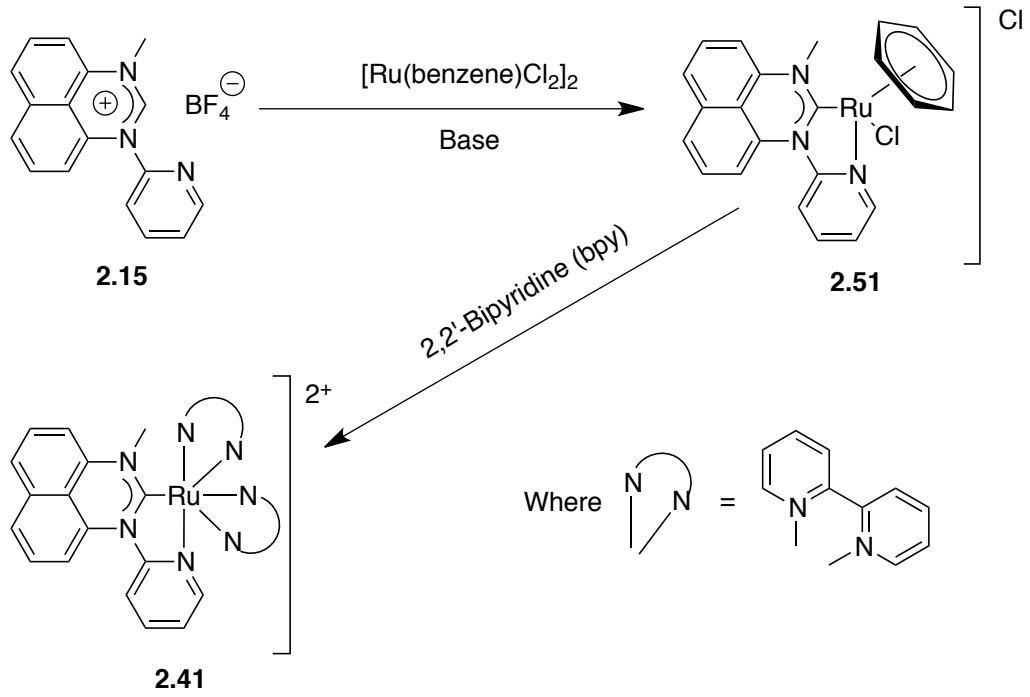
The use of d^{10} metals as a synthetic route to prepare metal-NHC complexes that can be transmetallated to give a ruthenium, palladium or other metal-NHC complexes was therefore abandoned. The synthesis of **2.42** was attempted via a microwave-assisted procedure in ethylene glycol with the NHC ligand, **2.16** as shown in scheme 2.17. The reaction was run 4x2 minutes and monitored by TLC. After eight minutes the NHC ligand, **2.16**, had almost been fully used up in the reaction with a distinctive new spot. After initial mass spectrometry analysis of the crude reaction mixture this showed a variety of ruthenium based complex peaks. ^{1}H-NMR could not be completed due to the abundance of ethylene glycol. Therefore as the product, **2.42**, was a chloride salt, a sephadex column was run to try and isolate these products. However, the only ruthenium product isolated was once again $[Ru(bpy)_3]^{2+}$, with no definitive sign of the desired product $[RuL(bpy)_2]^{2+}$, **2.42** (where L= **2.16** as the free NHC ligand).



2.16 **2.42**

Scheme 2.17: Attempted synthesis of **2.42** via a microwave assisted procedure.

A different ruthenium precursor was next utilised as reactions with $[Ru(bpy)_2Cl_2]$ were not proceeding. Therefore, $[Ru(benzene)Cl_2]_2$ was synthesised from $RuCl_3.xH_2O$ and cyclohexadiene and the NHC salt was to be coordinated prior to the pyridine ligands. The reaction with the NHC ligand, **2.15**, $[Ru(benzene)Cl]_2$ and a slight excess of sodium hydride as the base was used as shown in scheme 2.18.



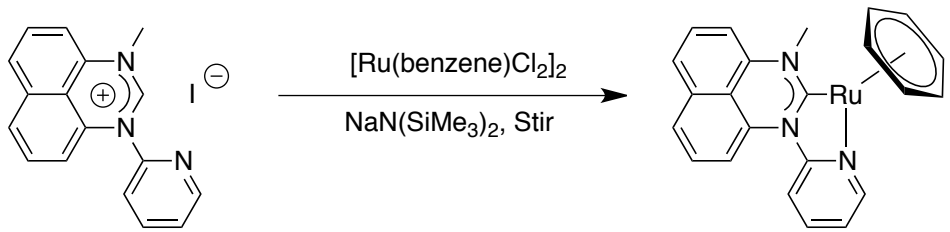
2.15 **2.51** **2.41**

Scheme 2.18: The attempted coordination of the NHC ligand, **2.15** prior to the pyridine ligands resulting in the ruthenium complex **2.51**. The coordinated benzene ligand can then be displaced with 2,2′-bipyridine to give, **2.41**.

The synthesis of **2.41** could subsequently be achieved by exchanging the coordinated benzene ring of, **2.51** with two equivalents of 2,2′-bipyridine to give the desired product, **2.42**. However, the synthesis of **2.41** was not achieved, as no evidence of the proposed complex, **2.51**, was visible according to mass spectrometry analysis. ^{1}H-NMR of the reaction was also inconclusive with no characteristic peaks

visible. The data retrieved from the mass spectrometry analysis did show the existence of **2.50**, thus giving evidence that water may be present in the reaction mixture, even though the reaction was performed as dry as possible. The source of the water was attributed to the sodium hydride due to the hydroscopic nature of the base. Therefore the reaction was performed again but in place of the NaH, dry NEt_3. This reaction preceded under an argon atmosphere and moisture restrictive conditions and in place of DMF, MeCN was used due to the easier removal of the solvent. The initial precipitate from the reaction was not of interest due to mass spectrometry and ^{1}H-NMR analysis. The filtrate showed presence of the ligand and the $[Ru(benzene)Cl_2]_2$ complex via mass spectrometry and the existence of **2.50**. The major product from ^{1}H-NMR analysis showed the characteristic singlet of the H2 proton of the NHC ligand, **2.15**. Thus showing that the triethylamine was not a strong enough base to deprotonate the NHC salt, **2.15**, to give the free carbene to react with ruthenium complex and if the NHC-Ru complex was formed any water present may displace the ruthenium to give **2.50**. Therefore a stronger base is needed in order to deprotonate the bulk sample of the NHC ligand rather than a small amount reacting with the ruthenium salt that is then displaced by a small amount of water that may be present in the reaction mixture. Hence why mass spectrometry gives evidence for the formation of the desired Ru-NHC complex, but ^{1}H-NMR highlights that the complex is definitely not the major product.

The following deprotonation utilised $NaN(SiMe_3)_2$ as the base in a THF solution. This base has shown to deprotonate perimidine NHC salts by Richeson *et al.*, as previously mentioned.[18] The NHC ligand, **2.13,** was used in this reaction, as the iodide anion should have no effect on the complexation process with ruthenium as shown in below in scheme 2.19.



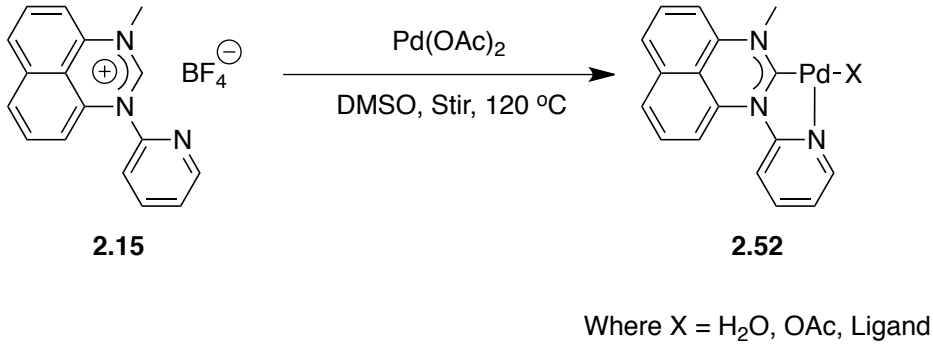
2.13 **2.51**

Scheme 2.19: The use of $NaN(SiMe_3)_2$ in the attempted synthesis of **2.51**.

To a solution of the NHC ligand, **2.13**, in THF and chlorobenzene one equivalent of $NaN(SiMe_3)_2$ was added under an argon atmosphere and moisture restrictive conditions. The reaction mixture was then stirred for two hours and after this time the $[Ru(benzene)Cl]_2$ was added and allowed to stir 18 hours at room temperature. After removal of the volatiles under vacuum the crude product was washed with DCM giving a precipitate that showed presence of a ruthenium complex potentially with the ligand **2.13**. Instead of continuing the purification of the potential NHC-complex this precipitate was then dissolved into a 4:1 EtOH:H_2O solution and refluxed over 48 hours with 2,2′-bipydridine to ideally give the complex **2.41**. Initially the reaction mixture showed that the complex **2.41**, was

present in solution via mass spectrometry analysis, but the ligand was also present in the solution, indicating that it was not fully deprotonated in the two hours it stirred with $NaN(SiMe_3)_2$. Once the reaction mixture was worked up the mass spectrometry analysis showed that $[Ru(bpy)_3]^{2+}$ had formed in solution and after ^{1}H-NMR analysis, proved to be the dominant species in the precipitate. Therefore the free NHC ligand may not have been generated or not have made a ruthenium-carbene bond as the NHC ligand shouldn't be displaced by a 2,2'-bipyridine ligand. However, a trace amount of the desired complex may have formed in solution as could be seen after mass spectrometry analysis.

The syntheses of palladium perimidine NHC complexes were also attempted. However, this had different problems associated with the complex synthesis compared to the ruthenium research conducted. The first synthetic approach attempted utilised the NHC ligand 2.15, and the oxidative addition of $Pd(OAc)_2$ as shown in scheme 2.20 following a preparation by Bielawski *et al*. in 2008.[79]

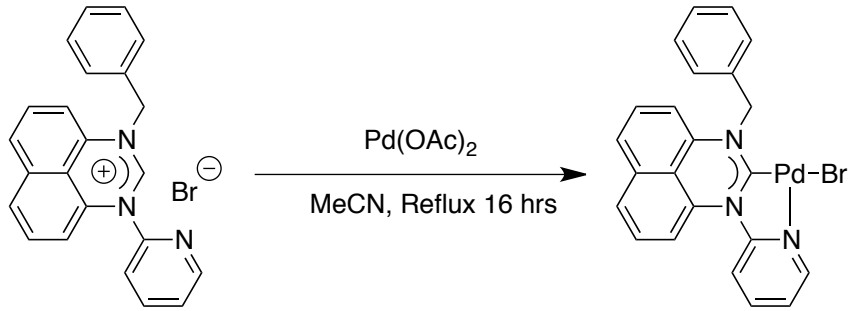


2.15 **2.52**

Scheme 2.20: The attempted synthesis of the proposed Pd-NHC complex, **2.52**.

The ligand, **2.15**, and $Pd(OAc)_2$ were combined in a schlenk tube under an argon atmosphere and moisture restrictive conditions and allowed to stir at 120 °C for three hours. Upon cooling to room temperature the DMSO was then removed by washing the crude product with DCM and water. The DCM layer was isolated and analysed by mass spectrometry and ^{1}H-NMR. The mass spectrometry showed the presence of ligand and three palladium complexes, but the specific structures could not be assigned solely from mass spectrometry analysis. However, assumptions could be made as peaks indicated the presence of mono and bis palladium complexes, **2.52**. The purification of the complex **2.52** could not be achieved and the mass spectrometry results indicated the variability in the number of coordinating ligands due to the easy displacement of the acetatate ligands from the palladium precursor. The ^{1}H-NMR that was collected for this reaction showed the presence of multiple products. Therefore crystallisations were set as a purification technique, however this did not yield any pure product. The reaction was repeated due to the promising, yet unobtainable results. The DMSO was exchanged for MeCN, because the work up of the reaction would be far simpler as the solvent could be removed under vacuum to ideally give a palladium complex. The reaction utilised the same starting materials, **2.15** and $Pd(OAc)_2$ and refluxed for 18 hours in MeCN. Upon removal of the

solvent crystallisations were set up to isolate a potential palladium complex. The ^{1}H-NMR obtained of the sample showed the disappearance of the characteristic H2 proton but was still not pure. The crystallisations that were set up did not yield any crystals therefore the reaction was repeated under the same conditions, but the NHC ligand, **2.14** was used in place of **2.15**. The reason for this was the bromide anion associated with the NHC salt, **2.14** would ideally be coordinated to the palladium and giving product, **2.53**, as shown in scheme 2.21.



Scheme 2.21: The attempted synthesis of the Pd-NHC complex, **2.53**.

The reaction was then performed with a slight excess of ligand. Upon removal of the MeCN after the reaction ran for 18 hours the crude product was analysed by mass spectrometry and ^{1}H-NMR. The mass spectrometry showed no existence of the product **2.53**. However, it did show the presence of two palladium complexes, **2.54** and **2.55** (assigned by mass only), that weren't expected as shown in figure 2.18

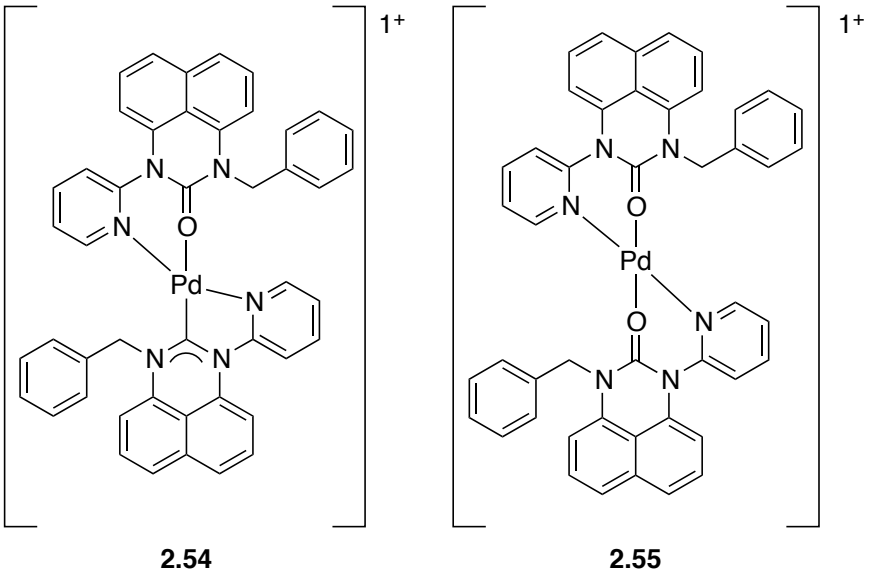
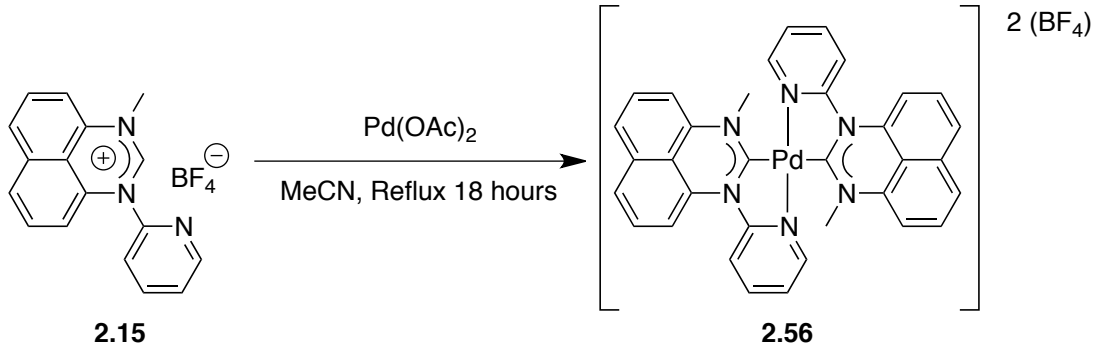


Figure 2.18: Mass spectrometry analysis of the reaction to give, **2.53**, and the proposed side products of the reaction, **2.54** and **2.55**.

Both the proposed complexes (**2.54** and **2.55**) have the oxidised form of the ligand **2.14** indicating the need to run the reaction under more rigorous air and moisture restrictive conditions. The complexes were unable to be isolated or characterised. ^{1}H-NMR of the crude product gave no information due to the poor purity of the sample. Therefore the following reaction reverted back to the tetrafluoroborate NHC ligand, **2.15**. The reaction was completed with a greater than two-fold excess of the ligand to $Pd(OAc)_2$ in order to give a bis NHC ligand palladium complex **2.56** as shown in scheme 2.22.



2.15 **2.56**

Scheme 2.22: The attempted synthesis of the Pd-NHC complex, **2.56**.

The reaction was run for 18 hours at reflux under an argon atmosphere and moisture restrictive conditions. The MeCN was removed under vacuum and the crude product was analysed by mass spectrometry and ^{1}H-NMR. The mass spectrometry analysis showed the presence ligand and the oxidised ligand, **2.50** present. There was existence of palladium complexes, but none could be assigned to a specific structure. The ^{1}H-NMR was also inconclusive as the ligand could be made out but there was little evidence of complex formation, once again showing that the mass spectrometry analysis may indicate the presence of various NHC-metal complexes yet the quantity of the complex may be negligible.

Conclusion

The investigation of perimidine based NHC ligands and their associated complexes was primarily a synthetic project due to the nature of the results. The synthesis of two 2,2′-bipyridine NHC perimidine analogues were synthesised both with halide anions (**2.13** and **2.14**) and as tetrafluoroborate salts **2.15** and **2.16**. The synthesis of these NHC salts were obtained in good yields and the only substantial method development was replacing Cu_2O with CuI in the Ullmann coupling to give **2.12**. The NHC salts, **2.17**, **2.22** and **2.32** were not synthesised, but synthetic routes have been described that should result in the products.

The successful synthesis of **2.29** provides three different reactions conditions to achieve the tridentate perimidine NHC salt, **2.32**. The isolation of **2.29** was achieved in a good yield via the Ullmann coupling with **2.26**. Significant method development was required in order to realise a substantial yield of **2.26**. The difficultly associated with the synthesis of **2.26** was attributed to the high reactivity of the starting materials chloro ethylformate and 1,8-diaminonaphthalene a known 'proton sponge.'

The organometallic synthesis was carried out in order to obtain ruthenium complexes with the perimidine based NHC ligands and investigate their physical properties. The synthesis of a ruthenium-NHC complex has not been achieved before and the NHC ligands had not been synthesised before either. The transmetallation with silver proved to be an unsuccessful route to obtain a NHC-metal complex. This was partially attributed to the formation of **2.50** via an attempted formation of a Cu(I)-NHC complex, **2.49**. A postulated mechanism for the formation of **2.50** was described in scheme 2.16, where the nucleophilic attack of water displaced the copper from the complex as Cu^0. However no evidence further studies were carried out to determine if this mechanism is possible. The isolation of a urea like compound has not been reported before and may be another reason as to why the formation of perimidine based complexes are difficult to realise.

The synthesis of palladium-NHC complexes was also attempted with no success either. Mass spectrometry analysis suggested the possible complexes **2.54** and **2.55** may have formed in the attempted synthesis of **2.53** but they could not be isolated.

The future work of this chapter should include isolation of **2.50** on a large scale and to determine a mechanism for its formation. The synthesis of **2.32** via the synthetic routes described in scheme 2.7 and if the attempted complexation with ruthenium undergoes similar difficulties as previously described. There is another couple of potential routes to explore to obtain a perimidine NHC-ruthenium complex. These include the use of different ruthenium precursors such as $Ru(COD)Cl_2$ and avoiding silver and instead utilising strong dry bases as a source to deprotonate the NHC salt under rigorous air and moisture restrictive conditions.

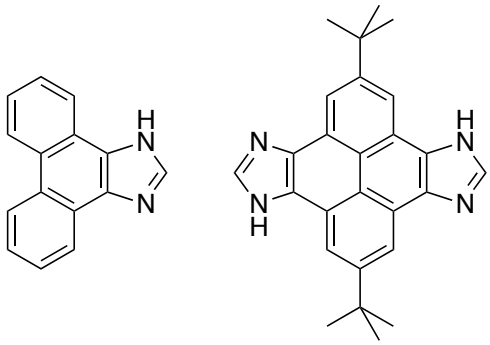
Chapter 3

Imidazole based NHC ligands

3. Imidazole based NHC ligands

Introduction

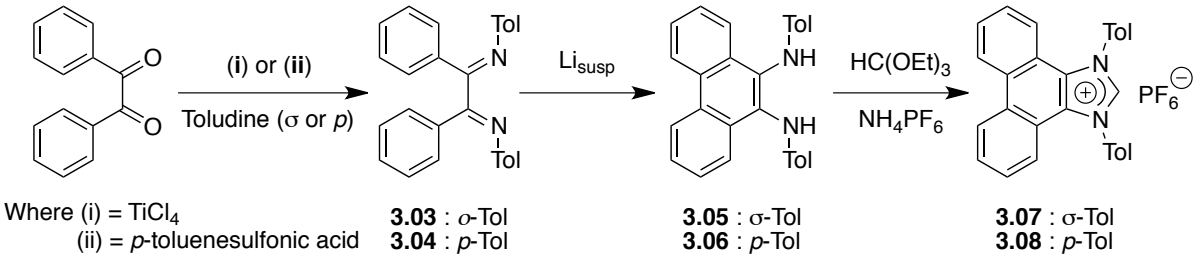
Imidazole based NHC ligands have been discussed extensively in the first chapter. However, an area that was only mentioned briefly was the larger aromatic core unit associated with an imidazole ring such as **3.01** and **3.02**, as shown in figure 3.1. The bis-imidazole pyrene moiety **3.02** has not been synthesised before, therefore giving a potential new NHC core unit.



