University of Strathclyde

Department of Pure and Applied Chemistry

Novel Imidazolium Salts, N-Heterocyclic Carbenes and their Coordination Polymers.

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"This thesis is the result of the author's original research. It has been composed by the author and has not been previously submitted for examination which has led to the award of a degree.

Signed:

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Abstract

N-heterocyclic carbenes (NHCs) have been developed in the last two decades as an important material in homogenous catalysis. Also MOFs have recently been receiving a great deal of attention due to their potential applications e.g. gas storage, adsorption and catalysis. This study involved the synthesis of new imidazolium salt functionalised with nitriles, carboxylates and pyridyl and their conversion into NHC complexes and porous coordination polymers.

A series of nitrile substituted imidazolium salts were synthesised. 1,1-bis(4-cyanophenyl)-3,3-methylenediimidazolium and 1-bromomethyl-3-(4-cyanophenyl)imidazolium salts were synthesised by N-arylation and N-alkylation of 4-cyanophenyl imidazole. The bisimidazolium salt was used to synthesise a dimeric silver(I) NHC complex. Reaction of this silver complex with $[Ru(p\text{-}cy)Cl_2]_2$ results in transmetallation and the formation of the NHC complex [Ru(**L**)Cl]BF_4. A platinum diNHC complex, [Pt(**L**)Br_2], was synthesized by *in situ* deprotonation of the bisimidazolium salt precursor, using NaOAc and $[Pt(COD)Cl_2]$. All were characterised crystallographically.

Picolyl substituted imidazolium salts were synthesised, 1,3-bis(4-picolyl)imidazolium, 1,3-bis(2-picolyl)imidazolium and 1-(4-cyanophenyl)-3-(4-picolyl)imidazolium salt were synthesised using solvothermal synthesis and were characterised spectroscopically, by elemental analysis and X-ray crystallographic analysis. 1,3-bis(2-picolyl)imidazolium chloride was prepared according to literature method while the 1-methyl-3-(4-picolyl)imidazolium salt was synthesised from the methyl imidazole and 4-picolyl chloride. All the picolyl substituted imidazolium salts were converted to Ag(I) NHC complexes of the type $[Ag(NHC)_2]^+$. The bis 4-picolyl imidazolium was used to synthesise two isostructural highly porous coordination polymers of Ag(I) and Cu(I).

New carboxylate imidazolium salts, 3,3'-methylenebis(1-(4-carboxyphenyl)-1H-imidazol-3-ium), 1,3-bis(4-carboxyphenyl)-1H-imidazol-3-ium, 1,3-bis(3-carboxyphenyl)-1H-imidazol-3-ium, 3-(4-carboxyphenyl)-1-methyl-1H-imidazol-3-ium

and 1-benzyl-3-(4-carboxyphenyl)-1H-imidazol-3-ium salts were prepared from hydrolysis of the corresponding nitrile imidazolium salts in HX (X = Br, Cl). The 1-benzyl-3-(4-carboxyphenyl)-1H-imidazol-3-ium imidazolium salt formed a rhodium diNHC complex [Rh(**L**)$_2$Br(CO)] by reacting the ligand with rhodium acetate in a solvothermal process. The 1,3-bis(4-carboxyphenyl)imidazolium salt reacted with $LnCl_3.XH_2O$ in DMF under a solvothermal process to give two isostructural MOFs of La(III) and Ce(III).

Abbreviations

Ac	acetyl
Bpy	bipyridine
BDC	benzene dicarboxylic acid
BTC	benzene tricarboxylic acid
CM	cross metathesis
COD	cyclooctadiene
Cy	cymene
1D	1 dimension
2D	2 dimension
3D	3 dimension
dba	dibenzylideneacetone
DCM	dichloromethane
DMF	dimethylformamide
DMSO	dimethylsulphoxide
En	ethylene diamine
Et	ethyl
IRMOF	isorectangular metal oganic frameworks
HMDS	hexamethyldisilazide
HKUST	Hong-Kong University of Science and Technology

IL	ionic liquid
Imid.	imidazole
INA	isonicotinic acid
KHMDS	potassium hexamethyldisilazide
Me	methyl
Mes	mesityl
MIL	Materiaux de I'Instiut Lavoisier
MOF	Metal organic framework
NMR	nuclear magnetic resonance
NHC	N – heterocyclic carbene
PCP	porous coordination polymer
PBU	primary building unit
PSM	post synthetic modification
Pyz	pyrazine
Pzdc	pyrazinedicarboxylic acid
RCM	ring closing metathesis
ROCM	ring opening cross metathesis
ROM	ring opening metathesis
ROMP	ring opening metathesis polymerisation
SNU	Seoul National University
Tbip	tert-butylisophthalic acid
Tf	trifluoromethylsulphonyl
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethyl silane/ trimethyl silyl
ZIF	Zeolitic Imidazolium Framework

TABLE OF CONTENTS

CHAPTER 1

N- Heterocyclic Carbene

1.1. A History of carbene

Carbenes are compounds with a divalent carbon atom which is linked to two adjacent groups by covalent bonds and has two non-bonding electrons (**1.1**) which are either in singlet or in triplet state (Figure 1.1). A singlet state is when in the ground state the two non bonding electrons are in the same orbital (**1.2**) with anti parallel spin while a triplet state is when they are in two different orbitals (**1.3**) with parallel spin.[1]

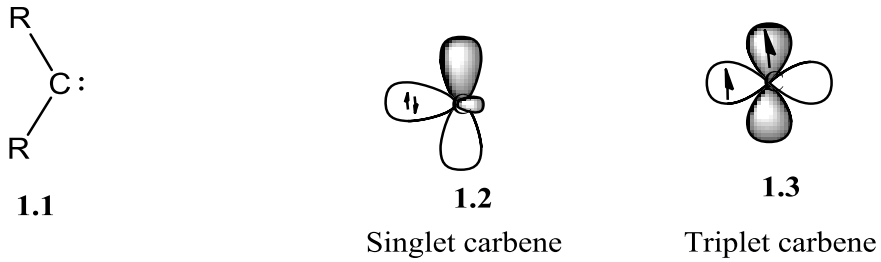
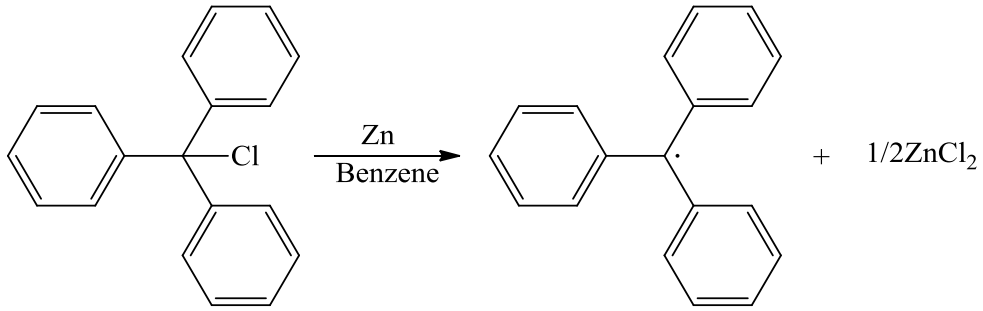


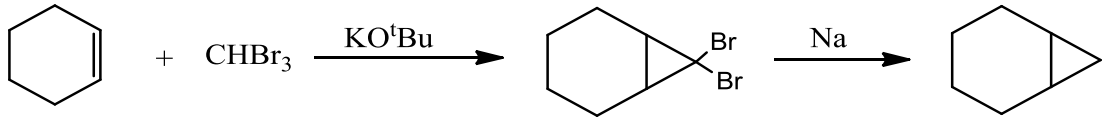
Figure 1.1: Carbene

The history of carbene chemistry can be traced to the mid 1800s, at a time when free radical chemistry was not fully understood. The idea of carbene-like species started as an assumption, most notably in works of Geuther and Hermann in 1855,[2] Nef in 1897[3] and through to 1900 when Gomberg characterised the first radical ($Ph_3C^{\cdot}$) (Scheme 1.1),[4] this was followed by the work of Staudinger in the 1910s[5] which contributed immensely to the recognition of carbenes as new reactive species. In the following years through to the 1930s free radicals were finally recognised and accepted, and their use in organic chemistry as reaction intermediates grew rapidly. Carbene moieties were then regarded as diradicals.[6]



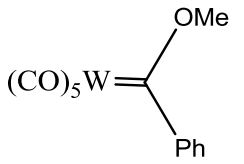
Scheme 1.1: First isolated free radical

Interest began to grow at the beginning of 1950s in the reactions of these diradicals (carbenes).[7, 8] In 1953, Doering and Knox reported a synthesis of tropolone from addition of carbene (methylene) and substituted benzene[9] and also proved the existence of dibromomethylene intermediates, through the addition of bromoform to an alkene (Scheme 1.2). Thereafter more organic syntheses involving the use of methylene intermediates were reported.[10, 11]



Scheme 1.2: Cyclopropanation of alkene via a dibromomethylene intermediate.

A major breakthrough was recorded when Fischer in 1964[12] isolated and characterised the first metal carbene complex; methoxyphenyl methylene tungsten (0) pentacarbonyl (**1.4**). In recognition of this work, these types of carbenes were called Fischer carbene, and they may best be considered as singlet carbenes, as the electron pair on the carbenic carbon atom occupies a single orbital.



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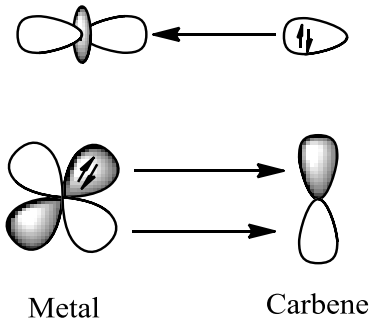
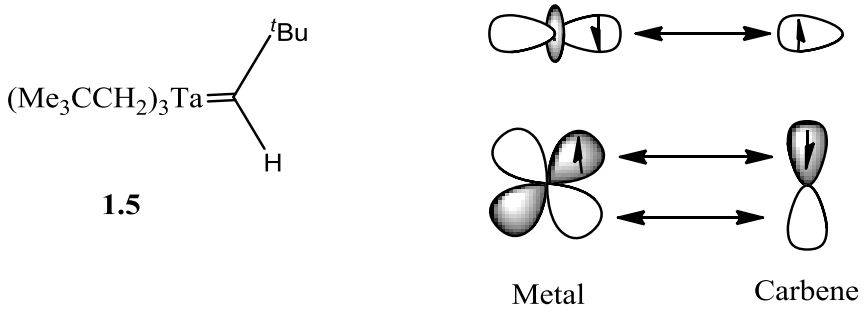


Figure 1.2: Fischer carbene

They form a metal-carbon bond by mutual donor acceptor interaction of two closed-shell fragments (Figure 1.2), the major bonding arising from carbene to metal σ-donation and a lesser π-back donation component from simultaneous metal to carbene π-back donation. The π-electrons are usually polarised toward the metal and the carbon-metal bond has a partial double bond character which diminishes with increasing stabilisation

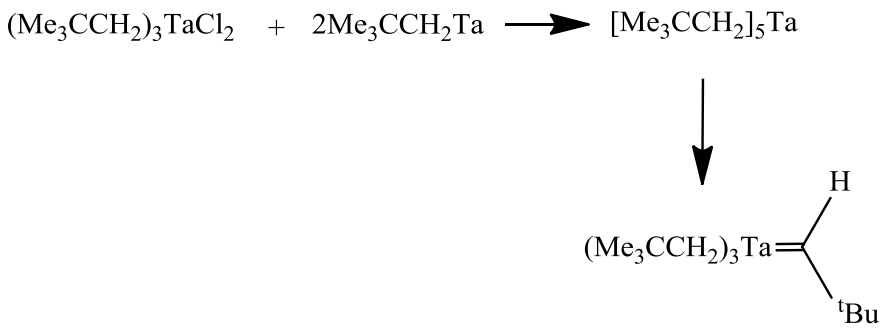
of the carbene by its α-groups. These groups on the carbene need to be π-donor substituents such as alkoxy and amino groups. Stable Fischer carbenes are mainly found with middle - late transition metals, typically in low oxidation states and they are electrophilic at the carbon-metal bond which makes it more prone to nucleophilic attack at the carbene centre.[13] Fischer carbene complexes are commonly used as reagents for the synthesis of organic compounds, most commonly in an annulation known as the Dötz reaction, which is a method used to prepare substituted aromatic ring system from non-aromatic precursors.[14]

Ten years later Schrock isolated and characterised the first high oxidation state metal alkylidine complex (**1.5**).[15] They are commonly synthesised through α-hydride elimination/alkane extrusion process. For example the formation of **1.5** results from rapid loss of neopentane from a penta(neo-pentyl)tantalum (V) intermediate (Scheme 1.3).



1.5

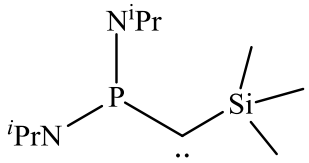
Figure 1.3: Schrock carbenes



Scheme 1.3: Synthesis of Schrock carbene (**1.5)**

Also in recognition of his work, these types of carbene were regarded as Schrock carbenes, and are best described as having their valence electrons residing in different orbitals and as such are triplet carbenes. They form a covalent metal-carbon bond created by both σ- and π-interactions (Figure 1.3). The π-electrons are nearly equally distributed between the carbon and the metal, and the metal-carbon bond is seen as a double bond. Schrock carbenes, unlike those of the Fischer type, form stable complexes with early transition metals in high oxidation states. They do not require π-donor substituents for stability as was the case with Fischer carbenes, and they are nucleophilic at the carbon- metal bond which makes them attract electrophiles at the carbene centre.[15] Schrock carbene complexes have been widely used in synthetic organic chemistry as catalysts in olefin metathesis reactions and also as a substitute for phosphorus ylides in the Wittig reaction.[16]

However, despite the significant interest in metal carbene species, it was not until 1988 that Bertrand and co-workers[17] isolated the first stable carbene (**1.6**) as red oil. Although it was successfully isolated, it proved not to be a material which is useful as a ligand for transition metals.[17] However, this paved the way for a now well established area of chemistry.



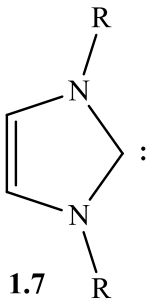
1.6

Figure 1.4: First isolated stable carbene

1.2. N-Heterocyclic carbenes (NHCs)

A class of these carbenes that has received the attention of many research groups are the N- heterocyclic carbenes (NHCs). These important carbenes are cyclic with the carbene carbon bearing at least one α-amino substituent (**1.7**). This field of chemistry

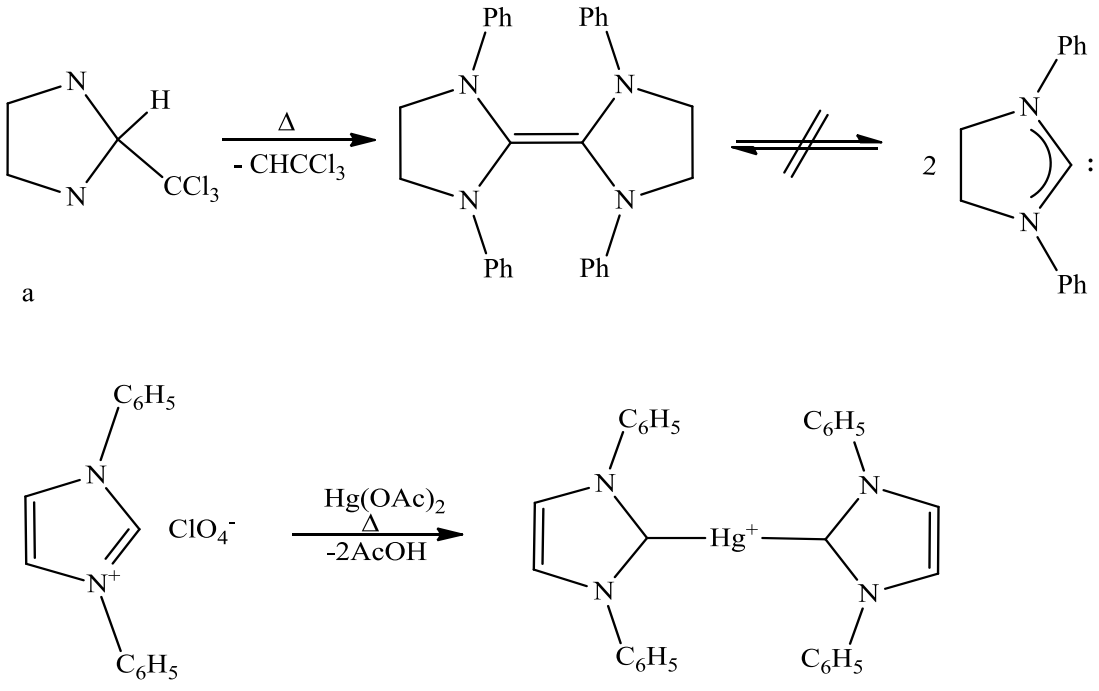
was born in the 1960s when Wanzlick et al[18] suggested the existence of the NHCs from the cleavage of enetetraamines according to Scheme 1.4.



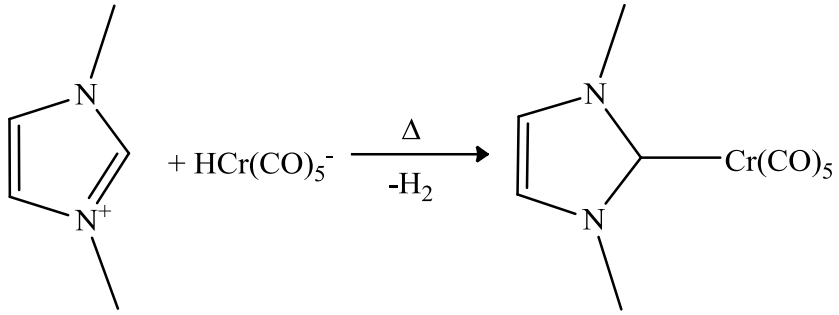
1.7

Figure 1.5: Typical NHC

While this was unsuccessful for the synthesis of a free carbene, it lead to the first NHC metal complexes containing mercury in 1968[18] followed in the same year by an independent report of Öfele on a chromium NHC Complex (Scheme 1.5).[19]



Scheme 1.4: Wanzlick's NHC complex, a) NHC postulation, b) NHC complex

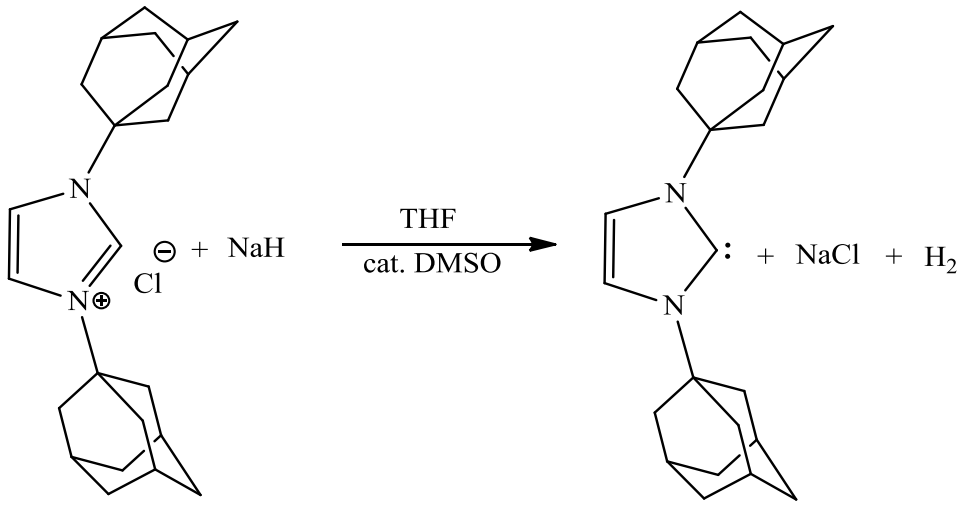


Scheme 1.5: Öfele's NHC complex

Lappert et al followed this work by investigating the NHC complexes obtained from thermolysis of electron rich olefins[20, 21] in the presence of metal salts. Additionally, some work by Taube et al on ruthenium NHC complexes in the middle of 1970s contributed to the emergence of this area of chemistry.[22]

In all these early studies a free NHC was not isolated, but was prepared *in situ* through deprotonation of the imidazolium salt by the basic ligand of the metal salt used in the process.[19] Little attention was given thereafter, to this amazing field of carbene chemistry until 1991 when Arduengo isolated the first free crystalline NHC (**1.8**).[23] This important and fantastic development opened up this area to the world of chemistry, which attracted a huge interest and advancement in the field of carbene chemistry, and immediately their use as ligands in organometallic chemistry hugely increased.

Arduengo prepared the free carbene by deprotonation of an imidazolium salt with sterically demanding substituents, N,N'–diadamantyl imidazolium chloride, using sodium hydride and catalytic amount of dimethylsulfoxide (Scheme 1.6).[23] Steric hindrance of the adamantyl substituents on the nitrogen atom prevents the free NHC from dimerising.



1.8

Scheme 1.6: Arduengo's isolation of the first free NHC

A year later Arduengo also reported the synthesis of a number of other NHCs (Figure 1.6), among which were 1,3-dimethylimidazol-2-ylidene (**1.9**) and 1,3,4,5–tetramethyl imidazol-2-ylidene (**1.10**), but unlike the previous isolated NHCs, they were less stable, could not be crystallised, and were only characterised as oils.[24] They later replaced the alkyl groups on the nitrogen atom with simple aromatic groups (**1.11**, **1.12**) but the free carbenes could not to be isolated. Introduction of methyl and chloro groups onto the aromatic ring resulted in stabilisation and permitted the free carbenes to be isolated, as a result they reported three more free NHCs; 1,3-bis(4-methylphenyl)imidazol-2-ylidene, bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (**1.13**) and 1,3-bis(4-chlorophenyl) imidazol-2-ylidene.[24] The isolation of the NHCs with less bulky N-substituents than adamantyl suggests that the steric hindrance suspected to be responsible for the stability of the first isolated free carbene may not be the only factor. Electronic stabilisation of the carbene carbon in imidazol-2-ylidenes may be enough to allow isolation of free NHCs even without the steric hindrance.[25] Several other free NHCs based on saturated heterocycles, the imidazolin-2-ylidenes, were isolated and reported by Arduengo and co workers.[26]

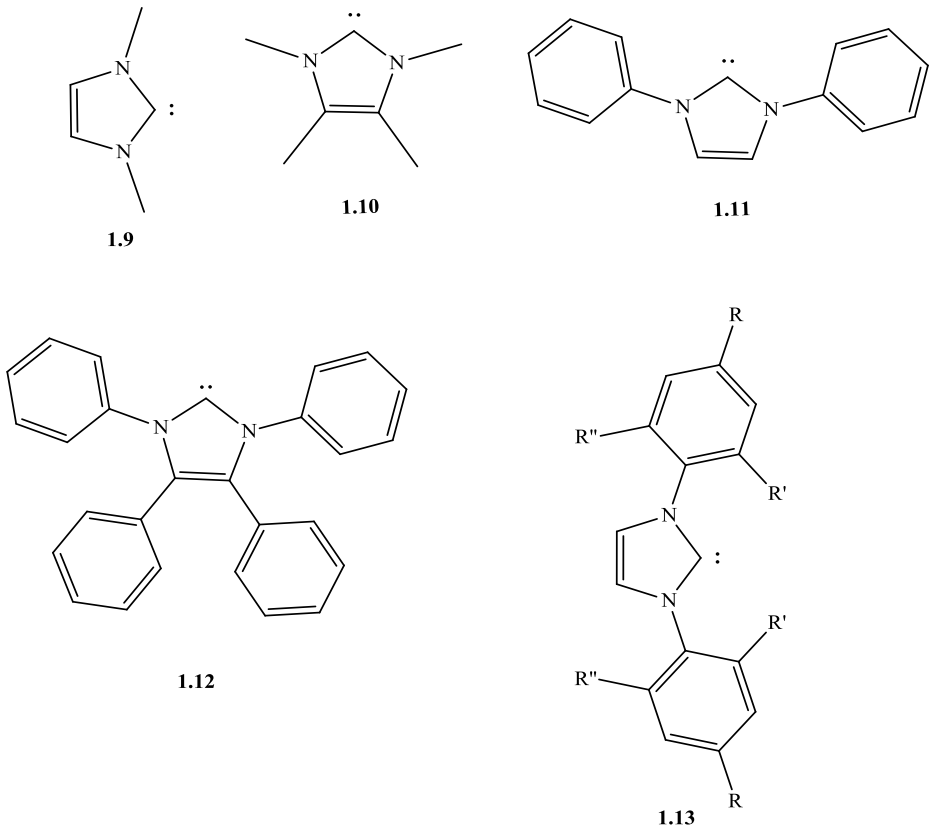


Figure 1.6: Examples of some early isolated NHC

Soon after, Herrmann and his group noted the existence of an analogy between phosphines and NHCs, in that they are both σ-donors and have low π-back-donating character, and this makes them able to behave in similar manner in metal complexation.[27] This suggests that phosphines could potentially be replaced by the NHCs which are often more easily synthesised and funtionalised. In addition, it is observed that NHCs generally form stronger bonds to metal centres than phosphines which results in more stable complexes than with phosphine ligands.[28]

Although the first free NHC isolated comes from five-membered rings having two nitrogen atoms, several other NHCs with rings ranging from four to seven membered and having 2 to 4 nitrogen atoms were reported in the literature (Figure 1.7).[29-33]

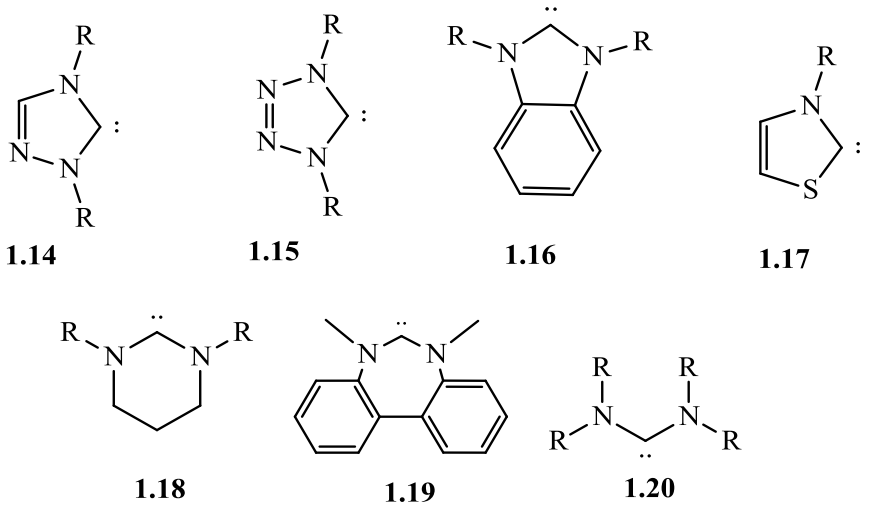


Figure 1.7: Examples of different types of carbenes

1.2.1. NHC electronic structure

Initially, when Arduengo isolated the first crystalline NHC (Figure 1.5) it was assumed that steric factors were necessary for NHC stabilisation, but evidence from subsequent NHCs isolated with low steric bulk (Figure 1.6) point to a different picture, suggesting that electronic factors may be primarily responsible for the stability of the NHCs. NHCs are bent carbenes which means that the frontier orbitals are sp^2-hybridized in-plane and a p-orbital orthogonal to the sp^2 plane, referred to as σ and pπ respectively.[32] NHCs have two α-amino substituents which play two electronic roles, firstly they stabilise the formally sp^2 hybridised non-bonding lone pair by σ-inductive withdrawing effect (Figure 1.8). Secondly, the vacant p-orbital is stabilised by a mesomeric effect, through donation of the α-amino lone pairs into vacant p-orbital (Figure 1.8). This push-push (mesomeric) and pull-pull (inductive) arrangement ensures the preservation of electroneutrality at the carbene centre making the singlet state dominant.[32]

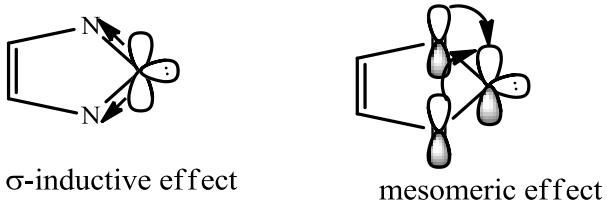


Figure 1.8: Electronic stabilisation in NHCs

1.2.2. NHC metal complexes

The first NHC metal complexes were reported in 1968, independently by Öfele and Wanzlick (Scheme 1.3 and 1.4).[19] However, thereafter few NHC metal complexes were reported until the isolation and characterisation of the free NHC (**1.8**) by Arduengo in 1991.[23] Thanks to this important discovery, an avalanche of reports of NHC metal complexes has occurred. Today complexes of NHCs with nearly all transition and main group metals are known.[1, 32-34] NHC ligands bind to both soft and hard metals; they primarily bind via a strong σ-donation of the carbene lone pair to the metal. Although NHCs are regarded mainly as σ–donors theoretical and structural studies suggest the existence of a π-back bonding component for certain metal centres.[35] Their excellent σ–donor properties make NHC metal complexes significantly different to their counterparts, the electrophilic Fisher carbene and the nucleophilic Schrock carbene metal complexes.[36] NHCs, like phosphines, are two electron-donors but they are more strongly electron donating than phosphine. As a result they often bind more strongly to the metal centre and tend to form more stable complexes than phosphines.[27, 36]

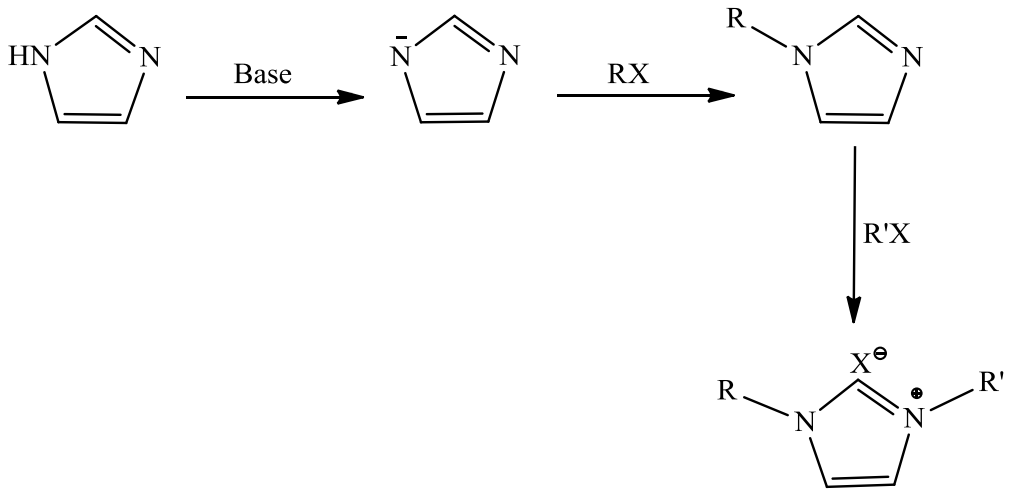
1.2.3. Synthesis of NHC precursors

In most cases the synthesis of NHCs and their complexes start from N,N' disubstituted azolium salts, which are used as precursors for the synthesis of imidazol-2-ylidenes, which constitute the largest group of stable NHC.[31] The imidazolium salt precursors are most commonly prepared by:

1) Stepwise N-alkylation of imidazole ring with the desired electrophile,[37] or
2) Building the heterocyclic ring with the appropriate substituents in one pot reaction using primary amines, glyoxal and paraformaldehyde in the presence of acid.[38] Other one pot synthetic strategies utilising different starting materials are in use and Cesar et al have reviewed this in more detail.[39]

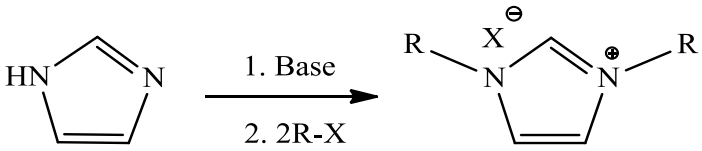
In the first process above, imidazole is deprotonated using a suitable base and two different substituents are introduced in a stepwise manner, allowing both symmetrical

and unsymmetrical imidazolium salts to be prepared (Scheme 1.7).[37] The major drawback of this method is that it is only readily applicable to alkyl halides.