3.01 **3.02**

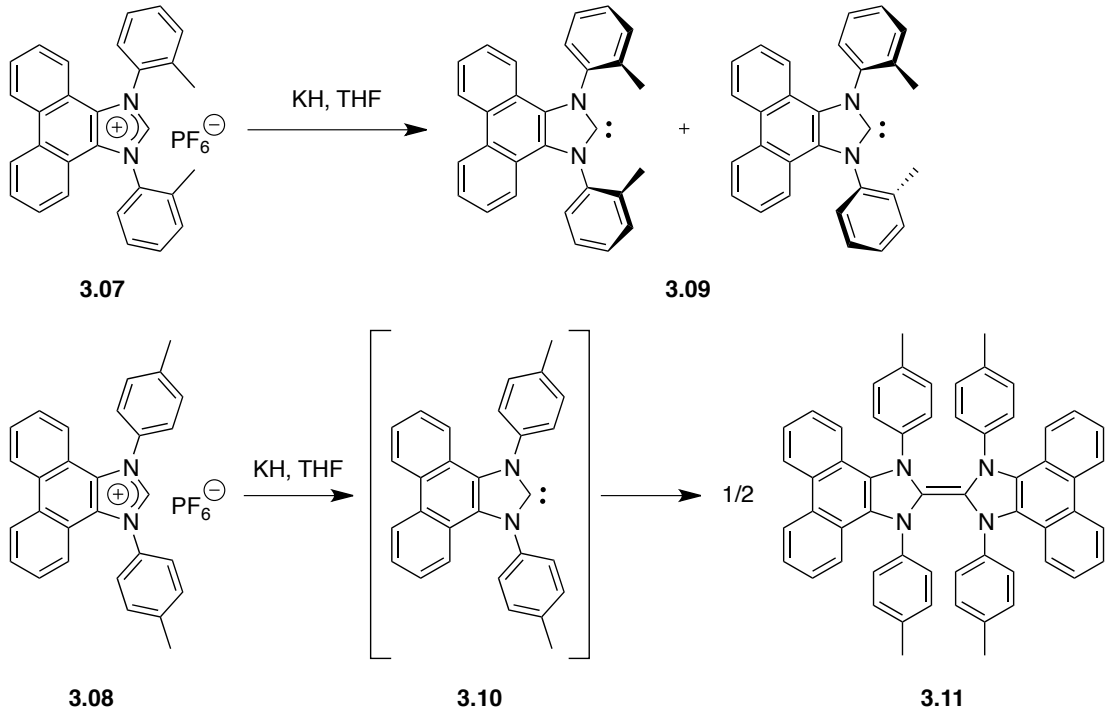
Figure 3.1: Phenanthrene (**3.01**) and pyrene (**3.02**) imidazole precursors to large potential NHC ligands.

There has been little research into these larger fused systems with only two publications of NHC ligands with the core unit of **3.01**. The research conducted by Tapu *et al*.[20] was highlighted in chapter one. Heinicke *et al*.[21] synthesised bis-toluene para and ortho derivatives **3.07** and **3.08**, respectively, following a different synthetic procedure compared to the work completed by Tapu *et al*. in 2008, as described in chapter one. Heinicke *et al*. were not able to achieve successful condensation of phenanthrenequinone and alkyl-amines to give the defined diimines, even under harsh reaction conditions (200 °C, 10 bar) to act as the precursor to give the desired NHC salts through a ring annulation reaction. However, the synthesis of benzil-bis-arylimines, **3.03** and **3.04** was achieved by condensation of benzil with *p*- and σ-toluidine and $TiCl_4$ or *p*-toluenesulfonic acid. Subsequent reductive cyclodehydrogenation of **3.03** and **3.04** resulted in the phenanthrene diamine compounds, **3.05** and **3.06** to which the cyclocondensation reaction with triethyl ortho formate resulted in the NHC salts **3.07** and **3.08**, as shown in scheme 3.1



Scheme 3.1: Synthetic route followed by Heinicke *et al*. to obtain the NHC salts, **3.07** and **3.08**.

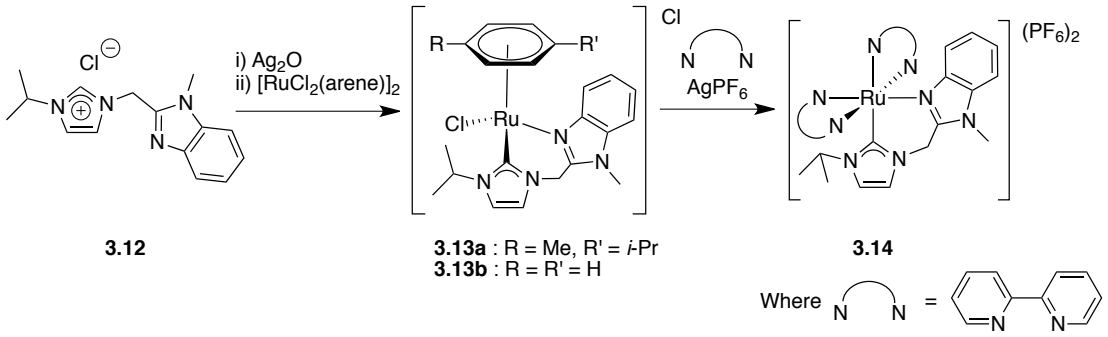
The NHC salts were able to form the free carbenes, **3.09** and **3.10** via deprotonation in THF with KH as the base, as shown in scheme 3.2. From this reaction two different results were obtained. The less hindered *p*-toluene derivative, **3.08** gave the entetramine, **3.11** rather than the free carbene **3.10**. Whereas the σ-toluene NHC salt, **3.07** was able to be isolated as the free carbene, **3.09** due to the greater steric bulk surronding the carbene carbon imposed by the methyl substituents. Silver complexes of both the σ- and *p*-toluene derivatives were obtained. However, the *p*-toluene NHC silver complex was obtained via reacting the NHC salt, **3.08** with Ag_2O due to the instability of the free carbene, whereas **3.07** is able to be deprotonated to give the free carbene, **3.09** and subsequently complexes with silver, palladium and rhodium were synthesised and isolated.



Scheme 3.2: Deprotonation of **3.07** and **3.08** giving the free carbene **3.09** and the entetramine **3.11**.

NHC ligands and ruthenium complexes have not been widely studied, with very little attention placed on bis-bipyridine ruthenium complexes with NHC ligands. In 2010 Albrecht *et al*. published the first NHC imidazolium ruthenium bis-bipyridine complex, **3.14**, as shown in scheme 3.3.[80] The

synthetic route to achieve this involved forming a silver complex first, and subsequent transmetallation to achieve ruthenium arene NHC complexes, **3.13a** and **3.13b**. The synthesis using the ruthenium arene complex was due to the lack of success with the transmetallation of the precursor silver NHC complex and $Ru(bpy)_2Cl_2$. The arene ancillary ligands of **3.13a** and **3.13b** can be exchanged with 2,2′-bipyridine and $AgPF_6$ displaces the chlorine counter anions, as shown in scheme 3.3. Albrecht *et al*. also completed the synthesis of ruthenium complexes with benzimidazole as the NHC ligand and with the same R-group substituents at the N1 and N3 positions compared to the NHC ligand **3.12**.



Scheme 3.3: The synthetic route to the first NHC imidazolium ruthenium bipyridine complex, **3.14**.

This chapter will describe the synthesis of various NHC salts with imidazole head groups, extended aromatic cores to the research described in chapter two substitution of the pyrid-2-yl functionality at the N1 position, as shown in figure 3.2. The NHC salts to be synthesised typically share a common feature similar to chapter two of a pyrid-2-yl substituent at the N1 position and various other alkyl groups at the N3 position. However, many synthetic challenges were met in the attempted synthesis of these NHC salts. There has been little attention placed on these 'extended' NHC salts and their associated ruthenium complexes, with no reported evidence of a ruthenium complex with the phenanthrene NHC salt and no synthesis of the potential NHC pyrene imidazole compound, **3.02** to date.

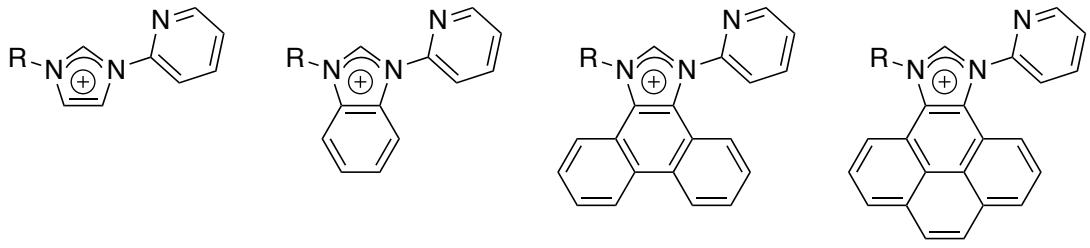
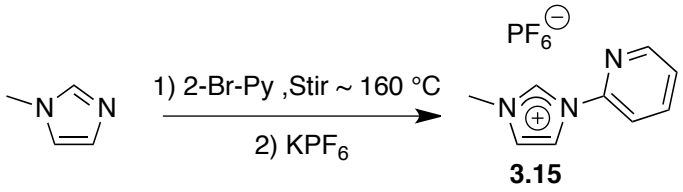


Figure 3.2: A general figure showing the extension of aromaticity of the NHC salts.

Ligand Synthesis

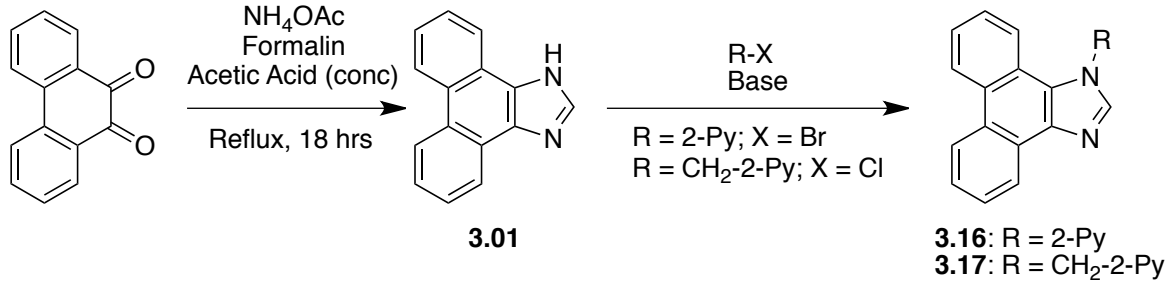
The imidazole NHC ligands followed a different synthetic route compared to the perimidine NHC ligands. The synthesis of an imidazole NHC salt began with the starting material 1-methyl-1*H*-imidazole and 2-bromo pyridine as shown in scheme 3.4.



Scheme 3.4: The synthetic route to obtain **3.15**.

The reaction ran for 21 hours at approximately 160 °C with 2-bromo pyridine as the solvent. Upon cooling to room temperature the reaction mixture was quenched with water and **3.15** was isolated via precitpitatation as a PF_6 salt. The reaction proceeded with a low yield (23.6%) and ^{1}H-NMR, mass spectrometry analysis supported the synthesis of the NHC salt **3.15**. [81]

However this research was focused on large fused imidazolae based NHC ligands. Therefore the phenanthrene core unit for imidazole based NHC ligands were studied following the procedures described earlier by Heinicke *et al*. and Tapu *et al*. Initially the synthetic route described by Tapu *et al*. was followed as it was perceived to be simpler. The general scheme of this route is shown below in scheme 3.5



Scheme 3.5: The synthetic route investigated to obtain the NHC salt precursor compounds, **3.16** and **3.17**.

The synthesis of **3.01** was achieved in a good yield (87.1%) after reflux of 9,10-phenanthraquinone in concentrated acetic acid with the reagents formaldehyde and NH_4OAc in a 4.5 fold and 20 fold excess, respectively.[20] The reaction was performed under an argon atmosphere. After the reaction ran for 18 hours at reflux the reaction mixture was cooled to room temperature and quenched with water and neutralised with ammonia. This caused a precipitate to form. The crude precipitate was filtered and

washed with water, acetone, DCM and Et_2O and allowed to dry. The precipitate was analysed by ^{1}H-NMR and mass spectrometry analysis confirming the synthesis of **3.01**.

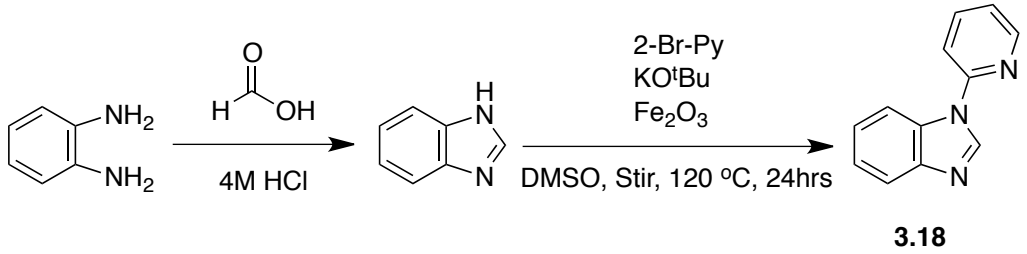
The synthesis of **3.16** could not be achieved. Many different conditions were attempted in order to realise the product, **3.16**. This initially began with Ullmann coupling that proved to be successful with the coupling of 1*H*-perimidine in chapter two. The reaction was monitored by TLC and ran for four days at 150 °C in DMSO with a catalytic amount of CuI (10 mol%), a slight excess (1.5 times) of 2-bromo pyridine and a two fold excess of K_2CO_3. Once the reaction had cooled to room temperature water and 15% ammonia were added. The reaction mixture was then set to stir at room temperature for one hour. DCM was then added and the organic fraction was isolated and dried with $MgSO_4$. The DCM was subsequently removed under vacuum giving an oily residue. This crude product was dried under a Hi-Vac system without any formation of a solid. Therefore Et_2O was added giving a precipitate that was isolated and both the precipitate and filtrate were analysed by ^{1}H-NMR showed the precipitate was the starting material **3.01**, while the filtrate was a mixture of undefinable products. Therefore in order to purify the filtrate column chromatography on silica with DCM as the eluent was performed, but the desired product, **3.16** could not be isolated from the reaction mixture.

Verma *et al*. showed that an Ullmann type coupling similar to the conditions described above worked for the reaction between benzoimidazole and 2-bromo-pyridine to give 1-(pyrid-2-yl)-benzoimidazole in a 98% yield.[82] The reaction conditions differed due to the KO^{t}Bu that was used as the base in place of K_2CO_3, the CuI mol% was decreased to 5% and the introduction of 5 mol% of benzotriazole was used to further activate the copper catalysed coupling reaction. The reaction was performed at 150 °C in DMSO under an argon atmosphere and moisture restrictive conditions whilst stirring for 18 hours. TLC analysis showed the disappearance of the starting material (**3.01**) and the crude product was isolated following the same procedure described before. However, upon analysis of the crude product via ^{1}H-NMR and mass spectrometry, this determined the isolated precipitate to be the starting material, **3.01** and the identity of the filtrate was inconclusive due to a range of unknown peaks in the aromatic region. Therefore column chromatography was performed but with no success, as the desired product, **3.16** could not be isolated. The disappearance of **3.01** via TLC analysis could be attributed to a complex intermediate of the reaction that either required may have required a longer reaction time.

Due to the failure of the Ullmann coupling reactions with **3.01** in the attempt to synthesise **3.16** the copper and benzotriazole sources were abandoned. Therefore the reaction was attempted again with **3.01**, KO^{t}Bu and 2-bromo pyridine in a slight excess in DMF at 110 °C for two days. After allowing the reaction mixture to cool to room temperature and removal of DMF by washing with water and DCM. The organic fraction was isolated, dried over $MgSO_4$ and removed under vacuum. The crude precipitate isolated proved to be the starting material **3.01** via ^{1}H-NMR. Although the filtrate again showed promise to be the desired product **3.16**, a pure sample could not be obtained via column chromatography. This stepwise addition of R-groups to **3.01** proved to be unsuccessful in yielding a

pure product in a significant yield. The use of a different catalyst and conditions would have to be employed in order to realise **3.16**.

Periasamy *et al*. described the N-arylation of benzimidazole with 2-bromo pyridine and catalytic Fe_2O_3 in 2012 to proceed in an excellent yield of 97%.[83] The reaction was performed in DMSO with KO^tBu, as the base and stirred at 120 °C for 24 hours in an open atmosphere. Therefore in order to test the validity of the reaction, the synthesis of **3.18** was completed following the procedure described shown in scheme 3.6.



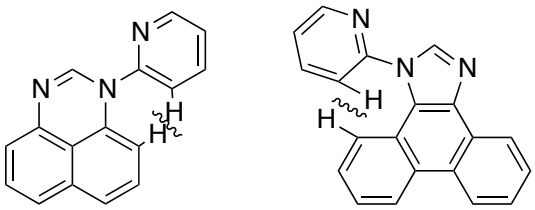
3.18

Scheme 3.6: The synthesis of benzimidazole and the subsequent N-arylation of benzimidazole with 2-bromo pyridine to give **3.18**.

In order to synthesise **3.18**, the precursor benzimidazole had to be made. This followed a similar ring annulation as described in the synthesis of 1*H*-perimidine in chapter two. *o*-phenylenediamine and formic acid were combined in a solution of 4M HCl and set to reflux for 24 hours. Upon cooling the reaction mixtrure to room temperature charcoal was added and filtered over celite. The filtrate was then basified with ammonia and the crude product was isolated with EtOAc. The organic fraction was dried over $MgSO_4$ and removed under vacuum. The crude product was washed with hexanes and the precipitate isolated proved to be the desired product benzimidazole via ^{1}H-NMR analysis. Benzimidaole was combined with 2-bromo pyridine, KO^tBu and a catalytic amount of Fe_2O_3. In DMSO and was set to stir at 120 °C. After 24 hours, the reaction was allowed to cool to room temperature and was quenched with water. The reaction mixture was then washed with EtOAc and the organic fraction was isolated, dried upon $MgSO_4$ and removed under vacuum. A yellow oil was isolated and from ^{1}H-NMR confirmed the synthesis of **3.18**. Therefore the reaction was repeated with **3.01** as the starting material in the attempted synthesis of **3.16**. The reaction was monitored by TLC on silica with DCM, after 72 hours of stirring at 120 °C there was no change in the products according to TLC analysis. Therefore the reaction was allowed to cool to room temperature and the reaction was quenched with water. The organic fraction was then isolated with DCM and washed with water and brine, dried upon $MgSO_4$ and the solvent removed under vacuum. This resulted in an oily residue which was stirred with Et_2O for an hour and a precipitate was isolated. The ^{1}H-NMR analysis showed the crude precipitate was the starting material **3.01**. Subsequent analysis of the filtrate showed an impure sample that could include the desired product, **3.16**. However, purification of this crude product was not performed due to the low yield isolated from the reaction mixture. This could be a

feasible route to obtain **3.16**, but the reaction may need to be performed for a longer duration or excess catalyst may be required. Nonetheless method development is needed in order to obtain **3.16**

An explanation as to why the synthesis of **3.16** proved to be difficult could be the steric hinderance of the H3 proton of the pyridine ring and its adjacent proton of the phenanthrene core, as shown in figure 3.3. Comparing **3.16** to **2.12** shows that there is a greater steric hinderence between the two protons of **3.16** explaining why the synthesis of **2.12** could be synthesised, whereas **3.16** could not be produced.



2.12 **3.16**

Figure 3.3: Highlighting the difference in steric repulsion between **2.12** and **3.16**.

The compound **3.17** was investigated as it potentially provided a similar bidentate functionalilty compared to **3.16**. However, different synthetic reactions differentiate the two compounds. The synthesis of **3.17** was readily achieved via the following reaction conditions, where **3.01** was reacted with an excess (1.2 times) of 2-picolyl chloride hydrochloride in the presence of K_2CO_3 (2.5 times excess) in DMF under an argon atmosphere and moisture restrictive conditions. The reaction stirred for 72 hours at 120 °C and upon cooling to room temperature the crude reaction mixture was diluted with water and DCM. The organic fraction was isolated and dried upon $MgSO_4$ and subsequently removed under vacuum to give the product **3.17** with no further purification required. This reaction to give **3.17** proceeded with ease compared to the attempted synthesis of **3.16**. This was attributed to the different type of reactions to give the desired product and the reduced steric hinderence on the phenanthrene core imposed by the 2-picolyl group. The synthesis of **3.16** is an S_NAr reaction whereas **3.17** undergoes an S_N2 type reaction. The ^{1}H-NMR of **3.17** was measured and shown below in figure 3.4. The characteristic singlet peak of the H2 proton was measured at 8.47 ppm and the ethyl peak was at 6.10 ppm. The ^{13}C-NMR showed the C2 peak at 144.12 ppm.

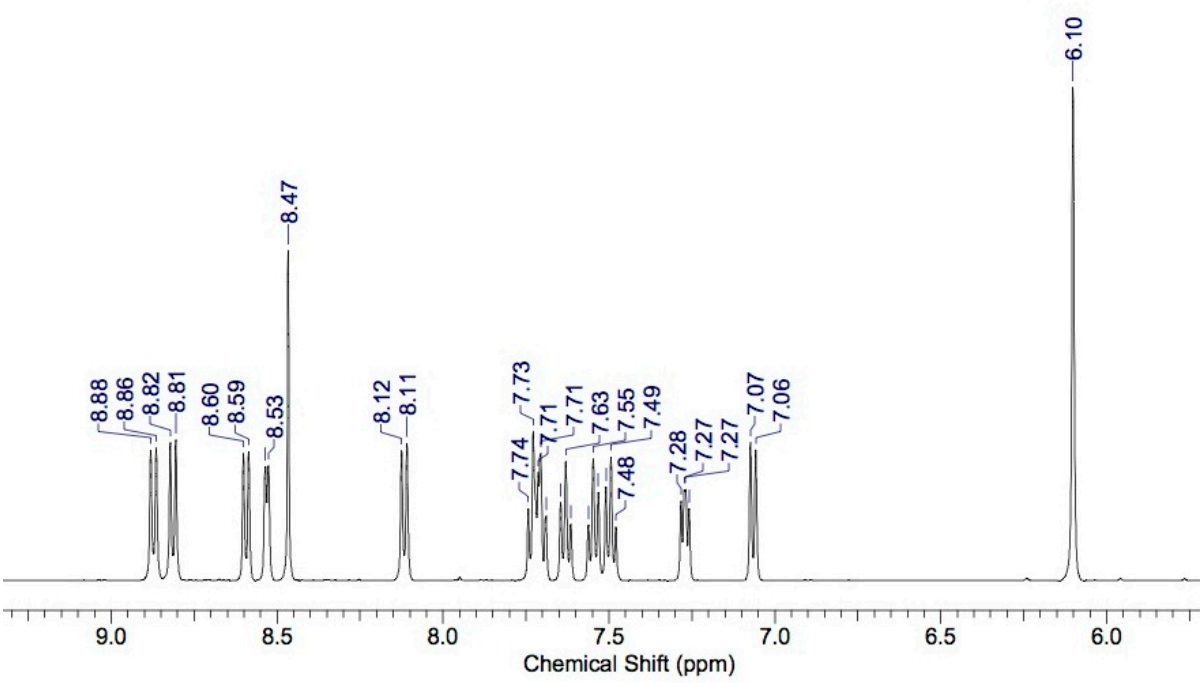
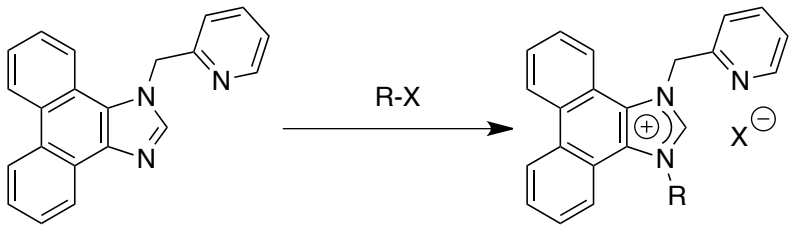


Figure 3.4: Aromatic region of **3.17** in DMSO-d_6.

The synthesis of NHC salts, **3.19** and **3.20** could be achieved following the synthesis of **3.17**. Different synthetic conditions resulted in the formation of these NHC salts with a general scheme for their formation shown in scheme 3.7.



3.17

3.19: R = Bn; X = Br
3.20: R = Me; X = I

Scheme 3.7: General route to obtain the NHC salts, **3.19** and **3.20**.

The synthesis of **3.19** was completed first by reacting **3.17** in a DCM:MeOH solution (4:1, respectively) with benzyl bromide (1.5 times excess) at reflux for 48 hours. Upon removal of the solvent mixture under vacuum, analysis of the crude product showed the existence of **3.19** via mass spectrometry analysis. Therefore column chromatography was performed on alumina with DCM:MeOH (80:20) as the solvent mixture. The starting material, **3.17** was able to be removed as it was the first fraction to be isolated, the other fractions showed the final product **3.19** and slow evaporation of the solvent mixture allowed single crystals to be grown and subsequently a crystal structure to be determined of the NHC salt **3.19** via X-ray diffraction studies. The overall yield of the reaction was determined to be

very low. Therefore further method development is required in order to realise a useful amount of product so complexation reactions can be attempted. The ^{1}H-NMR in DMSO-d_6 showed the characteristic H2 singlet peak at 10.01 ppm and the ^{13}C-NMR measured the C2 carbon at 143.54 ppm.

The synthesis of **3.20** was achieved by completing the reaction in a sealed tube vessel with methyl iodide as the solvent and **3.17** as the starting material. The reaction was stirred at 80 °C for 18 hours and upon cooling to room temperature the methyl iodide was removed under vacuum resulting a fine grey precipitate. Methanol was added to the grey precipitate giving an orange solution and a pale yellow precipitate. The pale yellow precipitate proved to be the NHC salt **3.20** and was isolated in a moderate yield (30.1%) with no further purification required. The ^{1}H-NMR in DMSO-d_6 is shown in figure 3.5 with the characteristic H2 singlet peak at 9.86 ppm and the ^{13}C-NMR showed the C2 carbon at 142.85 ppm. The synthesis of the benzyl derivative, **3.20** could not be achieved under these conditions, as the removal of benzyl bromide under vacuum is difficult due to its high boiling point (198 °C). The tetrafluoroborate salt derivative of **3.20** was not prepared because of time restraints.

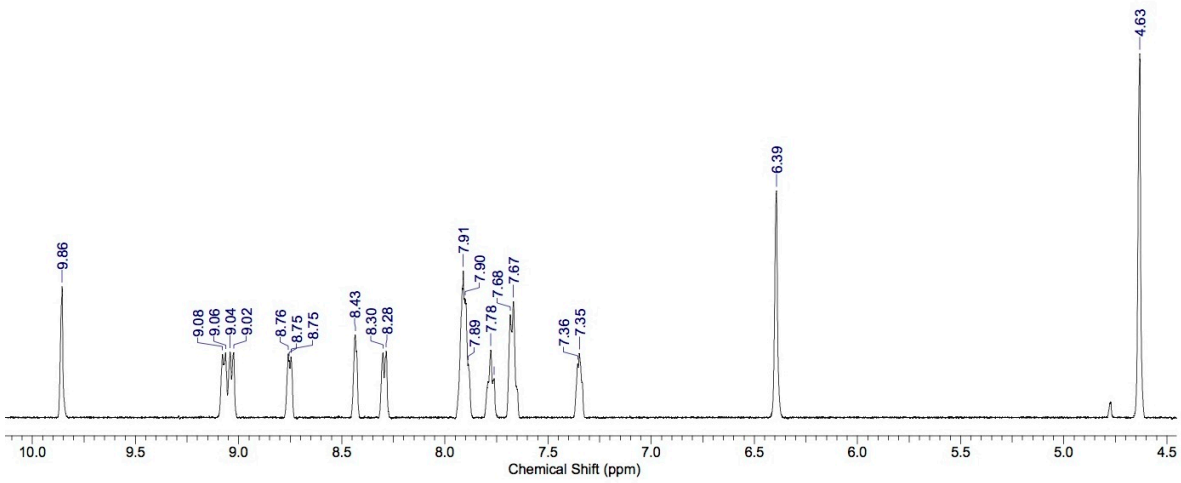
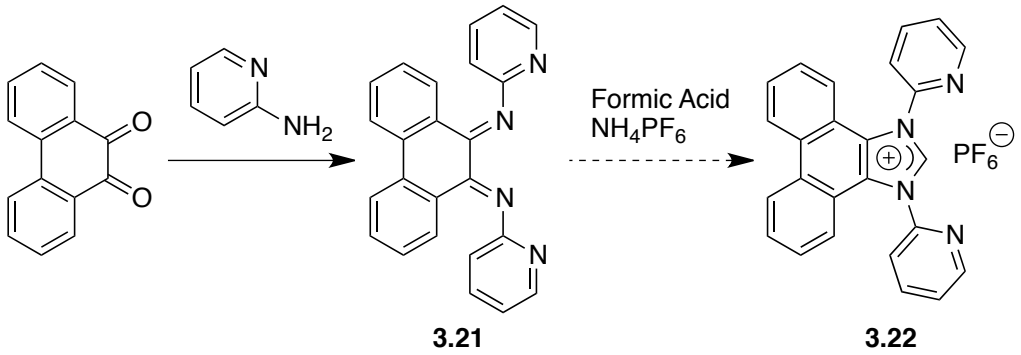


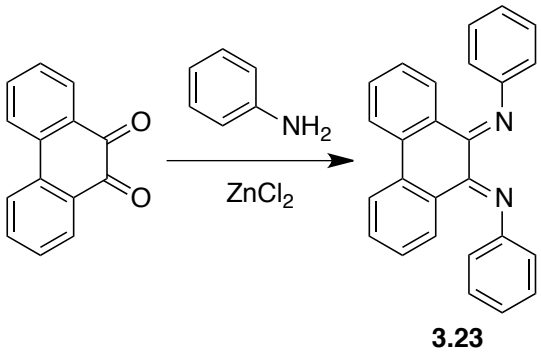
Figure 3.5: The ^{1}H-NMR of **3.20** in DMSO-d_6

The synthesis of **3.16** could not be achieved via the stepwise addition of 2-bromo pyridine to **3.01**. Therefore the synthetic strategy described earlier that Heinicke *et al*. utilised offered another potential route to achieve a pyrid-2-yl group at the N1 position with the added advantage of preparing the di-pyrid-2-yl functionality into the molecule, **3.22**, as shown in scheme 3.8.



Scheme 3.8: Synthetic route attempted to achieve **3.21** and the NHC salt **3.22**.

Initially the synthesis of **3.21** was attempted by reacting 9,10-phenanthraquinone with 2-amino pyridine (six times excess) and with a catalytic amount of *p*-toluenesulfonic acid in a toluene solution. The reaction was conducted at reflux with a Dean Stark apparatus and monitored by TLC. The reaction ran for a total of 48 hours with another six-fold excess of 2-amino pyridine added to the crude reaction mixture after 24 hours. After allowing the reaction to cool to room temperature the crude product was washed with toluene and filtered. The precipitate isolated was excess 2-amino pyridine and the toluene filtrate was removed under vacuum. The filtrate proved to be 9,10-phrenanthraquinone via ^{1}H-NMR analysis. The reaction conditions were deemed to mild, as the formation of the product **3.21** was not observed. The nucleophilicity of 2-amino pyridine was also questioned due to the electron withdrawing properties of the pyridine ring. Therefore aniline was used in place of 2-amino pyridine in order to establish a methodology for the synthesis of compounds similar in structure to **3.21**. The synthetic strategy employed was to use $ZnCl_2$ as a Lewis acid catalyst in order to promote the formation of the imine species, **3.23** as shown in scheme 3.9.

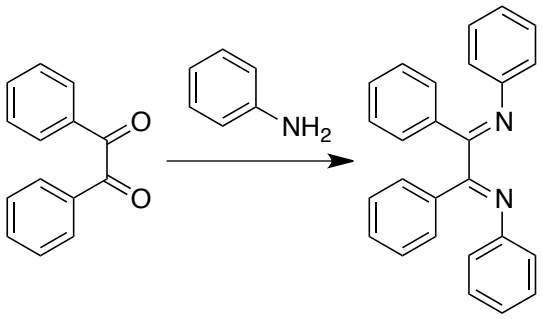


Scheme 3.9: Synthetic route to obtain **3.23** utilising $ZnCl_2$ as a lewis acid.

The attempted synthesis of **3.23** was performed in an open atmosphere with aniline used as the solvent (15x excess) and one equivalent of $ZnCl_2$. The reaction ran for 18 hours at ~165 °C and resulted in a black crude precipitate. After allowing the reaction to cool down to room temperature the crude product was stirred with Et_2O giving an orange solution that was isolated from the black precipitate. The Et_2O filtrate was subsequently removed under vacuum and upon analysis of the

crude product via ^{1}H-NMR and mass spectrometry analysis showed numerous products were present in none of which could be assigned by mass or data from the ^{1}H-NMR. Therefore column chromatography on silica with DCM was performed yet the products isolated proved to be impure as well and mass spectrometry and ^{1}H-NMR analysis gave no further information to the identity of the products.

The failure to synthesise **3.23** was attributed to the $ZnCl_2$, as upon its addition to the reaction mixture resulted in a viscous precipitate that prevented stirring of the reaction mixture. This was believed to prevent the reaction from going to completion, as the reaction mixture was unable to stir continuously due to the viscosity of the precipitate/solution formed. Therefore the reaction conditions were slightly modified so the $ZnCl_2$ was not used in the reaction to give **3.23**. The following reaction was performed neat, where an excess of aniline (20 times) was used as the solvent in the presence of 9,10-phenanthraquinone and stirring the reaction mixture at ~160 °C for 48 hours. The reaction was monitored by TLC analysis and after allowing to cool to room temperature the reaction mixture was quenched with 2M HCl and washed with Et_2O. This crude solution was allowed to stir for an hour and the organic and aqueous fractions were isolated. The Et_2O fraction was washed with a significant amount of 2M HCl to remove the aniline in the crude product. The Et_2O was dried with $MgSO_4$ and removed under vacuum. The crude product isolated proved to be unidentifiable again via ^{1}H-NMR and mass spectrometry analysis with no evidence for the starting material, 9,10-phenanthraquinone or potential intermediates from the crude product isolated. Therefore due to the unsuccessful synthesis of **3.23** with under harsh conditions further method development was required. The starting material 9,10-phenanthraquinone was exchanged for benzil giving the product **3.24** as shown in scheme 3.10.



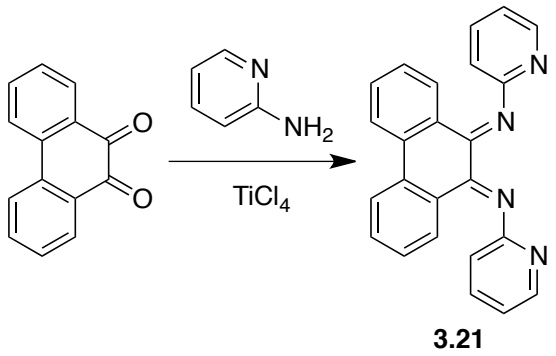
3.24

Scheme 3.10: The synthetic scheme to obtain **3.24**.

The reaction to give **3.24** was performed under the same conditions as described earlier with a neat reaction performed initially. Benzil was stirred in a hot solution of aniline at 160 °C for four hours. The time of the reaction was modified as it was suspected that stirring over an extended period of time was leading to the degradation of the desired product, giving various side products. This reaction was allowed to cool to room temperature and the crude product was stirred with Et_2O and

2M HCl as described earlier. This reaction potentially gave the desired product **3.24**, but in an insignificant yield as determined by the integrals of the ^{1}H-NMR. Therefore the addition of the lewis acid to the reaction conditions was attempted again in order to force the reaction. The presence of one equivalent of $ZnCl_2$ with ~40 times excess of aniline (in order to prevent the reaction forming a viscous solution) under a continous flow of argon (to protect the reaction mixture from oxygen and water) and was run for five hours at ~160 °C. The reaction mixture was subsequently cooled to room temperature and quenched with 2M HCl and Et_2O was added. The crude product was filtered to give a precipitate that was isolated and analysed by ^{1}H-NMR and mass spectrometry giving evidence of a protonated aniline salt. The filtrate fraction that was isolated showed the presence of the starting material, benzil and aniline as the only two products from TLC analysis. This shows that the $ZnCl_2$ was not aiding the reaction to give the desired product in both the benzil and phenanthrene examples described.

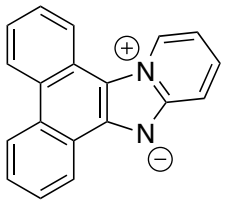
Shavyrin *et al*. described the synthesis of phenanthrene diimines with aryl substituents in moderate yields by using $TiCl_4$ as a lewis acid to catalyse their formation.[84] Due the exhaustion of methods to obtain a diimine compound with either a benzil or phenanthranene core unit without using the strong lewis acid $TiCl_4$, this synthetic route was justified. Therefore the synthesis of **3.1** was attempted in the presence of $TiCl_4$, as shown in scheme 3.11.



Scheme 3.11: The use of $TiCl_4$ to give the desired product, **3.21**.

The synthesis of **3.21** was attempted due to the greater interest of the potential NHC ligand that would result from the precursor (**3.21**) compared to the compounds **3.23** and **3.24** and their associated potential NHC ligands. The 9,10-phenanthraquinone and 2-amino pyridine (four times excess) were combined in a two-necked round bottom flask with toluene as the solvent. To this solution $TiCl_4$ was added dropwise and was set to reflux for 18 hours. This method is slightly modified from the procedure described by Shavyrin *et al*. where their reactions were stirred at ambient temperature for 10-20 hours compared to reflux. The procedure was attempted at ambient temperature. However, the products isolated could not be determined, as mass spectrometry and ^{1}H-NMR data was inconclusive with poor yields overall. Undertaking the reaction to give **3.21** with $TiCl_4$ at reflux resulted in the excess 2-amino pyridine present forming a hard solid upon the addition of the $TiCl_4$. This was a

contributing factor as to why the reaction did not proceed to give **3.21**, as it potentially prevented the aniline from participating in the reaction. However, water was added to the reaction mixture to quench the reaction and the toluene fraction was isolated and removed under vacuum. This was then further extracted with DCM and washed with water. The DCM fraction was subsequently dried upon $MgSO_4$ giving a crude product. However mass spectrometry analysis did not support the synthesis of **3.21**. The crude product was stirred with Et_2O giving a precipitate that was isolated pure and proved to be the side product **3.25** (shown in figure 3.6) due to mass spectrometry and ^{1}H-NMR analysis.

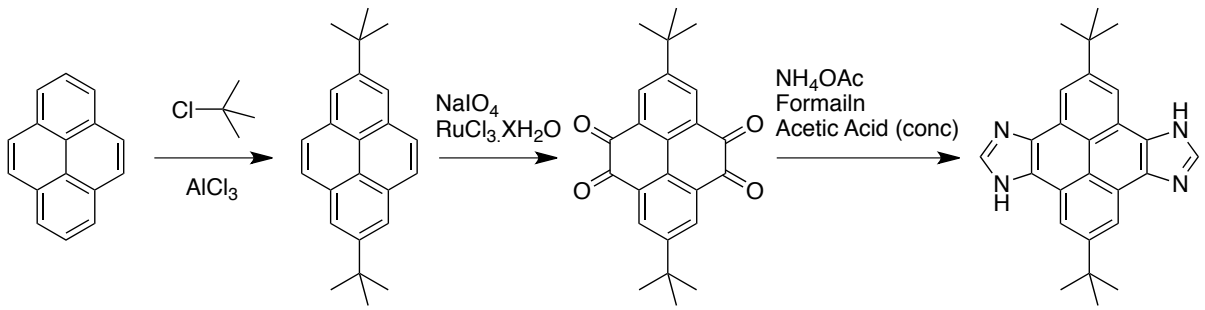


3.25

Figure 3.6: Side product, **3.25** isolated from the attempted synthesis of **3.21**.

This side product may suggest that the reaction conditions are too harsh as the elimination of the hydroxy group from the intermidiate product aided by the presence of $TiCl_4$ may suggest a mechanism for the formation of this compound. The isolation of **3.25** is a positive result in the attempted synthesis of **3.20** as this gave evidence for the sucessful imine condensation on 9,10-phenanthraquinone with 2-amino pyridine. Therefore with further method development the desired diimine species, **3.20** could be realised and subsequent formation of the NHC salt, **3.22**. However this method development was not attempted due to time constraints.

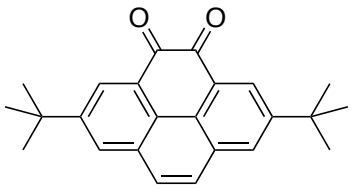
The synthesis of imidazole NHC salts with a pyrene core unit was also investigated. The pyrene core unit with imidazole head groups (**3.02**) has not been synthesised before and represents a new NHC moiety to be studied. The reason for investigating pyrene as a core unit is due to the luminescent properties associated with pyrene and its derivatives due to the large delocalistion of electrons over the molecule. The general synthetic strategy to realise **3.02** is shown in scheme 3.12.



3.26 **3.27** **3.02**

Scheme 3.12: The synthetic route to obtain a di-imidazole pyrene NHC precursor, **3.02**.

The synthesis of **3.26** was completed to counter potential insolubility issues that are associated with large extended aromatic units such as pyrene. The reaction followed a modified procedure described by Mateo-Alonso *et al*. and was achieved in a good yield (77.7%) after reacting pyrene with ^{t}BuCl and $AlCl_3$.[85] The product, **3.26** was confirmed due to supporting evidence from ^{1}H-NMR data and HRMS analysis. Harris *et al*. described a procedure for the oxidation of **3.26** to give **3.27**, this reaction was completed under the same conditions as described resulting in a relatively low yield (27.1%) compared to Harris *et al*. reported yield of 47%.[86] The synthesis was completed by combining **3.26**, $NaIO_4$ and $RuCl_3.XH_2O$ in a schlenk flask and performing the reaction for 18 hours at ~40 °C under an argon atmosphere. Upon cooling to room temperature water was added to quench the reaction and the crude product was isolated with DCM and washed with water. The organic fraction was subsequently dried over $MgSO_4$ and the solvent was removed under vacuum resulting in a dark green/black precipitate. A silica plug was eluted with EtOAc:Hexanes; 5:2 to remove the green/black residue from the crude product. Column chromatography on silica with DCM as the eluent was used to isolate the pure product **3.27**. The synthesis of **3.27** was confirmed due to mass spectrometry and ^{1}H-NMR analysis. The synthesis of the dione pyrene compound **3.28** (as shown in figure 3.7) was also completed under similar reaction conditions that were described for the synthesis of **3.27**. The only difference in the reaction conditions were the reaction temperature that it was conducted at room temperature rather than ~40 °C and ~ half the molar eqivalents of $NaIO_4$ was required to give the **3.28**. However a ^{1}H-NMR of the crude product showed the presence of **3.26** in an approxiamte 50:50 ratio of **3.27**:**3.28**, respectively determined from the integration of the ^{1}H-NMR peaks. The purification of **3.28** was not completed due to time constraints.



3.28

Figure 3.7: The dione pyrene compound, **3.28**, that was not successfully isolated.

The synthesis of **3.02** proceeded in a quantitative yield via the same reaction conditions described to give the product **3.01**. However, the reaction was run for two days compared to one resulting in a pure product. This is a new compound and was therefore fully characterised and the ^{1}H-NMR of **3.02** shown below in figure 3.8.

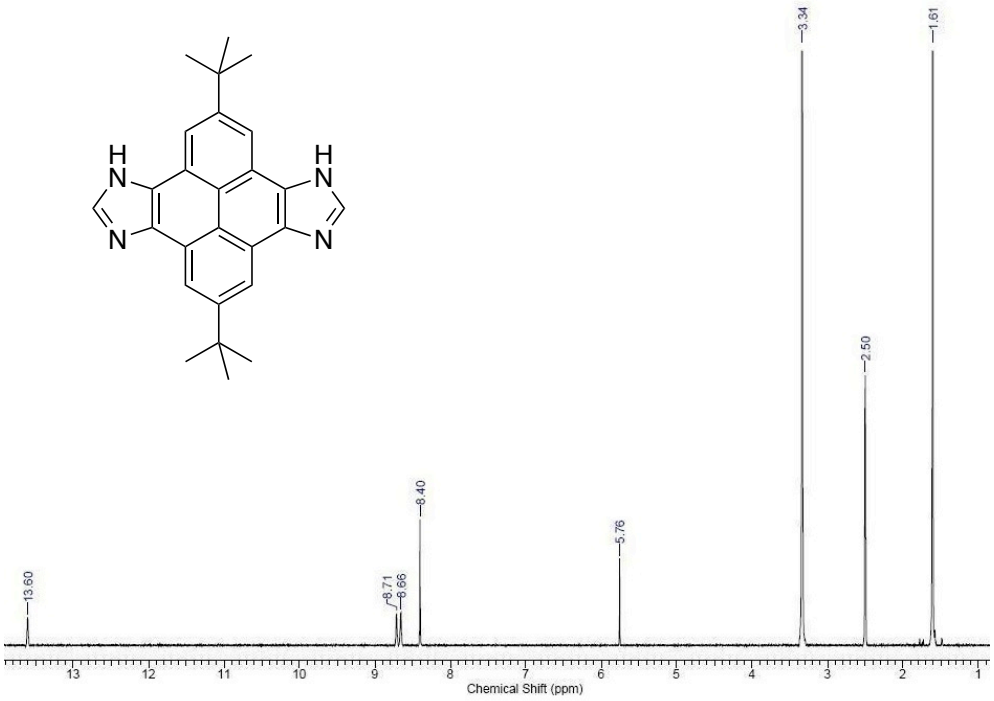
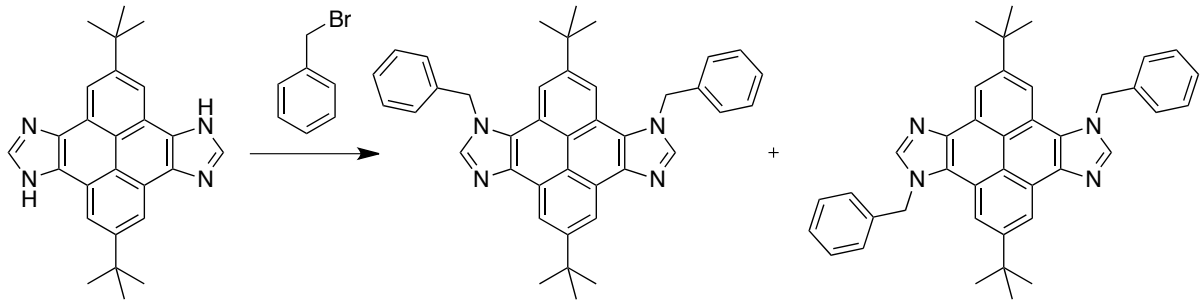


Figure 3. 8: The ^{1}H-NMR of the di-imidazole pyrene compound, **3.02** in DMSO-d_6.