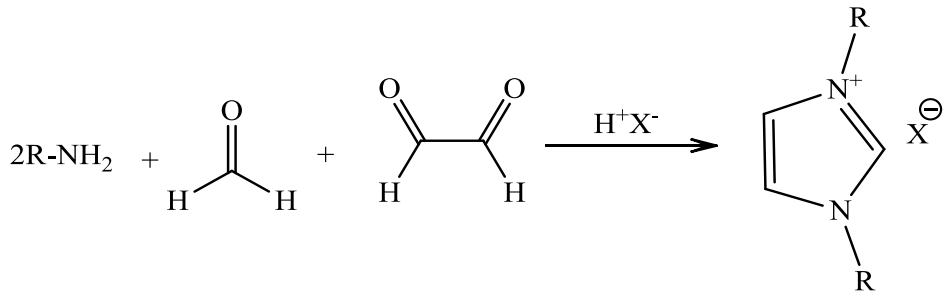
Scheme 1.7: Formation of imidazolium salt by stepwise alkylation of imidazole

Both symmetrical and unsymmetrical imidazolium salts can be prepared using this method with a suitable base.[40] The base, imidazole and two equivalents of the alkylating agent are all taken in one step (Scheme 1.8), it works well for N,N-diallyl imidazole.[41, 42]



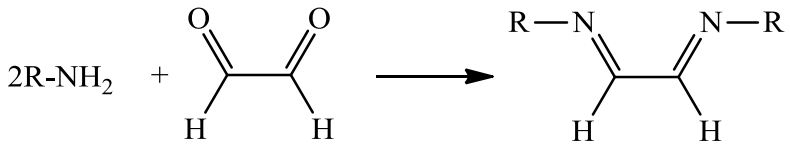
Scheme 1.8: One pot synthesis of symmetrical imidazolium salt

The second method of building the heterocyclic ring in a one pot synthesis involves the coupling of two equivalents of primary amine with glyoxal and completing the ring with formaldehyde in the presence of an acid (Scheme 1.9).[38, 42]



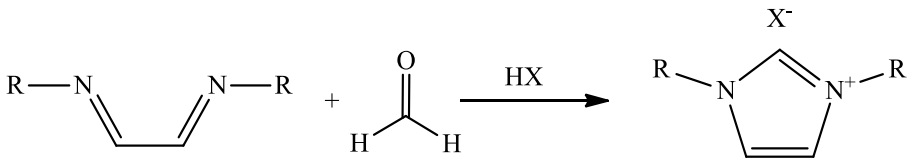
Scheme 1.9: Building of heterocylic ring in imidazolium salt synthesis

The reaction can be split into two steps which involve treating two equivalents of primary amine with glyoxal and isolating the Schiff's base (diimine) in the first step (Scheme 1.10).[40]



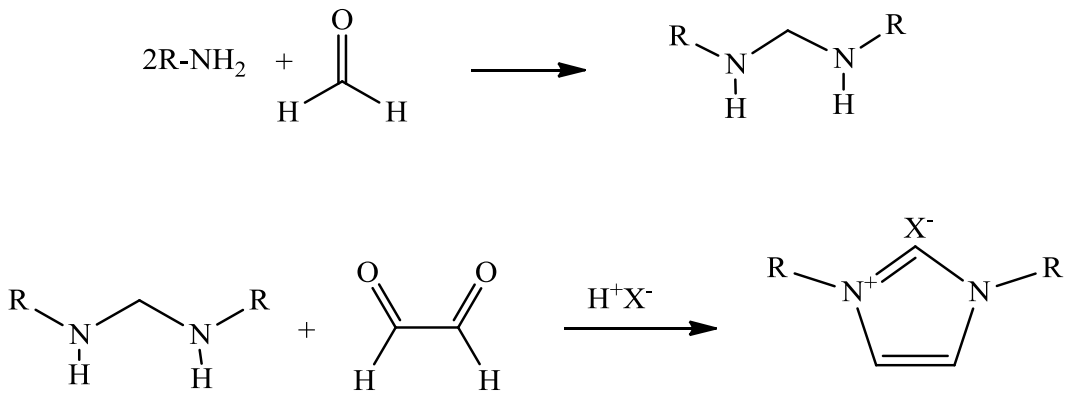
Scheme 1.10: Diimine formation

Then the ring is closed in the second step using paraformaldehyde, triethyl orthoformate or chloromethyl ethyl ether (Scheme 1.11). The method works most successfully in symmetrical systems.[40]



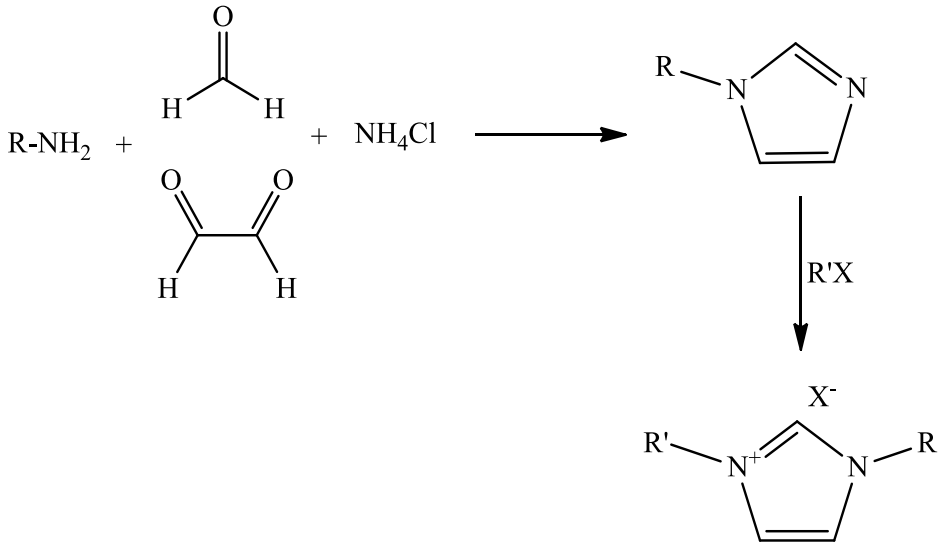
Scheme 1.11: Synthesis of imidazolium salt

Alternatively two equivalents of primary amine can be treated with paraformaldehyde. triethyl orthoformate or chloromethyl ethyl ether resulting in the formation of a diamine which is then closed with glyoxal in the second step (Scheme 1.12).



Scheme 1.12: Two step synthesis of imidazolium salt

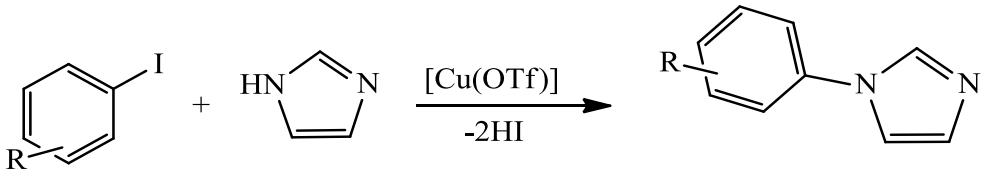
Grindnev and Mihaltseva[42] proposed a method which allows the combination of the two processes above by first synthesizing 1-alkylimidazole by a multi-component reaction involving primary amine, formaldehyde, glyoxal and ammonium chloride, which is subsequently alkylated at the second ring nitrogen atom with alkyl/aryl halide to give the desired imidazolium salt precursor (Scheme 1.13).[42]



Scheme 1.13: One pot synthesis followed by alkylation

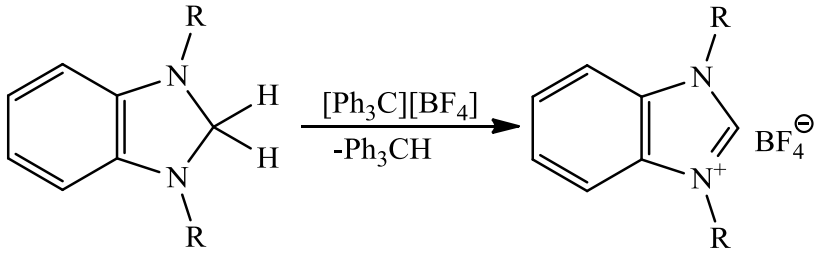
Another method involves direct coupling of imidazole with aryl halide in the presence of copper(I) salts to yield an aryl substituted imidazole, which may be followed by

alkylation to give the corresponding imidazolium salt. There are a wide range of copper catalysed aryl coupling reactions, for instance, with copper(I) triflate as shown in Scheme 1.14.[41]



Scheme 1.14: Coupling of imidazole with aryl halide

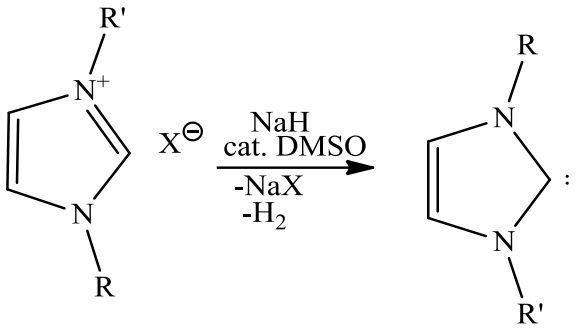
For benzimidazolium salts, the route involves hydrogen abstraction by treatment with tritylium tetrafluoroborate (Scheme 1.15).[43]



Scheme 1.15: Synthesis of benzimidazolium salt

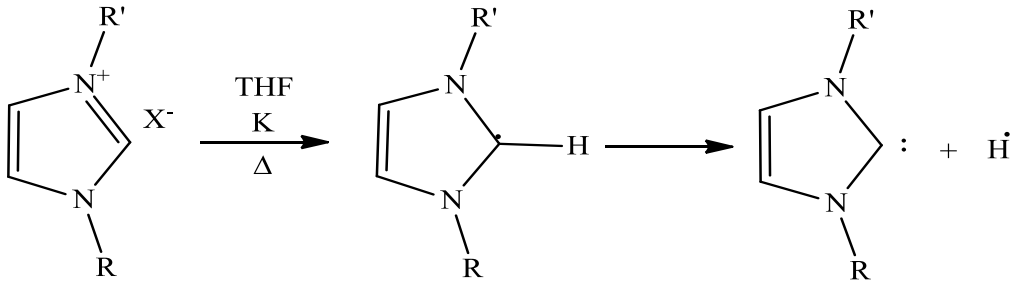
1.2.4. Free NHC synthesis

The most common method for the formation of imidazolylidenes is the deprotonation of imidazolium salts. The deprotonation can be carried out in ammonia or non- protic solvents under anhydrous conditions in the presence of a strong base such as potassium or sodium hydride, K^{t}BuO, HMDS etc.[37-39] In some cases a catalyst (e.g tert-butoxide, lithium aluminium hydride) may also be added (Scheme 1.16)



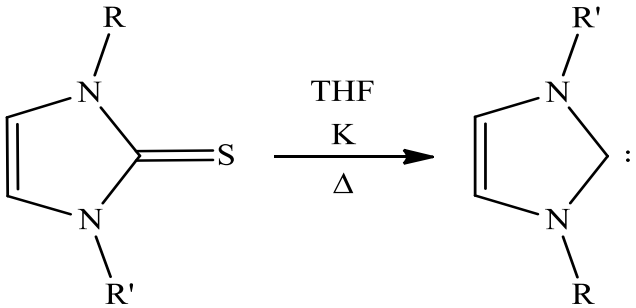
Scheme 1.16: Free NHC preparation from imidazolium salt

Clyburne et al reported the reduction of imidazolium salt to imidazol-2-ylidene by using an excess of potassium in boiling THF (Scheme 1.17).[44]



Scheme 1.17: Chemical reduction of imidazolium salt

Imidazol-2-ylidenes can also be obtained from imidazoline-2-thiones by reduction, which is also normally carried out in boiling THF with an excess of potassium (Scheme 1.18).[45]



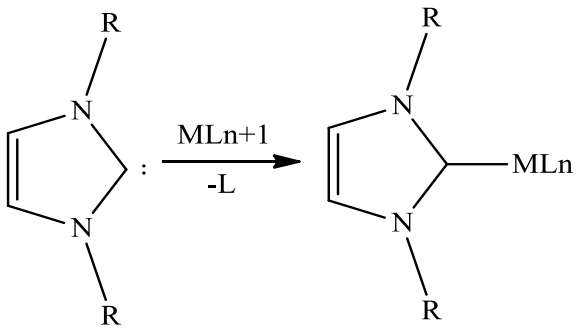
Scheme 1.18: Reduction of imidazol-2-thione

1.2.5. Complexation

Due to the usefulness of the metal-NHC complexes several synthetic methods have been used for their preparation. A detailed review of all these methods may not be possible in this brief introduction, but the most common methods are summarised below.

1.2.5.1. Free carbene route

The simplest and most direct method for the generation of NHC complexes is the reaction of the free carbene (NHC) with suitable metal precursor complexes (Scheme 1.19). The free carbene can be obtained through the methods described in 1.2.4 above. However this method has some limitations due to difficulty of generating many free NHCs which are generally highly sensitive to moisture and air,[34, 46, 47] requiring the use of dry, degassed solvents and Schlenk apparatus.



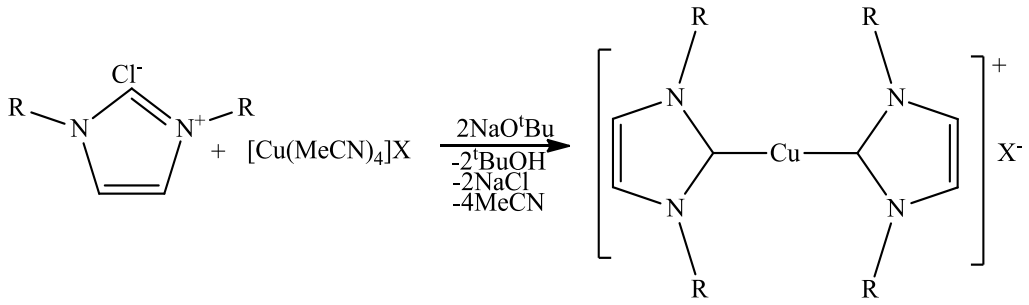
Scheme 1.19: Free NHC metallation

1.2.5.2. *In situ* deprotonation of imidazolium salt

Wanzlick and Öfele[18, 19] in their first report of NHC complexes have shown that NHC complexes can be prepared by *in situ* deprotonation of imidazolium salts in the presence of a suitable metal complex, without the necessity of isolating a free carbene. In both cases a ligand in the metal precursors acted as a base, deprotonating the imidazolium salt which then complexed the metal *in situ*. A more recent example is the reaction of $Ti(NMe_2)_4$ with an imidazolium chloride salt to yield $[Ti(NHC)_2Cl_2]$.[48] The major problem with this method is the limited availability of suitable metal precursors.

1.2.5.3. Deprotonation by external base

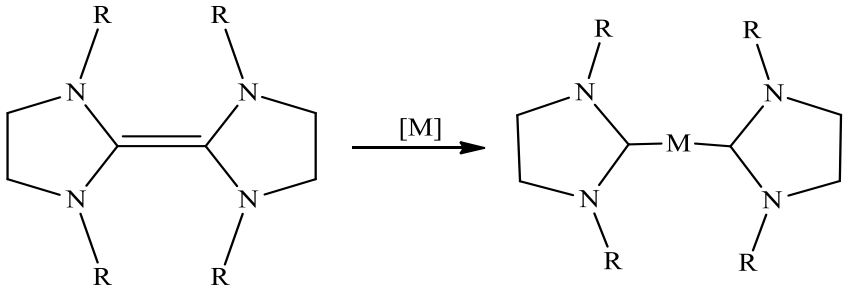
The carbene can also be generated *in situ* by treating the precursor imidazolium salt with an additional external base such as NaH, NaOAc, KO*t*Bu or MHMDS (M= Li, Na, K) in the presence of an appropriate metal salt. Many NHC complexes have been synthesised by this method (Scheme 1.20).[34] It was found to be suitable for many NHC systems ranging from three up to seven membered heterocycles.



Scheme 1.20: NHC - metal complex by deprotonation

1.2.5.4. Insertion into C=C bonds

In this method electron rich entetraamines are cleaved into the carbene monomer in the presence of coordinatively unsaturated electrophilic metal complexes (Scheme 1.21), which are later stabilised by coordination to the metal center. This method was first reported by Lappert et al,[49, 50] it is one of the earliest methods used for the synthesis of carbene complexes and it has been used mainly for unsaturated NHCs and benzimidazole based ligands for quite a number of metals. The method was also used to obtain metal complexes of chelating bis NHCs by insertion into N,N'-bridged tetraazafulvalenes.[49, 50]

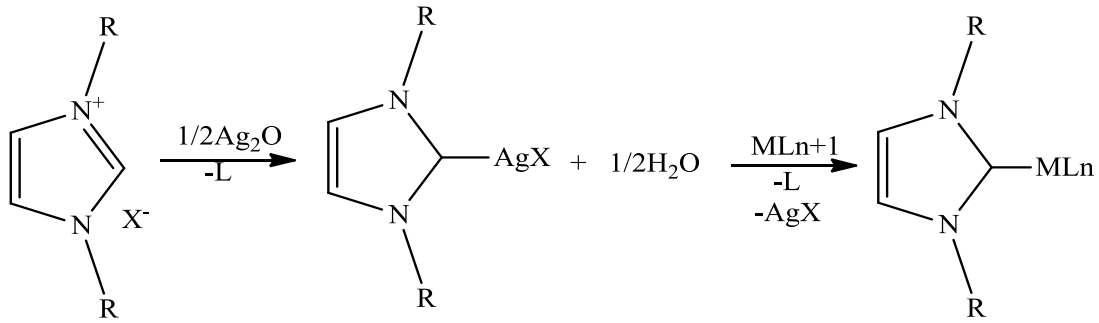


Scheme 1.21: Insertion of metal into C=C

1.2.5.5. Transmetallation method

NHC metal complexes have also been prepared by trans-metallation via silver complexes, also called the Ag_2O route. The silver complex is obtained by treating imidazolium salts with basic Ag_2O in a suitable solvent. The NHC is then transferred from the silver atom to another transition metal (Scheme 1.22), eg. Rh, Pd, Ir, Pt, Cu, Au, usually with deposition of silver halide.[47, 51] This method has become a standard procedure for preparation of NHC complexes with late transition metals; although it is not universally successful. It proves to be very useful in accessing NHC complexes where alternative syntheses are tedious or unsuccessful. It was first reported by Lin in 1998,[51] and continues to be widely used.

In addition to the popular Ag_2O route, other basic metal oxides M_2O (M = Cu, Hg,) have been used (albeit to a lesser degree) for formation of their corresponding NHC complexes[52, 53] and then used to transfer the NHC on to other transition metals. More recently the use of a Ni(I) NHC complex has been reported as an agent for NHC transfer.[54]



Scheme 1.22: Example of NHC metal complexes by transmetallation

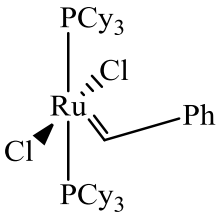
1.2.6. NHC in catalysis

The use of NHC complexes in homogenous catalysis has received a huge interest from different research groups, and has been a major driving force in the development of NHC chemistry. The extensive work of Hermann has been particularly important in this field.[27] The potential of NHCs was explored because of their perceived similarities to

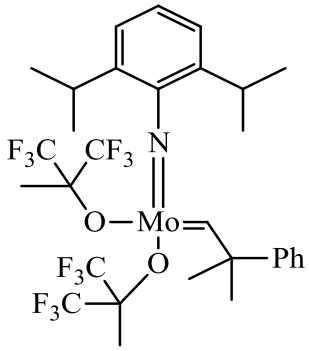
phosphine ligands. Quite a number of examples in which a known phosphine based catalyst has been modified by replacing one or more of the phosphine ligands with an NHC have been reported.[55] The catalytic activities of the NHC incorporated catalysts were almost always found to be more suited for many catalytic reactions than the original phosphine catalysts. Part of the possible reasons for the enhanced performance of these new catalysts may be that the non–labile, bulky NHC ligand provides the metal centre with considerable steric protection, and as a good σ-donor, stabilises the precatalyst and coordinatively unsaturated, catalytically relevant, intermediate.

1.2.6.1. Olefin metathesis using Ru-NHC catalysts

Ruthenium based olefin metathesis catalysts received a tremendous amount of attention after their introduction to the field by the work of Grubbs in the 1990s, who reported the synthesis of a phosphine ruthenium complex **1.21**, which was later called Grubbs' catalyst or the first generation Grubbs' catalyst.[55] These types of catalyst were found to be less reactive than the Schrock molybdenum based alkylidine complex **1.22** but they have a greater functional group tolerance and simplified handling characteristics.[56]



1.21

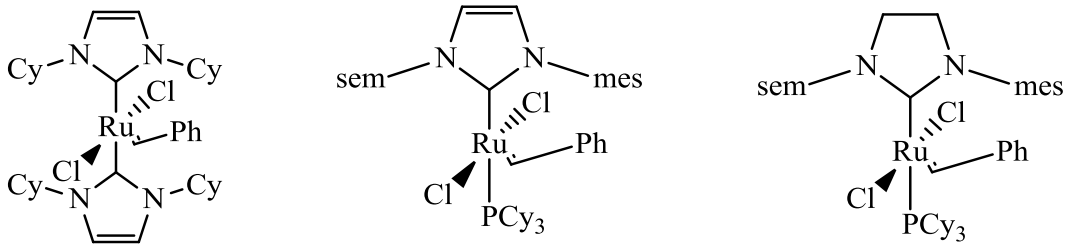


1.22

Figure 1.9: Grubbs (**1.21**) and Schrock (**1.22**) catalysts

Despite these important characteristics, they tend to show low thermal stability, decomposing at elevated temperature through P-C bond degradation and shows relatively low activity towards substituted double bonds.[57] It was at this point that Hermann in 1998 reported the ruthenium NHC complex **1.23** which reveals the potential

to serve as better alternative.[58] The NHCs prove to rival phosphines, because they are easier to produce and handle, they are also stronger σ-donors and weak π-acceptors and bind more strongly to the metal centre making dissociation less favourable. Although complex **1.23** was observed to be active in ROM and RCM, little or no improvement was noticed compared to the normal ruthenium phosphine catalyst **1.21**.[58] This low activity may not be unconnected to the strong bond between the NHC ligand and ruthenium. For olefin metathesis to begin at least one of the ancillary ligands must be labile enough for catalyst activation which was not the case in complex **1.23**.[59]



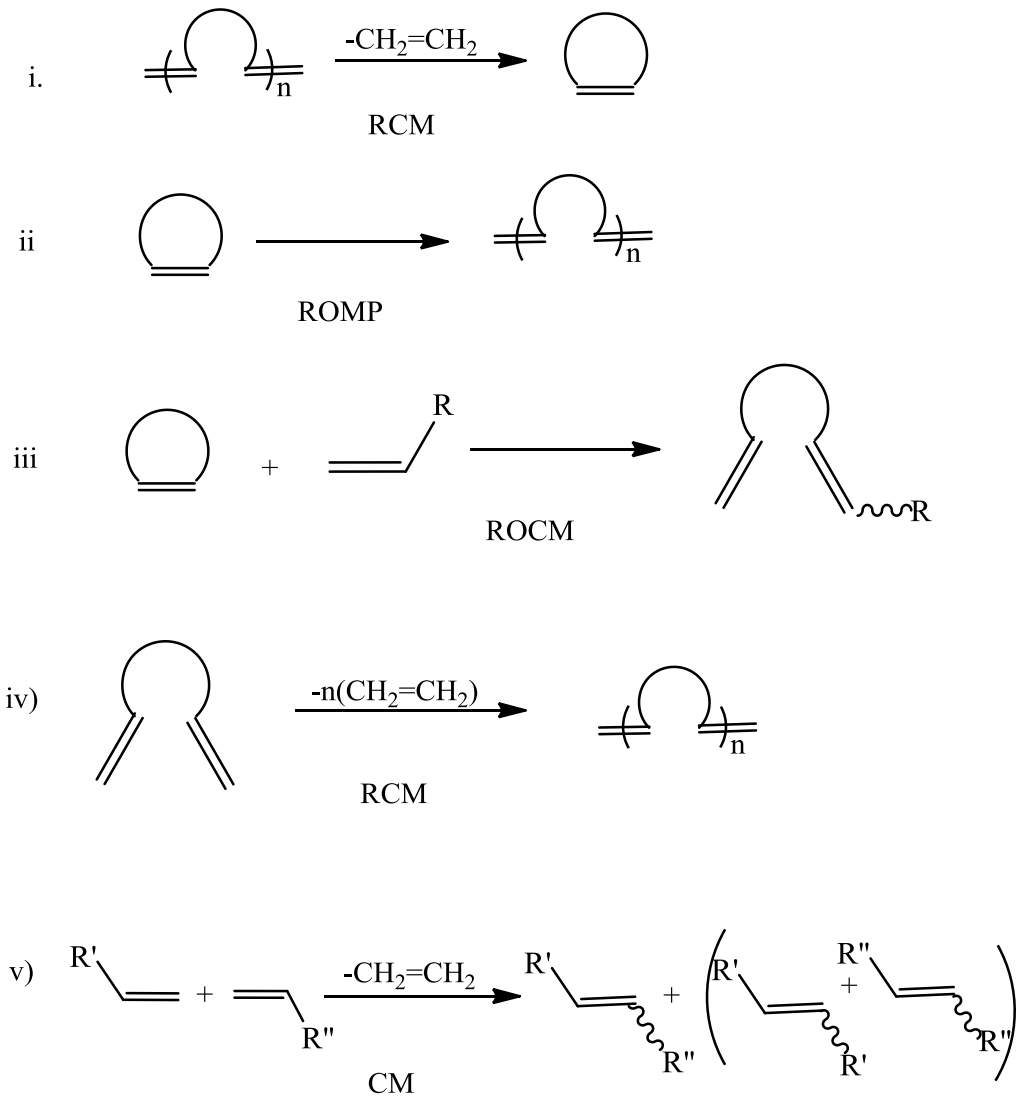
1.23 **1.24** **1.25**

Figure 1.10: NHC- Ru catalysts

Based on all the observations it was proposed that a complex combining both NHC and phosphine ligands may prove effective, the more strongly donating NHC may improve the dissociation of the more labile *trans*- phosphine from metal centre. The steric bulk and electron donating properties of the NHC will also help to effectively stabilise the electron deficient intermediates and promote olefin metathesis.