There were two synthetic strategies investigate in order to obtain pyrene NHC salts. The first synthetic route was the stepwise addition of benzyl groups to **3.02** as shown in scheme 3.13. The reaction conditions followed a modified procedure described by Salvio *et al*. in 2011 where 1*H*-imidazole was reacted with benzyl bromide at reflux in MeCN in the presence of K_2CO_3 over 30 mins to give 1-benzyl-1*H*-imidizaole resulting with a good yield (80%).[87] The reaction was conducted over 48 hours due to the two equivalents of benzyl bromide required for the di substitution reaction to proceed.



Scheme 3.13: Synthesis of di benzyl NHC precursors, **3.29** and **3.30**.

The reaction was monitored by TLC on silica with EtOAc as the eluent until it showed the disappearance of the starting material, **3.02**. The precipitate produced from the reaction was isolated and the MeCN from the filtrate solution was removed under vacuum. Mass spectrometry analysis of

the crude product showed the presence of mono-, di-, (**3.29** and **3.30**, respectively) and tetra, benzyl derivatives as well as the starting material, **3.02**. However, ^{1}H-NMR confirmed the di-benzyl species, **3.29** and **3.30** as the major products from the reaction in a 3:1 ratio with one another, as shown in figure 3.9. The ^{1}H-NMR also shows remaining starting material, **3.02** is present in the crude sample with the H2 proton measured at 8.54 ppm and the H2 proton of **3.29** and **3.30** were measured further downfied at 8.84 and 8.75 ppm in DMSO-d_6.

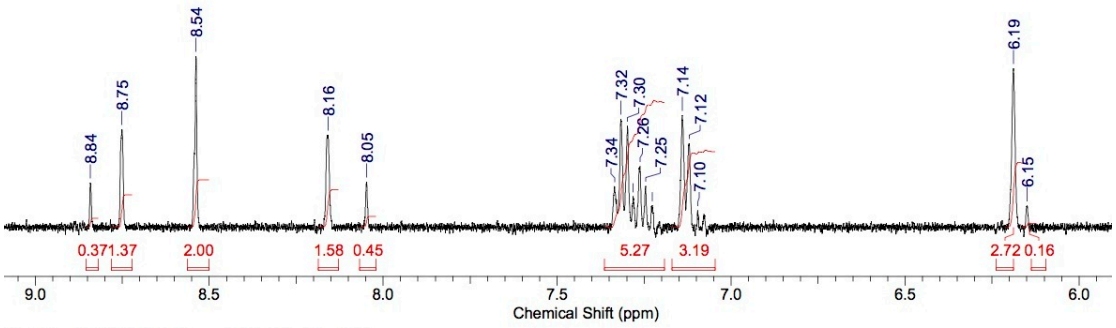
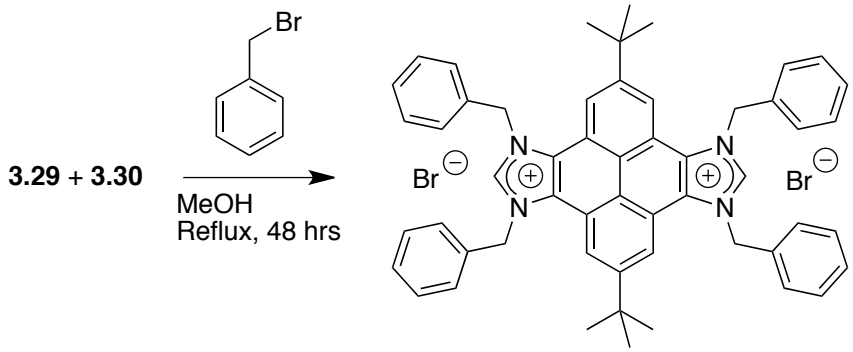


Figure 3.9: The ^{1}H-NMR of **3.29** and **3.30** isolated as the crude product in DMSO-d_6.

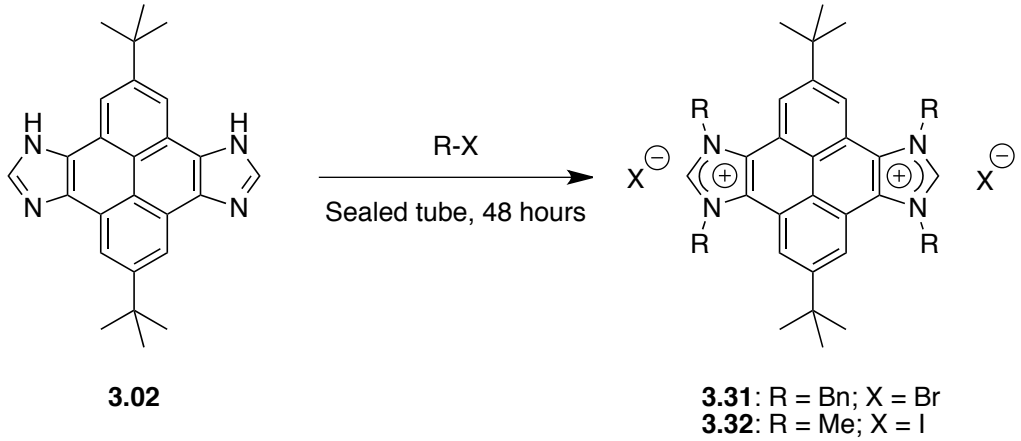
Attempts to isolate the two constitutional isomers via recrystallisations with MeCN failed and column chromatography on silica with EtOAc was also unsuccessful. The synthesis of the di-benzyl pyrene derivatives was not attempted again, but in the synthetic route to an NHC salt these products were only an intermediate. The advantage of isolating **3.29** and **3.30** could lead to NHC salts with different R group alkyl substituents at the N3 position and investigations into the different enantiomers and if they would exhibit similar or different the structural properties of their subsequent NHC-complexes. Therefore if this structural difference were significant does that translate to different physical properties? However, as the initial goal is to synthesise tetra alkyl NHC salts of **3.02** the crude product isolated of **3.29** and **3.30** was set to reflux with an excess of bromo benzene in MeOH for 48 hours, as shown in scheme 3.14. Upon removal of the MeOH, analysis of the crude product showed no evidence of **3.31**.



3.31

Scheme 3.14: Attempted synthesis of tetra benzyl NHC salt, **3.31**.

The synthesis of the tetra alkyl pyrene NHC salts was then attempted in a single step reaction, rather than isolation of the di-alkyl pyrene imidazole compounds due to the difficulty in purification. Therefore the synthetic procedure described for the synthesis of **3.19** was utilised in an attempt to obtain the NHC salts **3.31** and **3.32**, as shown in scheme 3.14.



3.02

3.31: R = Bn; X = Br
3.32: R = Me; X = I

Scheme 3.15: Attempted synthesis of tetra alkylimidazole pyrene NHC salts, **3.31** and **3.32**.

Reacting **3.02** with the alkyl halide as the solvent began the attempted synthesis of **3.31** and **3.32** in a sealed tube vessel for 48 hours. The two reactions were performed at slightly different temperatures due to the different volatility of the alkyl halides as solvents where the reaction to give **3.31** was run at 60 °C in a sealed vessel. The reaction to give **3.32** was performed at a slightly elevated temperature of 80 °C. The crude product, **3.31** was difficult to isolate due to the high boiling point of benzyl bromide (198 °C). Therefore the reaction mixture was washed with excess EtOAc as the product **3.31** was suspected to be insoluble in the organic solvent. Upon analysis of the precipitate remaining after its washes with ethyl acetate, mass spectrometry gave no evidence for the formation of the product, **3.31** and the resulting peaks could not be identified. ^{1}H-NMR data also gave inconclusive evidence to what was present in the crude product and time constraints prevented purification of the crude material in order to establish what had been synthesised. The reaction to give **3.32** was allowed to cool to room temperature, and the methyl iodide was removed under vacuum. The crude product of **3.32** was analysed by mass spectrometry giving evidence for the formation of the product as the correct mass could be observed. However, ^{1}H-NMR analysis did not support that the isolated product was pure. Therefore several attempts at recrystallisations with MeOH were made, but the pure product could not be isolated and time constraints prevented further purification.

Crystal Structures of NHC salts.

The crystal structure of **3.19** was obtained from the single crystals that were grown via slow evaporation of a DCM/MeOH solution, 4:1, respectively. The NHC salt crystallised in the monoclinic space group C2/*c*, with one molecule of the imidazolium salt and its associated counter anion, bromine and a water molecule disordered over four positions. The asymmetric unit is shown in figure 3.10.

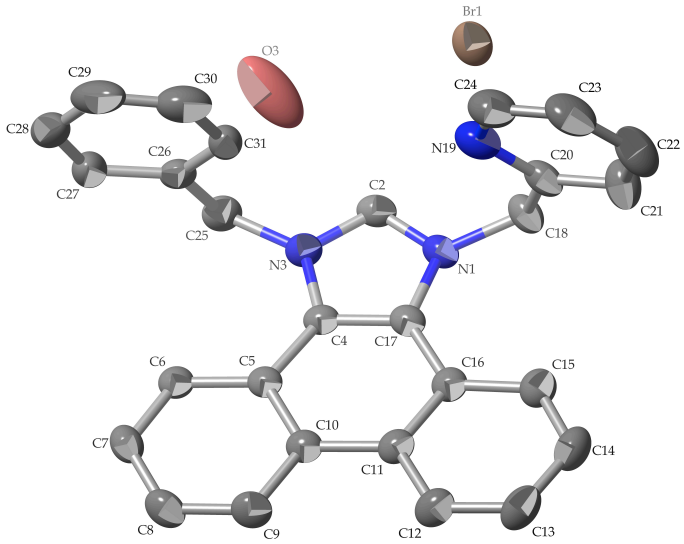


Figure 3.10: The asymmetric unit of **3.18** with a numerical assignment with one position of the water molecule only shown for clarity.

The bond distances of the two nitrogen atoms adjacent to the C2 atom are 1.330(3) Å and 1.327(3) Å for N1 and N3, respectively. Heinicke *et al*. reported a crystal structure of a similar ligand as a di-NHC-Ag complex. The bond distances between the C2 atom and the respective nitrogen atoms (N1 and N2) were 1.356 (2) Å and 1.353(2) Å.[21] The angle of the pyrindine ring to the central imidazole ring was 99.07(5)°, and the phenyl ring attached to the C25 atom to the same central imidazole ring had an angle of 96.48(5)°. The crystal packing of **3.19** is dominated by face-face π-π interactions between the aryl groups of the NHC salt. The phenyl substituents have π-π interactions with a counterpart ring on an adjacent molecule, as shown in figure 3.11(a).

(**a**) (**b**)

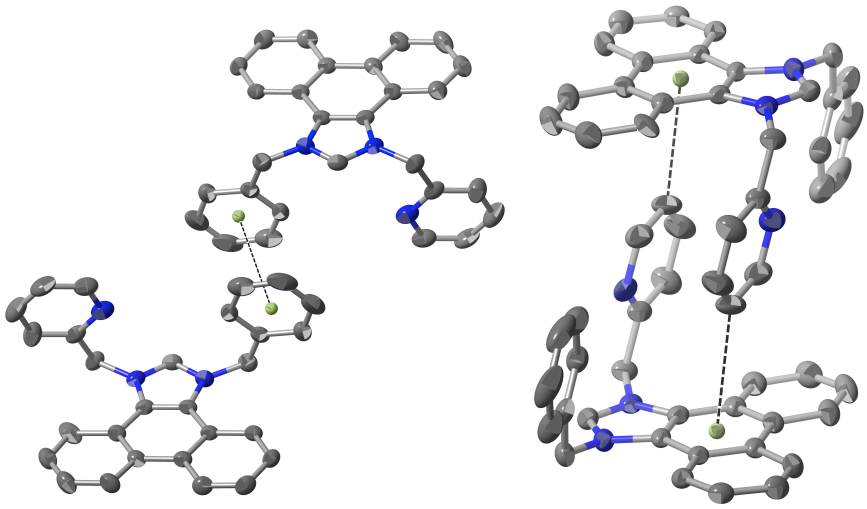


Figure 3.11: Intermolecular interactions of the R group substituents of **3.18**, (a), vv interactions of the benzyl substituents; (b), edge-face interactions between the pyridine ring and the central benzene ring of the phenanthrene moiety.

The face-face π-π interactions of the two phenyl subtituents (3.10a) have a typical plane-plane shift distance of 1.468(6) Å and a plane-plane centroid distance of 3.440(2) Å. The pyridine rings also exhibit edge-face interactions with the adjacent central ring of the phenanthrene core as shown in figure 3.10(b). The edge-face interaction distance was measured between the C23 atom and the calculated centroid of the central ring in the phenanthrene core resulting in a distance of 3.412(4) Å. The imidazole-fused backbone of the NHC salt, **3.19** exhibts face-face π-π interactions with the imidazole head group as shown in figure 3.12(a) and figure 3.12(b).

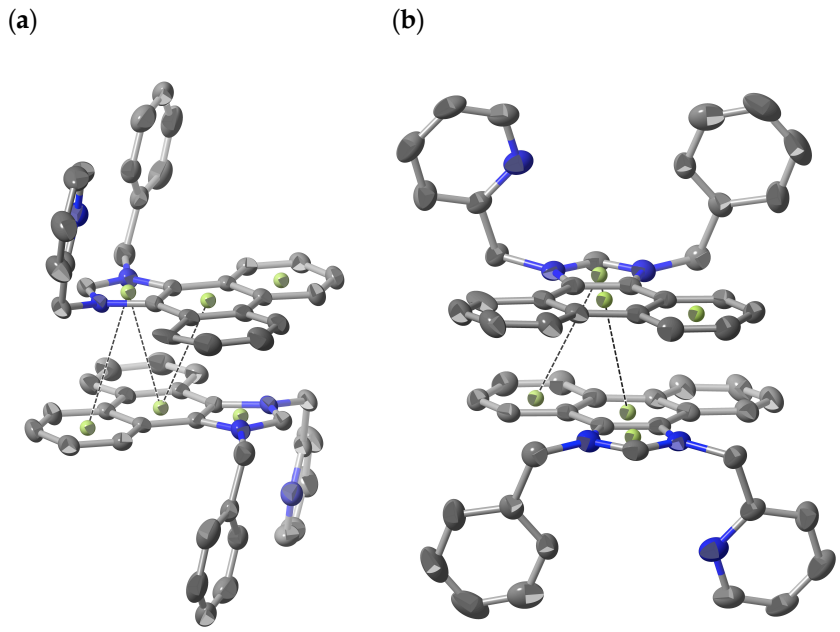
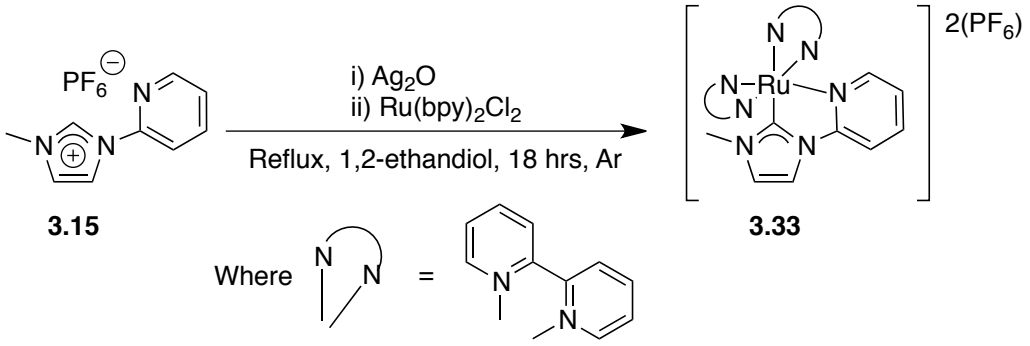


Figure 3.11: The π-π interactions of the fused backbone of **3.18**.

The imidazole ring and the central ring show π-π interactions with a plane-plane angle of approxiamatly 0°, plane-centroid distance 3.281(4) Å and a plane shift distance of 0.938(11) Å. The imidazole ring also shows π-π interactions with one phenyl ring of the phenanthrene core (C11,C12,C13,C14,C15,C16) rather than the other, with a of plane-plane angle 1.448(2)°, plane-plane centroid distance of 3.264(4) Å and a plane-plane shift distance of 1.608 (8) Å. This results in the NHC salts, 3.19 stacking slightly offset down the molecule due to π-π interactions between the imidazole ring and the central ring and offset across the molecule due to the π-π interactions with the imidazole ring and the phenyl ring (C11,C12,C13,C14,C15,C16) of the phenanthrene core unit.

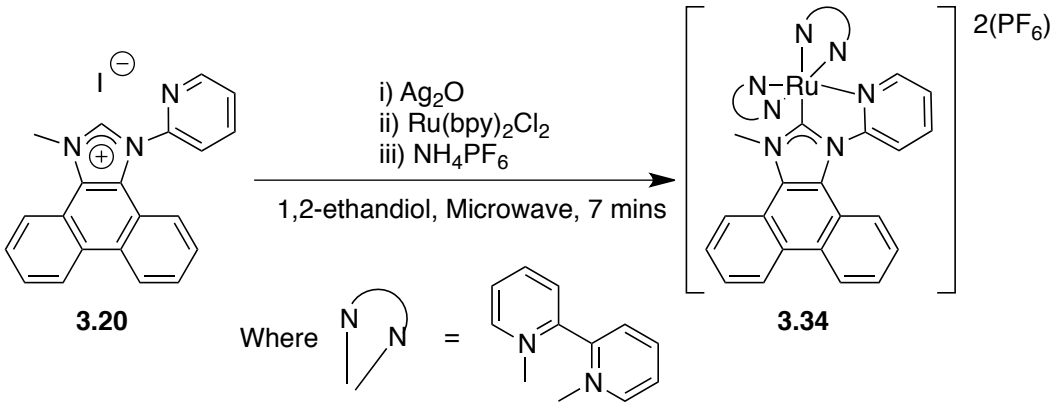
Synthesis of NHC complexes

The synthesis of NHC-ruthenium complexes with 2,2'-bipyridine ancillary ligands was the objective of this investigation. However due to time constraints and difficulty associated with the NHC ligand synthesis, only two complex formation reactions were performed. The NHC ligands utilised were **3.15** and **3.20**. The NHC ligand, **3.15**, was reacted with Ag_2O and $Ru(bpy)_2Cl_2$, as shown in scheme 3.16.



Scheme 3.16: Synthesis of the Ru-NHC complex, **3.33**, via transmetallation with Ag_2O

The NHC ligand, **3.15** was combined with Ag_2O in a schlenk tube under an argon atmosphere. 1,2-ethandiol was added to the reaction mixture and sparged with argon for five minutes. This was then set to reflux for 30 minutes to obtain the Ag-NHC complex. To the hot reaction one equivalent of $Ru(bpy)_2Cl_2$ was added and the reaction ran at reflux for 18 hours. Upon cooling the reaction mixture was quenched with water and filtered isolating a precipitate assumed to be AgCl. To the filtrate fraction NH_4PF_6 was added resulting in an orange precipitate that was identified as the desired ruthenium complex, **3.33**. The product, **3.33** was purified via slow diffusion of diisopropyl ether into MeCN resulting in orange needle like crystals. Formation of complex **3.33** was confirmed via mass spectrometry, $[Ru(bpy)_2\mathbf{3.15}]^{2+}$ = 286.5607. ^{1}H-NMR analysis was carried out confirming the disappearance of the H2 peak, unfortunately the rest of the spectrum is more complex than expected, this may be attributed to a dilute sample and prevented clear integration assignment. ^{13}C-NMR was also collected with the C2 carbene carbon having a chemical shift of 193.3 ppm. Luminescent investigations were to be performed but because of time constraints they were not completed. Due to the successful synthesis of **3.33**, the reaction was repeated again but with the NHC ligand, **3.20**. However, because of time constraints the reaction conditions were slightly modified, as the reaction was microwave assisted rather than heated to reflux over 18 hours. The NHC ligand, **3.20** was also an iodide salt compared to the hexafluorophosphate salt of **3.15**. The reaction is shown below in scheme 3.17.



Scheme 3.17: The attempted synthesis of **3.34** via a microwave assisted procedure.

The NHC ligand, **3.20** and Ag_2O were combined in ethylene glycol resulting in a yellow solution with Ag_2O, as a solid remaining. The reaction was conducted via a microwave-assisted procedure for two minutes in one minute intervals and monitored by TLC. Analysis of the TLC plate indicated the NHC ligand, **3.20** had formed a Ag-NHC complex a distinctive new product was evident. Therefore, $Ru(bpy)_2Cl_2$ was added to the reaction mixture and was heated for five minutes with one minute intervals. TLC analysis showed the formation of a new ruthenium complex after five minutes and the reaction was allowed to cool to room temperature and NH_4PF_6 was added resulting in a dark red precipitate to form. This precipitate was isolated and mass spectrometry confirmed the presence of the complex **3.34** in the crude sample. However, other ruthenium species were also present, one of which was determined to be $Ru(bpy)_2$(1,2-ethandiol) by mass spectrometry analysis. ^{1}H-NMR data confirmed that the bulk sample of the precipitate was the NHC ligand, **3.20**, as the characteristic H2 proton remained. Therefore this could indicate that the reaction was not conducted over a long enough period and/or it proceeded in a poor yield. This reaction was to be repeated but time constraints prevented this and subsequent analysis of the complex could not be completed.

Conclusion

The investigation of imidazolium based NHC ligands with large aromatic cores and subsequent attempted/completed complex formation has highlighted the difficulty associated with organic and inorganic synthesis. The synthesis of **3.16** expected to proceed via an Ullmann coupling reaction that proved to be successful with 1*H*-perimidine. However, upon its failure different synthetic conditions/reactions were investigated all of which gave no evidence of the desired product, **3.16**. Therefore the synthetic route to obtain **3.16** (described in scheme 3.5) was abandoned. This synthetic route did yield a positive result, with the synthesis of **3.17**. This success was attributed to the different chemical reactions, steric influences and electronic effects. The compound **3.17** lead to the synthesis of two NHC salts, **3.19** and **3.20**, but method development is required in order to realise **3.19** in a substantial yield.

The synthesis of **3.21** was attempted in order to realise the NHC salt, **3.22**. However, the imine condensation reaction required to obtain **3.21** was unsuccessful. This was attributed to the poor nucleophilicity of 2-amino pyridine. Therefore to force the reaction to completion $ZnCl_2$ was utilised as a lewis acid to further activate the carbonyl functionality to nucleophilic attack. The $ZnCl_2$ proved to be unsuccessful and was concluded to not be a strong enough lewis acid to promote the imine condensation. $TiCl_4$ was then used returning unexpected results with the product, **3.25** isolated from the reaction. This gives evidence that the imine condensation reaction was proceeding but the harsh conditions the reaction was performed under resulted in the elimination of water. Therefore modification of the reaction conditions could give the product **3.21** and the subsequent NHC salt, **3.22**.

The most promising reaction conditions to give the NHC salts, **3.31** and **3.32** utilises a sealed tube procedure. The products could not be isolated pure due to insolubility issues of the NHC salts. The reaction conditions to realise the products require modification where performing the reaction in the dark may result in a better yield and storage of the crude products in the freezer to slow down any decomposition of the NHC salt. The synthesis of the mono imidazole pyrene derivative via **3.28** is another reaction that should be performed but wasn't completed due to time constraints.

The synthesis of the ruthenium complex, **3.33** was successful via the transmetallation of the Ag-NHC complex *in situ*. However the insignificant yield obtained prevented further charachterisation. The luminescent studies of the complex were not achieved due to time constraints but will be investigated in the future. The Ru-NHC complex, **3.34** was not isolated but the reaction completed showed promise via mass spectrometry and if the reaction was performed for a longer duration the desired complex could have been realised.

Chapter 4

Experimental

4. Experimental

General Information

Unless otherwise specified, all reagents and starting materials were reagent grade, purchased from standard suppliers and used as received. Water was purified by reverse osmosis in-house. Where anhydrous solvents were required, the HPLC-grade solvent was either distilled from standard drying agents or dried by passing over a sealed column of activated alumina. Melting points were recorded on an electrothermal melting point apparatus and are uncorrected. Except where otherwise specified, all reactions were carried out in air.

Synthetic proceedures described with an asterisk (*) next to the numerical assignment of the reaction, i.e. **2.17***; indicate the reaction did not go to completion with no supporting evidence for the formation of the desired product.

Infrared Spectroscopy

All infrared spectra were recorded on a Perkin-Elmer Spectrum One FTIR instrument operating in diffuse reflectance mode with samples prepared as KBr mulls (KBr). The following abbreviations are used: s: strong, m: medium, w: weak, sh: sharp, br: broad.

Nuclear Magnetic Resonance

All spectra were recorded on a Varian INOVA 500 or an Agilent MR400 NMR spectrometer, operating at 500 and 400 MHz, respectively, for ^{1}H, and 125 MHz for ^{13}C on the 500 NMR spectrometer. All samples were dissolved in commercially available deuterated solvents DSMO-d_6 (^{1}H-NMR ref: 2.50 ppm, ^{13}C-NMR ref: 39.52 ppm), $CDCl_3$ (^{1}H-NMR ref: 7.26 ppm, ^{13}C-CNMR ref: 77.16) or CD_3CN (^{1}H-NMR ref: 1.94 ppm, ^{13}C-NMR ref: 1.32 ppm). 1D-nOesy, COSY, TOCSY, HSQC and HMBC experiments were employed where required.

UV/Visible Spectroscopy

UV/Visible spectra were recorded on a Varian CARY UV/Visible spectrometer in the range 200 – 800 nm for MeCN. Samples were measured in quartz curvettes of path length 1 cm and approximate capacity 3 ml.

Mass Spectrometry

Mass spectra were recorded by Dr Marie Squire and Dr Meike Holzenkaempfer on either a DIONEX Ultimate 3000 or Bruker MaXis 4G spectrometer, both of which were operated in high resolution positive ion electrospray mode. Samples were dissolved and diluted to the required concentration in HPLC grade MeCN or MeOH.

X-ray Crystallography

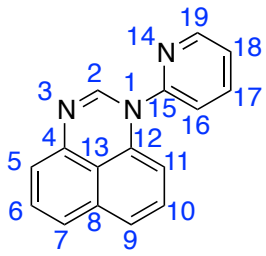
Refinement data is presented in Appendix 1. X-ray crystallographic data collection and refinement was carried out with either a Bruker APEXII instrument, using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, or an Oxford-Agilent SuperNova instrument with focused microsource Cu Kα (λ = 1.5418 Å) radiation and an ATLAS CCD area detector. All structures were solved using direct methods with SHELXS[88] and refined on F^2 using all data by full matrix least-squares procedures with SHELXL-97[89] within OLEX-2.[90] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions, or were manually assigned from residual electron density where appropriate, with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier atoms. The functions minimized were $\Sigma w(F2o\text{-}F2c)$, with $w=[\sigma 2(F2o)+aP2+bP]^{-1}$, where $P=[\max(Fo)2+2F2c]/3$. Some of the refinements reported may change a little upon preparation for final publication. Graphical representations of crystallographic data were prepared using the CrystalMaker. Crystallographic data for all compounds can be provided upon application.

Ligand Synthesis

1*H*-perimidine.

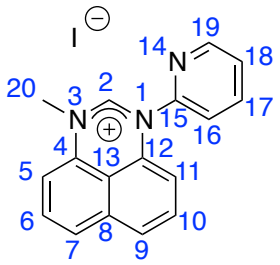
Following a modified literature procedure.[63] A solution of 1,8-diaminonaphthalene (4.0 g, 25.3 mmol) and formic acid (5.45 ml, 145.0 mmol) in ethanol (20 ml) was combined in a round bottom flask and set to reflux under an argon atmosphere for 15 hours. Upon cooling to room temperature the reaction mixture was quenched with water (50 ml). The mixture was then basified with 10% ammonia solution (50 ml) and the resulting precipitate was collected and dried giving the desired product, 1*H*-Perimidine. The product was then recrystallised from aqueous EtOH resulting in very dark orange crystals. Yield = 3.60 g (5.51 mmol, 85%), mp = 212-215 °C. ^{1}H-NMR (500 MHz, DMSO): δ 8.14 (1H, s, H1), 7.31 (1H, s, H2), 7.1]08 (2H, t, J = 8.1 hz, H6), 7.08 (2H, d, J= 7.7 hz, H5), 6.38 (2H, d, J = 5.2 hz, H1). ESMS: Found MH^+ 169.0764, $C_{11}H_9N_2$ requires MH^+ 169.0760.

1-(pyrdin-2-yl)-perimidine, **2.12.**



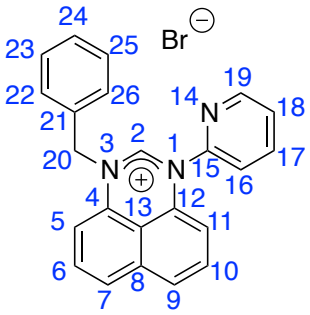
Following a modified literature procedure.[70] 1*H*-Perimidine (1.412 g, 8.40 mmol) was stirred with 2-Bromo-Pyridine (1.202 ml, 12.61 mmol), K_2CO_3 (2.323 g, 16.81 mmol) and CuI (0.160 g, 0.840 mmol) at 150^{0}C in dry DMSO (15 ml) under argon for 18hrs. The reaction mixture was quenched with 20% ammonia solution (50 ml) and stirred for 4hrs. DCM (50 ml) was then added and continued to stir for 18 hours. The solution was filtered and washed with DCM. After filtration the aqueous and organic layers were separated. The aqueous layer was washed with DCM (3x100 ml) and the organic fractions were combined and washed with water (3x100 ml) and brine (100 ml). The DCM fraction was dried over $MgSO_4$ and removed under vacuum, resulting in a yellow precipitate. Yield = 1.624 g (78.9%), mp = 158 °C. ^{1}H-NMR (500MHz, DMSO): δ 8.68 (1H, d, J = 4.5 hz, H19), 8.11 (1H, t, J = 7.7 hz, H17), 7.72 (1H, d, J = 7.7 hz, H16), 7.60 (1H, s, H2), 7.57 (1H, dd, J = 4.9 hz, 7.7 hz, H18), 7.28 (1H, t, J = 7.8 hz, H6), 7.24 (1H, d, J = 7.8 hz, H7), 7.19 (1H, d, J = 7.8 hz, H9), 7.08 (1H, t, J = 7.8 hz, H10), 6.78 (1H, d, J = 7.4 hz, H5), 6.22 (1H, d, J = 7.8 hz, H11). ^{13}C-NMR (125 MHz, DMSO): 151.9 (1C, C15), 150.2 (1C, C19), 146.8 (1C, C2), 142.3 (1C, C4), 140.3 (1C, C17), 137.2 (1C, C12), 135.0 (1C, C8), 128.8 (1C, C6), 127.5 (1C, C10), 124.2 (1C, C18), 122.2 (1C, C13), 121.0 (2C, C7, C16), 119.8 (1C, C9), 115.3 (1C, C5), 102.5 (1C, C11). UV-Vis: 333 nm (5210). ESMS: Found MH^+ 246.1026, $C_{16}H_{12}N_3$ requires MH^+ 246.1026.

1-(pyridin-2-yl)-3-methyl-perimidinium; Iodide, **2.13.**



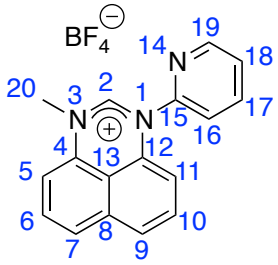
2.12 (1.244 g, 5.08 mmol) and MeI (0.791 ml, 12.70 mmol) were combined in a 100 ml round bottom flask. To this degassed EtOAc (60 ml) was added under an argon atmosphere conditions. The yellow solution was set to reflux for 18 hours resulting in a yellow precipitate. Upon cooling to room temperature the precipitate was isolated and dried. Yield = 1.584 g (80.6%), mp = 140-142 °C. ^{1}H-NMR (500 MHz, DMSO): δ 9.22 (1H, s, H2), 8.81 (1H, d, J = 4.1 hz, H19), 8.32 (1H, t, J = 7.5 hz, H17), 7.95 (1H, d, J = 7.5 hz, H16), 7.80 (1H, dd, J 4.1 hz, 7.5 hz, H18), 7.67 (1H, d, J = 7.5 hz, H7), 7.62 (1H, D, J = 7.5 hz, H9), 7.55 (1H, d, J = 7.5 hz, H6), 7.37 (1H, t, J = 7.5 hz, H10), 7.11 (1H, d, J = 7.5 hz, H5), 6.53 (1H, d, J = 7.5 hz, H11), 3.61 (3H, s, H20). ^{13}C-NMR (125 MHz, DMSO): δ 153.2 (1C, C2), 150.4 (1C, C19), 148.7 (1C, C15), 141.3 (1C, C17), 134.1 (1C, C8), 132.5 (1C, C12), 132.5 (1C, C4), 128.4 (1C, C6), 128.4 (1C, C10), 126.5 (1C, C18), 124.4 (1C, C7), 123.77 (1C, C9), 121.8 (1C, C16), 120.4 (1C, 13), 108.6 (1C, C11), 108.5 (1C, C5) 108.5 (1C, C5). 39.0 (1C, C20). UV-Vis: 328 (4743), ESMS: Found M^+ 260.1190, $C_{17}H_{14}N_3$ requires M^+ 260.1188.

1-(pyridin-2-yl)-3-benzyl-perimidinium; bromide, **2.14.**



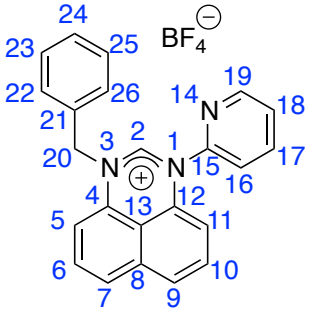
2.12 (1.324 g, 5.39 mmol) and benzyl bromide (1.604 ml, 13.49 mmol) were combined in a 100 ml round bottom flask. To this degassed EtOAc (60 ml) was added resulting in a yellow solution and the reaction mixture was set to reflux for 18 hours resulting in a yellow precipitate. Upon cooling to room temperature the precipitate was isolated and dried. Yield = 1.65 g (73.8%), mp = 128-130 °C. ^{1}H-NMR (500 MHz, DMSO): δ 9.62 (1H, s, H2), 8.84 (1H, d, J = 3.5 hz, H19), 8.35 (1H, t, J = 8.0 hz, H17), 8.01 (1H, d, J = 8.0 hz, H16), 7.83 (1H, dd, J = 3.5 hz, 8.0 hz, H18), 7.72 (1H, d, J = 7.5 hz, H7), 7.63 (1H, t, J = 8.0 hz, H24), 7.42 (5H, m, J = 7.5 hz, H9), 6.96 (1H, d, J = 7.5 hz, H5), 6.61 (1H, d, J = 7.5 hz, H11), 5.41 (1H, s, H20). ^{13}C-NMR (125 MHz, DMSO): δ 154.0 (1C, C2), 150.5 (1C, C19), 148.9 (1C, C15), 141.3 (1C, C17), 134.3, 132.6, 131.3, 128.9, 128.5, 128.2, 127.5 (1C, C7), 126.7 (1C, C18), 124.5, 124.1, 122.1 (1C, C16), 121.1, 109.7 (1C, C5), 108.9 (1C, C11), 54.9 (1C, C20). UV-Vis: 329 nm (5483). ESMS: Found M^+ 336.1506, $C_{23}H_{18}N_3$ requires M^+ 336.1501.

1-(pyridin-2-yl)-3-methyl-perimidinium; tetrafluoroborate, **2.15.**



2.13 (1.584 g, 4.09 mmol) and $AgBF_4$ (0.797g, 4.09 mmol) were combined in a round bottom flask with MeOH (50 ml) and set to stir for 15 hours at room temperature resulting in a yellow/white precipitate. The precipitate was then filtered upon celite and the MeOH was removed under vacuum to give the desired product, **2.15**. Yield = 1.369g (96.4%). ^{1}H NMR (500 MHz, DMSO): δ 9.23 (1H, s, H2), 8.81 (1H, d, J = 4.1 hz, H19), 8.33 (1H, t, J = 7.5 hz, H17), 7.97 (1H, d, J = 7.5 hz, H16), 7.80 (1H, dd, J = 4.1 hz, 7.5 hz, H18), 7.68 (1H, d, J = 7.5 hz, H7), 7.63 (1H, d, J = 7.5 hz, H9), 7.55 (1H, d, J = 7.5 hz, H6), 7.37 (1H, t, J = 7.5 hz, H10), 7.12 (1H, d, J = 7.5 hz, H5), 6.54 (1H, d, J = 7.5 hz, H11), 3.61 (3H, s, H20). ^{13}C-NMR (125 MHz, DMSO): δ 153.4 (1C, C2), 150.6 (1C, C19), 149.0 (1C, C15), 141.4 (1C, C17), 134.2 (1C, C8), 132.7 (1C, C12), 132.6 (1C, C4), 128.5 (1C, C6), 128.3 (1C, C10), 126.6 (1C, C18), 124.6 (1C, C7), 123.9 (1C, C9), 121.9 (1C, C16), 120.6 (1C, 13), 108.7 (1C, C11), 108.6 (1C, C5) 108.5 (1C, C5). ESMS: Found M^+ 260.1179, $C_{17}H_{14}N_3$ requires M^+ 260.1182.

1-(pyridin-2-yl)-3-benzyl-perimidinium; tetrafluoroborate, **2.16.**



2.14 (0.123 g, 0.305 mmol) and $AgBF_4$ (0.0593 g, 0.305 mmol) were combined in a round bottom flask with MeOH (50 ml) and set to stir for 15 hours at room temperature resulting in a yellow/white precipitate. The precipitate was then filtered upon celite and the MeOH was removed under vacuum to give the desired product, **2.16**. Yield = 0.119 g

(95.3%), mp = 110-114 °C. ^{1}H NMR (500 MHz, DMSO): δ 9.51 (1H, s, H2), 8.84 (1H, d, J = 3.5 hz, H19), 8.34 (1H, t, J = 8.0 hz, H17), 8.04 (1H, d, J = 8.0 hz, H16), 7.82 (1H, dd, J = 3.5 hz, 8.0 hz, H18), 7.70 (2H, d, J = 7.5 hz, H7, H9), 7.64 (2H, t, J = 8.0 hz, H6, H10), 7.41 (5H, m, H22 – H26), 6.95 (1H, d, J = 7.5 hz, H5), 6.62 (1H, d, J = 7.5 hz, H11), 5.36 (2H, s, H20). ^{13}C NMR (125 MHz, DMSO): δ 154.7 (1C, C2), 151.0 (1C, C19), 149.4, 141.8 (1C, C17), 134.8, 133.1, 131.8, 129.4, 128.7, 127.9, 127.2 (1C, C18), 124.9, 124.75, 124.6, 122.5, 121.6, 110.1 (1C, C5), 109.4 (1C, C11), 55.4 (1C, C20). ESMS: Found M^+ 336.1499, $C_{23}H_{18}N_3$ requires M^+ 336.1495.

1-(pyridn-2-yl)-3-(pyridin-2-methyl)-perimidinium; chloride, **2.17.***

2.12 (0.100 g, 0.408 mmol) and 2-picolyl chloride, hydrochloride (0.168g, 1.02 mmol) were combined in a round bottom flask with EtOAc (15 ml) and set to reflux for 18 hours. Upon cooling to room temperature the EtOAc was removed under vacuum giving a crude product.

1-(pyridn-2-yl)-3-(pyridin-2-methyl)-perimidinium; chloride, **2.17.***

2.12 (0.100 g, 0.408 mmol), 2-picolyl chloride hydrochloride (0.168g, 1.02 mmol) and Et_3N (1 ml, 7.17 mmol) were combined in a round bottom flask with toluene (15 ml) and the reaction mixture was set to reflux for 48 hours. Upon cooling to room temperature the toluene was removed under vacuum giving a crude product.

1,3-bis-(pyridn-2-yl)-perimidinium; bromide, **2.18***

2.12 (0.100 g, 0.408 mmol) and 2-bromo pyridine (0.0974 ml, 1.02 mmol) were combined in round bottom flask with EtOAc (15 ml) and set to reflux for 18 hours. Upon cooling to room temperature the EtOAc was removed under vacuum to give a crude product.

1,3-bis-(pyridn-2-yl)-perimidinium; bromide, **2.18.***

2.12 (0.100 g, 0.408 mmol) and 2-bromo pyridine (0.0974 ml, 1.02 mmol) were combined in a round bottom flask with toluene (15 ml) and the reaction mixture was set to reflux for 48 hours. Upon cooling to room temperature the toluene was removed under vacuum to give a crude product.

1,3-bis-(pyridn-2-yl)-perimidinium; bromide, **2.18.***

1*H*-perimidine (0.336 g, 2.00 mmol), 2-bromo pyridine (0.477 ml, 5.00 mmol), K_2CO_3 (0.415 g, 3.00 mmol) and Cu_2O (0.016 g, 0.200 mol) were combined in a schlenk tube under an argon atmosphere. To this dry DMSO (10 ml) was added and the reaction mixture was set to stir for 24 hours at 100 °C. Upon cooling to room temperature the reaction mixture was quenched with water (50 ml) and continued to stir for a further 48 hours at room temperature. A black insoluble precipitate was able to be isolated from the reaction mixture.

1,3-bis-(pyridn-2-yl)-perimidinium; bromide, **2.18.***

2.12 (0.0725 g, 0.296 mmol) and 2-bromo pyridine (0.42 ml, 4.40 mmol) were combined in a sealed vessel and set to stir at 180 °C for 24 hours. After cooling to room temperature the precipitate was isolated.

N^1,*N*^{8}-bis-(pyrid-2-yl)-1,8-diaminonaphthalene, **2.19.***

1,8-diaminonaphthalene (1.58g, 10.00 mmol), 2-bromo pyridine (4.062 ml, 30.00 mmol), K_2CO_3 (2.764 g, 20.00 mmol) were combined in a schlenk tube and set to reflux in dry DMF (15 ml) under an argon atomosphere for 48 hours. The reaction was monitiored by TLC on silica with DCM as the eluent. After cooling to room temperature the reaction mixture was quenched with water (100 ml) and Et_2O (100 ml) and filtered. The organic and aqueous fractions were isolated. The aqueous fraction was washed with Et_2O (3x100 ml) and the organic fractions were combined and washed with water (3x100 ml) and dried over $MgSO_4$ and removed under vacuum giving a crude product.

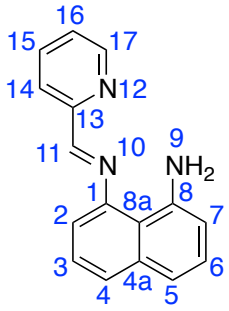
N^1,*N*^{8}-bis-(pyrid-2-methyl)-1,8-diaminonaphthalene, **2.20.***

1,8-diaminonaphthalene (1.58g, 10.00 mmol), 2-picolyl chloride hydrochloride (4.10 g, 25.00 mmol) and K_2CO_3 (8.292 g, 60.00 mmol) were combined in a schlenk tube and set to reflux in dry DMF (15 ml) under an argon atmosphere for 48 hours. The reaction was monitiored by TLC on silica with DCM as the eluent. Upon cooling to room temperature the reaction mixture was quenched with water (100 ml) and Et_2O (100 ml) and filtered giving a black precipitate. The organic and aqueous fractions were isolated. The aqueous fraction was washed with Et_2O (3x100 ml). The organic fractions were combined and washed with water (3x100 ml) and dried over $MgSO_4$ and removed under vacuum to give a crude product. Purification of the crude product was attempted via cloumn chromatography on silica with DCM:MeOH; 95:5 respectively.

N^1,*N*^{8}-bis-(pyrid-2-methylene)-1,8-diaminonaphthalene, **2.23.***

2-pyridinecarboxaldehyde (1.071 g, 10.00 mol) was combined through drop wise addition with 1,8-diaminonaphthalene (0.79, 5.00 mol) in Ar grade MeOH (50 ml). The reaction mixture was refluxed for 5hrs and left to evaporate after. Purification of the crude product was completed by column chromatography with EtOAc:PET; 30:70 respectively increasing to 100% EtOAc. The product, **2.25** was obtained as the first organic fraction to elute.

N[1]-(pyridin-2-yl-methylene)-1,8-diaminonaphthalene, **2.25.**



Yield = 0.265 g (21.5%), mp = 144-148 °C. ^{1}H-NMR (500 MHz, DMSO): δ 10.95 (1H, s, H11), 8.72 (1H, d, J = 4.8 hz, H17), 8.29 (1H, d, J = 8.0 hz, H14), 8.00 (1H, dt, J = 7.2, 1.5 hz, H15), 7.62 (1H, dd, J = 4.8, 6.4 hz, H16), 7.18 (1H, t, J = 8.0 hz, H3), 7.10 (1H, t, J = 8.1 hz, H6), 7.07 (1H, d, J = 8.3 hz, H4), 7.00 (1H, d, J = 8.1 hz, H5), 6.75 (1H, d, J = 7.3 hz, H2), 6.70 (1H, d, J = 7.3 hz, H7). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.6 (1C, C17), 138.2 (1C, C15), 129.4 (1C, C3), 128.9 (1C, C6), 127.0 (1C, C16), 122.6 (1C, C14), 120.4 (1C, C4), 118.2 (1C, C5), 114.8 (1C, C7), 104.2 (1C, C2). UV-Vis: 276 nm (94811), 351 nm (79288), 455 nm (9646). ESMS: Found MH^+ 246.1027, $C_{16}H_{12}N_3$ requires MH^+ 246.1026.