A phosphine-NHC ruthenium complex of this type, **1.24,** was synthesised and found to be the perfect choice, it was independently and almost simultaneously reported by the Grubbs,[59] Hermann[60] and Nolan[61] groups. This new generation of Grubbs' catalyst, which are called second generation Grubbs catalysts or simply Grubbs II, as expected were observed to be very stable to air and water, with greater functional group tolerance and to possess higher activity than the first generation catalyst, and in some cases even

higher than the molybdenum Schrock catalyst (**1.22**) (which had been established to be an active catalyst but with poor functional group tolerance).

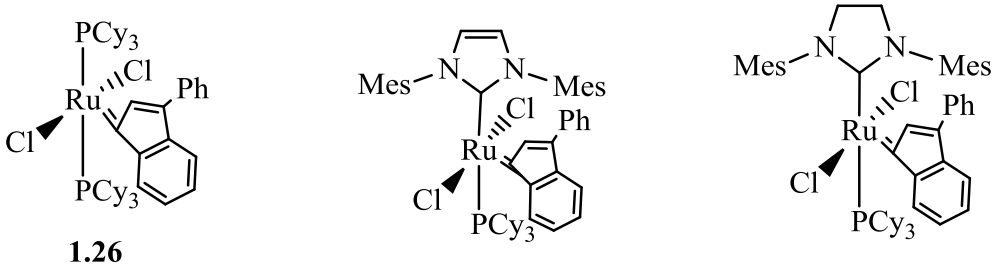


Scheme 1.23: Different types of olefin metathesis reaction

Grubbs later reported that catalyst **1.25** which contains a mesityl substituted NHC with a saturated backbone is even more active. It has a high rate of ROMP for low strain substrates and even catalyses the ROMP of sterically hindered substrates containing trisubstituted olefins.[62] Both complexes **1.24** and **1.25** were able to perform the RCM of

sterically demanding dienes to form tri- and tetra- substituted olefins[62] which were previously only possible using the Schrock catalyst **1.22**. In addition complex **1.25** produced the first example of CM to yield a trisubstituted olefin,[63] and was found to be effective even at 0.05mol% for RCM reactions and 0.0001 mol % for ROMP[64].

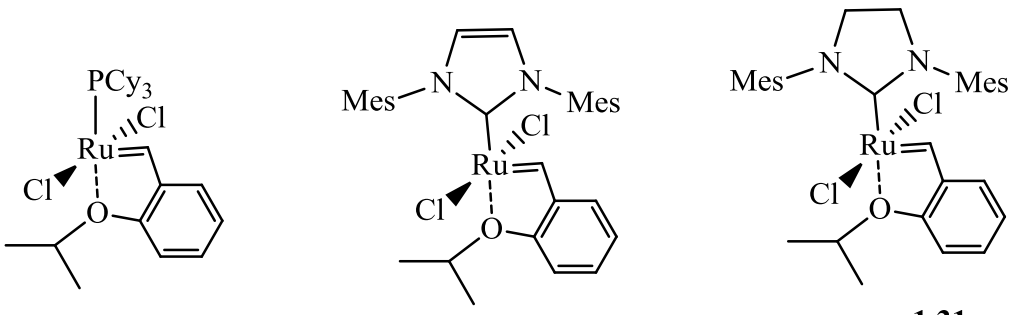
NHC bearing Ru-3-phenylindenylidene complexes **1.27** and **1.28** were developed as an altenative to Ru-benzylidine catalyst **1.26** and proved to be effective in natural product synthesis. They showed a higher thermal stability than their benzylidine counterparts and also showed a good activity and selectivity.[65]



1.26 **1.27** **1.28**

Figure 1.11: Examples of indenylidene catalyst

Another highly successful complex, the Hoveyda-Grubbs catalyst, **1.29,** was discovered by Hoveyda and coworkers by introduction of a styrene ether moiety.[66] The phosphine free Hoveyda – Grubbs catalysts were reported simultaneously in 2000 by groups of Hoveyda[67] and Blechart.[68] They bear an isopropoxy ether ligand tethered to the benzylidene group, and demonstrated an improved activity towards electron deficient alkenes. They are robust, easy to handle, stable in air and they have possibility for immobilization and catalyst re-use.

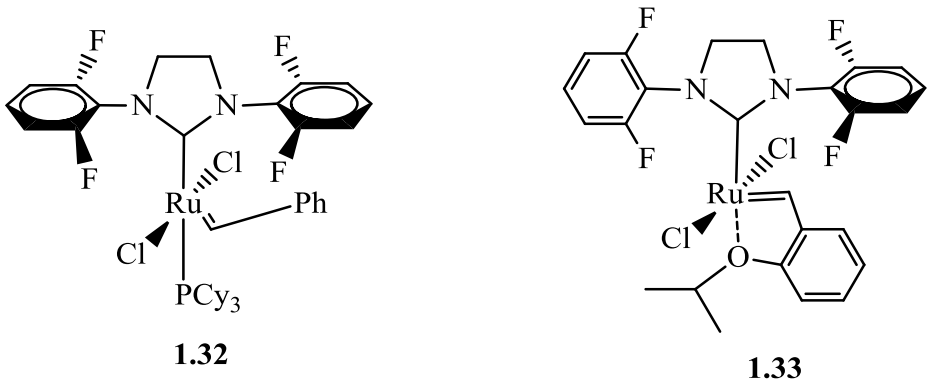


1.29 **1.30** **1.31**

Figure 1.12: Examples of Hoveyda - Grubbs catalyst

Ruthenium complexes bearing imidazol-2-ylidine or imidazolin-2-ylidine ligands are the most widely studied second generation olefin metathesis catalysts. The substituent on the NHC has a greater role in the activity of the complex, incorporating better donor substituents with larger steric requirement improves the catalytic activity of the complex as demonstrated by Nolan in 2000.[69] Today a large library of ruthenium complexes exists with the NHC (imidazol-2-ylidine or imidazolin-2-ylidine) having different types of substituent at position 1,3 or 4,5 of the NHC either symmetrically or unsymmetrically for both Grubbs and Hoveyda-Grubbs types of catalyst.[64] A few examples of these catalysts will be given below, however, detailed reviews on these catalysts and many others coupled with their catalytic activities have been presented in the literature.[1, 28, 52]

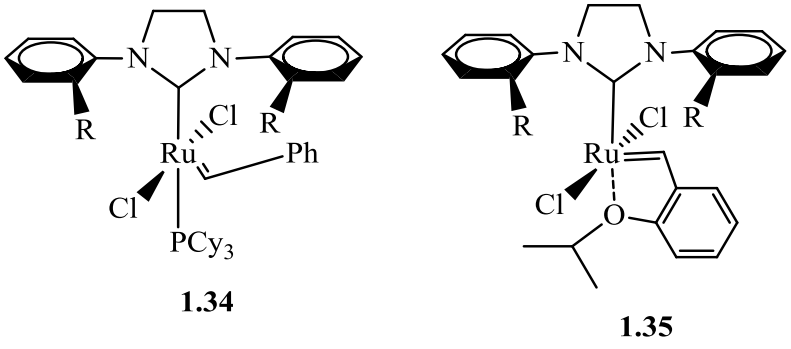
In 2006 Grubbs reported the synthesis and activity performance of some fluorinated NHC Grubbs and Hoveyda catalysts, **1.32** and **1.33**.[70] They are stable to air in the solid state and their activity was tested using standard RCM (Scheme 1.23). Although all are active, complex **1.33** was observed to be poorer than the parent Hoveyda catalyst **1.31** while complex **1.32** was more active than its parent complex **1.25.** This increased activity may be due to fluorine – ruthenium interaction which facilitates phosphine dissociation from the complex, which is the rate - limiting step in Grubbs type catalyst initiation.[70]



1.32 **1.33**

Figure 1.13: Symmetrical NHC- Ru catalyst

Schrodi et al[71] prepared a number of Ruthenium-NHC catalysts, changing the substituent on the NHC. They observed improved activity in RCM of sterically cumbersome substrates. The phosphine based complexes **1.34** were found to be better than Hoveyda type catalyst **1.35** in RCM (ring closing of dimethylmalonate was used as test reaction). Among the complexes prepared **1.34a** and **1.35a** containing methyl as substituent on the NHC were more active than the ethyl- and isopropyl analogues. These complexes were more active than their parent system **1.25** and **1.31** for the formation of tetrasubtituted olefins which may be due to open steric environment around the ruthenium centre which allows the catalytic site to accommodate larger organic fragments.[71]



1.34 **1.35**

a, R = Me
b, R = Et
c, R = *i*Pr

Figure 1.14: Symmetrical NHC - Ru complexes bearing different alkyl substituents

Grubbs et al[72] synthesised complexes **1.36** and **1.37** bearing unsymmetrical NHC groups and their activity was tested in CM, RCM and ROMP. Catalyst **1.36** proved to be superior to the traditional Grubbs and Hoveyda catalysts **1.25** and **1.35** in RCM reactions. Although they were found to be active, both complexes **1.36** and **1.37** were not much better than **1.25** or **1.31** in CM and ROMP.[72]

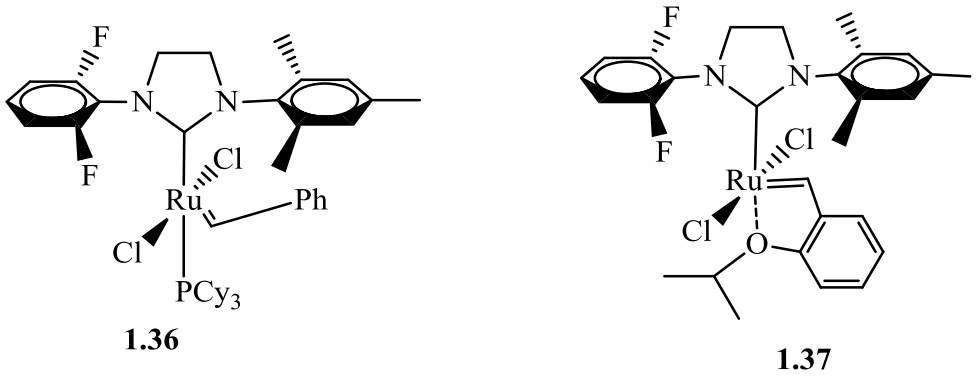


Figure 1.15: Unsymmetrical NHC- Ru catalyst

Ruthenium NHC catalysts with other substituted functional groups including carboxylate and nitrile have been synthesised and have shown various degrees of activities in metathesis reaction.[73]

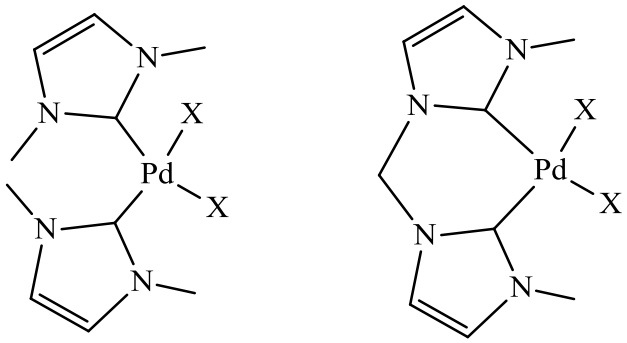
1.2.6.2. NHC catalysts for cross-coupling reactions

Cross coupling reactions involve joining two different organic fragments, forming a new carbon-carbon bond to give a new compound in the presence of catalyst. This method has been significantly used in synthesizing many organic compounds and it is due to its significance that Heck, Negishi and Suzuki were jointly awarded 2010 Novel prize in chemistry in recognition of their contribution in different cross coupling reactions. NHC ligands have been used in place of sterically demanding electron-rich phosphine ligands to support cross-coupling catalysts. The phosphine catalysts are often unstable as they are sensitive to air and moisture. They also dissociate at elevated temperature and need to be handled in an air free environment to reduce oxidation tendencies. The NHC

ligands tend to be more desirable as they form catalysts that posses higher thermal stability, and their activity is often comparable to or better than that of phosphine-supported systems.[74] In some cases they even catalyse reactions not observed with the phosphine catalysts. Herrmann and co-workers reported the first use of NHC metal catalysts in this context, demonstrating that biscarbene palladium complexes were active catalysts for the Heck reaction. Shortly thereafter the groups of Herrmann and Nolan reported that NHC palladium complexes are also effective catalysts for Suzuki coupling reactions and Sonogashira reactions.[34, 74]

1.2.6.2.1. Heck coupling

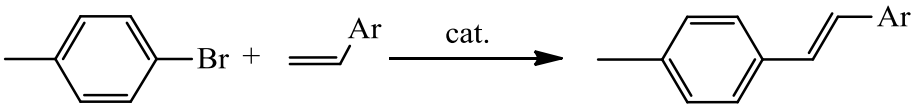
Excellent results have been reported for palladium catalysed Heck reactions with the traditional phosphine containing complexes. However, the phosphine ligand and its complexes with palladium are sensitive to air and moisture, thus putting a limit to their application. In addition, under Heck conditions, phosphines and their palladium complexes are subject to decomposition, therefore excess phosphine needs to be used. However the use of excess phosphine slows the rate of the reaction and also the phosphines are expensive and cannot be recovered (due to the decomposition).[75] This prompted chemists to look for other options in the quest to find another ligand that would be less expensive, easy to prepare and easy to handle. In addition these new catalysts need to withstand high temperatures in order to effectively activate traditionally more inert bonds. At high temperature the P-C bond in the normal phosphine catalyst is cleaved, which mostly deactivates the catalyst.[75] NHC complexes appeared to have excellent stability towards heat, air and moisture owing to the stronger σ-binding ability of the NHC ligands than phosphine. This enables NHCs to answer most of these challenges as the first complexes with palladium were synthesised at high temperature (170^{o}C) which shows it can withstand substantial amount of heat therefore solving the P-C cleavage problem, therefore Pd NHC complexes can be potential catalysts for the Heck reaction.[76]



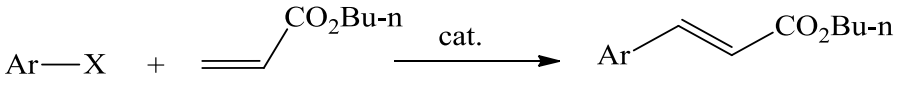
1.38 **1.39**

Figure 1.16: Examples of the first Pd NHC catalysts

The first application of palladium-NHC complexes in the Heck reaction was reported by Hermann in 1995.[74] Thereafter many other research groups reported the synthesis and application of various palladium and some nickel NHC complexes as catalysts in Heck reactions. Complexes **1.38** and **1.39** were tested for Heck reaction and were revealed to be promising. They were observed to show good activities in Heck coupling of both aryl bromides and aryl chlorides.[27]



Scheme 1.24: Typical Heck reaction involving aryl coupling

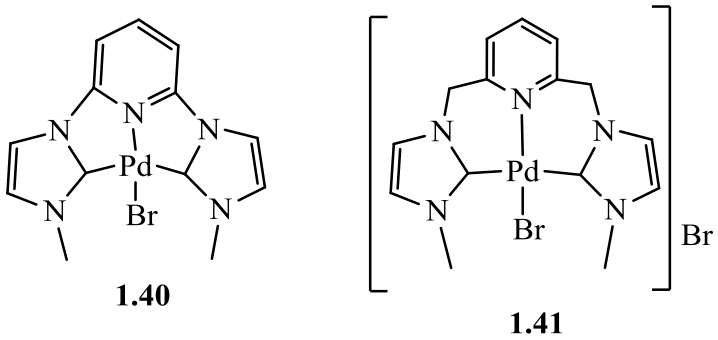


X = halide

Scheme 1.25: Generalised Heck coupling of aryl halide with acrylate

Also, Peris et al reported the synthesis and use of complex **1.40** in the reaction of iodobenzene and styrene to give trans stilbene in the presence of NaOAc as a base with a

very low catalyst loading of 0.2% (Scheme 1.24).[75] Similarly bromobenzene and styrene were converted to trans-stilbene in high yield at a catalyst loading of 5%.[75]



1.40 **1.41**

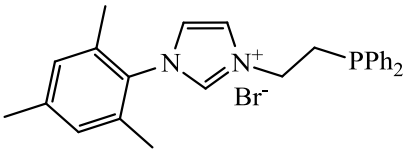
Figure 1.17: Examples of Pd tridentate pincer CNC bis carbene

There was little difference between the use of the above catalysts and the traditional phosphine catalyst in terms of activity, but one favourable observation was that the Heck reaction could now be carried out in the presence of air with these new palladium-NHC catalysts, therefore demonstrating that the problem of air sensitivity of the conventional phosphine Heck catalysts had been solved.[75] These new catalysts were observed to have higher thermal stability and required lower catalyst loadings to provide acceptable yields.[75]

Modification of complex **1.40** by introducing methylene spacers between the rings gave a more soluble and more active cross-coupling catalyst **1.41**[75] and was observed to show a very good activity for the olefination of chlorobenzaldehyde at a very low catalyst loading of 0.002%, giving a very high yield.[75] Nolan reported the first application of phosphino-NHC catalysts in Heck reaction,[76] the phosphine-NHC ligand **1.42** was synthesised, and its palladium complex prepared *in situ* using $Pd(dba)_2$ in the presence of Cs_2CO_3.

Zhou et al synthesised phosphine-functionalised NHC ligands **1.43** and **1.44** with stable diarylphosphines as pendant functional groups.[77] These ligands were coordinated to palladium *in situ* using $Pd(dba)_2$ in the presence of K_2CO_3. The *in situ* formed palladium complexes of these ligands proved to be effective for the coupling of a wide range of

aryl bromides or iodides with acrylates (Scheme 1.25). It was also observed to be effective in the coupling of aryl bromide with styrene derivatives (Scheme 1.26).[77]



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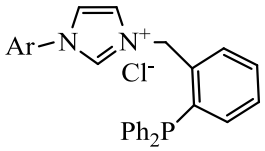

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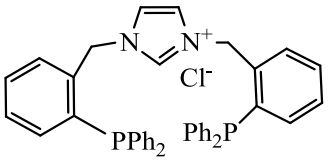

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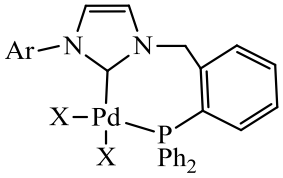


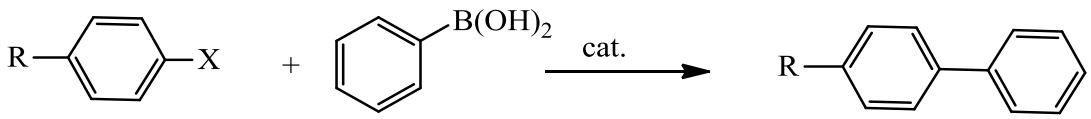
1.45

Figure 1.18: Examples of phosphino NHC Pd catalysts

Complex **1.43** (Ar = Phenyl) was observed to show low activity but introduction of alkyl groups to the N-phenyl ring of the NHC ligand increased the activity,[77] with the highest activity observed when the Ar was 2,6-diisopropylphenyl. This suggest that introduction of bulky groups to the phenyl ring of the phosphine functionalised NHC ligand is increasing the activity of the palladium catalyst.

1.2.5.2.2. Suzuki reaction

Herrmann reported the use of complex **1.39**, which was active in Heck reaction, to also be active in Suzuki coupling of aryl bromides with aryl boronic acids (Scheme 1.26). The catalyst was observed to be very active in a wide variety of bromo arene and chloroarene systems.[37]



X = Halide cat = Pd NHC complex

Scheme 1.26: Generalized Suzuki coupling reaction

Also the phosphine free Pd complex of the first crystalline free NHC (**1.7**) was found to be very active as a coupling agent for aryl chlorides to form biphenyl (substituted) in Suzuki cross couplings.[37]

Lee et al reported the synthesis of phosphine functionalised NHC ligand precursors and their subsequent complexation with palladium. Their activity in Suzuki coupling with many bromide and phenyl boronic acid was also reported. The catalysts were discovered to be active with aryl bromides as substrate while it was ineffective with aryl chlorides (Scheme 1.26).[78]

Other cross coupling reactions that were catalysed by NHC complex catalysts include Negishi coupling, Sonogashira coupling, and Kumada cross coupling. Detailed reviews are available in the literature.[79, 80]

1.2.6.3. Other catalytic reactions of NHCs

Today a large library of transition metal- NHC catalysts exists for both industrial and research purposes. These NHC-Metal catalysts have been reported to catalyse one reaction or the other, which we cannot give in detail in this introduction, but some other reactions are summarized below (Table 1.1).

Table 1.1: Some reactions involving NHC complexes as catalysts.

Reaction	**Metal Centre**	**Reference**
Hydrogenation	Ru, Ir, Pd	[81]
Hydrosilylation of alkynes	Rh, Pt,	[82]
Furan Synthesis	Ru	[83]
Aryl halide amination	Pd	[27]
Ethene Polymerisation	Ti, V, Cr	[83]
Hydroformylation	Co. Rh	[84]
Atom transfer radical Polymerisation	Fe	[85]

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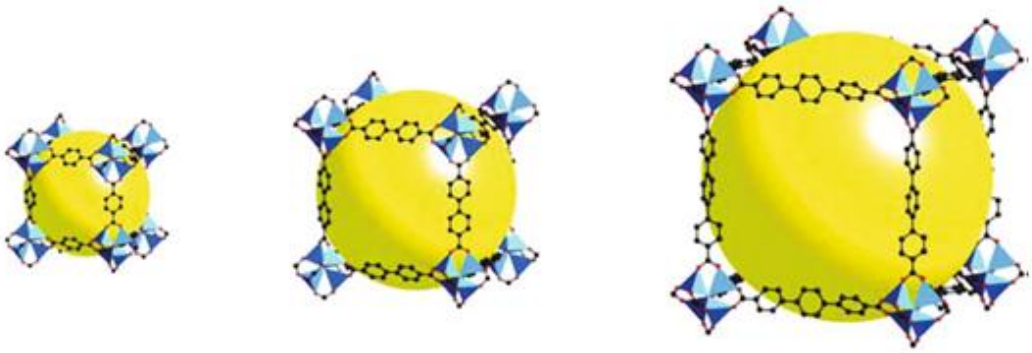
CHAPTER 2

Metal Organic Frameworks

2.1. Introduction

Metal organic frameworks (MOFs) or porous coordination polymers (PCP) have emerged to be an interesting type of porous inorganic – organic hybrid materials which contain organic ligands linking metal ions or metal ion clusters giving well characterised crystalline architectures.[1] The striking features of this class of porous materials are their exceptional stability, their tunabilty, their very high porosity and their large internal surface area.[2] These properties can be controlled by the successive changes in the organic linkers (Figure 2.1). For instance, MOFs with surface areas extending beyond 6000m^2/g have been synthesised by increasing the chain length of the organic linkers.[3] These properties make MOFs important candidates for a number of applications which include gas storage,[3-6] catalysis,[7, 8] chemical sensing,[9, 10] drug delivery[10] and gas separation,[11] among others.



MOF-5 IRMOF-10 IRMOF-16

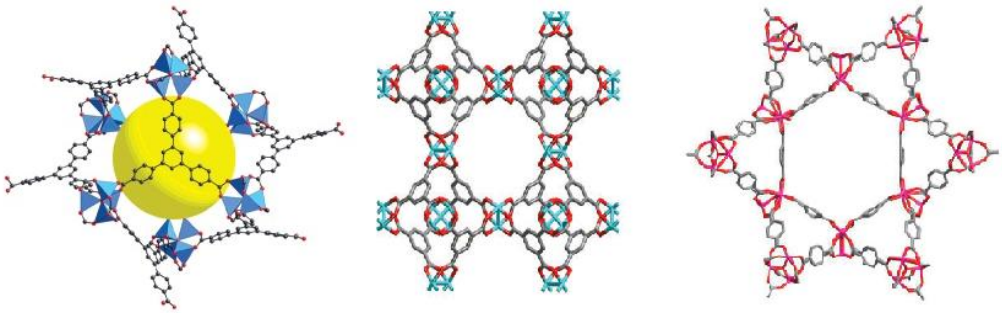
Figure 2.1: Examples of MOFs showing an increase in surface area[2] (reprinted with permission from Ref. 2)

The chemistry of these materials has evolved gradually through decades from the knowledge of coordination and solid state zeolite chemistry. In 1897 Hofmann discovered the first recognised coordination network, with a chemical formula of $Ni(CN)_2(NH_3).C_6H_6$, by the reaction of C_6H_6 and a NH_3 solution of $Ni(CN)_2$.[12] This complex leads a series of other Hofmann complexes which were later structurally characterised to have a 2-dimensional layer based architecture.[12] In 1936 the 3-dimensional compounds called the Prussian blue complexes were synthesized.[12] All

these complexes utilise inorganic CN^- as the bridging ligands, and as such do not have large cavities, but they were able to alert researchers to look for coordination networks with greater cavities which may be achieve by replacing the CN^- linker with larger organic ligands. This type of metal organic coordination network was reported by Robson and Hoskin in 1989[13] and 1990,[14] when they detailed the synthesis of infinite frameworks utilising Cu(I) metal centres linked with the organic $C(C_6H_4.CN)_4$ giving a solid polymeric material. These reports marked a key point point in the research of metal organic frameworks, in fact many assume that this is the birthday of MOFs.

In 1995 Yaghi and Zawarotko, separately and at almost the same time, reported metal organic frameworks containing larger channels. Zaworotko et al[15] reported the synthesis of Zn and 4,4-bpy coordination network with a large pore size, comparable to that of larger zeolites. Yaghi et al[16] same time in 1995 reported the synthesis of metal organic frameworks containing Cu centres linked also with 4,4-bpy ligand forming an extended 3D network. Yaghi et al further reported on some other porous metal organic frameworks utilising carboxylate linkers BTC and BDC.[17-20] Two of the most popular MOFs, MOF-5 $(ZnO_4(BDC)_3).(DMF)_8C_6H_5Cl$[21] and HKUST-1 $(Cu_3(BTC)_2(H_2O)_3)_n$[22] were separately synthesised and reported in 1999 by Yaghi et al and Williams et al respectively. MOF-5 was synthesised by diffusing Et_3N into a solution of $Zn(NO_3)_2$ and H_2BDC in DMF/chlorobenzene while HKUST-1 was synthesised from the reaction of $CuNO_3.H_2O$ with H_3BTC using hydrothermal method in 50:50 water:ethanol mixture. The following years saw an explosion of interest among different research groups around the world resulting in many reports of this type of materials under different terminologies[23]. Non-flexible and flexible MOFs were reported in 2002 by Ferey et al,[24] MIL-74 and MIL-53 respectively. Also in 2005[25] they reported the synthesis of MIL-101 which is among reported MOFs with highest surface area of around $6000m^2/g$.[25] In the following years many other interesting MOFs have been reported, and more recently the use of imidazolium salts (NHC precursors) as building blocks for MOF synthesis has been attempted,[26-29] with some being converted to NHC complex containing MOFs.[29-31] Several terminologies are in use for naming these materials which normally follow the

traditional naming methodology adopted by the zeolite chemistry which comprises letters (representing the laboratory or country where those material are made) followed by an integer (n) (Figure 2.2). Metal Organic framework (MOF-n) and Porous Coordination Polymers (PCP) are the more common names in use, originally proposed by the Yaghi[2] and Kitagawa[1] groups respectively. Other names in use include HKUST-n (Hong-Kong University of Science and Technology)[22], CUK-n (Cambridge University – KRICT), MIL-n (Materiaux de I'Institut Lavoisier), SNU-n (Seoul National University),[24] ZIF-n (Zeolitic Imidazolium Framework)[32] etc. Although each different group uses different terminologies in naming these types of coordination polymers, MOFs was generally being adopted in describing them in most literature material as such we intend to use MOFs in describing these porous materials in this thesis.