1*H*,3*H*-perimid-2-one, **2.26.***

NaOCN (1.234 g, 18.98 mmol) was slowly added to a hot solution (80 °C) of 2M HCl (150 ml). This resulted in efervescence and a pale white clear solution remained. To this solution 1,8-diaminonaphthalene (3 g, 18.99 mmol) was added and this was set to stir for one hour. After cooling to room temperature the reaction mixture was placed in the freezer for 18 hours resulting in a precipitate.

1*H*,3*H*-perimid-2-one, **2.26.***

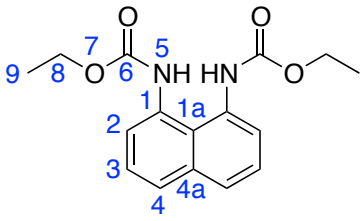
1,8-diaminonaphthalene (4 g, 25.32 mmol) and K_2CO_3 (3.499g, 25.32 mmol) were added to a 500 ml round bottom flask under an argon atmosphere. Dry THF (200 ml) was added and cooled to 0 °C. The chloroethylformate (3.13 ml, 32.91 mmol) was added to a 100 ml schlenk flask containing dry THF (50 ml), the solution of chloroethylformate and THF was added to the reaction mixture slowly over 30 mins at 0 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 18 hours at room temperature, after this the reaction mixture was heated to 40 °C for 2 hours. The reaction mixture was filtered and washed with THF (100 ml) and water (100 ml). The majority of the precipitate dissolved upon the addition of water and the filtrate was cooled in the freezer for 30 mins. A precipitate from this solution was obtained and isolated and proved to be the product **2.28**.

1*H*,3*H*-perimid-2-one, **2.26.**

Following a modified literature procedure.[72] To a 100 ml Schlenk flask, 1,8-diaminonaphthalene (1.00 g, 6.33 mmol) and K_2CO_3 (0.875 g, 6.33 mmol) were dried and sparged with argon. To this dry THF (40 ml) was added resulting in a dark red solution. The Schlenk flask was back filled with Ar and to this chloro ethylformate (1.3 eq) was added (dry) with 8 mls of THF dropwise over 30mins at 0^0C. The reaction mixture was then allowed to warm up to room temperature and was flushed with Ar for an hour. This was then set up to reflux for 18 hours. The contents of the flask were then cooled to 0 °C and isolation of the precipitate gave the desired product, **2.26**. Yield = 0.55 g (48.3%), mp =

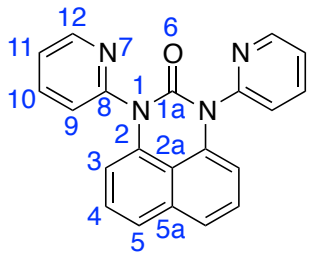
268-270 °C. ^{1}H-NMR ((500MHz, DMSO): δ 10.05 (2H, s, H2), 7.21 (2H, t, J = 7.8 hz, H4), 7.10 (2H, d, J = 8.2 hz, H3), 6.51 (2H, d, J = 7.4 hz). IR: 3096 (br), 1731 (s), 1666 (sh), 1648 (sh), 1471 (sh), 1382 (s), 1269 (sh). ESMS: Found MH^+ 185.0709, $C_{11}H_9N_2O$ requires MH^+ 185.0709

N^1,*N*^{8}-diethyl carbamate-1,8-diaminonaphthalene, **2.28.**



Yield = 1.06 g (13.8%), mp = 154-158 °C. ^{1}H-NMR (500MHz, $CDCl_3$): δ 7.70 (4H, d, = J = 8.1 hz H2, H4), 7.43 (2H, t, J = 8.1 hz, H3), 4.24 (4H, q, J = 6.9 hz, H8), 1.31 (6H, t, J = 6.4 hz, H9). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 155.2 (2C, C6), 136.2 (2C, C1), 132.3 (1C, C1a), 127.1 (2C, C2), 125.9 (4C, C3, C4), 123.0 (1C, C4a), 61.8 (2C, C7), 14.7 (2C, C8). UV-Vis: 306 (3452). ESMS: Found MNa^+ 325.1157, $C_{16}H_{18}N_2O_4Na$ requires MNa^+ 325.1159.

1,3-bis-(pyridn-2-yl)-perimidin-2-one, **2.29.**



2.26 (0.523 g, 2.91 mmol), CuI (0.111 g, 0.581 mmol) and K_2CO_3 (1.205 g, 8.72 mmol) were combined in a Schlenk tube under an argon atmosphere. To this 2-bromo pyridine (0.693 ml, 7.27 mmol) and dry DMSO (5 ml) were added. The reaction mixture was then set to stir for two days at 150 °C whilst monitored by TLC on silica with EtOAc as the eluent. Upon cooling to room temperature 15% NH_3 solution (100 ml) was added and allowed to stir for one hour at room temperature. After this DCM (100 ml) was added and the reaction mixture was allowed to stir for 18 hours at room temperature. The precipitate was filtered and washed with water (100 ml) and DCM (100 ml). The DCM layer was then washed with water (3x100 ml) and the aqueous layer was washed with DCM (3x100 ml). The DCM fractions were combined, isolated and dried over $MgSO_4$ and removed under vacuum. TLC analysis showed the existance of two products and therefore the crude product was washed with Et_2O (200 ml) and the precipitate was filtered and gave a pure product as a light sand colour powder, **2.29**. Yield = 0.725 g (73.7%), mp = 230 °C. ^{1}H-NMR (500 MHz, DMSO): δ 8.73 (2H, d, J = 4.4 hz, H12), 8.12 (2H, t, J = 7.1 hz, H10), 7.64 (2H, d, J = 7.1 hz, H9) 7.56 (2H, dd, J = 4.5 hz, 7.1 hz, H11), 7.38 (2H, d, 7.6 hz, H5), 7.26 (2H, t, J = 7.6 hz, H4), 5.84 (2H, d, J = 7.6 hz, H3). ^{13}C-NMR (125 MHz, DMSO): δ 150.5 (2C, C12), 150.3 (2C, C8), 149.0 (1C, C1a), 140.1 (2C, C10), 137.8 (2C, C2), 134.0 (1C, C5a), 127.7 (2C, C4), 124.9 (2C, C9), 124.6 (2C, C11), 119.6 (2C, C5), 113.6 (1C, C2a), 106.0 (2C, C3). IR: 3066 (w), 1668 (s), 1586 (s), 1566 (sh), 1524 (sh), 1464 (sh), 1435 (sh), 1435 (sh), 1328 (s). UV-Vis: 323 nm (3608). ESMS: Found MH^+ 339.1245, $C_{21}H_{15}N_4O$ requires MH^+ 339.1240.

2.33.*

The preparation of PPA was conducted initially with 1.8:1, P_2O_5 (1.928 g):H_3PO_4 (1.071 g); by combining the reactants in a Schlenk flask and stirring the reaction mixture at ~140 °C for two hours resulting in a hot solution of PPA. To this solution 1*H*-perimidine (0.200 g, 1.19 mmol) and 2-

chlorobenzoic acid (0.279 g, 1.78 mmol) were added and the reaction vessel and set to stir for 2 hours. Upon cooling to room temperature the reaction mixture was quenched with water (20 ml) and the organic fraction was isolated with DCM. Column chromatography was performed on silica with DCM and Hexanes (80:20, respectively) in an attempt to isolate the product, **2.33**.

2.36.*

The preparation of PPA was conducted initially with a ratio of 2.4 g of P_2O_5 (2.188 g) per ml of H_3PO_4 (0.882 ml). The H_3PO_4 and P_2O_5 were stirred at 200 °C for 30 mins. 1*H*-permidine (0.200 g, 1.19 mmol) and 2-chloronicotinic acid (0.281 g, 1.79 mmol) were added to this hot solution of PPA and stirred at 130 °C for two hours. Water (20 ml) was added to the reaction mixture to quench the reaction and the organic fraction was isolated with DCM and dried over $MgSO_4$. Isolation of the precipitate and filtrate gave the crude products from the reaction.

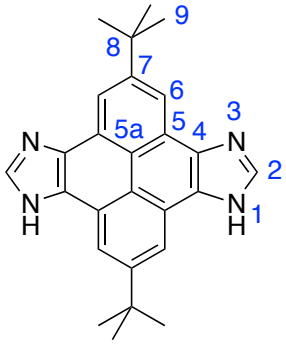
2.37.*

1*H*-perimidine (0.750 g, 4.46 mmol), K_2CO_3 (1.234 g, 8.93 mmol), CuI (0.0849 g, 0.446 mmol) and 2-chloronicotinic acid (1.055 g, 6.70 mmol) were combined in a Schlenk tube under an argon atmosphere. To this dry DMSO (10 ml) was added and the reaction mixture was set to stir at 150 °C for 3 days. Upon cooling to room temperature the reaction mixture was quenched with water (100 ml) and 15% NH_3 (25 ml) and set to stir for one hour. To this DCM (100 ml) was added and to stir for another hour. The crude precipitate was filtered and the organic fraction was isolated and washed with water (3x100 ml) and subsequently dried over $MgSO_4$. The DCM was removed under vacuum giving the crude product.

1*H*-phenanthro-(9,10)-imidazole, **3.01.**

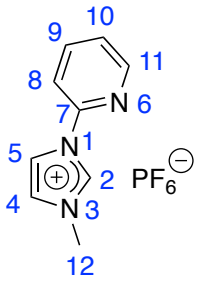
Following a modified literature procedure.[20] Phenanthraquinone (3.00 g, 14.4 mmol), NH_4OAc (23.07 g, 0.299 mol) and formalin (2.31ml, 65.5 mmol) were combined in a Schlenk flask under an argon atmosphere. To this concentrate acetic acid (56 ml) was added and the reaction mixture was set to reflux for 18 hours. Upon cooling to room temperature the reaction mixture was quenched with water (200 ml) and neutralised with concentrate ammonia resulting in the formation of a cream colour precipitate. The precipitate was washed with water (50 ml), acetone (50 ml), DCM (50 ml) and Et_2O (50 ml). The precipitate was proved to be the desired product, **3.01**. Yield = 0.314 g (11.0%), mp = 302 – 308 °C. ^{1}H-NMR (500MHz, DMSO): δ 13.44 (1H, s, N1), 8.84 (2H, d, J = 8.3 hz, ArH), 8.44 (2H, d, J = 5.5 hz, HX), 8.30 (1H, s, ArH), 7.71 (2H, t, J = 7.4 hz, ArH), 7.62 (2H, t, J = 7.4 hz, ArH). ESMS: Found MH^+ 219.0911, $C_{15}H_{11}N_2$ requires MH^+ 219.0917.

3.02



Following a modified literature procedure.[20] **3.27** (0.650 g, 1.74 mmol), NH_4OAc (5.36 g, 69.5 mmol) and formalin (0.500 ml, 14.2 mmol) were added to a Schlenk tube under an argon atmosphere. To this concentrate acetic acid (6.8 ml) was added and the reaction mixture was set to reflux and was run for 48 hours. Upon cooling to room temperature the reaction mixture was quenched with water (25 ml) and neutralised with 20% NH_3. The precipitate isolated was washed with water (100 ml), acetone (100 ml), DCM (100 ml) and Et_2O (100 ml) resulting in the pure product **3.02**. Yield = 0.675 g (98.5%), mp = > 324 °C. ^{1}H-NMR (500 MHz, DMSO): δ 13.61 (2H, s, H1), 8.71-8.66 (4H, m, H6), 8.40 (2H, s, H2), 1.61 (18H, s, H9). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 146.6 (1C, C7), 139.2 (1C, C2), 137.3 (1C, C4), 117.8, 114.4, 54.9 (1C, C8), 31.8 (1C, C9). ESMS: Found MH^+ 395.2238, $C_{26}H_{27}N_4$ requires MH^+ 395.2230.

1-(pyrid-2yl)-3-methyl-imidazolium; hexafluorophosphate, **3.15**.



Following a modified literature procedure.[81] 1-methyl-imidazole (0.824 g, 9.353 mmol) and 2-bromo pyridine (1.503 g, 9.513 mmol) were added to a 25 ml round bottom flask and heated to 160 °C for 21 hours. Upon cooling to room temperature water (10 ml) was added and saturated KPF_6(aq) was added resulting in a precipitate. The precipitate was filtered and washed with water (2x5 ml) and Et_2O (2x5 ml) giving a red powder. The powder was recrystallised from acetone/Et_2O to give the pure product, **3.15**. Yield = 0.314 g (11.0%), mp = 120 °C. ^{1}H-NMR (400 MHz, CD_3CN): δ 9.25 (1H, s, H2), 8.59 (1H, d, J = 4.7 hz, H11), 8.09 (1H, t, J = 8.2 hz, H9), 8.06 (1H, s, H4), 7.72 (1H, d, J = 8.2 hz, H8), 7.58 (1H, q, J = 4.7, 7.4 hz, H10), 7.55 (1H, s, H5), 3.96 (3H, s, H12). ESMS: Found M^+ 160.0872, $C_9H_{10}N_3$ requires M^+ 160.0869.

1-(pyrid-2-yl)-phenanthro-(9,10)-imidazole, **3.16.***

3.01 (1.000 g, 4.59 mmol), 2-bromo pyridine (0.656 ml, 6.88 mmol), K_2CO_3 (1.268 g, 9.17 mmol) and CuI (0.0874 g, 0.459 mmol) were combined in a Schlenk tube under an argon atmosphere and moisture restrictive conditions. To this dry DMSO (10 ml) was added and the reaction mixture was set to stir for 96 hours at 150 °C. Upon cooling to room temperature water (50 ml) was added to quench the reaction and 15% NH_3 (20 ml) and was set to stir at room temperature for one hour. To this reaction mixture DCM (100 ml) was added and the organic fraction was isolated and washed with water (3x100 ml). The organic fraction was dried over $MgSO_4$ and removed under vacuum giving an oily residue. Et_2O (100 ml) was added to the crude product resulting in a precipitate that was isolated by filtration. Column chromatography was completed on silica with DCM.

1-(pyrid-2-yl)-phenanthro-(9,10)-imidazole, **3.16.***

3.01 (0.5 g, 2.29 mmol), 2-bromo pyridine (0.262 ml, 2.75 mmol), KO^{t}Bu (0.386 g, 3.44 mmol), CuI (0.0218 g, 0.115 mmol) and benzotriazole (0.0273 g, 0.229 mmol) were combined in a Schlenk tube under an argon atmosphere and moisture restrictive conditions. To this dry DMSO (5 ml) was added and the reaction mixture was set to stir for 18 hours at 150 °C. Upon cooling to room temperature water (50 ml) was added to quench the reaction and 15% NH_3 (10 ml) and was set to stir at room temperature for one hour. To this reaction mixture DCM (100 ml) was added and the organic fraction was isolated and washed with water (3x100 ml). The organic fraction was dried over $MgSO_4$ and removed under vacuum giving an oily residue. Et_2O (100 ml) was added to the crude product resulting in a precipitate that was isolated by filtration. Column chromatography was performed on silica with DCM.

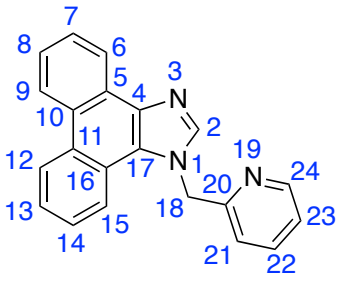
1-(pyrid-2-yl)-phenanthro-(9,10)-imidazole, **3.16.***

3.01 (0.5 g, 2.29 mmol) and KO$_t$Bu (0.386 g, 3.44 mmol) were combined in a Schlenk tube under an argon atmosphere and moisture restrictive conditions. To this dry DMF (10 ml) was added resulting in a dark red/purple solution. To this 2-bromo pyridine (0.262 ml, 2.75 mmol) was added and the reaction mixture was set to stir for 48 hours (monitored by TLC on silica with DCM). Upon cooling to room temperature, water (50 ml) and DCM (50 ml) were added to the reaction mixture and set to stir for one hour. The organic fraction was then isolated and washed with water (3x100 ml), dried over $MgSO_4$ and removed under vacuum. This resulted in an oily residue; therefore Et_2O was added to the giving a precipitate to form in solution. This was isolated and determined to be the starting material **3.01**. Removal of the Et_2O under vacuum was completed giving a crude product. Column chromatography of the crude product was performed on silica with DCM.

1-(pyrid-2-yl)-phenanthro-(9,10)-imidazole, **3.16.***

3.01 (1.5 g, 6.88 mmol), 2-bromo pyridine (1.312 ml, 13.8 mmol), Fe2O3 (0.110 g, 0.0688 mmol) and KO^{t}Bu (1.548 g, 13.8 mmol) were combined in a Schlenk tube under an argon atmosphere and moisture restrictive conditions. To this reaction mixture dry DMSO (15 ml) was added and the reaction was set to stir for 72 hours at 120 °C. TLC monitored the reaction on silca with DCM. Upon cooling the reaction to room temperature water (50 ml) and DCM (100 ml) were added to the crude reaction mixture. This was stirred for one hour at room temperature. The organic fraction was then isolated and washed with water (3x100 ml), dried over $MgSO_4$ and removed under vacuum. This resulted in an oily residue. The crude residue was stired with Et_2O resulting in the formation of a precipitate. The precipitate was isolated via filtration and the filtrate was isolated.

1-(pyrid-2-methyl)-phenanthro-(9,10)-imidazole, **3.17.**



3.01 (1.50 g, 6.88 mmol), 2-picolyl chloride hydrochloride (1.35 g, 8.26 mmol) and K_2CO_3 (2.38 g, 17.22 mmol) were combined in a 100 ml round bottom Schlenk flask to this dry DMF (30 ml) was added. The reaction vessel was then sparged with argon and was set to stir at 120 °C for 72 hours. Upon cooling the reaction mixture to room temperature it was quenched with water (100 ml) and DCM (100 ml). This was then stirred vigourously for ten minutes. The two fractions were separated and the aqueous phase was washed with DCM (3x50 ml) and the DCM fraction was washed with water (3x50 ml). The DCM fraction was dried over $MgSO_4$ and removed under vacuum giving the pure product **3.17** as a cream coloured precipitate. Yield = 1.245 g (58.9%), mp = 158 – 162 °C. ^{1}H-NMR (500 MHz, DMSO): δ 8.88 (1H, d, J = 7.8 hz, H9), 8.82 (1H, d, J = 8.1 hz, H12), 8.59 (1H, d, J = 8.1 hz, H15), 8.53 (1H, d, J = 3.9 hz, H24), 8.45 (1H, s, H2), 8.12 (1H, d, J = 8.1 hz, H6), 7.72 (2H, m, H22 and H14), 7.63 (1H, t, J = 7.1 hz, H13), 7.55 (1H, t, J = 7.1 hz, H8), 7.50 (1H, t, J = 7.8 hz, H7), 7.28 (1H, t, J = 4.7 hz, H23), 7.07 (1H, d, J = 7.6 hz, H21), 6.10 (1H, s, H18). ^{13}C-NMR (125 MHz, DMSO): δ 156.4 (1C, C20), 149.5 (1C, C24), 144.1 (1C, C2), 138.0 (1C, C17), 137.4 (1C, C22), 128.0 (1C, C16), 127.4 (1C, C11), 127.3 (1C, C14), 127.1 (1C, C10), 126.8 (1C, C7), 125.4 (1C, C13), 125.0 (1C, C8), 124.97 (1C, C4), 124.2 (1C, C9), 123.5 (1C, C12), 122.8 (1C, C23), 122.6 (1C, C5), 121.8 (1C, C15), 121.2 (1C, C6), 120.8 (1C, C21), 51.9 (1C, C18). ESMS: Found MH^+ 310.1347, $C_{21}H_{16}N_3$ requires MH^+ 310.1339.

1*H*-Benzimidazole

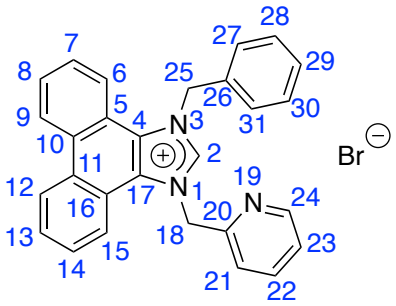
o-Phenylenediamine (2.00 g, 18.50 mmol) and formic acid (1.05 ml, 27.82 mmol) were combined in a 25 ml round bottom flask. To this 4M HCl (10 ml) was added and the reaction mixture was set to reflux for 24 hours. Upon cooling to room temperature, charcoal was added and filtered over celite. The filtrate was basified to pH 10-12 with NH_3, giving a white precipitate. This was extracted with EtOAc and quenched with water. The aqueous layer was washed with EtOAc (3x50 ml) and the organic fractions were combined and washed with water (3x50 ml). The EtOAc fraction was then dried over $MgSO_4$ and removed under vacuum. The resulting precipitate was washed with hexanes and isolated giving the desired product, 1*H*-benzimidazole. Yield = 1.302 g (59.6%). ^{1}H-NMR (400 MHz, DMSO): δ 12.43 (1H, s, H1), 8.21 (1H, s, H2), 7.57 (2H, s, HX), 7.18 (2H, m, HX).

1-(pyrid-2-yl)-benzimidazole, **3.18**.

Following a modified literature procedure.[83] 1*H*-Benzimidazole (0.400 g, 3.39 mmol), 2-bromo pyridine (0.646 ml, 6.78 mmol), KO^{t}Bu (0.761 g, 6.78 mmol) and Fe_2O_3 (0.054 g, 0.339 mmol) were combined in a Schlenk tube with dry DMSO (10 ml) and an air condensor and set to stir for 24 hours at 120 °C. Upon cooling to room temperature the reaction mixture was quenched with water (20 ml)

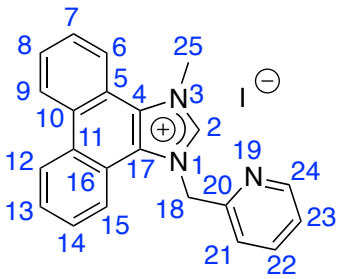
and EtOAc (20 ml) and continued to stir for a further ten minutes. The organic fraction was isolated and the aqueous layer was washed with EtOAc (3x20 ml). The organic fractions were combined and washed wih water (3x20 ml) and brine (1x20 ml). The organic fraction was dried over $MgSO_4$ and removed under vacuum. A yellow oil was isolated and proved to the desired product, **3.18**. Yield = 0.448 g (67.7%). ^{1}H-NMR (400 MHz, DMSO): δ 8.62 (1H, d, J = 3.9 hz), 8.59 (1H, s), 8.06 (1H, d, J = 7.4 hz), 7.92 (1H, t, J = 7.4 hz), 7.86 (1H, d, J = 7.4 hz), 7.60 (1H, d, J = 7.4 hz), 7.37 (2H, m), 7.31 (1H, m).

1-(pyrid-2-methyl)-3-benzyl-phenanthro-(9,10)-imidazolium; bromide, **3.19.**



3.17 (0.250 g, 0.801 mmol) and benzyl bromide (0.144 ml, 1.21 mmol) were combined in a round bottom flask with solvent mixture of DCM:MeOH; 4:1 (20 ml:5 ml, respectively). The reaction mixture was set to reflux for 76 hours. Upon cooling removal of the solvent mixture resulted in the crude product, **3.19**. This was purified by column chromatography on alumina with DCM:MeOH; 4:1 ratio to give the isolated product, **3.19**. Crystals of the NHC salt were grown by slow evaporation of DCM:MeOH solution. Yield = 0.314 g (11.0%), mp = 219 °C. ^{1}H-NMR (500 MHz, DMSO): δ 10.01 (1H, s, H2), 9.02 (2H, d, J = 8.6 hz, H9 and H12), 8.45 (2H, d, J = 8.8 hz, H24 and H15/H6), 8.39 (1H, d, J = 8.3 hz, H6/H15), 7.93 (1H, t, J = 7.6 hz, H7 and H14), 7.79 (3H, m, H8, H13 and HX), 7.71 (2H, m), 7.45 (4H, m), 7.37 (2H, m), 6.48 (2H, s, H18), 6.39 (2H, s, H25). ^{13}C-NMR (125 MHz, DMSO): δ 153.0 (1C, C20), 149.7 (1C, C24), 143.5 (1C, C2), 137.7 (1C, C22), 133.9 (1C, C26), 129.4, 129.3, 129.2, 128.6, 128.4, 128.3, 126.9, 126.7 (1C, C17), 126.1 (1C, C4), 124.7, 124.6, 123.7, 122.7, 122.3, 122.2, 120.2, 120.1, 54.0 (1C, C18), 53.1 (1C, C25). ESMS: Found M^+ 400.1817, $C_{28}H_{22}N_3$ requires M^+ 400.1808.

1-(pyrid-2-methyl)-3-methyl-phenanthro-(9,10)-imidazolium; iodide, **3.20.**



3.17 (0.300 g, 0.971 mmol) and methyl iodide (3 ml) were combined in a sealed tube and stirred at 80 °C for 18 hours. Upon cooling to room temperature the methyl iodide was removed under vacuum resulting in a fine grey precipitate. To this MeOH (10 ml) was added giving an orange solution and a pale yellow precipitate. This was filtered and washed with MeOH (10 ml) and the pale yellow precipitate proved to be the desired NHC salt, **3.20**. Yield = 0.132 g (30.1%), mp = 308 °C. ^{1}H-NMR (500 MHz, DMSO): δ 9.86 (1H, s, H2), 9.07 (1H, d, J = 7.1 hz), 9.03 (1H, d, J = 8.6 hz), 8.75 (1H, d, J = 6.6 hz), 8.44 (1H, s), 8.29 (1H, d, J = 8.3 hz), 7.90 (3H, m), 7.78 (1H, t, J = 8.5 hz), 7.68 (2H, d, J = 7.3 hz), 7.35 (1H, t, J = 3.6 hz), 6.39 (2H, s, H18), 4.63 (3H, s, H25). ^{13}C-NMR (125 MHz, DMSO): δ 153.2 (1C, C20), 149.7 (1C, C24), 142.8 (1C, C2), 137.7 (1C, C22), 129.3, 128.6, 128.3, 128.1, 126.8 (1C,

C4), 125.9 (1C, C17) 124.7, 123.7, 122.6, 122.3, 122.1, 120.9, 120.2, 53.7 (1C, C18), 48.7 (1C, C25). ESMS: Found M+ 324.1502, $C_{22}H_{18}N_3$ requires M^+ 324.1512.

N^9,N^{10}-bis-(pyrid-2-yl)-phenathro-(9,10)-diime, **3.21.***

9,10-phenanthraquinone (0.500 g, 2.40 mmol), 2-amino pyridine (1.354 g, 14.40 mmol) and a catalytic amount of *p*-toluenesulfonic acid were combined in a 100 ml rond bottom flask with toluene (60 ml) and a Dean-Stark trap. The reaction mixture was set to reflux for 24 hours. After 24 hours another six equivalents of 2-amino pyridine (1.354 g, 14.40 mmol) were added to the reaction mixture and continued to reflux for another 24 hours. Upon cooling to room temperature the precipitate was isolated and the filtrate was removed under vacuum.

N^9,N^{10}-bis-(pyrid-2-yl)-phenathro-(9,10)-diime, **3.21.***

9,10-phenanthraquinone (0.500 g, 2.40 mmol) and 2-amino pyridine (1.354 g, 14.40 mmol) were combined in a two necked round bottom flask. To this dry toluene (15 ml) was added and the reaction mixture was set to stir at room temperature. To this $TiCl_4$ (0.266 ml, 2.40 mmol) was added dropwise to the reaction mixture and continued to stir for 18 hours. Upon cooling to room temperature the reaction mixture was quenched with water (100 ml) and the tolunene was isolated and removed under vacuum. The organic fraction was then further extracted with DCM (3x50 ml) and water (3x50 ml). The organic fractions were combined and dried over $MgSO_4$ and removed under vacuum giving a crude product.

N^9,N^{10}-bis-(pyrid-2-yl)-phenathro-(9,10)-diime, **3.21.***

9,10-phenanthraquinone (1.500 g, 7.20 mmol) and 2-amino pyridine (2.71 g, 28.83 mmol) were combined in a Schlenk round bottom flask. To this dry toluene (45 ml) was added and the reaction mixture was set to stir at room temperature. To this $TiCl_4$ (0.950 ml, 8.65 mmol) was added dropwise to the reaction mixture and was set to reflux for 18 hours under an argon atmosphere. Upon cooling to room temperature the reaction mixture was quenched with water (100 ml) and the tolunene was isolated and removed under vacuum. The organic fraction was then further extracted with DCM (3x50 ml) and water (3x50 ml). The organic fractions were combined and dried over $MgSO_4$ and removed under vacuum giving a crude product. This crude product was then washed with Et_2O (100 ml) giving a precipitate that was found to be **3.25**.

N^9,N^{10}-bis-phenyl-phenathro-(9,10)-diime, **3.23.***

9,10-phenanthraquinone (0.500 g, 2.40 mmol) and 2-amino pyridine (3.00 ml, 32.91 mmol) were added to a Schlenk tube. To this $ZnCl_2$ (0.330 g, 2.42 mmol) was added resulting in a thick viscous solution. The reaction mixture was set to stir at 165 °C for 18 hours. Upon cooling to room temperature the

crude product was stirred with Et_2O (20 ml) and filtered giving a black precipitate and an orange Et_2O filtrate. The filtrate was removed under vacuum however could not be identified. Therefore column chromatographty was performed on silica with DCM as the eluent to give crude products.

N[9],*N*[10]-bis-phenyl-phenathro-(9,10)-diime, **3.23.***

9,10-phenanthraquinone (0.200 g, 0.961 mmol) and aniline (2.00 ml, 21.94 mmol) were combined in a Schlenk tube under an argon atmosphere. The reaction mixture was stirred at 160 °C for 48 hours. Upon cooling to room temperature the reaction mixture was quenched with 2M HCl (100 ml) and Et_2O (100 ml). This solution was then set to stir for one hour at room temperature. The organic fraction was then isolated and washed with 2M HCl (3x100 ml). The organic fraction was then dried over $MgSO_4$ and the Et_2O was removed under vacuum to give a crude product.

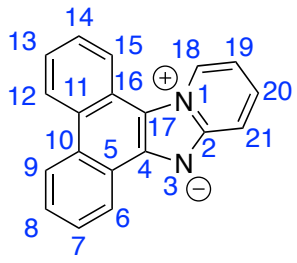
N[1],*N*[4]-bis-phenyl-2,3-bis-phenyl-(2,3)-diimine, **3.24.***

Benzil (0.500 g, 2.38 mmol) and aniline (3.00 ml, 32.91 mmol) were combined in a Schlenk tube under an argon atmosphere. The reaction mixture was stirred at 160 °C for four hours under a continous flow of argon. Upon cooling to room temperature the reaction mixture was quenched with 2M HCl (100 ml) and Et_2O (100 ml) and set to stir at room temperature for one hour. The organic fraction was isolated and washed with 2M HCl (500 ml). The organic fraction was dried over $MgSO_4$ and the Et_2O was removed under vacuum giving a crude product.

N[1],*N*[4]-bis-phenyl-2,3-bis-phenyl-(2,3)-diimine, **3.24.***

Benzil (0.400 g, 1.903 mmol) and aniline (3.00 ml, 32.91 mmol) were combined in a Schlenk tube and the reaction mixture was heated to 160 °C and set to stir. To the reaction mixture $ZnCl_2$ (0.260 g, 1.903 mmol) and more aniline (3.00 ml, 32.91 mmol) were added and continued to stir for five hours under a continuous flow of argon. Upon cooling to room temperature Et_2O (50 ml) was added and the precipitate and filtrate were isolated.

3.25.



Yield = 0.293 g (15.2%), mp = 130 – 134 °C. ^{1}H-NMR (500MHz, DMSO): δ 9.58 (1H, d, J = 6.6 hz, H18), 8.99 (1H, d, J = 8.3 hz, H12), 8.89 (1H, d, J = 7.8 hz, H9), 8.83 (1H, d, J = 8.3 hz, H15), 8.76 (1H, d, J = 7.8 hz, H6), 7.96 (1H, d, J = 9.1 hz, H21), 7.83 (1H, t, J = 7.8 hz), 7.77 (2H, m), 7.70 (1H, t, J = 7.6 hz), 7.60 (1H, t, J = 7.8 hz, H20), 7.23 (1H, t, J = 7.23 hz, H19). ^{13}C-NMR (125 MHz, DMSO): δ 147.1 (1C, C2), 140.3, 129.2, 128.0 (1C, C18), 127.8, 127.5, 127.3, 127.1, 127.0, 126.6, 124.9 (1C, C12), 124.6 (1C, C9), 123.7 (1C, C6), 123.2 (1C, C6), 123.1, 120.6 (1C, C15), 118.7, 117.5 (1C, C21), 112.8 (1C, C13). ESMS: Found MH_+ 269.1075, $C_{19}H_{13}N_2$ requires MH^+ 269.1073.

2,7-di tert-butyl pyrene, **3.26**.

Following a modified literature procedure.[85] Pyrene (5.00 g, 24.75 mmol) was added to a 100 ml round bottom Schlenk flask to this dry DCM (50 ml) was added. Tert butyl chloride (6.81 ml, 61.84 mmol) was added and the reaction mixture was set cooled to 0 °C. Once the reaction mixture was cold $AlCl_3$ (6.61 g, 49.52 mmol) was added in small portions whilst stirring. The reaction mixture was then warmed to room temperature and stirred for another four hours. The reaction mixture was then added to ice water resulting in a precipitate that filtered and upon recrystallisations from hexanes the desired product **3.26**. Yield = 6.04 g (77.7%), mp = > 324 °C. ^{1}H-NMR (500 MHz, DMSO): δ 8.30 (4H, s, ArH), 8.13 (4H, s, ArH), 1.55 (18H, s, ^{t}BuH).

2,7-di tert-butyl pyrene-(4,5,9,10)-tetraone, **3.27**.

Following a modified literature procedure.[86] **3.26** (2.00 g, 6.47 mmol), $NaIO_4$ (11.30 g, 52.83 mmol) and $RuCl_3.XH_2O$ (0.161 g, 0.776 mmol) were combined in a Schlenk round bottom flask, to this DCM (25 ml), MeCN (25 ml) and water (30 ml) were added and the reaction mixture was set to stir for 18 hours at 40 °C. Upon cooling to room temperature the reaction mixture was quenched with water (50 ml) and DCM (50 ml). The aqueous fraction was washed with DCM (3x100 ml) and the organic fractions were combined and washed with water (3x100 ml). The DCM fraction was then dried over $MgSO_4$ and removed under vacuum giving a dark green/black precipitate. A silica plug was run with EtOAc:Hexanes; 5:2, respectively followed by a silica column with DCM as the eluent giving the pure product **3.27** as a yellow/orange powder. Yield = 0.646 g (27.1%), mp = > 300 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.47 (4H, s, ArH), 1.42 (18H, s, ^{t}BuH).

2,7-di tert-butyl pyrene-(4,5)-dione, **3.28**.*

Following a modified literature procedure.[86] **3.26** (2.00 g, 6.47 mmol), $NaIO_4$ (6.48 g, 30.28 mmol) and $RuCl_3.XH_2O$ (0.129 g, 0.6.21 mmol) were combined in a Schlenk round bottom flask, to this DCM (25 ml), MeCN (25 ml) and water (30 ml) were added and the reaction mixture was set to stir for 18 hours at room temperature. Upon cooling to room temperature the reaction mixture was quenched with water (50 ml) and DCM (50 ml). The aqueous fraction was washed with DCM (3x100 ml) and the organic fractions were combined and washed with water (3x100 ml). The DCM fraction was then dried over $MgSO_4$ and removed under vacuum giving a dark green/black precipitate. A silica column with DCM as the eluent was run giving a crude product as a mixture of **3.27** and **3.28**.

3.29 & **3.30**.*

Following a modified literature procedure.[87] **3.02** (0.200 g, 0.493 mmol), benzyl bromide (0.293 ml, 2.46 mmol) and K_2CO_3 (0.204 g, 1.48 mmol) were combined in a Schlenk tube under moisture

restrictive conditions and an argon atmosphere. To this dry MeCN (10 ml) was added and the reaction mixture was set to reflux for 48 hours. Upon cooling a white cream precipitate was isolated and the showing the existence of **3.29** and **3.30** with **3.02** present in the sample. The filtrate was removed under vacuum giving a crude product.

3.31.*

The crude sample of **3.29** and **3.30** (0.0408 g, 0.0711 mmol) and benzyl bromide (0.0211 ml, 0.178 mmol) were combined in a 50 ml round bottom flask. To this MeOH (20 ml) was added and the reaction mixture was set to reflux for 48 hours. Upon cooling to room temperature the MeOH was removed under vacuum giving a crude product.

3.31.*

3.02 (0.100 g, 0.246 mmol) and benzyl bromide (3 ml) was added to a sealed tube and set to stir at 60 °C for 48 hours. After 48 hours the reaction mixture continued to stir but at room temperature for another 24 hours. The reaction mixture was subsequently quenched with EtOAc (50 ml) and the remaining precipitate was isolated.

3.32.*

3.02 (0.100 g, 0.246 mmol) and methyl iodide (3 ml) was added to a sealed tube and set to stir at 80 °C for 48 hours. After 48 hours the reaction mixture continued to stir but at room temperature for another 24 hours. The methyl iodide was removed from the reaction mixture under vacuum giving a crude product.

Synthesis of NHC complexes

2.39.*

2.13 (0.100 g, 0.258 mmol) and Ag_2O (0.0891 g, 0.385 mmol) were combined in a 50 ml Schlenk flask and placed under an argon atmosphere and moisture restrictive conditions. To this dry MeCN (25 ml) was added and the reaction mixture was set to reflux for 72 hours. The solution changed from yellow to brown as the reaction was run. Upon cooling to room temperature the reaction mixture was filtered on celite giving a dark orange solution.

2.40.*

2.14 (0.020 g, 0.0481 mmol) and Ag_2O (0.138 g, 0.0596 mmol) were combined in a Schlenk tube under an argon atmosphere and moisture restrictive conditions. To this dry MeCN (5 ml) was added and the reaction was set to reflux for 72 hours. Upon cooling to room temperature the reaction mixture

was filtered on celite and the MeCN. The filtrate (MeCN) was removed under vacuum giving the crude product.

2.41.*

2.13 (0.010 g, 0.0254 mmol) and Ag_2O (0.0178 g, 0.0768 mmol) were combined in a 25 ml RB flask to which ethylene glycol (5 ml) was added and sparged with argon for five minutes. The reaction mixture was placed under an argon atmosphere and set to reflux for one hour. To this hot solution $Ru(bpy)_2Cl_2$ (0.020 g, 0.0384 mmol) was added and continued to reflux for a further 18 hours. Upon cooling to room temperature H_2O (50 ml) was added and filtered over celite. To the isolated filtrate NH_4PF_6 was added. The crude product was with DCM (3x100 ml) and dried upon $MgSO_4$ and subsequently removed under vacuum. ^{1}H-NMR and mass spectrometry confirmed the desired product, **2.41** was not realised. Therefore crystallisations were set up with diffusion of Hexanes into MeCN and Acetone. This did not yield any crystals.

2.41.*

2.15 (0.020 g, 0.0577 mmol) and Ag_2O (0.0281 g, 0.121 mmol) were combined in a Schlenk tube to which 1,2-ethandiol (5 ml) was added and sparged with argon for five minutes. The reaction mixture was placed under an argon atmosphere and set to reflux for 30 minutes. To this hot solution $Ru(bpy)_2Cl_2$ (0.030 g, 0.0577 mmol) was added and continued to reflux for a further 18 hours. Upon cooling to room temperature H_2O (50 ml) was added and filtered over celite. To the isolated filtrate NH_4PF_6 was added resulting in a precipitate. The crude precipitate was washed with H_2O (10 ml) and Et_2O (10 ml) and 1H-NMR and mass spectrometry analysis confirmed ruthenium species present. Therefore then cyrstallisations were set up via diffusion of Et_2O and $^iPr_2O$ into MeCN with 1 drop of toluene. However, no crystals were obtained.

2.42.*

2.16 (0.0231 g, 0.0562 mmol) and Ag_2O (0.0281 g, 0.121 mmol) were combined in a Schlenk tube to which ethylene glycol (5 ml) was added and sparged with argon for five minutes. The reaction mixture was placed under an argon atmosphere and set to reflux for 30 minutes. To this hot solution $Ru(bpy)_2Cl_2$ (0.029 g, 0.0562 mmol) was added and continued to reflux for a further 18 hours. Upon cooling to room temperature H_2O (50 ml) was added and filtered over celite. To the isolated filtrate NH_4PF_6 was added resulting in a precipitate. The crude precipitate was washed with H_2O (10 ml) and Et_2O (10 ml) and ^{1}H-NMR and mass spectrometry analysis confirmed ruthenium species present. However the desired product, **2.24** could not be isolated.

2.42.*

2.15 (0.0231 g, 0.0562 mmol) and $Ru(bpy)_2Cl_2$ (0.029 g, 0.0562 mmol) were combined in a 25 ml RB flask with ethylene glycol (5 ml). The reaction mixture was set to reflux utilising a microwave. The reaction ran for 4x2 minutes, and monitored via TLC with silica. TLC analysis showed the existence of a new product. Therefore the crude product was purified via column chromatography on sepahdex and gradient concentrations of NaCl as the solvent. However, the desired product was not isolated.

2.43.*

2.15 (0.0342 g, 0.0990 mmol) and Ag_2O (0.0057 g, 0.0248 mmol) and a catalytic amount of Bu_4NHSO_4 were combined in a 50 ml RB flask with DCM (25ml) and allowed to stir for one hour in the dark. After one hour NaOH (1M, 3ml) was added and continued to stir for a further 10 minutes. The reaction mixture was then filtered over celite and the filtrate was removed under vacuum. Analysis via mass spectrometry and ^{1}H-NMR confirmed the desired product, **2.43** was not realised.

2.43.*

2.15 (0.0195 g, 0.0563 mmol) and Ag_2O (0.0281 g, 0.121 mmol) were comn=bined in a 10 ml RB flask with ethylene glycol (5 ml) giving a pale yellow solution with yellow precipitate (**2.15**) remaining. This was irradiated in a microwave reactor for 3x1 minutes. The solution became a dark yellow cloudy solution with a white/grey precipitate remaining suspected to be Ag^0. Mass spectrometry analysis showed the existence of only ligand, with no silver complex present.

2.44.*

2.16 (0.119 g, 0.0282 mmol) and Ag_2O (0.0171 g, 0.0738 mmol) and a catalytic amount of Bu_4NHSO_4 were combined in a 50 ml RB flask with DCM (25 ml) and allowed to stir for one hour in the dark. After one hour NaOH (1M, 3 ml) was added and continued to stir for a further 10 minutes. The reaction mixture was then filtered over celite and the filtrate was removed under vacuum. Analysis via mass spectrometry and ^{1}H-NMR confirmed the desired product, **2.44** was not realised.

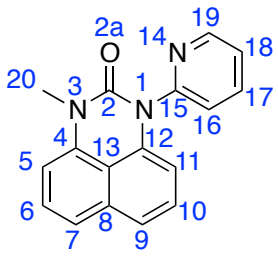
2.48.*

2.15 (0.030 g, 0.08651 mmol) was placed in a Schlenk tube. To the Schlenk tube, KO^tBu (0.0204 g, 0.182 mmol) in dry MeOH (5 ml) was added at 0 °C. The Schlenk tube was then made dark and AgOTf (0.033 g, 0.130 mmol) was added and the reaction was set to stir for one hour at 0 °C. TLC analysis showed ligand present and an unknown purple species. The reaction was filtered over celite and the MeOH was removed under vacuum. Crystallisations were set up with Heptane, Et_2O and $^iPr_2O$ diffusing into MeCN, DCM and MeOH. However, no product was isolated.

2.49.*

2.15 (0.100 g, 0.288 mmol), CuI (0.0659 g, 0.346 mmol) and KO^{t}Bu (0.0485 g, 0.433 mmol) were combined in a Schlenk tube under an argon atmosphere and moisture restrictive conditions. To this dry MeCN (7 ml) was added and the reaction mixture was set to reflux. Upon running the reaction for 48 hours at reflux another equivalent of KO^{t}Bu (0.0324 g, 0.288 mmol) was added. The reaction ran for a total of 72 hours whilst monitored by TLC on silica with EtOAc. Upon cooling to room temperature the reaction mixture was filtered over celite and the MeCN filtrate was removed under vacuum. In order to purify the cruse product column chromatography was performed on silica with EtOAc:DCM; 80:20. Only one product was isolated from the column to be pure being **2.50**. The desired product **2.49** was not observed.