MOF-177 HKUST-1 MIL-101

Figure 2.2: Examples of some popular MOFs with different terminologies[33]

Porous materials are classified mainly into 3 groups, based on their pore sizes; those with a pore diameter <2 nm are regarded as microporous (most of the original porous zeolite falls into this category), those with a diameter in the range 2 – 50 nm are mesoporous MOFs[34] and those with pore diameters over 50 nm are macroporous MOFs.[1]

MOFs or porous coordination polymers according to Kitagawa,[35] evolved through three generations; the first generation are those microporous frameworks which are only sustained with the presence of guest molecules and easily collapse on removal of this molecule. That means they are not reversible to their original state once the guest

molecules are removed. The second generation, are those porous materials that are more rigid, more stable and have permanent porosity even on removal of guest molecules, indicating that the guest molecule has no effect on the framework topology. The third generation are those with flexible and dynamic frameworks which change reversibly with stimuli, (which may include temperature, pressure, guest molecule, light) by either expanding or contracting depending on the external effect.[24]

2.2. Synthesis of MOFs

One of the major advantages and turning point for MOFs are their potential to be tailored to give a desired topology to suit a particular application unlike the more traditional porous zeolites and activated carbon. These are achieved by carefully selecting the appropriate primary building units (PBUs), i.e the metal ion connectors and the organic ligand linkers (Figure 2.3) to give the desired structural motif.[36] It should be noted that MOFs may contain two or more different metal ions linked to a ligand (heterometallic or mixed metal MOFs) or having two or more ligands linked to a metal ion (mixed ligand MOFs).[37] In addition there are other important components that need to be taken into consideration, such as the choice of solvents, which sometimes provide guest molecules which stabilise the framework. In fact many MOFs are observed to be supported by solvent molecules and collapse on their evacuation.[38] Also the counterions associated with the metal may in some cases influence the framework structure, and in some materials may participate as connectors in the framework forming an integral part of the structure.[1, 36] Quenching or blocking ligands like pyridine or other monodentate ligands may also need to be selected to block a particular metal coordinating site which, if available, may alter the desired framework topology. Generally in MOF synthesis obtaining crystalline materials good enough for single crystal X-ray diffraction directly from the reaction mixture is preferred, since many MOFs, once formed, are difficult to re-crystallise because of poor solubility, as is common with many coordination polymers. MOFs have been synthesised using a variety of methodologies and strategies by different research groups around the world.[39] In general the choice of the organic ligand and its preferred topology plays a greater role in determining the appropriate

methods and the reaction conditions to be employed. The major conditions that affect the formation of MOFs include the temperature, pH, concentration and pressure.[24]

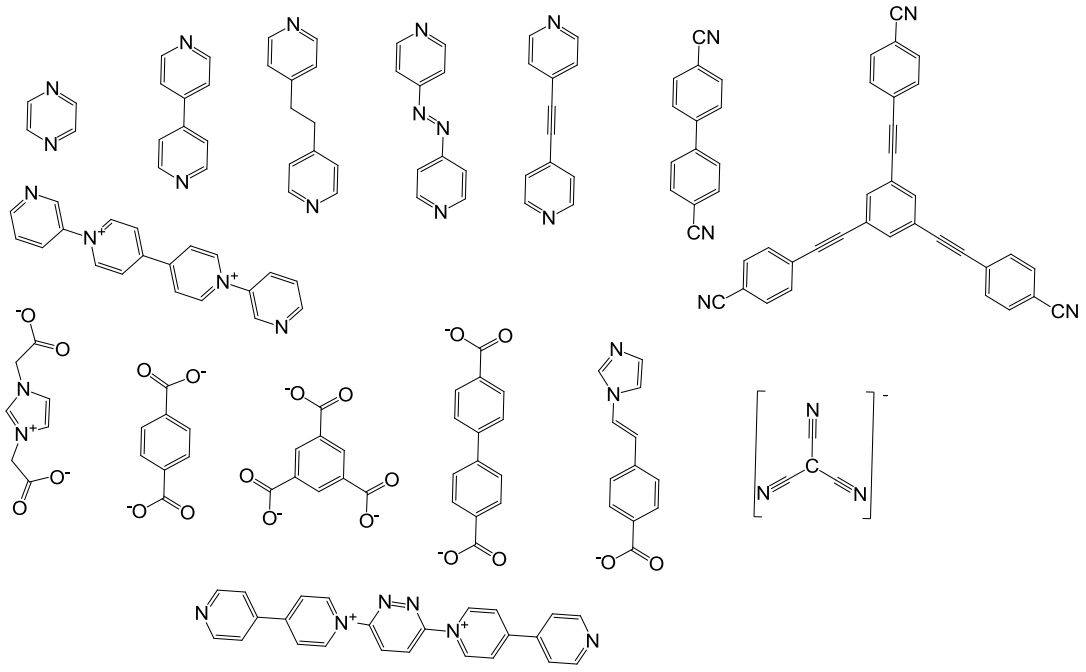


Figure 2.3: Some common organic linkers use in MOF synthesis

The most widely used synthetic method is conventional self assembly, in which a metal ion and organic linkers are assembled together giving MOFs under wide variety of reaction conditions. One of the earliest methods is the diffusion technique, where solutions of a metal ion and organic linkers are allowed to slowly diffuse in to each other, forming the desired MOF at the interface. Most of the earlier work in this field including reports of Robson and Hoskins[13, 24] utilises this method and it is still in use to the present day. One major advantage of this process is it often gives a very good quality of crystals making characterisation much easier. Although the processes are straight forward and give a quality crystal, it is mostly very slow (it may take weeks or even months) and it often gives a very low yield. Alternatively the solutions of the metal ion and the organic linkers may be layered on to each other, slowly diffusing forming crystalline material at the interface.

Another straight forward process widely used in synthesising MOFs is the self-assembly of the metal ion and organic linkers in solution at room temperature or in some cases with mild heating (usually less than 100^{o}C). The metal ion and the organic linkers are dissolved in an appropriate solvent and allowed to evaporate at room temperature, in the process assembling together giving crystalline MOF material. Alternatively the mixtures are concentrated at elevated temperature and allowed to slowly cool forming a crystalline material.[39] This method works best where the metal-ligand interaction is rapidly reversible.

A more recent method employed with high success to prepare more robust frameworks is solvothermal synthesis which involves a one pot reaction.[24, 39] In this method all the reactants, which may include the metal source, organic linkers and the solvent(s) are taken in one vessel, sealed, and heated at elevated temperature (from 100^{o}C to 250^{o}C) thereby forming an autogenous pressure. Because high temperatures are used especially with the alkyl formamide solvents, solubility is not usually a problem (most reactants may be soluble at usually higher reaction temperature). Where deprotonation is needed (e.g in carboxylates) it is accomplished by gradual decomposition of the amide solvent (which is very popular in solvothermal synthesis) during the reaction.[2] Other widely used solvents in solvothermal synthesis include acetonitrile, amines, and pyridine. Hydrothermal synthesis is a sub-set of solvothermal methods, in which water is used as the solvent. In this case the organic linkers must be soluble or at least partially soluble in water at that higher temperature.

Another method that employs the help of microwave called microwave irradiation assisted synthesis, initially used by organic chemists, has been tested and employed to prepare many microporous MOFs with greater ease.[40] This method has drastically reduced the time required to form MOFs, often from several days using other methods (like solvothermal, diffusion etc) to a few minutes. Despite reducing the time, it is still capable of giving a good quality crystalline product and improving the purity of the compounds. Several MOFs have been reported to be synthesised using this method, Cr-MIL-100 was the first of the MOFs to be synthesised in this way.[41] Microwave

synthesis was tested and found to improve the synthesis of many MOFs including the most popular materials like MOF-5, HKUST-1 and the MIL-101[40,42] giving nanocrystalline products, significantly improving the yield, and shortening the reaction time to less than an hour instead of days.

Currently there are other new techniques being developed in the synthesis of MOFs which are not yet widespread, but which have potential, including

i) Solid state grinding of the reactants, or mechanochemistry, which involves mechanical breakage of intramolecular bonds which is followed by chemical transformations.[40, 43] Although it has been long in used in synthesis, its application in MOF synthesis was first reported in 2006,[44] MOFs produce this way include [Cu(INA)$_2$], HSKUT-1, ZIF-4, ZIF-8 etc.[39]

ii) Sonochemistry, which involves application of high energy ultrasound to the reaction mixture was reported to be used for MOF synthesis in 2008.[39, 45] It was intended to make MOF synthesis greener, i.e producing MOFs in an environmentally friendly synthetic method that is fast, and consuming less energy with commercial production in mind. Several MOFs including MOF-5,[46] MOF-177,[47] HKUST-1,[48] Ln(BTC)(H_2O) (Ln = Ce, Tb or Y)[49] and others were reported to be produced in higher yield, and just like microwave methods significantly reducing the reaction time from days to minutes.

iii) Electrochemistry is also a synthetic method that is being developed for MOF synthesis. A first report in 2005,[50] detailed the synthesis of Cu-MOF using an electrochemical cell set up, where copper plates were used as the anode, the carboxylate (BTC) dissolved in methanol was use as the solvent, while copper also served as the cathode. This resulted in a greenish precipitate of the Cu-MOF being formed.

2.3. Post synthetic modification.

Although MOFs have outstanding qualities which make them interesting materials in a wide range of applications, there are situations when they may require further functionalisation or modification to suit a particular purpose e.g. in catalysis, gas separation, gas storage. These modifications may be achieved by either functionalising the starting organic linkers before constructing the frame work (pre-synthetic modification) or functionalisation after the framework has been established i.e. post synthetic modification (PSM) as shown in Figure 2.4.[33, 51, 52]

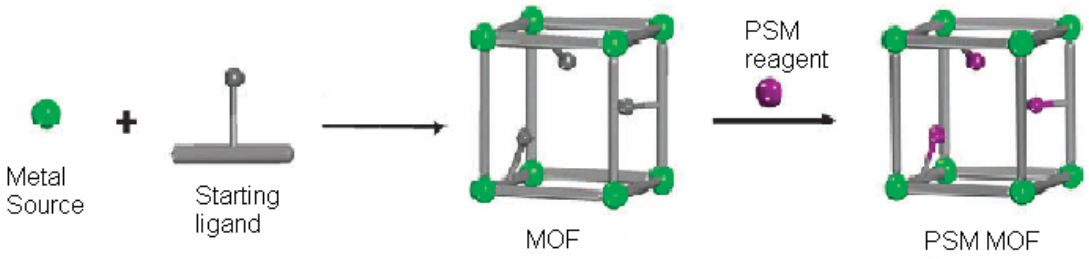


Figure 2.4: Schematic representation of post synthetic modification[33,51](reprinted with permission from Ref. 51)

Pre-synthetic modification of the organic linker prior to MOF formation may be problematic due to the fact that the functionalities introduced may not withstand the MOF synthetic conditions, particularly if a solvothermal synthetic method (which to date remain the most common synthetic process for MOFs) is used, or may interfere with the chemical processes and thus hinder the formation of the desired MOFs. Although any process that may alter the initial composition of MOFs may be regarded as post synthetic modification, e.g. removal of solvent (desolvation) or counter ion exchange, a stricter definition of post synthetic modification limits it to modifications involving formation of covalent or dative bonds within the framework (Figure 2.5).[52] Such alterations are normally achieved by modifying an unsaturated metal coordination site or by the reaction of functional groups on the organic linkers of the MOF framework. PSM allows many functional groups to be added to framework, which may not be possible using the normal solvothermal process due to the harsh reaction

conditions of this process. These modifications may enhance the overall properties and applicability of the materials towards gas adsorption, catalysis, etc. Several methods are being employed and currently many materials are being modified using this processes.[33, 51, 52]

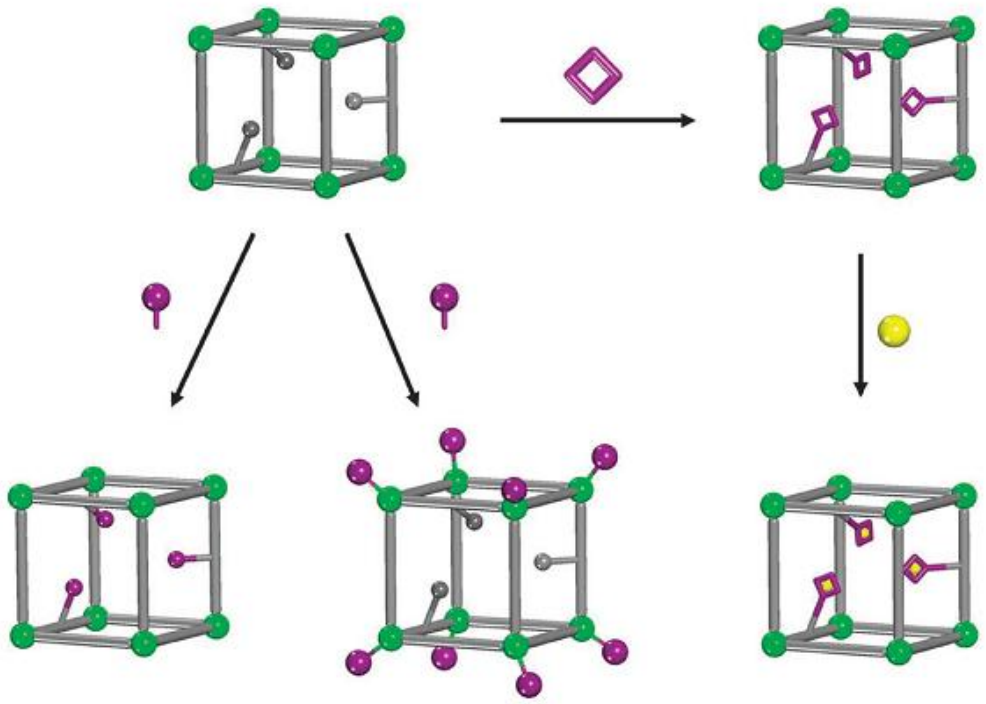


Figure 2.5: Representation of covalent (left), coordinate covalent (middle), and a combination of PSM strategies (right) for PSM of MOFs.[33,51] (reprinted with permission from Ref. 51)

2.4. Applications of MOFs

Applications of porous materials are mostly dependent on framework features, and in particular the nature of the pore. Consequently, the dimensions and accessibility of the pore defines the scope of its applications.[10] For these reasons, the traditional zeolites, which have limited functionalities and a much smaller pore, have restricted applications. MOFs, on the other hand, possess most of these favourable features and in addition the framework can be tailored to give the pore the desired functionality, size, shape, surface area and easy accessibility. For instance, these tunable tendencies have resulted in the

design and synthesis of MOFs with exceptionally high pore size and surface area. These are found to have a wide range of applications from the traditional gas storage, catalysis, and gas separation and more recently extending their applications to sensing and biomedical problems is getting attention.[10, 53, 54]

2.4.1 Gas storage

Gas storage is one of the first and most promising applications of MOFs, due to their higher sorption properties which in turn arise from their enormous surface area and low density.[55] With current challenges in the available energy sources, including the decrease in fossil fuel reserves and issues with climate change, alternative energy sources will be highly prized. MOFs may prove to be a source of materials due to their large pores capable of adsorbing large amount of fuel gases like H_2, CH_4, CO_2, C_2H_2 etc.[3, 4, 6, 55, 56]
The major challenge is to develop materials capable of storing enough gases for practical usage and transportation. The US Department of Energy (DOE) has set a revised target for materials to be used for onboard hydrogen storage. It set a 5.5 wt %, 40g L^{-1} within an operating temperature range of -40 to 85^{o}C under a maximum delivery pressure of 100 atm, (2015 hydrogen storage target)[55] and 5.6 wt% for CO_2.[55] Many MOFs have shown an appreciable storage capacity, but to date none of those known have met these targets for onboard hydrogen storage and usage.

Kitagawa in 1997[57] reported the introduction of large amounts of methane into the coordination polymer $[Co_2(4,4\text{-bpy})_3(NO_3)_4.4H_2O]_n$. Several other porous materials with higher methane capacity have been reported.[1, 5, 24, 54, 56] The most studied gas storage applications of MOFs is their hydrogen storage capacity due to its significance as a cleaner energy source. Some of the most successful MOFs for hydrogen storage include MOF-5 with up to 5.1 wt% at 77K, HKUST-1, 3.6 wt% , MIL-58 4.1 wt%.[54] It was experimentally established that there is a correlation between surface area and the hydrogen uptake of the MOFs, the higher the surface area the more hydrogen it can accommodate. MIL-101 and MOF-177 which are among the highest surface area and the hydrogen uptakes at 77K of 6.1 wt% (80 bar) and 7.5 wt% (70 bar)[54] respectively.

2.4.2. Catalysis

Metal organic frameworks, like the traditional porous zeolite catalysts, such as aluminosilicates, have uniform pore and channel sizes in the framework which is an important feature for catalysis, hence the widely held belief that they can be used in this manner.[58] But, unlike zeolites MOFs have tunable pores such that the pore size and functionality can be tailored to suit a particular catalytic reaction, which makes it possible to be used in reactions that perhaps cannot be realised using zeolite catalysts. Although MOFs for gas storage and separation need to have a permanent porosity, this is not necessary for catalysts, since most of catalytic reactions take place in the presence of solvent. MOFs are said to be functionalised catalytically when they i) contain active metal nodes, ii) contain catalytically active functional sites on the organic linkers, or iii) they are able to encapsulate catalytically active guest molecules or clusters.[58] These conditions are normally achieved by i) carefully selecting the primary building units such that they contain the desired functionalities, ii) synthesising the ligand and metal clusters with the desired catalytic functionalities before MOF synthesis or iii) modifying already synthesised MOFs (PSM) to contain the desired functionality for the particular catalytic reaction. Other catalytically functionalised MOFs being developed are the homochiral MOFs[7, 8] and mesoporous MOFs.[34] Despite the huge potential and the large library of MOFs that exist, relatively few reports on their catalytic application have been reported.

One of the earliest reports on the use of MOFs for catalysis was reported in 1994 by Fujita et al.[59] They reported the use of $\{[Cd(4,4\text{-bpy})_2](NO_3)_2\}_n$ in cyanosilation of aldehydes. The following years have seen an increase in catalytic investigations of these materials, as evidenced from a number of good reviews[8, 10, 24, 54, 58] in the literature.

2.4.3. Gas separation

Another important application of these porous materials is their ability to use their pore size, shape and functionality to select a particular molecule through an adsorptive separation process. The separation is made possible when shape, size or chemical properties of one of the components of a mixture prevents access of selected molecules

into the pores of the framework, while others are allowed and can be adsorbed. This illustrates the possible usage of MOFs, with proper tailoring, to act as selective molecular sieves. A number of reports on this application have been forthcoming. For instance, Manganese formate was reported to selectively adsorb H_2 over N_2 and Ar at 78K and also it selectively adsorbed CO_2 over CH_4 at 195K.[60] In all the cases it shows almost zero adsorption capacity for the excluded gases i.e. N_2, Ar, and CH_4. MIL-96 was also reported to adsorb CO_2 over CH_4 based on size and shape of the gases and the framework pore.[60] Another report by Li et al indicates Zn(tbip) adsorbed paraffin, methanol and dimethyl ether while excluding aromatics.[61] Kitagawa et al reported on selective adsorption of acetylene over CO by Cu(Pzdc)(Pyz).[62] Several other MOFs were reported to selectively adsorb certain gases over others.[11, 60]

A possible use of MOFs to selectively separate harmful gases including Cl_2, SO_2, CO, NH_3 etc from air was reported by Yaghi et al.[11, 63] They used a series of MOFs (MOF-5, MOF-177, HKUST-1 and IRMOF-62), and found that pore functionality and open metal sites play a key role in sorption abilities of these MOFs and indicates that all these MOFs are capable of removing toxic gases from air in a dry environment but failed to do so in a humid environment. Many other unwanted gases were found to be separated by MOFs.

2.5. Overall aims and objectives

Although significant progress has been made in terms of the design and application of MOFs in various fields, work is on-going to further develop these materials to improve a particular application, or to develop entirely new MOFs for some specific purposes. For this reason a great deal of research is directed at the design and synthesis of novel organic linkers[53] to produce new families of MOFs with well arranged features like the pore size, surface area, functionality within the pores for particular applications. It is in line with these observations that we aim to synthesise some new imidazolium salts with non chelating donor subsitituents (pyridyl, nitriles, and carboxylates) capable of permitting their assembly into coordination polymers and will attempt to produce novel cationic MOFs with large cavities using suitable metal sources.

NHC ligands have had a remarkable degree of success because of their versatility toward transition metals and their outstanding catalytic applications[64-66] (as described in more detail in Chapter 1). In mind of this success it is intended to convert these new imidazolium salts into novel NHC complexes and to use various techniques to study their properties, which will give an insight into their potential applications.

These NHC complexes will have potential to be used as building blocks for MOFs, and will produce materials that are likely to be very good in catalysis, gas storage and some other applications. This is because the metal NHC complexes will provide additional unsaturated metal sites (active sites) within the MOFs and functionalities that may improve the activity of these materials.

Although such an approach seems highly promising, it has only attracted the attention of few research groups around the world, and only a handful of reports on the use of imidazolium salts as building blocks for MOFs have been forthcoming.[26-28,67] Furthermore only a very few of these imidazolium salt containing MOFs have been converted into NHC complex containing frameworks. In 2009 Son et al[30] reported the formation NHC–Cu(I) complex in the self-assembly of dicarboxylate imidazolium salt and $Cu(NO_3)_2$ in a solvothermal process using DMF solvent. It was reported that Cu (I)

was formed by an *in situ* reduction of the Cu(II) during the reaction process (Figure 2.6) Cu(II) ions bind to the carboxylates and as such serve as the connecting metal centre, while the reduced Cu(I) coordinates to the carbene carbon forming an NHC complex.

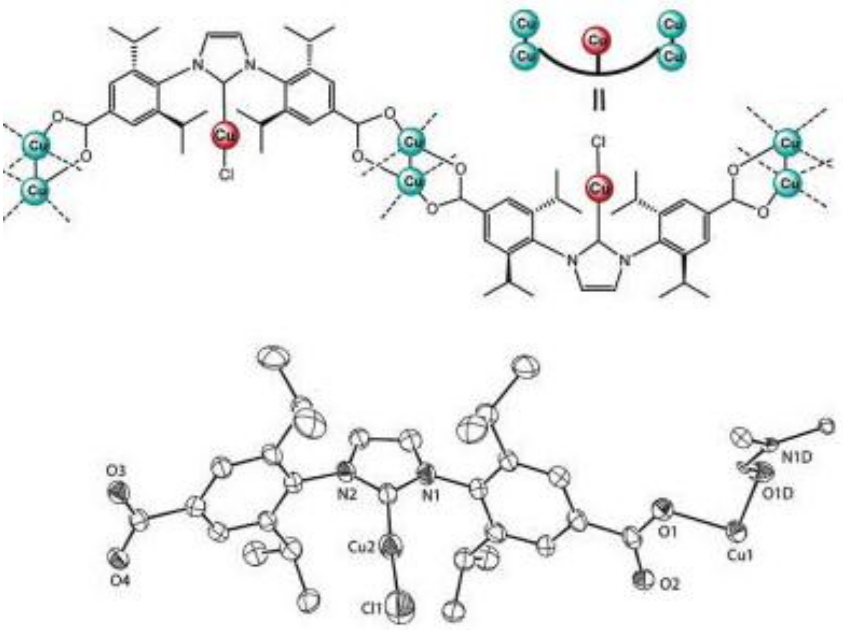


Figure 2.6: Example of a MOF containing NHC building block[30] (reprinted with permission from Ref. 30)

A year later in 2010[31] the same group also reported the formation of heterometallic MOFs connected through Ce(III) centres while forming a Cu(I) NHC complex. It was observed that the harder metal ion Ce(III) binds to the carboxylate and the softer Cu(I) coordinates to the carbene carbon of the NHC formed *in situ*. In 2010 Yaghi et al[29] reported the synthesis of two MOFs (Figure 2.7), one containing imidazolium salts as building blocks, the IRMOF-76 and the other IRMOF-77 containing its corresponding NHC as the building block. The IRMOF-76 containing the imidazolium salt was obtained in a straightforward solvothermal process; attempts to convert this imidazolium salt linker to corresponding NHC complex (via post synthetic modification) failed. Alternatively, the imidazolium salt was first converted to a palladium NHC complex (pre-synthetic modification) by reacting with $[Pd(CH_3CN)_2Cl_2]$ in presence of pyridine

before the MOF synthesis. The NHC palladium complex thus obtained was used directly in a solvothermal process forming IRMOF-77.

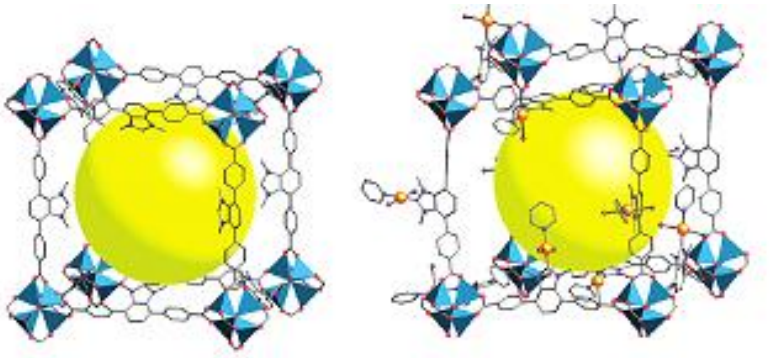


Figure 2.7: Imidazolium and NHC complex containing MOFs[29] (reprinted with permission from Ref. 29)

Therefore due to these huge successes of the MOFs and NHC complexes, coupled with the potentials of inter-marrying the two to give unique NHC coordination polymers or MOFs, we aim to utilise our new NHC complexes as building blocks to prepare new families of these important NHC containing MOFs. Alternatively, the constructed cationic imidazolium-linked polymers may be modified by introducing metal sources capable of producing our desired NHC containing MOFs. Also some characterisation techniques will be employed to study their properties which will give an insight into their potential applications.

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CHAPTER 3

Nitrile Functionalised Imidazolium Salts and Some of Their N-Heterocyclic Carbenes

3.1. Introduction

NHC ligands have attracted a huge amount of interest over the last two decades[1] as a result of isolation of a free crystalline carbene by Arduengo et al in 1991.[2] Their subsequent complexation, primarily with late transition metals,[3] and to a lesser degree with main group elements have been widely reported.[4] Their resemblance to phosphines, coupled with the fact that they are more electron rich makes them excellent co-ligands in homogenous catalysis.[4] A large body of research on the use of NHCs and their complexes as homogenous catalysts has been reported,[5] including the areas of olefin metathesis and hydroformylation,[6] coupling reactions,[5] and polymerisation reactions.[5] More recently, NHC ligands and their metal complexes have been found to be potentially useful building blocks in the formation of many coordination polymers or metal–organic frameworks (MOFs).[7]

The substituents on the NHCs play a significant role in their stability and selectivity as catalyst and will also determine their ability to form coordination polymers or MOFs. Imidazolium salts and their corresponding carbenes with donor functionalities have been receiving a great deal of attention[8, 9] in the design of homogenous catalysts. In particular, steric control of the catalyst active site *via* the ligand architecture and substituent steric bulk has been studied, while the use of labile substituents capable of generating coordinative unsaturation has also been of interest.

Many functionalised NHCs with pendant groups consisting mainly of N and O donors have been synthesised and reported. Substituents on the NHCs containing S and P donor groups have also been reported, but to a lesser degree.[8, 10] Although a number of N-functionalised NHCs have been reported, only few contain nitrile functionalities, despite their ligating potentials. In 2004 Zhou et al[11] reported a series of ionic liquids based on imidazolium salts with nitrile functionalities attached to alkyl side chains. Although none of these salts prepared were converted to NHCs, they were found to be very useful in hydrogenation catalysis. This work was followed in 2007[12] by preparation of another series of imidazolium salts based ionic liquids (ILs) containing both mono and bis nitrile functionalisation and tested their performances in C-C coupling reactions in

which they were found to show some appreciable activity. One of the bis nitrile functionalised imidazolium salts was converted to a palladium NHC complex (Figure 3.1b), but it has not significantly affected the catalytic reactions, rather it helped in stabilising the ionic liquids (ILs) which were established to be useful as immobilization media in multiphasic catalysis.[12]

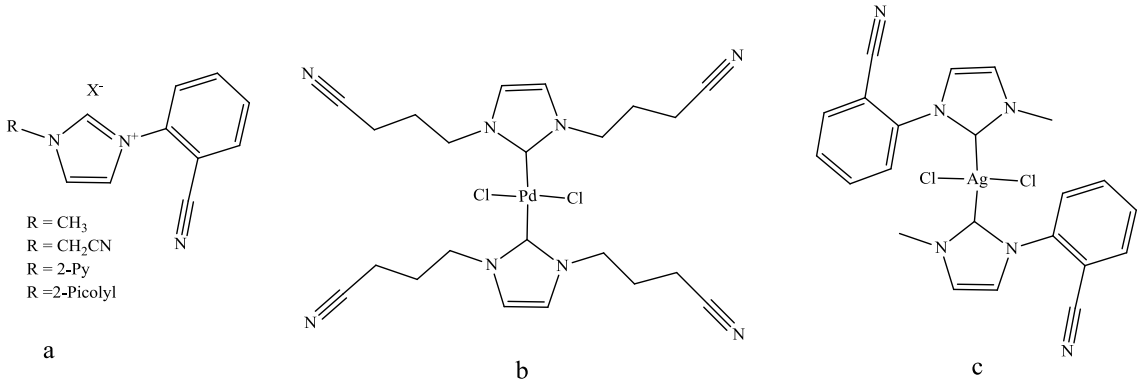


Figure 3.1: Examples of nitrile functionalised NHC complexes

Morris et al in 2009[13] reported the synthesis and X-ray crystal structures of some unsymmetrical nitrile functionalised imidazolium salts (Figure 3.1a) and subsequently converted them into silver(I) (Figure 3.1c) and rhodium(I) carbene complexes. The same group also[14] reported the synthesis and characterisation of nitrile functionalised NHC complexes from palladium(II) and platinum(II) through transmetalation of their corresponding silver(I) complexes.

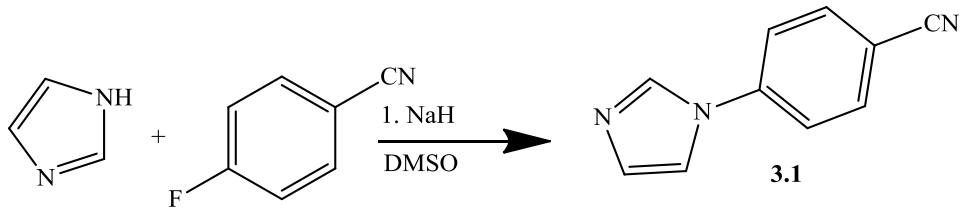
We are interested in the development of functionalised imidazolium salts bearing non-chelating coordinating groups (e.g. nitrile, carboxylate, pyridine), which can be used to form NHC. We also intend to investigate the assembly of these imidazolium salts into MOFs. Either pre- or post-synthetic modification will then allow conversion of the imidazolium salt to a metal NHC complex. Hence, mono- or bimetallic functional MOFs can be envisaged.

This chapter describes the synthesis and characterisation of 1-(4-cyanophenyl) imidazolium salts, their conversion to metal NHC complexes and attempts to assemble these into polymeric materials.

3.2. Results and discussion

3.2.1. Ligand synthesis

The synthesis of the nitrile functionalised imidazolium salt precursors was accomplished in two steps. The first involved the synthesis of 1-(-4-cyanophenyl) imidazole (**3.1**), and initially a procedure used by Amouyal et al[15] was adopted. It involves reaction of 4-fluorobenzonitrile and imidazole in DMSO at 90^{o}C for 4 days according to Scheme 3.1. Although the targeted 1-(-4-cyanophenyl) imidazole was formed, as confirmed spectroscopically using mass spectrometry, IR and NMR (^{1}H and ^{13}C), the yield was poor (about 15%) despite taking 4 days to accomplish.

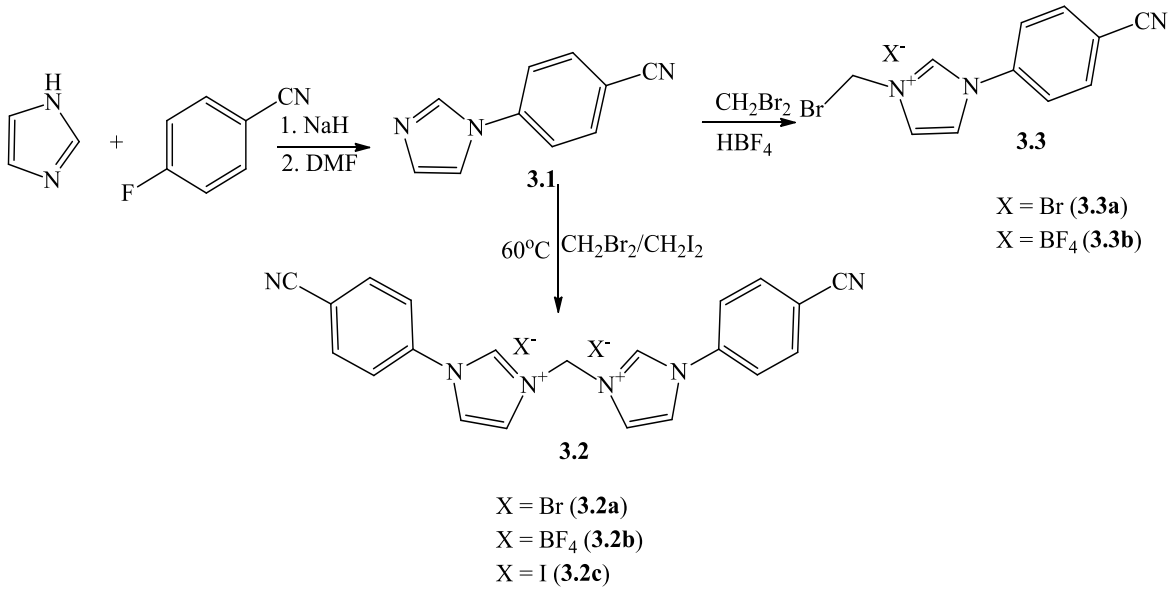


Scheme 3.1: Synthesis of 1-(-4-cyanophenyl)imidazole

A modification of another procedure reported by Molt et al[16] shortens the reaction time to a day and also significantly improves the yield to 95%. It involves refluxing a mixture of 4-fluorobenzonitrile, imidazole and sodium hydride in DMF (Scheme 3.2) and subsequent precipitation of the product in cold H_2O.

In the second step, the 1-(4-cyanophenyl) imidazole synthesised was then heated at 60-65^{o}C in neat dibromomethane for 2-3 days according to Scheme 3.2 to form the bis imidazolium salt (**3.2a**) in high yield. The imidazolium salt(s) gradually precipitated throughout the time of the reaction to give a white compound which was filtered, washed with THF and dried. Because excess dibromomethane was used, at higher temperatures (above 70^{o}C) a mixture of the bisimidazolium bromide salt (**3.2**) and

mono-imidazolium bromide (**3.3**) were obtained, which were tedious to separate. The methylene bridged imidazolium iodide salt was better synthesised following the same method but using diiodomethane at a lower temperature (40-50^{o}C) to prevent a mixture of both bis and mono imidazolium salt being obtained.



Scheme 3.2: Synthesis of the benzonitrile imidazolium salts

To improve solubility, the halide anion was exchanged for tetrafluoroborate by addition of HBF_4 dropwise to an aqueous solution of the halide salt. The formation of these imidazolium salts was confirmed spectroscopically. ^{1}H NMR (Figure 3.2) indicates the appearance of a new peak at 6.95ppm for **3.2** and 6.26ppm for **3.3** which were attributed to the bridging methylene groups, while the resonance at 7.95ppm in 4-cyanophenyl imidazole has shifted significantly to 10.48ppm for **3.2** and 10.22ppm for **3.3**, which is typical of imidazolium salts.[17] Ions in the mass spectrum (M^{+}) at m/z = 351 and 264 for **3.2** and **3.3** respectively, supported by good agreement between theoretical and observed result in the microanalysis further confirmed the synthesis of these precursors. The nitrile functionality on the imidazolium salts was indicated by presence of peak at 2232 cm^{-1} in the IR-spectra.

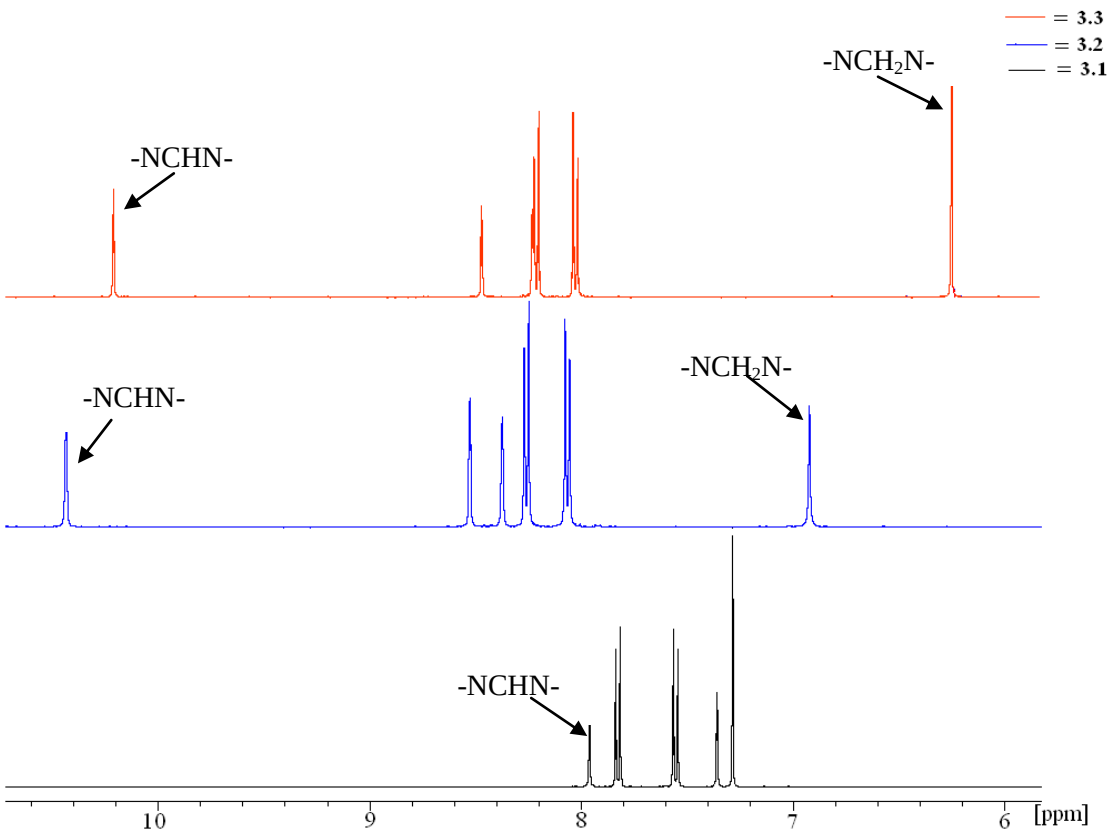


Figure 3.2: ^{1}H NMR (400MHz, DMSO-d_6) of the aryl imidazole **3.1**, bisimidazolium salt **3.2** and mono imidazolium salts **3.3**

Single crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into concentrated acetonitrile solutions of **3.2b**. The crystallographic information is presented in Table 3.1. As expected, one asymmetric unit of the bowl-shaped bisimidazolium salt contains one 1-(-4-cyanophenyl) imidazole attached to a methylene group which is on a two-fold special position, and one tetrafluoroborate counter ion (Figure 3.3). The bond distances and angles are within the range of similar imidazolium salts.[17, 18]

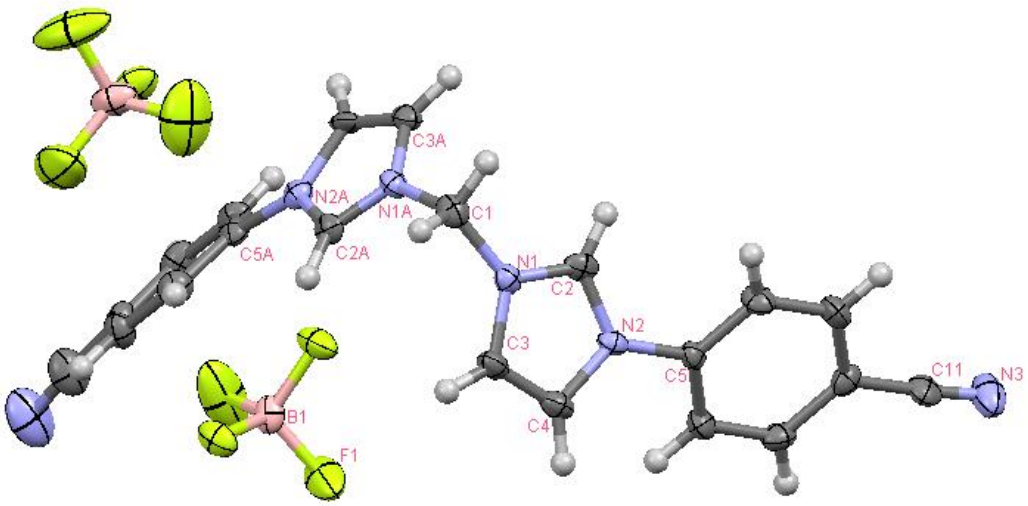


Figure 3.3: X-ray crystal structure of **3.2b,** thermal ellipsoids drawn at 50% probability level. Some selected bond lengths (Å) and bond angles (°). N(1) – C(1) = 1.461(5), N(2) –C(5) = 1.436(4), N(3) – C (11) = 1.139(5), N(1a) –C(1) = 1.484(5), N(2a)– C(5a) = 1.436(5), N(1) – C(1) – N(1a) = 109.8(3), C(2) – N(1) – C(1) =124.6(3), C(2a)– N(1a) – C(1) = 124.0(3), C(2) – N2 – C5 =124.6(3), C(2a) – N(2a) – C(5a) = 124.9(3)

There are significant hydrogen bonding interactions between the fluorines of the BF_4 anion and 4 different hydrogens of the cation (Figure 3.4). They make contact with the most acidic proton (NCHN) on C(2A), the imidazole ring hydrogen on C(3), the methylene hydrogen on C(1) and the phenyl ring hydrogen on C(10A). The F--H contact distances are 2.426 Å, 2.424 Å, 2.439 Å and 2.416 Å respectively. Each of these distances is less than the sum of the van der Waals radii of H and F (2.70 – 3.05)[19] therefore falls within hydrogen bonding. The more acidic hydrogen atoms on C(2A) and C(3), as might be expected, are more willing to form hydrogen bonding interactions, with each being attracted to 2 different fluorine atoms of the BF_4^- anion. A weak interaction was also observed between the BF_4^- anion and the π-system of a second cation imidazolium ring as shown in Figure 3.4. The interaction is between each of the NCN carbon (C(2) and C(2A)), N(2A) and the BF_4^- through F(2) and F(3) with a contact

distances of 2.830 Å, 2.961 Å and 3.037 Å thus encapsulating the BF_4^- anion within the two imidazolium rings.

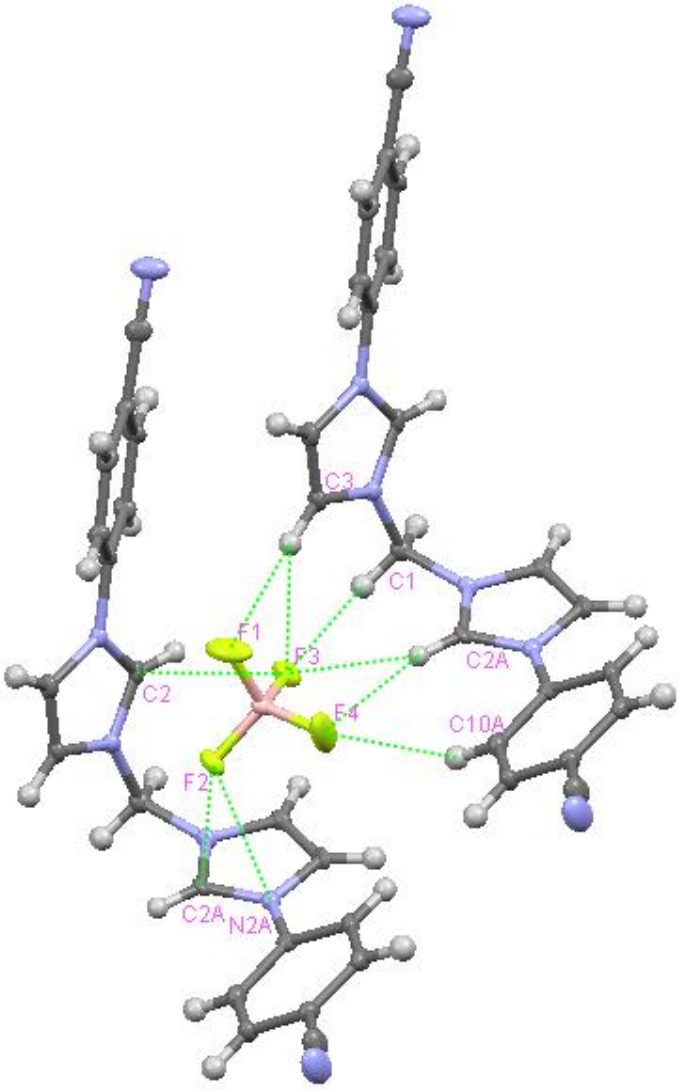


Figure 3.4: Crystal structure of **3.2b** showing the BF_4^- anion coordination environment

No aromatic π-π stacking is observed in the packing of the molecule but apart from the anion – cation contacts described above the molecules are also weakly assembled by contact between the nitrile nitrogen and the π system of imidazolium ring through the NCN carbon with a distance of 2.834 Å. In addition the other nitrile nitrogen links two cations through weak interaction with a hydrogen atom on the phenyl ring as shown in Figure 3.5. This nitrile interaction gives an extended array of the molecule when viewed along the crystallographic a-axis.

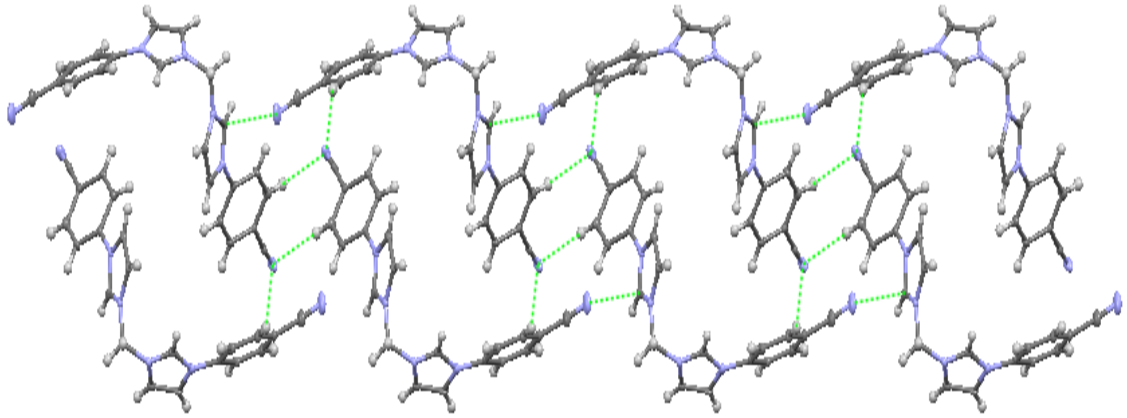


Figure 3.5: Extended crystal structure of **3.2b** viewed along the crystallographic a-axis showing weak C---H---N and N---C interactions. BF_4^- counter ions omitted for clarity.

Table 3.1. Selected crystallographic data for **3.2b**, and **3.3b**

Compound	**3.2b**	**3.3b**
Chemical Formula	$C_{21}H_{16}N_6B_2F_8$	$C_{11}H_9N_3BrBF_4$
Formula weight	526.02	349.92
Colour	Colourless	Colourless
Lattice Type	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
a/Å	6.5768(4)	8.9505(3)
b/ Å	2.9966(9)	8.4051(4)
c/ Å	27.067(2)	18.2696(9)
α/°	90	90
β/°	90	101.840(4)
γ/°	90	90
V/ Å	2313.6(3)	1345.18(10)
Z	4	4
T/K	293(2)	123(2)
μ/mm^{-1}	0.137	3.094
F000	1063.8	687.9
No of reflection collected	6699	8765
No of independent reflections/(R_{int})	4732/0.0382	3564/0.0218
No of observed Reflection ($I>2\sigma(I)$)	2188	2064
No of parameters Refined	334	176
R1 (obsd/all)	0.0481/0.1192	0.0305/0.0517
wR2 (obsd/all)	0.0746/0.0653	0.068/0.071
Largest difference in peak and hole $eÅ^{-3}$	0.441, -0.361	0.602, -0.482

Single crystals of the monoimidazolium salt (**3.3b**) suitable for X-ray diffraction were obtained directly from the BF_4^- anion exchange reaction. It crystallises in the monoclinic space group $P2_1/c$, with each asymmetric unit containing the 4-cyanophenyl linked to an imidazolium ring. The cyanophenyl and the imidazolium rings are co planer, with the terminal bromine pointing upward (Figure 3.6)

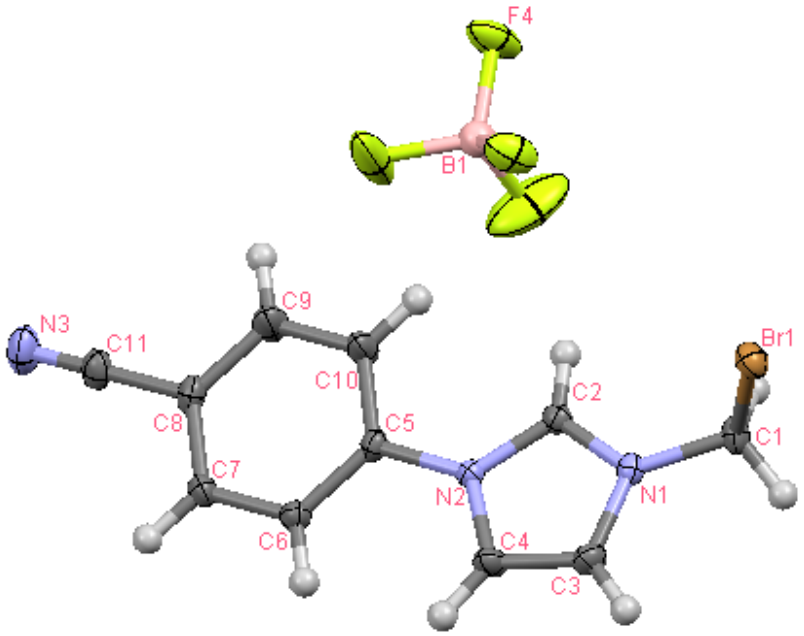


Figure 3.6: Crystal structure of **3.3b,** thermal ellipsoids drawn at 50% probability level. Some selected bond length (Å) and angles (°). C(1) – Br(1) = 1.939(2), C(1) – N(1) = 1.447(3), N(1) – C(2) = 1.326(2), N(1) – C(3) = 1.371(3), C(2) – N(2) = 1.331(3), N(2) – C(4) = 1.390(3), N(2) – C(5) = 1.443(2), N(3) – C(11) = 1.141(3), C(1) – N(1) – C(2) = 124.9(2), N(1) – C(1) – Br(1) = 110.5(1), C(2) – N(2) – C(5) = 125.7(2), N(2) – C(5) – C(10) = 119.3(2), N(2) – C(5) – C(6) = 119.2(2).

Figure 3.7 shows the BF_4^- anion environment, weakly linking up four cationic molecules of **3.3b** through hydrogen bonds, which are shorter than those in ligand (**3.2b**)**.** The contact in the first molecule is between F(1) and hydrogens on C(2) and on the methylene carbon C(1) with average contact distances of 2.454 Å and 2.386 Å respectively. The contact with the second molecule is between F(4) and hydrogen on

C(1) and also between F(3) and the C(3) hydrogen with an average distance of 2.305 Å. Contact with the third molecule is between F(3) and hydrogens on C(4) and C(6) with average contact distance of 2.324 Å, and also F(1) and the C(6) hydrogen, with a distance of 2.662 Å. Finally, contact with the fourth molecule is between F(2) and hydrogen on C(2) with a distance of 2.370 Å. All the contact distances in this molecule are within 2.305 – 2.454 Å which are within the van der Waals radii of F and H.[19]

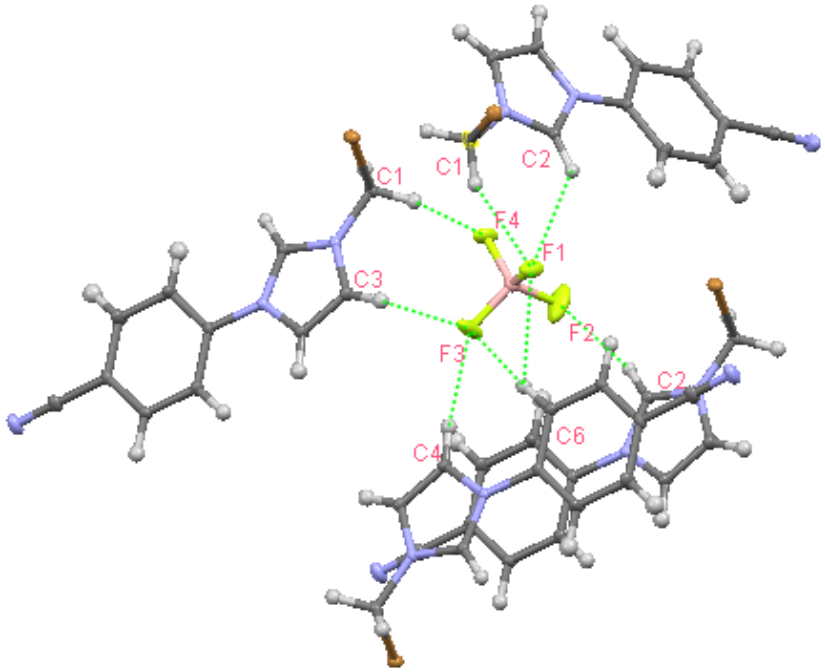


Figure 3.7: Crystal structure of **3.3b** showing the BF_4 anion interaction environment.

The bromine on the cationic molecule was observed to also weakly interact with two other molecules through hydrogen bonding (Figure 3.8). It interacts with C(1) hydrogen on one molecule and the phenyl ring hydrogen on C(10) in the other molecule. Interestingly a halogen-halogen interaction was observed between the bromine and F(4) of the BF_4^- anion, with a Br---F distance of 3.273 Å. Such halogen---halogen interactions have been a matter of interest and debate in recent years.[20]

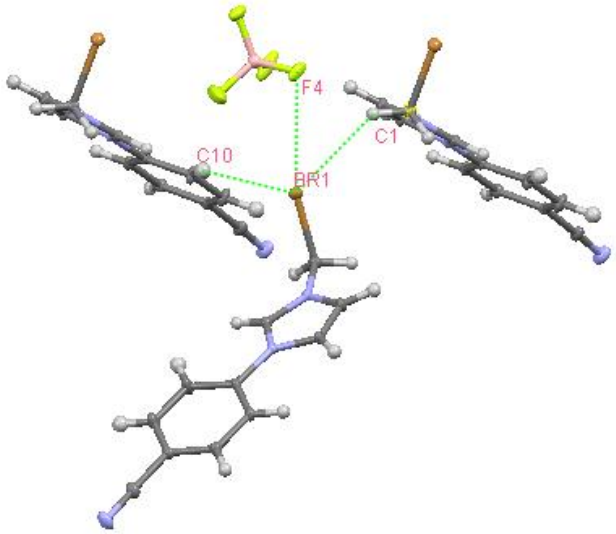


Figure 3.8: Crystal structure of **3.3b,** showing the Br interaction environment.

The packing of this molecule also does not show π-π stacking (just like **3.2b** above), but the nitrile nitrogen atoms are in contact with a hydrogen atom on the phenyl ring arranging the molecule to be in pairs with head to tail arrangement (Figure 3.9) given an extended array with a beautiful architecture.

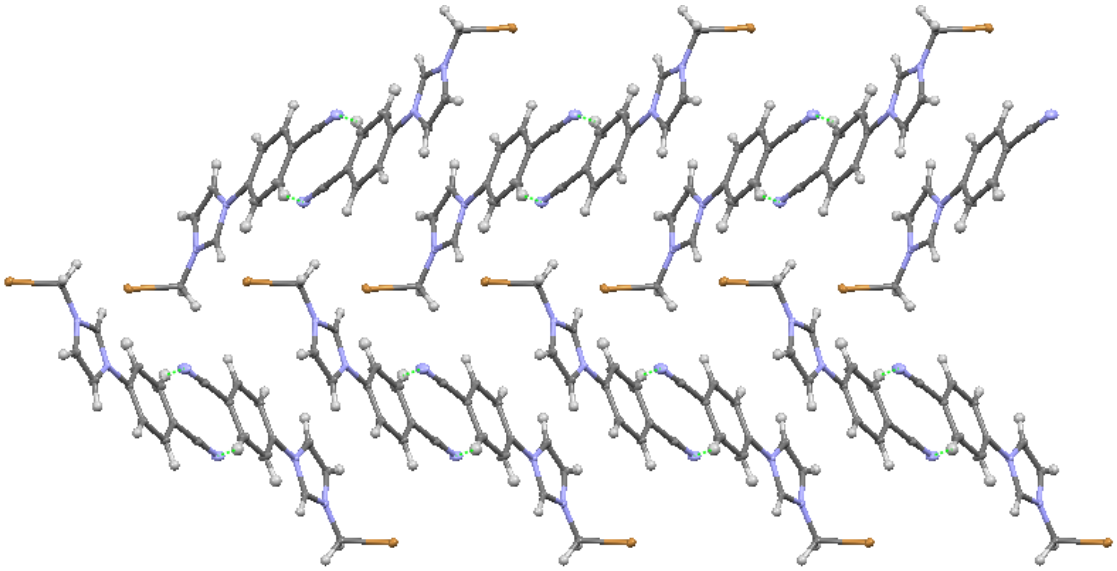
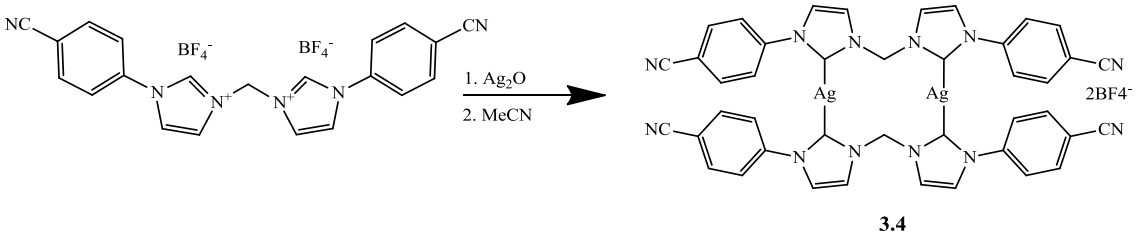


Figure 3.9: Extended crystal structure of **3.3b**, viewed along the crystallographic a-axis showing the C---H---N interaction. BF_4^- anions omitted for clarity.