1-(pyrid-2-yl)-3-methyl-perimid-2-one **2.50.**



Yield = 0.0053 g (6.67%) mp = 184 – 186 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.76 (1H, d, J = 3.9 hz, H19), 7.98 (1H, t, J = 7.6 hz, H17), 7.42 (3H, m), 7.29 (2H, m), 7.16 (1H, t, J = 7.8 hz), 6.65 (1H, d, J = 7.6 hz, H5), 5.89 (1H, d, J = 7.6 hz, H11), 3.46 (3H, s, H20). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 151.9 (1C, C2), 151.1 (1C, C19), 139.8 (1C, C17), 138.2, 137.9, 134.6, 128.0, 127.6, 125.0, 124.3, 120.0, 106.0 (1C, C5), 104.9 (1C, C11), 30.4 (1C, C20). IR: 2923 (br), 2849, (m), 1677 (m), 1587 (m), 1465 (sh), 1438 (w), 1341 (br). UV-Vis: 322 nm (3576). ESMS: Found MH^+ 276.1133, $C_{17}H_{14}N_3O$ requires MH^+ 276.1131.

2.51.*

NaH (0.0083 g, 0.346 mmol) was placed in a Schlenk tube under an argon atmosphere and moisture restrictive conditions. Dry DMF (2.5 ml) was added at 0 °C. **2.15** (0.050 g, 0.144 mmol) was dissolved in dry DMF (2.5 ml) in a different Schlenk flask again under an argon atmosphere and moisture restrictive conditions. This solution containing **2.15** was added to the NaH solution and allowed to warm up to room temperature and set to stir for three hours. After this $[Ru(benzene)Cl_2]_2$ (0.036 g, 0.0721 mmol) was added to the reaction mixture and set to stir for 18 hours. The DMF was removed under vacuum and the crude product was analysed via mass spectrometry and ^{1}H-NMR giving no evidence for the formation of **2.51**.

2.51.*

2.15 (0.050 g, 0.144 mmol) was added to a Schlenk tube under an argon atmosphere and moisture restrictive conditions. To this dry MeCN (5 ml) was added and the reaction mixture was sparged for 10 minutes with argon. Dry NEt_3 (0.024 ml, 0.173 mmol) was added to the reaction mixture and allowed to stir for one hour at room temperature. After an hour of stirring $[Ru(benzene)Cl_2]_2$ (0.036 g, 0.0721 mmol) was added and the reaction was set to reflux for 18 hours. Upon cooling the reaction

mixture was filtered giving a precipitate that was of no interest according to mass spectrometry and ^{1}H-NMR analysis. The filtrate was removed under vacuum and analysis via mass spectrometry and ^{1}H-NMR showed the existence of the desired product, **2.51**, but was not able to be isolated as a pure sample.

2.51 - 2.41.*

2.13 (0.150 g, 0.388 mmol) was added to a schenk tube under an argon atmosphere and moisture restrictive conditions. To this dry THF (5 ml) and chlorobenzene (5 ml) were added and sparged with argon for five minutes. $NaN(SiMe_3)_2$ in a 1M THF solution (0.388 ml, 0.388 mmol) was added into a separate Schlenk tube containing dry THF (1 ml) and chlorobenzene (1.5 ml) and this solution was sparged for five minutes with argon. After sparging of the $NaN(SiMe_3)_2$ solution was complete this was added to the Schlenk tube containing **2.13** at room temperature and the reaction mixture was set to stir fortwo hours, where the original yellow solution with a yellow precipitate dissolved into an orange solution. After two hours of stirring $[Ru(benzene)Cl_2]_2$ (0.097 g, 0.194 mmol) was added and the reaction mixture was set to stir for 18 hours at room temperature. After stirring for 18 hours the volitles were removed under vacuum and the chlorobenzene was removed on a Hi-Vac line. The crude product was washed with DCM (20 ml) and Et2O (20 ml) resulting in a precipitate containing the desired product, **2.51**. This crude product was dissolved in EtOH:H_2O; 4:1, (25 ml) and set to reflux with 2,2'-bipyridine (0.181 g, 1.16 mmol) over 48 hours to give the desired complex **2.41**. Upon cooling to room temperature the EtOH and H2O were removed under vacuum and the crude product was analysed to be $[Ru(bpy)_3]^{2+}$.

2.52.*

2.15 (0.100 g, 0.288 mmol) and $Pd(OAc)_2$ (0.0647 g, 0.288 mmol) were added to a Schlenk tube under an argon atmosphere and moisture restrictive conditions. To this dry DMSO (5 ml) was added and was set to stir for three hours at 120 °C. Upon cooling to room temperature the reaction mixture was quenched with H_2O (20 ml) and allowed to stir for another hour. The reaction mixture was then washed with DCM (3x100 ml). The DCM was subsequently dried upon $MgSO_4$ and removed under vacuum. The crude product showed the existence of palladium complexes but they could not be isolated and purified.

2.52.*

2.15 (0.050 g, 0.144 mmol) and $Pd(OAc)_2$ (0.0307 g, 0.137 mmol) were combined in a Schlenk tube under an argon atmosphere and moisture restrictive conditions. To this dry MeCN (5 ml) was added and the reaction mixture was set to reflux for 18 hours. Upon cooling the reaction mixture was filtered and the MeCN filtrate was removed under vacuum. The crude product was attempted to be purified by vapour diffusion of Et_2O, $^iPr_2O$ and Hexanes diffusing into MeCN and MeOH and the

slow evaporation of MeCN and MeOH solutions. However the crude product could not be purified or isolated.

2.53.*

2.14 (0.050 g, 0.124 mmol) and $Pd(OAc)_2$ (0.0264 g, 0.118 mmol) were combined in a Schlenk tube under an argon atmosphere and moisture restrictive conditions. To this dry MeCN (5 ml) was added and the reaction mixture was set to reflux for 18 hours. Upon cooling the MeCN was removed under vacuum and the crude product could not be purified.

2.56.*

2.15 (0.100 g, 0.288 mmol) and $Pd(OAc)_2$ (0.0307 g, 0.137 mmol) were combined in a Schlenk tube under an argon atmosphere and moisture restrictive conditions. To this dry MeCN (5 ml) was added and the reaction mixture was set to reflux for 18 hours. Upon cooling the MeCN was removed under vacuum and the crude product could not be purified to isolate the unidentified palladium complexes that were present.

3.33.

3.15 (0.0171 g, 0.0562 mmol) and Ag_2O (0.0280 g, 0.121 mmol) were combined in a Schlenk tube under moisture restrictive conditions and an argon atmosphere. To this 1,2-ethandiol (5 ml) was added and the reaction mixture was sparged with argon for five minutes. The reaction mixture was then set to reflux for 30 minutes. After this $Ru(bpy)_2Cl_2$ was added to the reaction mixture and continued to reflux for 18 hours. Upon cooling to room temperature the reaction mixture was quenched with water (15 ml) and filtered over celite. To the isolated filtrate NH4PF6 was added resulting in a precipitate that was isolated (0.0157 g). Single crystals were grown via slow diffusion of diisopropyl ether into MeCN. Yield = 0.0030 g (6.1%), mp = > 300 °C. ^{1}H-NMR (500 MHz, DMSO): δ 8.49 (d, J = 7.8 hz), 8.44 (d, J = 8.5 hz), 8.40 (d, J = 8.8 hz), 8.10 (t, J = 9.4 hz), 8.00 (m), 7.90 (d, J = 7.8 hz), 7.72 (d, J = 4.9 hz), 7.61 (m), 7.48 (m), 7.39 (m), 7.30 (t, J = 6.4 hz), 7.20 (m), 7.15 (m), 3,14 (m), 3.01 (m), 2.98 (m). ^{13}C-NMR (125 MHz, DMSO): δ 193.3 (1C, C2), 151.9, 127.6, 126.2, 124.3. UV-Vis: 287 nm (39445), 435 (6411). ESMS: Found M^{2+} 286.5607, $C_{29}H_{25}N_7Ru$ requires M^{2+} 286.5606.

3.34.*

3.20 (0.030 g, 0.0665 mmol) and Ag_2O (0.0334 g, 0.115 mmol) were combined in a 10 ml round bottom flask. To this 1,2-ethandiol (5 ml) was added and irradiated in a microwave reactor and was run for 2x1 minutes. After this time $Ru(bpy)_2Cl_2$ (0.0342 g, 0.0658 mmol) was added and was irradiated in a microwave reactor and run for 5x1 minutes. Upon cooling to room temperature the reaction mixture was quenched with water (10 ml) and NH_4PF_6 was added resulting in a precipitate.

Appendix 1

Crystal data and X-ray experimental details

Appendix 1.

Crystal data and X-ray experimental details for compounds **2.14**, **2.15**, **2.50** and **3.18**.

Compound	**2.14**	**2.15**	**2.50**	**3.18**
Empirical formula	$C_{24}H_{18}BrClN_3$	$C_{34}H_{28}B_2F_8N_6$	$C_{32}H_{18}N_8O_2$	$C_{28}H_{23}BrN_3O$
Radiation Wavelength	0.71073	0.71073	0.71073	1.54184
Formula weight	461.76	694.24	546.54	497.40
Temperature (K)	120.01(10)	120.01(10)	120.00(10)	120.01(10)
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	Pnma	C2/c
Unit cell dimensions: a (Å)	12.1144(7)	11.5352(3)	21.7888(6)	35.935(15)
b (Å)	14.7957(12)	10.42022(17)	6.8163(3)	13.1325(6)
c (Å)	11.7319(10)	13.6153(4)	8.9477(2)	21.416(9)
α (°)	90.00	90.00	90.00	90.00
β (°)	105.887(3)	112.892(3)	90.00	153.09(12)
γ (°)	90.00	90.00	90.00	90.00
Volume($Å^3$)	2022.5(3)	1507.66(7)	1328.89(7)	4574(3)
Z	4	2	2	8
Density (calculated) (Mg/m^3)	1.516	1.529	1.366	1.445
Absorption coefficient (mm^{-1})	2.173	0.126	0.735	2.651
F(000)	936.0	712.0	564.0	2040.0
Crystal size (mm)	0.59×0.51×0.39	0.31 × 0.27 × 0.13	0.31×0.16×0.21	0.19×0.15×0.03
Theta range for data collection (°)	3.5 to 55	5.48 to 65.68	10.68 to 147.7°	8.34 to 148.16
Reflections collected	9977	25172	7161	21613
Independent reflections [R(int)]	4116[0.0351]	5273[0.0289]	1432[0.0280]	4569[0.0323]
Data / restraints / parameters	4116/0/279	5273/0/255	1432/0/134	4569/0/298
Goodness-of-fit on F^2	1.037	1.071	1.136	1.358
R_1 [I>2sigma(I)]	0.0354,	0.0446	0.0658,	0.0395,
wR_2 (all data)	0.0937	0.1236	0.1896	0.1545
Largest diff. peak/hole / e $Å^{-3}$	0.76/-0.34	0.43/-0.26	0.33/-0.22	0.46/-0.61

Chapter 5

References

5.References

[1] P. S. Skell, S. R. Sandler, *J. Am. Chem. Soc.* **1958**, *80*, 2024-2025.

[2] E. O. Fischer, A. Maasböl, *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 580-581.

[3] W. A. Herrmann, C. Köcher, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162-2187.

[4] F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122-3172.

[5] H. Tomioka, T. Watanabe, K. Hirai, K. Furukawa, T. Takui, K. Itoh, *J. Am. Chem. Soc.* **1995**, *117*, 6376-6377.

[6] A. J. Arduengo, H. Bock, H. Chen, M. Denk, D. A. Dixon, J. C. Green, W. A. Herrmann, N. L. Jones, M. Wagner, R. West, *J. Am. Chem. Soc.* **1994**, *116*, 6641-6649.

[7] L. Cavallo, A. Correa, C. Costabile, H. Jacobsen, *J. Organomet. Chem.* **2005**, *690*, 5407-5413.

[8] E. A. Carter, W. A. Goddard, *J. Phys. Chem.* **1986**, *90*, 998-1001.

[9] W. M. Butler, J. H. Enemark, J. Parks, A. L. Balch, *Inorg. Chem.* **1973**, *12*, 451-457.

[10] A. Burke, A. L. Balch, J. H. Enemark, *J. Am. Chem. Soc.* **1970**, *92*, 2555-2557.

[11] H. W. Wanzlick, *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 75-80.

[12] A. J. Arduengo, J. R. Goerlich, R. Krafczyk, W. J. Marshall, *Angew. Chem.* **1998**, *110*, 2062-2064.

[13] A. J. Arduengo, *Acc. Chem. Res.* **1999**, *32*, 913-921.

[14] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361-363.

[15] D. Martin, A. Baceiredo, H. Gornitzka, W. W. Schoeller, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 1700-1703.

[16] F. E. Hahn, M. C. Jahnke, V. Gomez-Benitez, D. Morales-Morales, T. Pape, *Organometallics* **2005**, *24*, 6458-6463.

[17] E. Despagnet-Ayoub, R. H. Grubbs, *J. Am. Chem. Soc.* **2004**, *126*, 10198-10199.

[18] P. Bazinet, T.-G. Ong, J. S. O'Brien, N. Lavoie, E. Bell, G. P. A. Yap, I. Korobkov, D. S. Richeson, *Organometallics* **2007**, *26*, 2885-2895.

[19] C. C. Scarborough, M. J. W. Grady, I. A. Guzei, B. A. Gandhi, E. E. Bunel, S. S. Stahl, *Angew. Chem. Int. Ed.* **2005**, *44*, 5269-5272.

[20] D. Tapu, C. Owens, D. VanDerveer, K. Gwaltney, *Organometallics* **2008**, *28*, 270-276.

[21] F. Ullah, M. K. Kindermann, P. G. Jones, J. Heinicke, *Organometallics* **2009**, *28*, 2441-2449.

[22] P. L. Arnold, S. Pearson, *Coord. Chem. Rev.* **2007**, *251*, 596-609.

[23] R. Castarlenas, M. A. Esteruelas, E. Oñate, *Organometallics* **2005**, *24*, 4343-4346.

[24] D. J. Cardin, B. Cetinkaya, M. F. Lappert, *Chem. Rev.* **1972**, *72*, 545-574.

[25] K. Öfele, *J. Organomet. Chem.* **1968**, *12*, P42-P43.

[26] F. P. de, N. Marion, S. P. Nolan, *Coord. Chem. Rev.* **2009**, *253*, 862-892.

[27] H. W. Wanzlick, H. J. Schönherr, *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141-142.

[28] K. Öfele, *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 950-950.

[29] R. R. Schrock, *J. Am. Chem. Soc.* **1974**, *96*, 6796-6797.

[30] Y. Canac, M. Soleilhavoup, S. Conejero, G. Bertrand, *J. Organomet. Chem.* **2004**, *689*, 3857-3865.

[31] W. W. Schoeller, D. Eisner, S. Grigoleit, A. B. Rozhenko, A. Alijah, *J. Am. Chem. Soc.* **2000**, *122*, 10115-10120.

[32] T. E. Taylor, M. B. Hall, *J. Am. Chem. Soc.* **1984**, *106*, 1576-1584.

[33] S. F. Vyboishchikov, G. Frenking, *Chem. Eur. J.* **1998**, *4*, 1428-1438.

[34] I. J. B. Lin, C. S. Vasam, *Coord. Chem. Rev.* **2007**, *251*, 642-670.

[35] P. J. Fraser, W. R. Roper, F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* **1974**, 102-105.

[36] A. M. Voutchkova, M. Feliz, E. Clot, O. Eisenstein, R. H. Crabtree, *J. Am. Chem. Soc.* **2007**, *129*, 12834-12846.

[37] A. M. Voutchkova, L. N. Appelhans, A. R. Chianese, R. H. Crabtree, *J. Am. Chem. Soc.* **2005**, *127*, 17624-17625.

[38] P. L. Arnold, F. G. N. Cloke, T. Geldbach, P. B. Hitchcock, *Organometallics* **1999**, *18*, 3228-3233.

[39] Y. Ito, T. Hirao, K. Tsubata, T. Saegusa, *Tetrahedron Lett.* **1978**, 1535-1538.

[40] R. A. Michelin, L. Zanotto, D. Braga, P. Sabatino, R. J. Angelici, *Inorg. Chem.* **1988**, *27*, 93-99.

[41] S. Diez-Gonzalez, S. P. Nolan, *Coord. Chem. Rev.* **2007**, *251*, 874-883.

[42] S. Di□ez-Gonza□lez, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612-3676.

[43] W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. AU - Artus, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2371-2374.

[44] N. Marion, S. P. Nolan, *Acc. Chem. Res.* **2008**, *41*, 1440-1449.

[45] U. Christmann, R. Vilar, *Angew. Chem. Int. Ed.* **2005**, *44*, 366-374.

[46] P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100-110.

[47] S. T. Nguyen, L. K. Johnson, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1992**, *114*, 3974-3975.

[48] S. T. Nguyen, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1993**, *115*, 9858-9859.

[49] A. Fuerstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Stelzer, O. R. Thiel, *Chem.--Eur. J.* **2001**, *7*, 3236-3253.

[50] A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Stelzer, O. R. Thiel, *Chem. Eur. J.* **2001**, *7*, 3236-3253.

[51] C. W. Bielawski, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2000**, *39*, 2903-2906.

[52] M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953-956.

[53] M. Duati, S. Tasca, F. C. Lynch, H. Bohlen, J. G. Vos, S. Stagni, M. D. Ward, *Inorg. Chem.* **2003**, *42*, 8377-8384.

[54] K. O□fele, E. Tosh, C. Taubmann, W. A. Herrmann, *Chem. Rev.* **2009**, *109*, 3408-3444.

[55] G. Venkatachalam, M. Heckenroth, A. Neels, M. Albrecht, *Helv. Chim. Acta* **2009**, *92*, 1034-1045.

[56] J. M. Calvert, J. V. Caspar, R. A. Binstead, T. D. Westmoreland, T. J. Meyer, *J. Am. Chem. Soc.* **1982**, *104*, 6620-6627.

[57] J. R. Winkler, T. L. Netzel, C. Creutz, N. Sutin, *J. Am. Chem. Soc.* **1987**, *109*, 2381-2392.

[58] M. Maestri, N. Armaroli, V. Balzani, E. C. Constable, A. M. W. C. Thompson, *Inorg. Chem.* **1995**, *34*, 2759-2767.

[59] V. Friese, S. Nag, J. Wang, M.-P. Santoni, A. Rodrigue-Witchel, G. S. Hanan, F. Schaper, *Eur. J. Inorg. Chem.* **2011**, *2011*, 39-44.

[60] M. Alexandra Bernardo, F. Pina, B. Escuder, E. Garcia-Espana, M. Luz Godino-Salido, J. Latorre, S. V. Luis, J. A. Ramirez, C. Soriano, *J. Chem. Soc., Dalton Trans.* **1999**, 915-922.

[61] B. Bag, P. K. Bharadwaj, *J. Phys. Chem. B* **2005**, *109*, 4377-4390.

[62] A. J. Eastwood, A. E. A. Contoret, S. R. Farrar, S. Fowler, S. M. Kelly, S. M. Khan, J. E. Nicholls, M. O'Neill, *Synth. Met.* **2001**, *121*, 1659-1660.

[63] J. M. Herbert, P. D. Woodgate, W. A. Denny, *J. Med. Chem.* **1987**, *30*, 2081-2086.

[64] P. Bazinet, G. P. A. Yap, D. S. Richeson, *J. Am. Chem. Soc.* **2003**, *125*, 13314-13315.

[65] H. Tsurugi, S. Fujita, G. Choi, T. Yamagata, S. Ito, H. Miyasaka, K. Mashima, *Organometallics* **2010**, *29*, 4120-4129.

[66] L. V. Desai, K. J. Stowers, M. S. Sanford, *J. Am. Chem. Soc.* **2008**, *130*, 13285-13293.

[67] M. M. Heravi, B. Baghernejad, H. A. Oskooie, *Chin. J. Chem.* **2009**, *27*, 379-383.

[68] N. M. Starshikov, A. F. Pozharskii, *Khim. Geterotsikl. Soedin.* **1980**, 96-100.

[69] M. L. Kantam, J. Yadav, S. Laha, B. Sreedhar, S. Jha, *Adv. Synth. Catal.* **2007**, *349*, 1938-1942.

[70] Z. Xi, F. Liu, Y. Zhou, W. Chen, *Tetrahedron* **2008**, *64*, 4254-4259.

[71] M. Shakir, M. Azam, S. Parveen, A. U. Khan, F. Firdaus, *Spectrochim. Acta, Part A* **2009**, *71A*, 1851-1856.

[72] J. Gong, S. J. Sturla, *J. Am. Chem. Soc.* **2007**, *129*, 4882-4883.

[73] O. V. Vinogradova, E. A. Filatova, N. V. Vistorobskii, A. F. Pozharskii, I. V. Borovlev, Z. A. Starikova, *Russ. J. Org. Chem.* **2006**, *42*, 338-348.

[74] I. V. Borovlev, O. P. Demidov, A. F. Pozharskii, *Chem. Heterocycl. Compd. (N. Y., NY, U. S.)* **2002**, *38*, 1091-1095.

[75] C. Avendano, M. Espada, B. Ocana, S. Garcia-Granda, M. d. R. Diaz, B. Tejerina, F. Gomez-Beltran, A. Martinez, J. Elguero, *J. Chem. Soc., Perkin Trans. 2* **1993**, *0*, 1547-1555.

[76] C. Deissler, F. Rominger, D. Kunz, *Dalton Trans.* **2009**, 7152-7167.

[77] C. M. Fitchett, *Proposed communication*.

[78] V. J. Catalano, A. L. Moore, *Inorg. Chem.* **2005**, *44*, 6558-6566.

[79] D. M. Khramov, E. L. Rosen, J. A. V. Er, P. D. Vu, V. M. Lynch, C. W. Bielawski, *Tetrahedron* **2008**, *64*, 6853-6862.

[80] W. Ghattas, H. Mu□ller-Bunz, M. Albrecht, *Organometallics* **2010**, *29*, 6782-6789.

[81] S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller, R. H. Crabtree, *J. Am. Chem. Soc.* **2002**, *124*, 10473-10481.

[82] A. K. Verma, J. Singh, V. K. Sankar, R. Chaudhary, R. Chandra, *Tetrahedron Lett.* **2007**, *48*, 4207-4210.

[83] L. Alakonda, M. Periasamy, *Synthesis* **2012**, *44*, 1063-1068.

[84] V. K. Cherkasov, N. O. Druzhkov, T. N. Kocherova, A. S. Shavyrin, G. K. Fukin, *Tetrahedron* **2012**, *68*, 1422-1426.

[85] N. Kulisic, S. More, A. Mateo-Alonso, *Chem. Commun.* **2011**, *47*, 514-516.

[86] J. Hu, D. Zhang, F. W. Harris, *J. Org. Chem.* **2005**, *70*, 707-708.

[87] R. Salvio, R. Cacciapaglia, L. Mandolini, *The Journal of Organic Chemistry* **2011**, *76*, 5438-5443.

[88] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112-122.

[89] G. M. Sheldrick, *SHELXL-97, Programs for X-ray Crystal Structure Refinement* **1997**, *University of Gottingen*.

[90] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339-341.