3.2.2. Complex synthesis and structures

Having obtained these novel nitrile substituted imidazolium salts, we were interested in preparing their corresponding metal complexes. The stability of the silver-NHC complexes makes them a convenient precursor for synthesis of further metal NHC complexes, since they serve as carbene transfer agents to a number of transition metals, including ruthenium, rhodium and palladium.[21, 22]

Most of the NHC silver(I) complexes are conveniently prepared by the action of silver(I) oxide on the imidazolium salt pro-ligand in dichloromethane, either at room temperature, or with mild heating. The silver oxide normally serves a dual purpose, acting as a base to deprotonate the bis-imidazolium salt and also as a silver source which coordinates to the free carbene formed *in situ*. In this way NHC-silver(I) complexes are prepared in good yield and are relatively stable to moisture and air.



3.4

Scheme 3.3: Preparation of bis silver tetracarbene complexe.

Initial attempts to prepare a silver complex by stirring a mixture of the imidazolium salt **3.2b** with silver(I) oxide in dichloromethane, either at room temperature or at reflux, or in acetonitrile at room temperature, did not yield the desired complex. However, refluxing a small excess of silver(I) oxide and the bisimidazolium salt (**3.2b**) in acetonitrile overnight with total exclusion of light resulted in the formation of a bis silver tetracarbene complex (**3.4**) according to Scheme 3.3. It was isolated by filtration through celite to remove any unreacted silver(I) oxide, concentration of the resulting solution and addition of diethyl ether to precipitate the white NHC complex **3.4** in high yield. The formation of the silver NHC complex **3.4** was confirmed by the disappearance

of the NC(H)N singlet peak at 10.15 ppm in the ^{1}H NMR, due to the loss of the acidic proton of the imidazolium salt. It also suggests that all the imidazolium salt has been converted to the silver complex (**3.4**)**.** The ^{13}C NMR is also consistent with the formulation, with shifts of the resonances relative to the starting imidazolium salt, although the peak due to the carbenic carbon, expected at ca 180 ppm was not observed. Mass spectrometry shows the parent ion peak at m/z = 459 [M^{2+}] and 917 [M^{+}] (Figure 3.10) with an isotope pattern consistent with the presence of two silver atoms, confirming the formation of the disilver tetracarbene complex (**3.4**). The absence of the carbene peak in the ^{13}C NMR is very common within the silver NHC carbene family, in fact not many silver NHC complexes with well resolved silver – carbene coupling have been reported,[23] possibly due to exchange and long relaxation times.

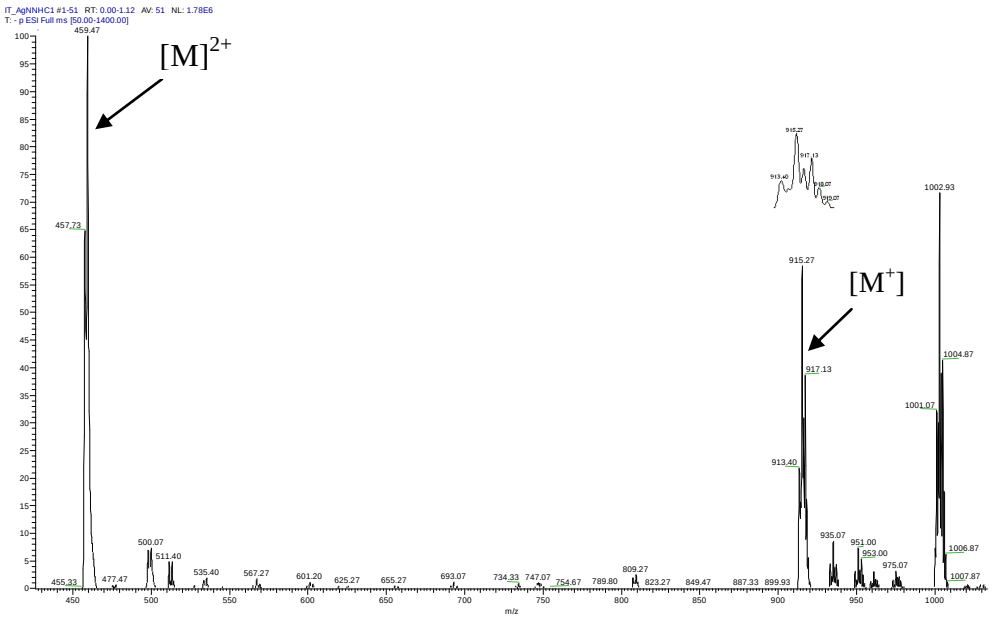


Figure 3.10: Mass spectrum of **3.4**

Single crystals of **3.4** suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a concentrated acetonitrile solution of the complex. It crystallises in orthorhombic space group Pbca, and the crystal data is presented in Table 3.2. The molecular structure revealed the bis silver tetracarbene complex, **3.4**, (Figure 3.11)

comprising two dicarbene ligands spanning two silver(I) atoms, with each silver bonded to two imidazol-2-ylidenes from the different sister ligands (Figure 3.11).

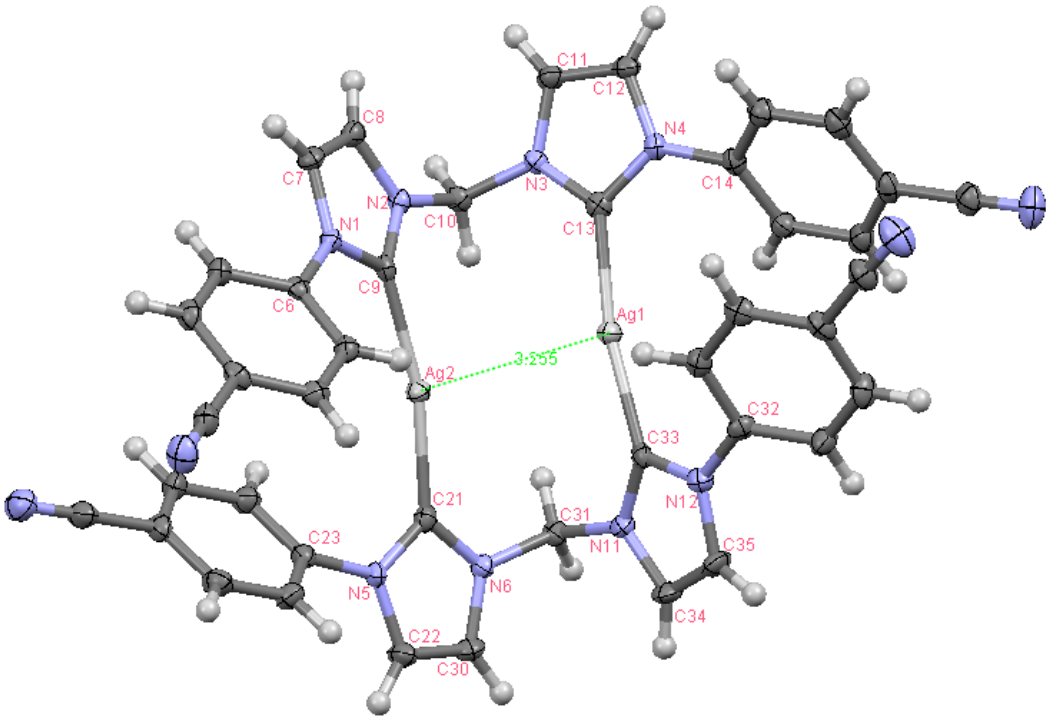


Figure 3.11: Crystal structure of **3.4,** thermal ellipsoids drawn at 50% probability level. BF_4 anions are omitted for clarity. Some selected bond length (Å) and bond angles (°). Ag(1) – C(13) = 2.093(3), Ag(1) – C(33) = 2.087(3), Ag(2) – C(9) = 2.085(3), Ag(2) – C(21) = 2.081(3), C(9) – Ag(2) – C(21) = 168.1(1), C(13) – Ag(1) – C(33) = 169.7(1), N(2) – C(10) – N(3) = 111.4(2), C(6) – N(1) – C(9) = 125.4(2), C(9) – N(2) – C(10) = 124.4(2).

The silver to carbenic carbon bond lengths (Ag-$C_{carbene}$) fall in a narrow range with an average bond length of 2.087(3) Å, which are within the expected range for this type of silver NHC compound.[23] Similarly, the C(13) – Ag(1) – C(33) bond angle (169.7(1)^o) and C(9) – Ag(2) – C(21) bond angle (168.1(1)^o) are similar both showing a deviation from linearity. Although these bond angles deviate from linearity and thus are less than typical bond angles for bis NHC silver(I) complexes, they are consistent with other similar silver(I) bis NHC and tetracarbene complexes.[22, 23] The two silver atoms are bent

toward each other suggesting a Ag---Ag interaction which is confirmed considering the distance between them is 3.255 Å, and this value is similar to other Ag---Ag interactions reported in similar complexes.[23] Another important feature of the structure is the close approach of the neighbouring two cyanophenyl rings, which are slightly twisted, adopting a face to face arrangement as shown in Figure 3.12. The phenyl rings make closest contact on the nitrile ends, with a distance of 3.376 Å indicating the presence of π-π stacking between the opposite phenyl rings. This types of interaction can be attributed to the nitrile functionalities as it was not observed when mesityl was used as a substituent in a similar silver tetra NHC complex.[23]

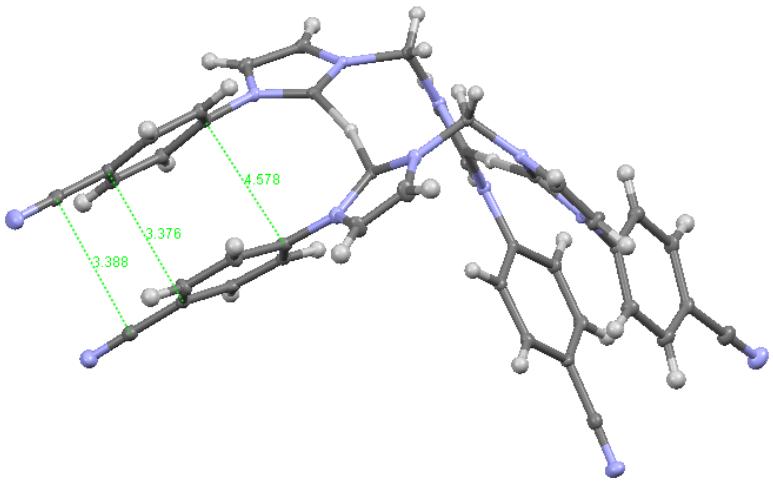
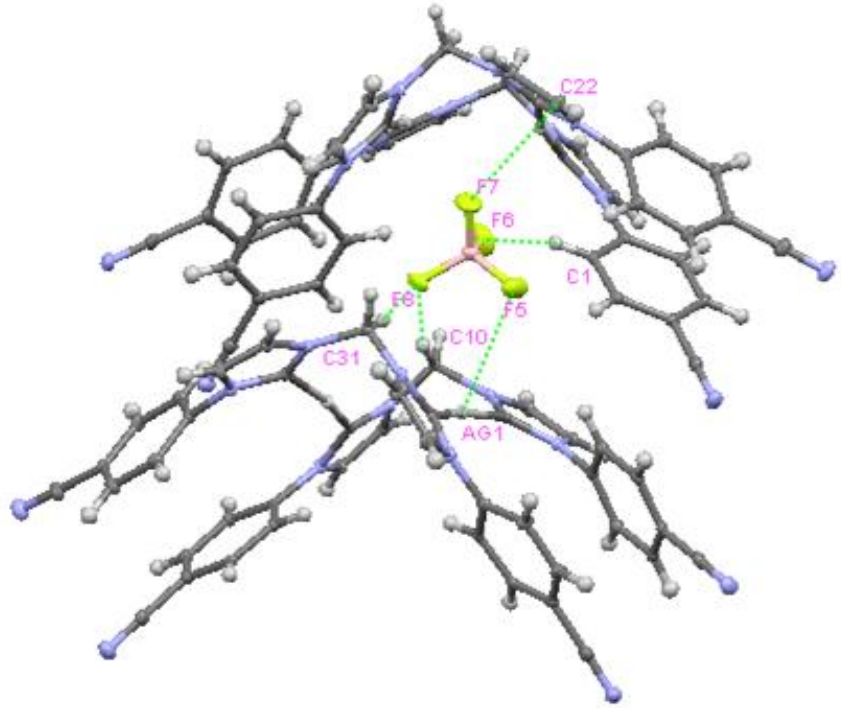
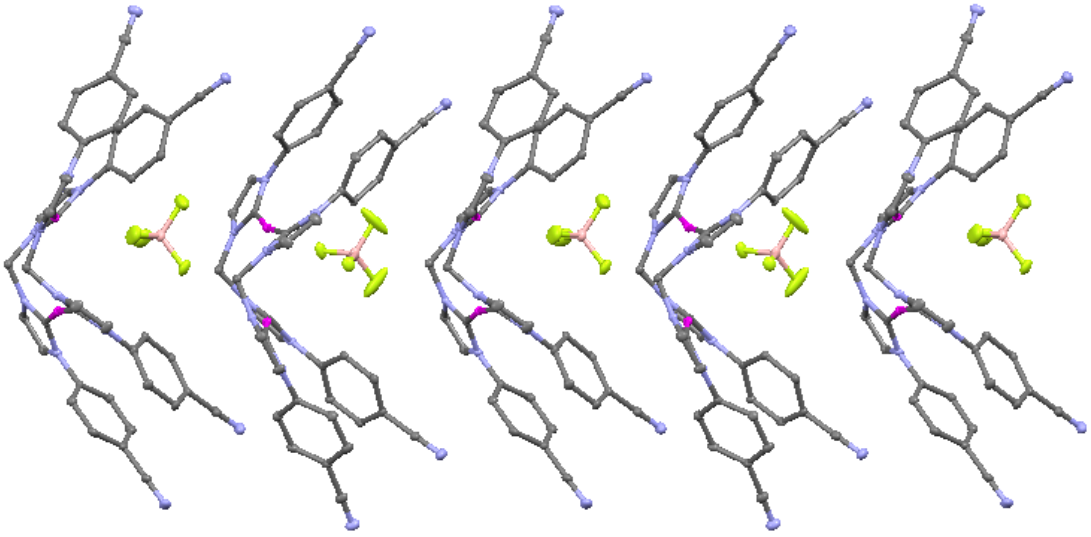


Figure 3.12: Crystal structure of **3.4,** showing the interaction of the aryl rings. BF_4 anions are omitted for clarity

The BF_4^- was observed to be weakly bonded to two separate molecules of the complex as shown in Figure 3.13 In one, F(5) was found to be weakly attracted to silver atom Ag(1) and F(8) was interacting with hydrogen of each of the methyl spacers C(10) and C(31) with average contact distance of 2.311 Å. The other bis silver NHC molecule interacted through hydrogen bonding between F(6) and hydrogen on C(1), while interaction between F(7) and C(22) shows involvement of the imidazolium ring π system at a distance of 3.114 Å



a



b

Figure 3.13: Crystal structure of **3.4,** (a) showing the BF_4^- anion interaction environment, (b) view along crystallographic b-axis, hydrogen omitted for clarity.

Weak bonding interactions between nitrile nitrogen on both ends of the molecule and hydrogen on the phenyl and imidazolium rings gives rise to a herringbone pattern structure along the crystallographic b-axis (Figure 3.14). N(7) was attracted to 2 different hydrogen atom one from the phenyl and the other from imidazolium rings with distances of 2.648 Å and 2.496 Å respectively. On the other end of the molecule N(14) was weakly bonded with the phenyl hydrogen on C(10) and N(13) with phenyl hydrogen on C(4)

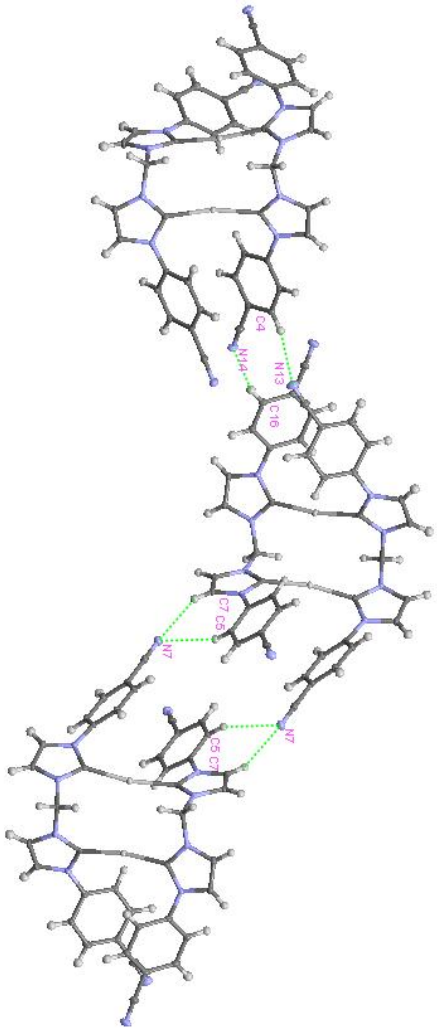
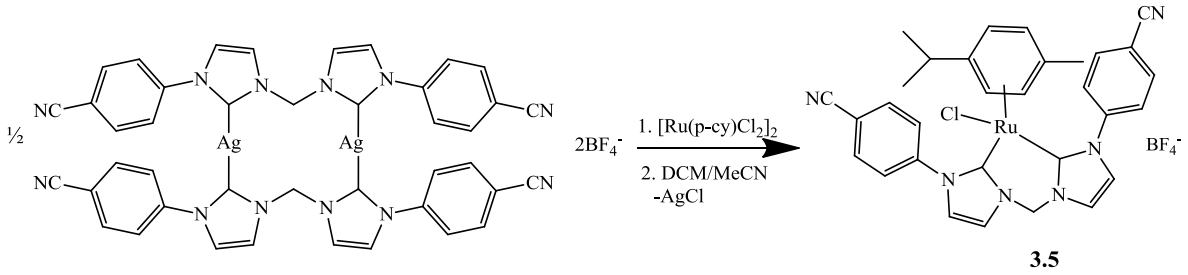


Figure 3.14: Crystal structure of **3.4,** showing the C---H---N interactions. BF_4^- anions are omitted for clarity

Table 3.2. Selected crystallographic data, for **3.4**, **3.5** and **3.6**

Compound	**3.4**	**3.5**	**3.6**	**3.8**
Chemical Formula	$Ag_2C_{42}H_{28}N_{12}B_2F_8$	$Ru_1C_{21}H_{14}N_6B_1F_4$	$Pt_1C_{21}H_{14}N_6Br_2$	$Pd_1C_{22}H_{22}N_8F_8$
Formula weight	1090	538.25	705.26	678.51
Colour	Colourless	brown	Colourless	colourless
Lattice Type	orthorhombic	monoclinic	Monoclinic	monoclinic
Spacegroup	p b c a	P 2_1/a	P 2/c	Pc
a/Å	15.2544(7)	9.3479(2)	14.4902(7)	12.2112(2)
b/ Å	22.3535(11)	16.9362(6)	8.6318(4)	6.6692(10)
c/ Å	27.8705(11)	18.9812(6)	24.9505(14)	16.6868(2)
α/°	90	90	90	90
β/°	90	93.688(2)	92.073(5)	92.504(10)
γ/°	90	90	90	90
V/ Å	9503.5(7)	2998.84(16)	3118.7(3)	1357.66(3)
Z	8	4	4	2
T/K	293(2)	123(2)	123(2)	123(2)
ρ/gcm-3	1.52	1.57	1.91	1.66
μ/mm^{-1}	0.899	0.67	7.265	0.767
F000	4319	1432	1716	676
No of reflections collected	37187	26263	19220	10522
No of independent reflections/R_{int}	12302/0.0473	6835/0.0829	7837/0.0555	6466/0.013
No of observed Reflection (I>2 σ(I))	6735	5079	4637	6383
No. parameters Refined	651	400	360	370
R1 (obsd/all)	0.0357/0.0837	0.076/0.112	0.0434/0.0884	0.0229/0.0235
wR2 (obsd/all)	0.0636/0.0695	0.136/0.154	0.0947/0.1016	0.0572/0.0576
Largest difference peak and hole e$Å^{-3}$	0.903, -0.773	0.725, -0.634	2.146, -1.035	0.800, -0.359

The use of silver carbene complexes as carbene transfer agents has been widely applied to the preparation of metal-NHC complexes, thanks to the initial work of Lin.[24] The ruthenium NHC complex (**3.5**), was prepared using this transmetalation method. Addition of $[Ru(p\text{-}cy)Cl_2]_2$ into a solution of the bis silver tetracarbene complex (**3.4**) (Scheme 3.4) resulted in immediate precipitation of white silver chloride. The mixture was stirred for 2 hours, the silver chloride was removed by filtration and the solution containing the ruthenium NHC complex was concentrated and precipitated using di-ethyl ether to give a brown complex in high yield.



Scheme 3.4: Synthesis of ruthenium complex through transmetalation reaction.

The expected coordination of the ruthenium by both NHC groups of the ligand was confirmed in the NMR analysis. The disappearance of the NCHN peak of the imidazole and the splitting of the methylene protons into a doublets of doublets in the ^{1}H NMR similar to **3.4** shows the formation of the Ru-NHC complex (**3.5**). This was further supported by the appearance of carbene-carbon peak in the high frequency region of the ^{13}C NMR (175.6 ppm). This carbene peak was slightly lower than some reported Ru-NHC complexes but is within the expected range of typical metal NHC complexes.[22, 25] The NMR data was further supported by the parent ion peak in the mass spectrum at m/z = 621.13 [M^+] with the appropriate isotope pattern and good agreement between observed and theoretical values of the elemental analysis.

The formation of this complex was further confirmed by X-ray structural analysis. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into concentrated acetonitrile solution of the compound **3.5**. It crystallises in monoclinic space group $P2_1/a$ and the crystal data are presented in Table 3.2. The

molecular structure shows the ruthenium atom in the classic piano-stool arrangement, coordinated to the two carbene carbon atoms and one chlorine atom capped with one p-cymene moiety (Figure 3.15).

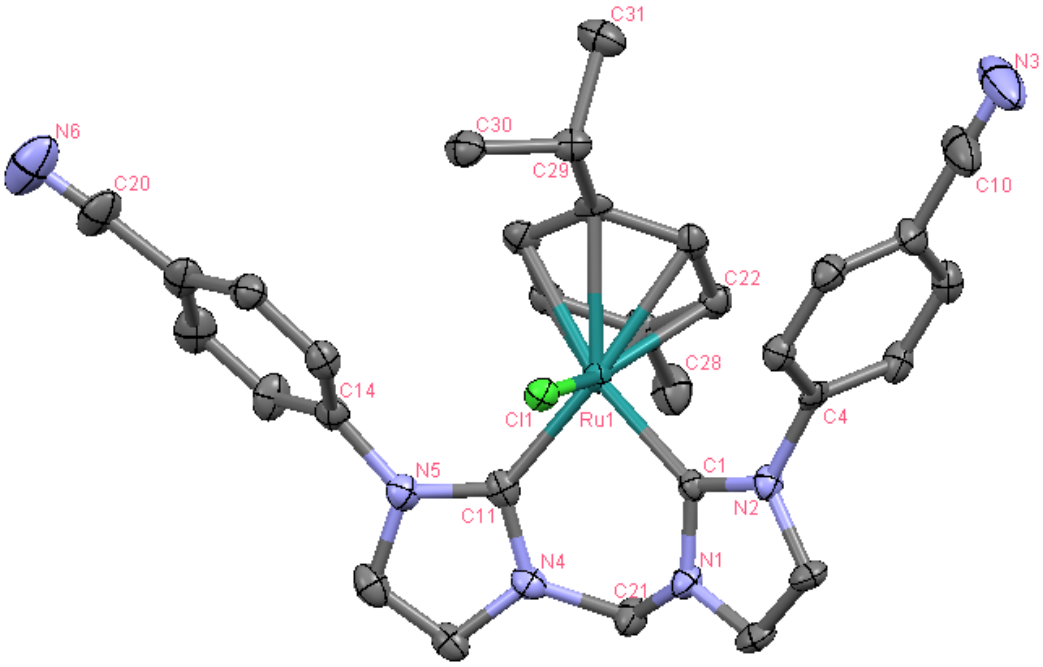


Figure 3.15: Crystal structure of **3.5,** thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and BF_4 anions omitted for clarity. Some selected bond lengths (Å) and bond angles(°), Ru(1) –C(1) = 2.043(5), Ru(1) – C(11) = 2.060(5), Ru(1) – Cl(1) = 2.423(1), Ru(1) – C(22) = 2.187(6), N(1) – C(21) = 1.441(7), N(4) – C(21) = 1.468(8), N(2) – C(4) = 1.455(7), N(3) – C(10) = 1.142(1), C(1) – Ru(1) – C(11) = 86.1(2), C(1) – Ru(1) – Cl(1) = 82.6(1), N(1) – C(21) – N(4) = 109.6(5), C(1) – N(2) – C(4) = 126.8(4), C(1) - N(1) – C(21) = 122.8(5), C(11) – N(4) – C(21) =124.4(5).

The Ru-$C_{carbene}$ bonds lengths (Ru(1) – C(1), 2.0418(1) Å and Ru(1) – C(11), 2.0604(1) Å are quite similar and are within the range of Ru-$C_{carbene}$ in other Ru-NHC complexes.[25] The C(1) – Ru(1) – C(11) bond angle (86.14^o) shows the imidazolium ring were brought closer and are within the region of bite angles for this type of ligand. The chlorine atom was pointing away from both rings in the structure with Ru-Cl bond length of 2.4235(1) Å which is unexceptional from typical Ru – Cl bond in Ru-NHC complexes. Both

cyanophenyl rings were observed to be twisted to almost perpendicular to the parent imidazole ring to minimise H----H repulsions.

There are no regular patterns in the packing of this molecule, they seem to be packed at random but held by different type of weak interactions. One of such interaction is a short contact between one of the carbon on the p-cymene and the cyanophenyl ring π-system other contacts include, C-H---N, Cl---H, and F---H as shown in Figure 3.16

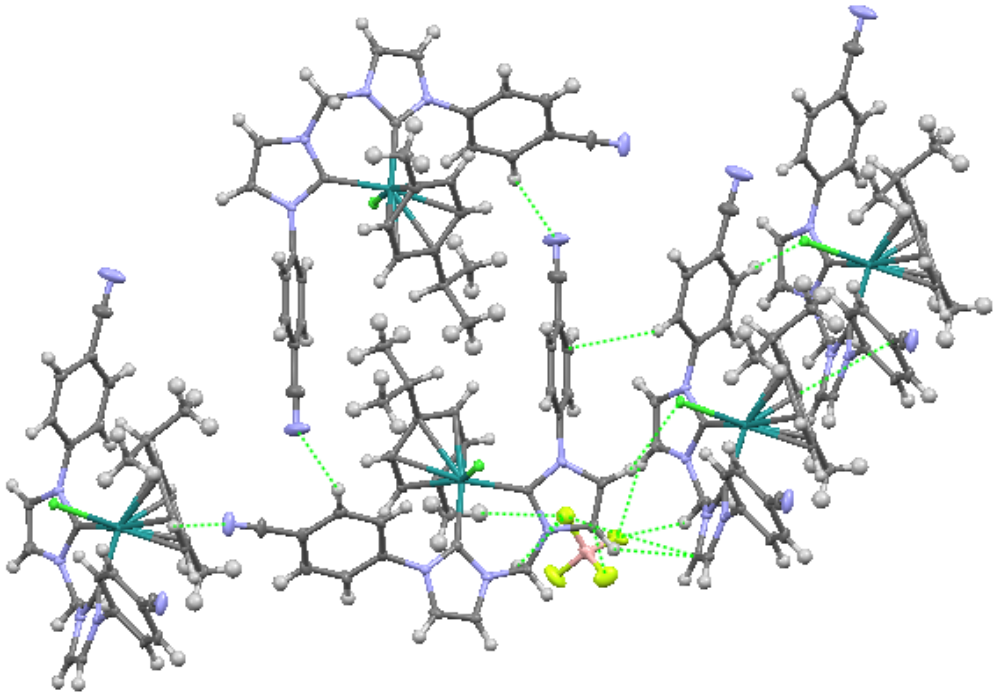
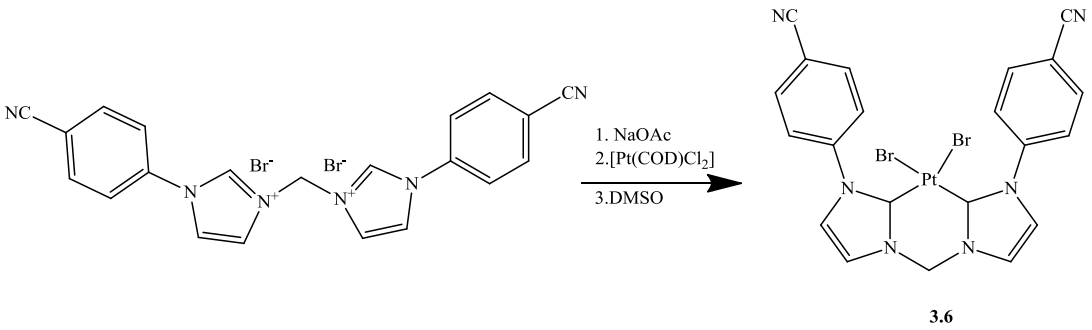


Figure 3.16: Crystal structure of **3.5,** showing different types of weak interaction binding the molecules. Some BF_4 anions are omitted for clarity.

Platinum NHC complexes have been prepared through deprotonation of the acidic proton of the imidazolium salt to give a free carbene before complexation or alternatively the deprotonation can occur *in situ*. The *in situ* deprotonation may be through addition of an external base or with the use of a mild base which may act as both deprotonating agent and metal source e.g platinum acetate. The platinum complex **3.6** was prepared according to Scheme 3.5, which involves taking a mixture of

bisimidazolium salt (**3.2a**), NaOAc and [Pt(COD)Cl_2] in DMSO and heating at 100^oC overnight. THF was used to precipitate a white product which was identified spectroscopically as the platinum bis NHC complex (**3.6**).



3.6

Scheme 3.5: Synthesis of the platinum bis NHC complex

The NMR showed signals attributable to the aryl and imidazole protons, and the loss of the signal at 10.40 ppm of the starting ligand attributed to the NC(H)N in imidazolium salt **3.2a** as found in the other complexes, **3.4** and **3.5** indicates the formation of our targeted compound (**3.6**). Furthermore the singlet signal of the methylene bridge appeared to split in to a doublet of doublets which is characteristic of chelated methylene bridged di-NHC complexes.[17] In addition a significant shift of the signal attributed to the carbene carbon is noticed in the ^{13}C NMR spectrum.

X-ray analysis was possible when a single crystal was grown from slow diffusion of THF into DMSO solution of the complex. It crystallises in the monoclinic space group P2/c, and the crystal data information is given in Table 3.2. The structure shows the platinum atom bonded to two carbenic carbon atoms and two bromine atoms in a distorted square planar geometry (Figure 3.17), with one well resolved DMSO molecule and another which is disordered. The bisimidazolium NHC ligand in this structure is more bent, bringing the two imidazolium ring more closely than in the bisimidazolium salt (**3.2a**) and the two complexes (**3.4** and **3.5**). The C(1) – Pt(1) – C(11) bond angle of 85.5(3)^o, is similar to previous platinum bis and tetracarbenes complexes reported.[17, 18, 26]

The Pt - $C_{carbene}$ (Pt(1) – C(1), 1.9786(1) and Pt(1) –C(11), 1.9795) are also identical with similar Pt-NHC complexes reported [18]. A slight deviation was observed in the Br(1)– Pt(1) – Br(2) bond angle (92.15°) which is slightly higher than similar Platinum complexes reported which has average bond angles of 85.50°, but the Pt-Br bond lengths (Pt(1) – Br(1), 2.4870(1) and Pt(1) – Br(2), 2.4749(1) are similar to those previously reported.[18, 26] The cyanophenyl rings unlike in complex **3.5** (where they are twisted to almost perpendicular to the imidazole ring) are only slightly twisted; in fact they are almost coplanar with their respective imidazole ring in the structure.

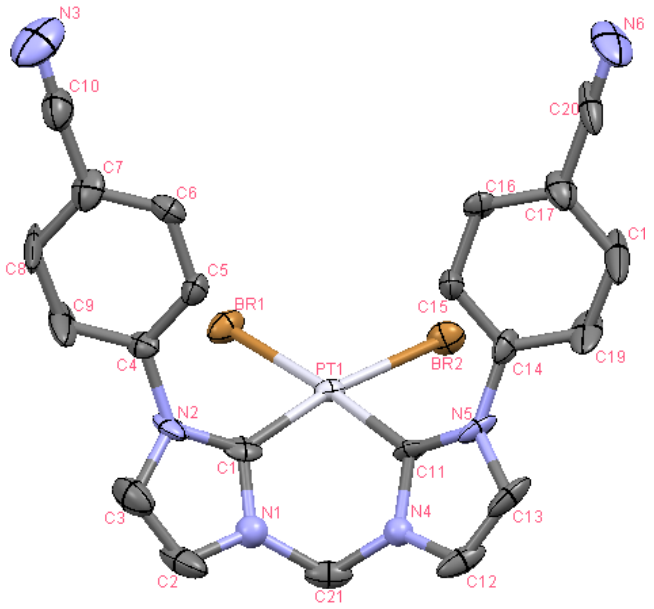


Figure 3.17: Crystal structure of **3.6,** thermal ellipsoids drawn at 50% probability level. Hydrogen atoms omitted for clarity. Some selected bond lengths (Å) and bond angles(°) Pt(1) - Br1 = 2.4861(8), Pt(1) – Br(2) = 2.4746(9), Pt(1) – C(1) = 1.963(8), Pt(1) –C(11) = 1.968(7), N(1) – C(21) = 1.460(10), C(21) – N(4) = 1.420(10), N(2) – C(4) = 1.429(9), N(3) – C(10) = 1.150(11), Br(1) – Pt(1) – Br(2) = 92.10(3), Br(1) – Pt(1) – C(1) = 92.4(2), Br(2) – Pt(1) – C(11) = 89.5(2), C(1) – Pt(1) – C(11) = 85.5(3), Pt(1) – C(1) – N(1) = 120. 0(6), Pt(1) – C(11) – N(4) = 119.7 (5), C(1) – N(1) – C(21) = 121.3(7), C(11) – N(4) – C(21) = 122.0(6), C(1) – N(2) – C(4) = 125.7(6), C(11) – N(5) – C(14) = 125.1(6).

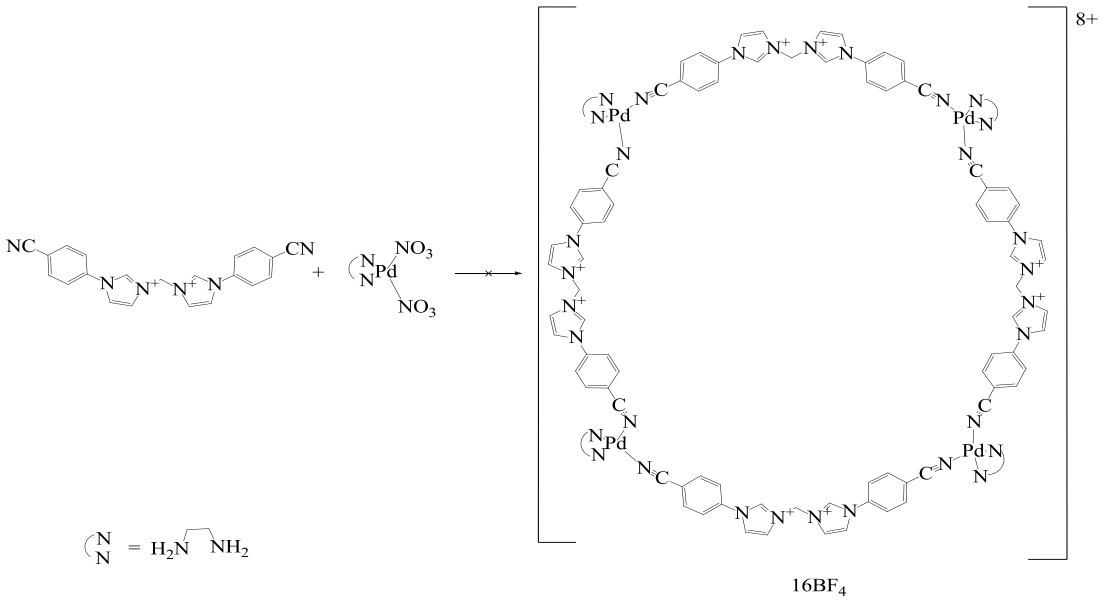
3.3. Attempted synthesis of cationic polymers

Having successfully synthesised these promising bisnitrile bisimidazolium salts (**3.2**) which have the potential to produce polymeric frameworks, attempts were made to assemble them into an array of polymeric materials. The initial attempt involved dissolving the imidazolium salts and various Zn(II), Cu(II), Ag(I), Cd(II), Ni(II) metal salts in water and allowing the solution to slowly evaporate in hope of obtaining crystals of cationic coordination polymers of **3.2**. But in every case the products obtained have their IR, NMR and mass spectra identical to that of **3.2,** indicating probable failure of the nitrile groups to complex with the metal. This was thought to be due to presence of two cations in the molecule which may render the terminal nitrile group less basic and as such having weaker coordinating ability. To remedy this various bases were tried to adjust the pH but all to no avails.

The second approach involved refluxing solutions of the imidazolium salt **3.2** and the various metal salts listed above in different types of organic solvents including methanol, ethanol, acetonitrile, DMF, DMSO, but again the spectroscopic data obtained are identical to the starting imidazolium salts (**3.2**). No evidence of complexation was found. In a further attempt, a layering method (as used by the Hanton group (personal communication)) was adopted in an effort to grow crystals of the targeted materials. The bisimidazolium salts were dissolved in methanol and layered with acetonitrile was allowed to diffuse into the solution of the metal salts in water for several days. But this also did not result in the formation of our target compound as evidenced from the spectroscopic data. Other solvent permutations were tried with less dense solvents layered on heavier ones, but once more our target compounds proved elusive. Similarly, attempts to covert the metal NHC complexes **3.4**, **3.5** and **3.6** into polymers following a similar method as with **3.2** did not yield the expected results. Although the acidic nature of the bisimidazolium salts **3.2** has been reduced through complexation steric factors may have played some role.

In an attempt to form a macrocylic complex $[(en)Pd(\mathbf{3.2})]_4(BF_4)_8$, which may act as a host to organic molecules owing to its potential framework design. The bisimidazolium

ligand, **3.2**, was dissolved in methanol and added to an aqueous solution of $[Pd(en)(NO_3)_2]$ at room temperature, and a solution of NH_4BF_4 was added to precipitate the targeted macrocycle (**3.7**) or higher oligomers according to Scheme 3.6. The resulting product was also observed to be the starting ligand, **3.2**, from the evidence of the spectroscopic data. The reaction was repeated with mild heating and at reflux, but that also did not give the expected compound.

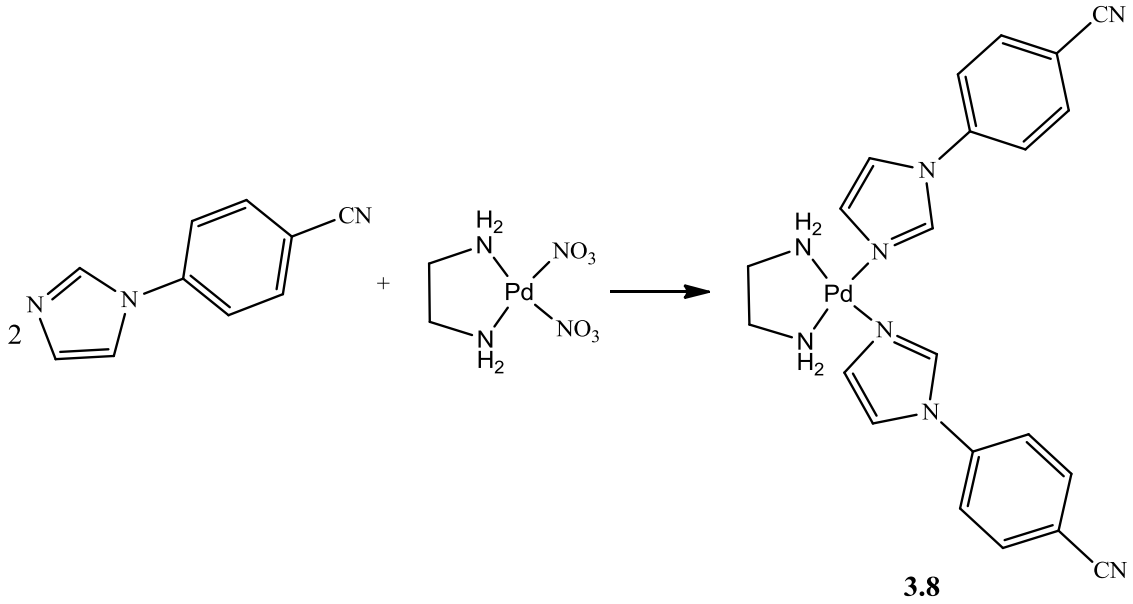


3.7

Scheme 3.6: Attempted synthesis of $[Pd(en)(\mu\text{-}\mathbf{3.2})]_2(BF_4)_2$ (**3.7**)

However when 1-(4-cyanophenyl) imidazole (**3.1**), was used in place of ligand **3.2**, according to Scheme 3.7 a crystalline material was obtained at room temperature. An IR spectrum shows a CN stretching vibration peak at ca 2232 cm^{-1} which is similar to that obtained in the ligand indicating a non-coordinating mode of the CN group. But the ^1H NMR spectrum indicates a significant shift of the signal attributed to NCHN from 7.95 ppm in the ligand to 8.91 ppm and also two new peaks absent in the imidazole ligand at 2.73 ppm and 5.56 ppm were attributed to the methylene and amine (NH_2) protons respectively. Other imidazole and phenyl peaks have shifted upfield suggesting complexation of the ligand through the imidazole nitrogen. ^{13}C NMR spectrum shows the eight ligand (**3.1)**, peaks and another peak at 46.81 ppm attributed to the methylene

protons. The good agreement between these NMR and mass spectral data which shows the isotope pattern similar to the formulation of compound **3.8** indicates its formation. This was supported by elemental analysis data, although the carbon and hydrogen values are not in agreement, but the ratios are consistent **3.8**. The significant shift of the NCHN proton peak in the NMR spectrum and the non-coordinating mode of the CN vibration peak in the IR indicates the coordination was only through the imidazole nitrogen but not through CN group or both as we expected. This inability of the nitrile to coordinate and form the macrocycle further highlighted the challenge in activating the coordinating abilities of the nitrile, suggesting that the cationic nature of ligand **3.2**, may not be the only factor hindering its coordination, since **3.1** is neutral and yet the coordination cannot be established. In addition to the spectroscopic and elemental analytical data, **3.8** was confirmed by X-ray crystallographic analysis.



Scheme 3.7: Synthesis of *cis*-[Pd(en)(**3.1**)$_2$](BF$_4$)$_2$ (**3.8)**

Single crystals suitable for X-ray diffraction were obtained directly from the slow evaporation of the solution of **3.8**, and it crystallised in monoclinic space group Pc, crystallographic information is given in Table 3.2. One asymmetric unit contained one palladium atom, one ethylene diamine, two ligand molecules and two BF_4^- anions. As

indicated from the IR spectrum, the palladium is coordinated through the imidazole nitrogen not through the nitrile, the Pd(1) – N(1) bond length is 2.013 Å which is similar to Pd(1) – N(6) at 2.001 Å, these bond length as expected due to aromaticity of the imidazole ring are slightly lower than palladium ethylene diamine nitrogen bond length at Pd(1) – N(4) 2.0410 Å and Pd(1) – N(5) 2.0306 Å.

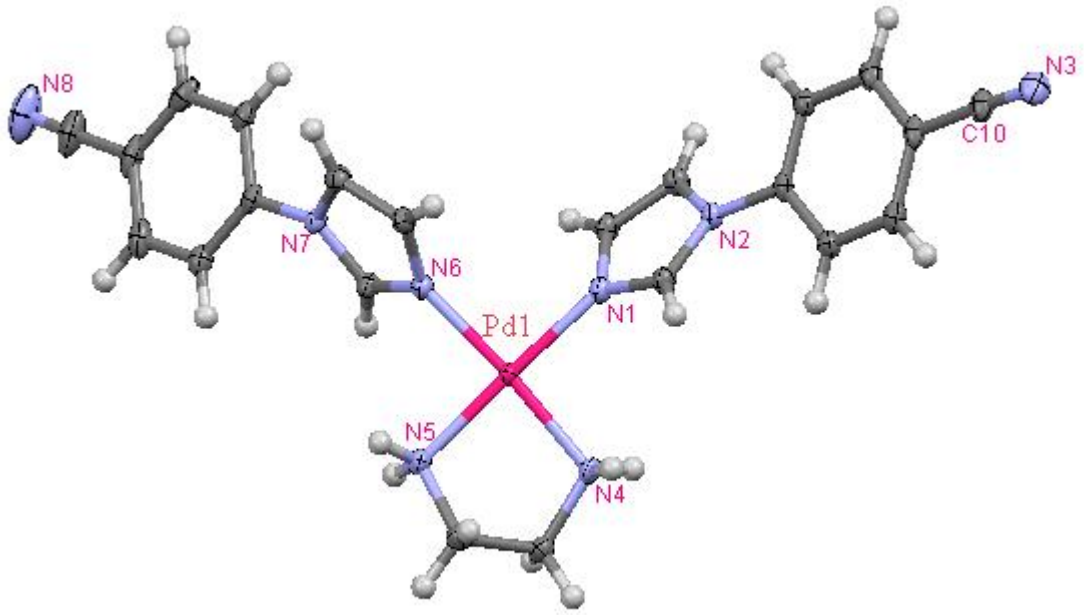


Figure 3.18: Crystal structure of **3.8,** thermal ellipsoids drawn at 50% probability level. BF_4^- anion omitted for clarity. Some selected bond lengths (Å) and bond angles (°) Pd(1) – N(1) 2.0134(19), Pd(1) – N(6) 2.0014(19), Pd(1) – N(4) 2.0411(18), Pd(1) – N(5) 2.0307(19), N(1) – Pd(1) – N(6), 90.81(7) , N(4) – Pd(1) – N(5) 84.38(7), N(1) – Pd(1) – N(4) 93.95(7), N(4) – Pd(1) – N(6) 175.23(8).

3.4. Conclusion

Our target was to synthesise new nitrile functionalised imidazolium salts that could be used as a ligand to form new NHC complexes. 4-cyanophenyl imidazole was synthesised and used to form two imidazolium salts (**3.2** and **3.3**) which were described. The bisimidazolium salt (**3.2**) on deprotonation has been an excellent ligand for the synthesis of our targeted NHC complexes. The synthesis and characterisation of a silver

NHC complex (**3.4**) formed from the reaction of silver(I) oxide and bis imidazolium salt (**3.2**) was described. A transmetalation protocol was employed in the preparation of the ruthenium complex (**3.5**) from the silver NHC complex. Also a platinum bis-carbene complex (**3.6**) was synthesised and characterised.

Several attempts were made to convert these imidazolium salts or their corresponding NHC complexes into coordination polymers but these did not yield the desired results. However it is believed that under appropriate conditions these species do have potential to form coordination polymers.

3.5. Experimental

3.5.1. General considerations. Unless otherwise stated all reactions were performed under nitrogen using standard Schlenk line techniques. 1-(4-cyanophenyl) imidazole,[16] $[Pt(COD)Cl_2]$,[27] $[Pd(en)(NO_3)_2]$[28] and $[Ru(p\text{-}cy)Cl_2]_2$[29] were prepared according to literature procedures. All other reagents were purchase from Aldrich and were used without further purification.

All infrared spectra (KBr disk, 400-4000 cm^{-1}) were recorded on Nicolet Avatar 360 FT-IR spectrometer. Mass spectra were recorded on a thermo Finnigan LCQDUO mass spectrometer using ESI. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE/DPX 400 (400 MHz) or AVANCE/DRX 500 (500 MHz) spectrometers in $CDCl_3$ or d_6-DMSO with tetramethylsilane as standard. Elemental analyses were carried out at the micro analytical laboratory at the University of Strathclyde, Glasgow. Single crystal measurements were made at 123K with graphite monochromated Mo-Kα1 radiation (wavelength 0.71073 Å) on an Oxford Diffraction Gemini S diffractometer equipped with a CCD detector and a variable temperature device. Data for **3.5** was collected by the EPSRC Crystallographic Service at Southampton University on a Bruker Nonius FR591 rotating anode source using Mo K_α radiation, focussed by a 10cm confocal mirror and detected using an APEX II CCD camera. Crystals were mounted in oil on a fibre loop and data collected at 120 K. Initial atomic sites were located using direct methods. Remaining non-hydrogen atom sites were calculated using difference

Fourier maps. Refinement of atomic co-ordinates and thermal parameters was to convergence and by full-least squares methods on F^2 within SHELX-97.[30] All H-atoms were placed in calculated positions and in a riding mode. Reported wR2 values are based on F^2 and all reflections, whilst reported R1 values are based on F and on observed reflections with $I>2\sigma(I)$

3.5.2. Synthesis of 1,1-Di (4-cyanophenyl)-3,3-methylenediimidazolium dibromide (3.2a)

1-(-4-cyanophenyl)imidazole **(3.1**) (1.5g, 8.87 mmol) was dissolved in excess dibromomethane (5 mL) and stirred for 3 days at 65^{o}C. A white solid formed was filtered, washed with THF and dried to give the bisimidazolium salt **3.2a**. Yield 2.95g, 65%. ^{1}H NMR (DMSO-d6 δ): 10.48(s, 2-CH of imid. 2H), 8.53 (s, 4-CH of imid. 2H), 8.40 (s, 5-CH of imid. 2H), 8.27 (d, 2-CH of Ph. 4H), 8.07 (d, 4-CH of Ph. 4H), 6.95 (s, CH_2 of methyl 2H). ^{13}C{^{1}H}NMR (DMSO-d6, δ): 138.09 (C_{Ph}), 137.03 ($NCN_{imid.}$), 134.85(C_{Ph}), 123.28 ($C_{imid.}$), 122.88 (C_{Ph}), 121.47 ($C_{imid.}$) 117.65(CN), 112.80 (C_{Ph}), 58.71(CH_2). IR (KBr, cm^{-1}): 2232 (ν(CN)). MS (ESI, methanol/water; m/z): 351.13$[M]^+$. Anal. Calculated for $C_{21}H_{16}N_6Br_2.H_2O$; C, 47.57; H, 3.42; N, 15.85%. Found C, 47.35; H, 3.03; N, 15.44%.

3.5.3. Synthesis of 1,1-Di (4-cyanophenyl)-3,3-methylenediimidazolium tetrafluoroborate(3.2b)

Bisimidazolium dibromide (**3.2a**) (1g, 1.95 mmol) was dissolved in water (5 mL) and fluoroboric acid was added in drops to give a white precipitate of bisimidazolium fluoroborate. X-ray quality crystals were grown by acetonitrile – diethyl ether using vapour diffusion. Yield 0.92g, 90%.

^{1}H NMR (DMSO-d6 δ): 10.15(s, 2-CH of imid. 2H), 8.52 (s, 4-CH of imid. 2H), 8.24 (s, 5-CH of imid. 2H), 8.28 (d, 2-CH of Ph. 4H), 8.03 (d, 4-CH of Ph. 4H), 6.82 (s, CH_2 of methyl 2H). ^{13}C {^{1}H} NMR (DMSO-d6, δ): 137.95 (C_{Ph}), 137.61 (NCN), 134.63(C_{Ph}), 123.28 ($C_{imid.}$), 122.94 (C_{Ph}), 121.73 ($C_{imid.}$) 117.63(CN), 112.92 (C_{Ph}), 59.09(CH_2). IR (KBr, cm^{-1}): 2232 (ν(CN)). MS (ESI, methanol/water; m/z): 351.13$[m]^+$. $C_{21}H_{16}N_6B_2F_8$; C, 47.95; H, 3.07; N, 15.98%. Found C, 47.21; H, 2.86; N, 15.61%.

3.5.4. Synthesis of 1,1-Di (4-cyanophenyl)-3,3-methylenediimidazolium diiodide (3.2c)

1-(-4-cyanophenyl) imidazole, **3.1**, (2g, 11.82 mmol) was dissolved in excess diiodomethane (10 mL) and stirred for 3 days at 55^{o}C. A yellowish precipitate was formed which was filtered, washed with THF and dried to give the bisimidazolium iodide (**3.2c**). Yield 5.10g, 72%.

^{1}H NMR (DMSO-d6 δ): 10.20 (s, 2-CH of imid. 2H), 8.53 (s, 4-CH of imid. 2H), 8.28 (s, 5-CH of imid. 2H), 8.27 (d, 2-CH of Ph. 4H), 8.04 (d, 4-CH of Ph. 4H), 6.84 (s, CH_2 of methyl 2H). ^{13}C {^{1}H} NMR (DMSO-d6, δ): 138.09 ($NCN_{imid.}$), 137.03 (C_{Ph}), 134.85 (C_{Ph}), 123.28 ($C_{imid.}$), 122.88 (C_{Ph}), 121.47 ($C_{imid.}$) 117.65 (CN), 112.80 (C_{Ph}), 58.71 (CH_2). IR (KBr, cm^{-1}): 2232 (ν(CN)). MS (ESI, methanol/water; m/z): 351.13[m] $^{+}$.

3.5.5. Synthesis of 1-bromomethyl 3- (4-cyanophenyl)imidazolium bromide (3.3a)

1-(-4-cyanophenyl) imidazole, **3.1**, (1.5g, 8.87 mmol) was dissolved in excess dibromomethane (5 mL) and stirred overnight at reflux. A white solid formed was filtered, washed with THF and dried to give **3.3**. X-ray quality crystals were obtained directly from BF_4^- anion exchange.

^{1}H NMR (DMSO-d6 δ): 10.22 (s, 2-CH of imid. 1H), 8.48 (s, 4-CH of imid. 1H), 8.20 (s, 5-CH of imid. 1H), 8.23 (d, 2-CH of Ph. 2H), 8.05 (d, 4-CH of Ph. 2H), 6.26 (s, CH_2 of methyl 2H). MS (ESI, methanol/water; m/z): 264.07[m]$^{+}$.

3.5.6. Synthesis of Silver Complex 3.4

Bisimidazolium tetraflouroborate, **3.2b**, (1g, 1.9 mmol) and silver(I) oxide (0.23g, 1.0 mmol) were added to 10 mL acetonitrile and reflux overnight. It was cooled and filtered through celite to remove any unreacted silver(I) oxide. The solvent was remove under reduced pressure to give a white solid complex **3.4**. X-ray quality crystals were grown by acetonitrile – diethyl ether using vapour diffusion. Yield 1.54g, 74%.

^{1}H NMR (DMSO-d6 δ): 10.48(s, 2-CH of imid. 2H), 8.53 (s, 4-CH of imid.. 2H), 8.40 (s, 5-CH of imid. 2H), 8.27 (d, 2-CH of ph. 4H), 8.07 (d, 4-CH of ph. 4H), 6.95 (s, CH_2 of methyl 2H). ^{13}C {^{1}H} NMR (DMSO-d6, δ): 142.61 (C_{ph}), 133.84 (C_{ph}), 124.86

(C_{imid}), 124.32 (C_{ph}.), 123.85 ($C_{imid.}$), 118.12 (CN.) 112.14 (CH_2), 64.78 (CH_2). IR (KBr, cm^{-1}): 2225 (ν(CN)). MS (ESI, methanol/water; m/z): 459.60 $[M]^{2+}$, 917 $[M]^{2+}$. $C_{42}H_{28}N_{12}Ag_2B_2F_8$; Anal. Calculated; C, 46.24; H, 2.59; N, 15.42%. Found C, 46.07; H, 2.73; N, 15.74%.

3.5.7. Synthesis of Ruthenium Complex 3.5

$[Ru(p\text{-}cy)_2Cl_2]_2$ (30.6mg, 0.05 mmol) dissolved in dichloromethane was added in drops to an acetonitrile solution of the disilver tetracarbene tetrafluoroborate, **3.4** (50mg, 0.05 mmol). An immediate precipitate of silver chloride was formed and the mixture was stirred for 2hrs and filtered. Removal of the solvent at reduce pressure afforded a brown product of the ruthenium complex **3.5**. X-ray quality crystals were grown by acetonitrile -diethyl ether using vapour diffusion. Yield 27mg, 83%.

^{1}H NMR (DMSO-d6 δ): 8.04 (d, 2-CH of Ph. 4H), 7.97 (d, 4-CH of Ph. 4H),, 7.54 (s, 4-CH of imid. 2H), 7.45 (s, 5-CH of imid. 2H), 6.30 (d, CH_2 of methyl 1H), 5.63 (d, CH_2 of methyl 1H), 5.04 (d, CH of P-cy, 2H), 4.68 (d, CH of P-cy, 2H), 2.05 (m, CH of P-cy 1H), 1.61 (s, $CH_{3(ortho)}$ of P-cy 3H), 0.83 (d, $CH_{3(para)}$ of P-cy 6H). ^{13}C {^{1}H} NMR (DMSO-d6, δ): 175.62 (C-Ru), 143.57 (C_{Ph}), 133.31(C_{Ph}), 130.30 (C_{Ph}), 126.24 ($C_{imid.}$), 122.75 ($C_{P\text{-}cy}$.) 118.66(CN), 112.80 (C_{Ph}), 91.47 ($C_{P\text{-}cy}$.), 88.11 ($C_{P\text{-}cy}$.), 61.91 (CH_2), 31.14 ($C_{P\text{-}cy}$.), 22.40 ($C_{P\text{-}cy}$.), 18.68 ($C_{P\text{-}cy}$.) . IR (KBr, cm^{-1}): 2235 (ν(CN)). MS (ESI, methanol/water; m/z):621.13$[M]^+$. $C_{31}H_{28}N_6ClRu$; Anal. Calculated; C, 52.56; H, 3.99; N, 11.87%. Found; C, 52.19; H, 3.93; N, 12.09%.

3.5.8. Synthesis of Platinum Complex 3.6

Bisimidazolium bromide **3.2a** (50mg, 0.1 mmol), sodium acetate (16.4mg, 0.2 mmol) and $[Pt(COD)Cl_2]$ (37.4mg, 0.1 mmol) were dissolved in 10 mL of dimethylsulphoxide and stirred at 80^{o}C for 2hrs and then at 100^{o}C overnight. It was allowed to cool and THF was added to precipitate the white platinum complex **3.6**. X-ray quality crystals were grown by DMSO – THF using vapour diffusion. Yield, 35mg, 51%.

^{1}H NMR (DMSO-d_6 δ): 7.82 (d, CH of imid. 4H), 8.08 (m, CH of Ph 8H), 6.39 (d, CH_2 of methyl 1H), 6.15 (d, CH_2 of methyl 1H). IR (KBr, cm^{-1}): 2228 (ν(CN)). MS (ESI,

methanol/water; m/z): 545.60 $[m]^+$. $C_{21}H_{14}N_6Pt_1I_2$; Anal. Calculated; C, 31.54; H, 1.77; N, 10.52%. Found C, 31.48; H, 1.89; N, 9.34%.

3.5.9. Synthesis of Palladium complex (3.8)

1-(4-cyanophenyl) imidazole **3.1** (0.1g, 0.6 mmol) was dissolved in 3 mL methanol and added to a solution of $[Pd(en)(NO_3)_2]$ in water (4 mL). It was stirred for 30 min at room temperature. Concentrated solution of NH_4BF_4 was added and the solution allowed to slowly evaporate over two days. The crystals obtained were collected and washed with diethyl ether and dried in vacuum. Yield 0.075g, 50%.

^1H NMR (DMSO-d_6 δ) 8.91 (s,NCHN of imid. 2H), 8.20 (s, -CH of imid. 2H), 8.17 (d, -CH of Ph 4H), 7.93 (d, CH of Ph. 4H), 7.31 (s, CH of Ph. 2H), 5.56 (s, NH_2 4H), 2.73 (s, $-CH_2$ 4H). ^{13}C {^1H} NMR (DMSO-d6, δ): 138.71 ($NCN_{imid.}$), 138.25 (C_{Ph}), 134.44 (C_{Ph}), 129.85 ($C_{imid.}$), 121.36 (C_{Ph}), 119.72 ($C_{imid.}$) 117.65 (CN), 111.05 (C_{Ph}), 46.81 (CH_2). IR (KBr, cm^{-1}): 2232 (ν(CN)). MS (ESI, methanol/water; m/z): 502.53$[m]^+$, $C_{22}H_{22}N_8Pd_1B_2F_8$; Anal. Calculated; C, 38.90; H, 3.27; N, 16.51%. Found C, 40.09; H, 2.63; N, 16.73%.

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CHAPTER 4

Pyridine Functionalised Imidazolium Salts, Their N-Heterocyclic Carbene Complexes and Their Coordination Polymers.

4.1. Introduction

The isolation and characterisation of a free N-heterocyclic carbene (NHC) by Arduengo in 1991[1] opened up this rather little known area of chemistry. NHCs emerged to be an interesting family of ligands in organometallic chemistry due to their versatility. They have been widely used as an alternative to the well known phosphine ligands in the field of catalysis.[2] Many NHCs have been synthesised and converted to metal complexes, their catalytic use has been well established, including in C-C coupling reactions, metathesis, hydroformylation, and polymerisation reactions to name but a few.[3, 4]

Initial reports on the NHCs centred towards exploring the chemistry of monodentate ligands like H_2Imes and their catalytic applications. Although the NHCs have recorded this huge success in replacing phosphine ligand due to their superior electron donating ability, the development of new NHCs functionalised with pendant donor groups may afford ligands with more than one coordinating site which may improve the hemilability or fine tune the electronic and steric properties of the ligand.[5]

Those functionalised with nitrogen donor atoms are the most studied, followed by those with oxygen donors,[5] which give rise to bidentate, tridentate or multidentate NHC ligands. Nitrogen heteroaromatic functionalised NHC are the most common, and among these pyridine substituted are the most reported group.[5] These pyridine functionalised imidazolium salts and their corresponding NHCs have long been of interest and several have been synthesised and reported.[5-7] Their popularity might arise from the ease in forming silver carbene complexes, which are a gateway for the synthesis of many other metal NHC complexes through transmetallation reactions.[8, 9]

In 2000 Danopoulos et al[10] reported an *in situ* formation of pyridine functionalised NHC complexes of palladium ((C-N)PdMeBr, C-N = 3-R-1(2-methylpyridine)-imidazolin-2-ylidene (R = ^{t}Bu or mes)). They were found to be excellent catalysts for Heck arylation and also to have good activity in amination reactions. In 2002, they also reported[11] the synthesis and isolation of a free pyridine functionalised NHC ligand from the reaction of 1-(2,6-diisopropylphenyl) imidazole and 2-bromo-6-trimethylsilyl pyridine and

subsequent deprotonation of the resulting imidazolium salt with $KN(SiMe_3)_2$ in THF at -10 to 0^oC.

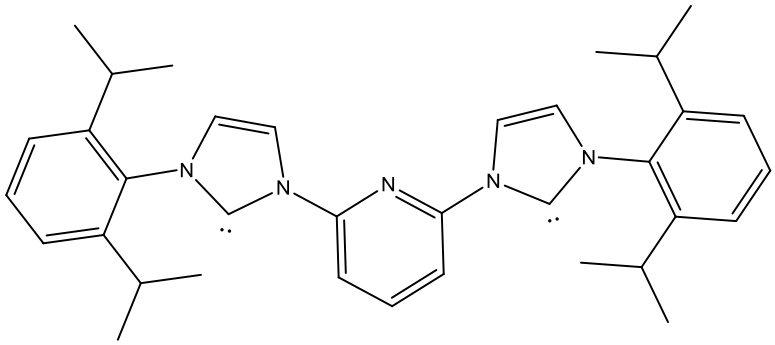


Figure 4.1: Free pyridine functionalised NHC

Although air sensitive, it was stable enough for its crystal to be isolated at room temperature and be analyzed by X-ray crystallography. In the same year, the group also reported the isolation and crystal structure of the first free pyridine functionalised bis NHC ligand (Figure 4.1).[12] Reacting the free ligand with $RuCl_2(PPh_3)_3$ produced a catalytically active Ruthenium bis carbene complex which catalyzed hydrogenation of C=O and C=N.

Danopoulos and coworkers reported several other pyridine functionalised imidazolium salts and their NHC complexes,[7, 13-15] while other notable contributors in the field of pyridine NHC organometallic chemistry include Cavell et al,[16] Peris et al,[17] Catalano et al.[18] In fact many pyridine NHC complexes utilising transition metals including Pd, Rh, Ir, Ni, Cu, Ag, Fe, and Co have been synthesised and reported by research groups across the globe.[7]

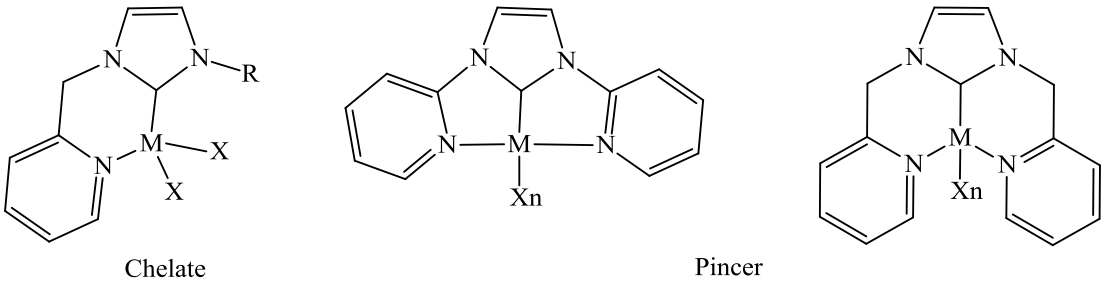


Figure 4.2: Pyridine functionalised chelating and pincer carbene complexes

Most of the reported pyridine functionalised imidazolium salts and their NHC complexes are mainly of 2-pyridine type, none utilises the 4-pyridine despite their enormous potential. The 2-pyridine functionalised NHCs, with all their success, have not been known to produce well defined coordination polymers, but instead they favour formation of chelating or pincer type carbene complexes (Figure 4.2). This is due to the close proximity the pyridine nitrogen to the carbene carbon. On the other hand, the terminal nitrogen containing 4-pyridine functionalised NHCs, when developed, will have potential to form the desired porous coordination polymers due to their non chelating geometries.

We aim to synthesise such pyridine containing imidazolium salts convert them into NHC complexes and explore the possibility of assembling them into well defined coordination polymers. In addition, the imidazolium salts will be assembled into polymers with the aim of later converting these into NHC containing porous coordination polymer by post-synthetic modification.

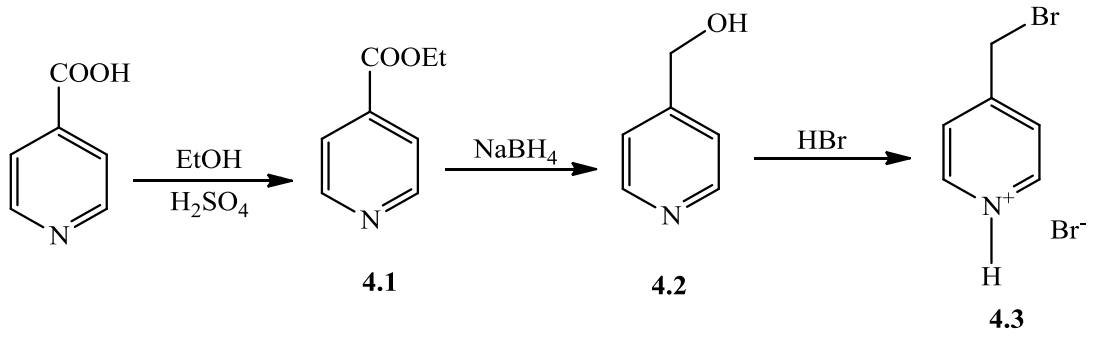
4.2. Results and discussion

4.2.1. Ligand synthesis

The synthesis of our targeted pyridine substituted imidazolium salts involves two major steps, the first being the generation of picolyl bromide hydrobromide from isonicotinic acid while the second step is the conversion of the picolyl bromide hydrobromide to the pyridine substituted imidazolium salts.

4.2.1.1. 4-Picolyl bromide hydrobromide

Isonicotinic acid was converted to 4-picolylbromide according to scheme 4.1 which is intended to be used as a substituent on the imidazolium nitrogen of our target NHC ligands. The conversion follows a procedure reported by Ferri *et al*.[19]



4.1 **4.2** **4.3**

Scheme 4.1: Synthesis of 4-bromomethylpyridine hydrobromide

The isonicotinic acid was treated with ethanol in the presence of an acid to form the corresponding ester (**4.1**). The absence of carboxylic acid peak and appearance of two new peaks in the ^{1}H NMR spectra assigned to the ethyl group indicates the conversion of the acid to the ester (**4.1**).

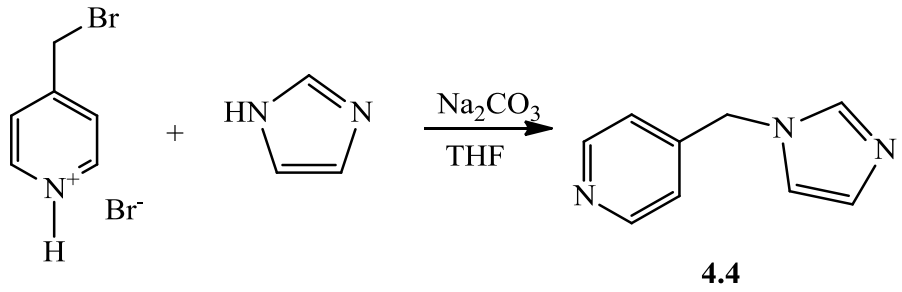
The yield obtained was low, which may be attributed to the formation of water in the process which favours the backward reaction. Thus the reported procedure was adjusted by making the ethanol in slight excess and more importantly by carrying out the reaction in the presence of molecular sieves. The molecular sieves absorbed the water produced in the course of the reaction, which favours the forward reaction resulting in formation of **4.1** in significantly higher yield.

The ester was reduced to the corresponding alcohol (**4.2**) in high yield by using sodium borohydride as reported in the literature.[19] The peaks assign to the ethyl protons of **4.1** were absent in the ^{1}H NMR and a new peak at 4.51 ppm assigned to the OH proton was observed, confirming the reduction of the ester to the alcohol and this was further supported by mass spectral data.

The alcohol (**4.2**) was easily converted to 4-picolyl bromide hydrobromide (**4.3**) through reaction with 48% HBr. The reaction was refluxed for a longer time than reported to move all the alcohol straight to the picolyl bromide hydrobromide. White crystals of **4.3** precipitated in high yield from cold ethanol, it was filtered, washed with cold ethanol and dried. Both NMR and mass spectral data were consistent with our desired product.

4.2.1.2. 1-(4-Picolyl)imidazole

The preparation of the imidazolium salts intended to be used for the generation of the NHCs, was initially expected to be a straightforward process as there were several related imidazolium salts prepared by a variety of simple methods, as described in Chapter 1. Although only few imidazolium salts had been prepared using picolyl as substituent, we did not anticipate any difficulties in the synthesis. However it proved to be very challenging. Initially the formation of the monosubstituted imidazole (**4.4**) was attempted by reaction of the deprotonated 4-picolyl bromide hydrobromide and imidazole in the presence of sodium carbonate under nitrogen at reflux temperature using THF as a solvent (Scheme 4.2). To avoid dimerisation the 4-picolyl bromide was added in parts over 30 minutes.



4.4

Scheme 4.2: Synthesis of 4-picolyl imidazole

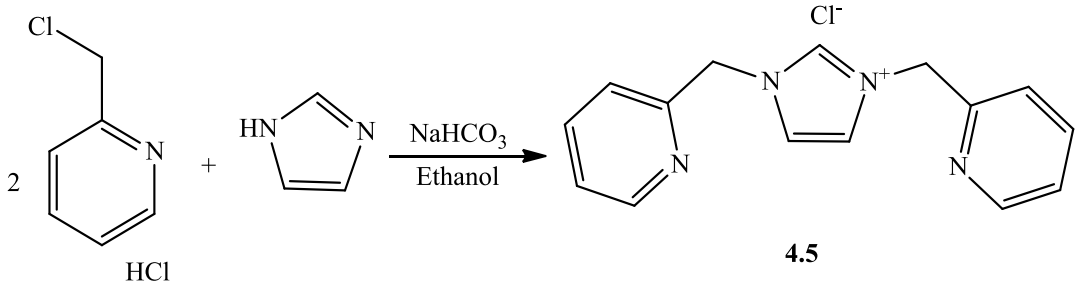
A dark brown oil was observed to form, and ^{1}H NMR and mass spectral analysis revealed it to be a mixture of many products, including the desired compound, **4.4,** but the spectra were so complex that it become difficult to identify the major product formed. Many overlapping peaks were observed between 7 ppm and 9 ppm making it very difficult to assign the ^{1}H NMR signals. Although a small ion peak in the mass spectrum at m/z = 170 indicates our desired product, the predominant positive ion peak was at m/z = 185 which might be due to the major product of the complex mixture of the compounds formed**.** Attempts were made to separate the products using both TLC and column chromatography, but those did not result in satisfactory separation, while attempts to grow crystals failed.

In a second attempt to synthesise the 1-substituted imidazole (**4.4**), one equivalent of 4-picolyl bromide hydrobromide and a base were taken in one pot and refluxed in DMF under nitrogen over night. The base served to deprotonate both the 4-picolyl bromide hydrobromide and the imidazole. As in the previous case the NMR (^{1}H) and mass spectra were also complex which was difficult to assign, again with some evidence in both analysis for the desired product (**4.4)**. Once more, TLC and column chromatography did not yield the desired pure compound (**4.4**). A range of different solvents such as methanol, ethanol and acetonitrile were used, but similar results were obtained.

At this point it was decided to prepare an imidazolium salt with 2-picolyl groups as substituents using a procedure reported by Cavell *et al*.[20]

4.2.1.3. 1,3-Bis(2-picolyl)imidazolium chloride

Bis-(2-picolyl)imidazolium chloride, **4.5**, was successfully synthesised by refluxing imidazole, two equivalents of 2-picolyl chloride hydrochloride and a base ($NaHCO_3$) in ethanol (Scheme 4.3) as reported by Cavell.[20] The $NaHCO_3$ was used to deprotonate both 2-picolyl chloride hydrochloride and the imidazole. Filtering the product and removing the solvent under vacuum afforded a dark brown oil, which was triturated with THF to produce a precipitate of compound **4.5** in good yield.



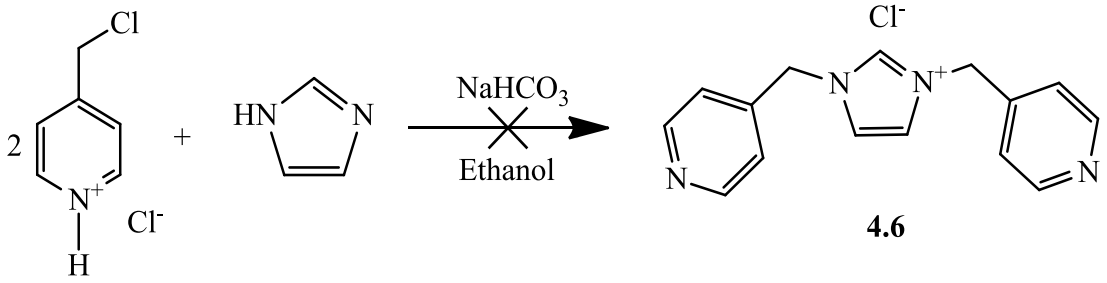
Scheme 4.3: Synthesis of 1,3-bis(2-picolyl)imidazole

The compound was confirmed spectroscopically to be the intended product (**4.5).** In the ^{1}H NMR spectrum the appearance of resonances downfield at 11.09 ppm assigned to acidic imidazolium proton (-NCHN-) is in keeping with most of the similar imidazolium

peaks reported in Chapter 3 and also in the literature.[21] The methylene spacers linked to the imidazole shows a resonance at 5.69 ppm**.** The appearance of positive ion peak at m/z = 251 as the major peak in the mass spectrum further indicates the formation of the compound **4.5.**

4.2.1.4. 1,3-Bis(4-picolyl)imidazolium chloride

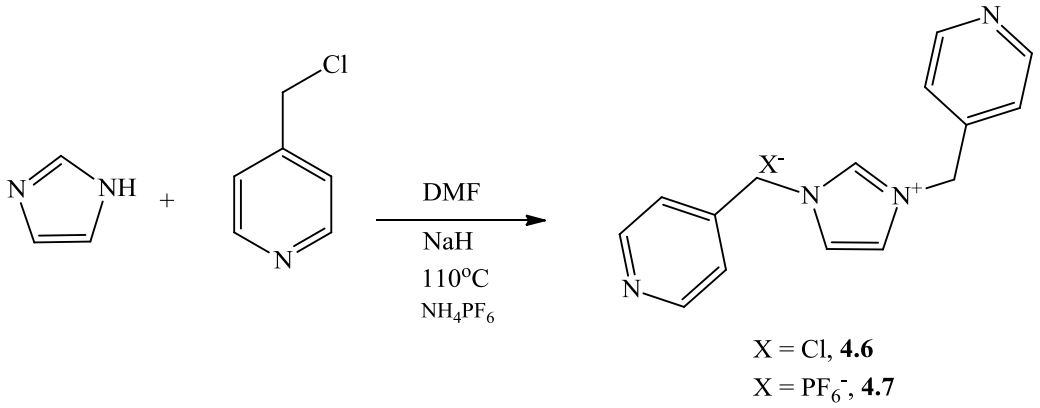
Having successfully prepared imidazolium salt **4.5**, an essentially identical procedure was followed in an effort to synthesise the bis-(4-picolyl)imidazolium chloride, but with little success. Initially the procedures were followed as described above, utilising each of the bromo and chloro picolyl and refluxing for 2 days. The product obtained proved to be impure. Spectroscopic analysis (NMR and mass spectra) shows the presence of our desired product (**4.6**), but just as in the previous cases, it is present as one component in a complex mixture of other by-products. Although peaks which may be attributed to our product are present, they are weak, once more suggesting that our desired compound is not the major product. It proved to be impossible to purify and isolate the target compound. Other attempts to improve on this procedures include changing the solvent to DMF, methanol, acetonitrile, and DMSO while appropriately adjusting the reaction temperatures to obtain the targeted bis 4-picolyl substituted imidazolium salts did not give satisfactory results.



Scheme 4.4: Attempted synthesis of 1,3-bis(4-picolyl)imidazole

Eventually, however the targeted 1,3-bis(4-picolyl)imidazolium salt (**4.6**), was prepared by adopting solvo-thermal synthetic procedures. 4-picolyl chloride, imidazole and sodium hydride (60%) were dissolved in DMF and heated at 110^{o}C in a sealed 20 mL

pressure tube for 48 hrs. The product was precipitated using diethyl ether, dissolved in methanol and precipitated again 3 times to give a dark brown oil which after further work up gave a dark brown powder. The chloride counter-anion was exchanged for hexafluorophosphate by dropwise addition of saturated solution of ammonium hexafluorophosphate to a solution of the imidazolium salt in water. Anion exchange was performed to improve the solubility giving more room for solvent selection, and it was also observed that, it further purified the product. In fact a more pure material was obtained when a mixture of ethanol and water was used in the exchange. The imidazolium hexafluorophosphate salt (**4.7**) was insoluble in water but soluble in methanol and therefore slow evaporation of the methanol solution at room temperature results in crystallisation of the product with little or no impurities. The formation of the products **4.6** and **4.7** was confirmed spectroscopically and **4.6** by single crystal X-ray analysis.



Scheme 4.5: Solvothermal synthesis of 1,3-bis(4-picolyl)imidazolium salts

The ^{1}H NMR, as expected, showed five peaks representing the five different hydrogen environments (Figure 4.3). The methylene spacer between the imidazole and the pyridine was observed at 5.63 ppm, a marked shift from the picolyl chloride starting material. There is also a significant shift of the -NCHN- proton, as expected to 9.44 ppm (Figure 4.3), which is an indication of the formation of the target imidazolium salt (**4.6**). This was further supported by the expected six peaks in the ^{13}C NMR spectra. Ions in the mass spectrum (M+) at m/z = 251 further confirm the synthesis of **4.6**. Both NMR (^{1}H

and ^{13}C) (Figure 4.3) and mass spectrometry suggest that the product has been purified but poor agreement between expected and observed values in microanalysis of the imidazolium chloride salt suggested otherwise. However the exchanged hexafluorophosphate salt, **4.7**, was much purer and gave a good agreement between expected and observed values, thus confirming the synthesis of the product.

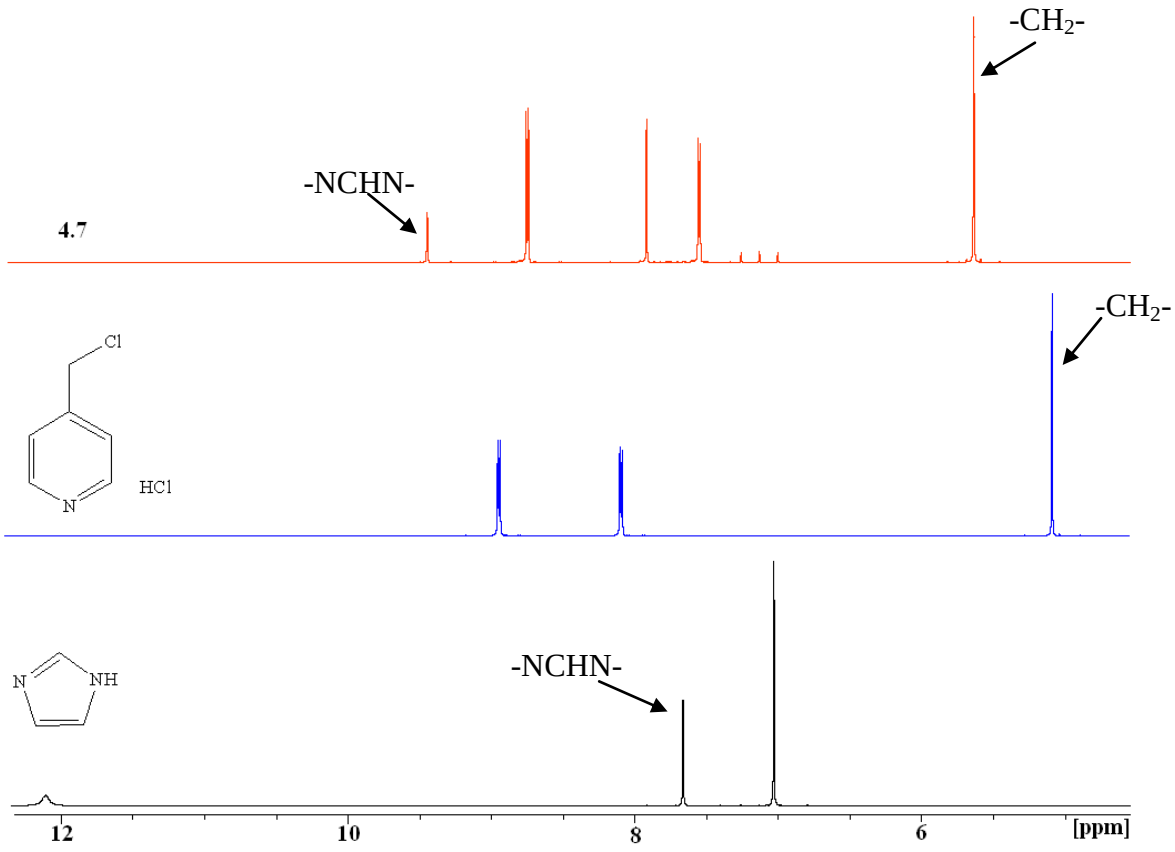


Figure 4.3: ^{1}H NMR (400 MHz, DMSO-d) spectra of imidazole, 4-picolyl chloride hydrochloride and 1,3-bis(4-picolyl)imidazolium salt, **4.7**

Single crystals suitable for X-ray analysis were grown by slow diffusion of diethyl ether into the methanol solution of the imidazolium salt **4.6**. It crystallises in monoclinic space group P $2_1/c$, and the crystallographic information is presented in Table 4.1. The asymmetric unit consists of one cationic imidazolium salt and one chloride counter ion (Figure 4.4). The new C(1) – N(2) and C(7) – N(1) bond lengths are 1.460 (2) Å and

1.472 (2) Å respectively, which shows their similarity. The pyridyl group attached to the imidazole has identical bond angles (C(1) – N(2) – C(13) 126.0(1)° and C(13) – N(1) – C(7) 126.0(1)°), which are all twisted assuming non planar conformation with respect to the attached imidazole ring and oriented facing in the opposite direction (Figure 4.4).

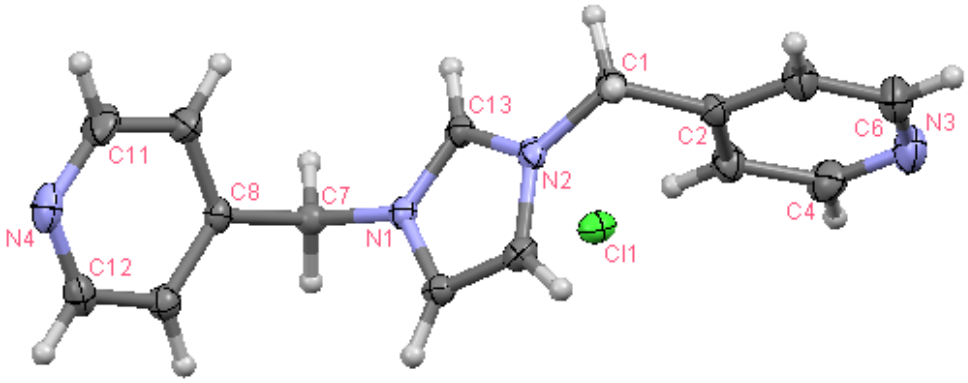


Figure 4.4: Crystal Structure of **4.6,** with thermal ellipsoids drawn at 50% probability level. Some selected bond length (Å) and bond angles (°). N(1) – C(7) = 1.472(2), N(2) – C(1) = 1.461(2), N(3) – C(4) = 1.336(2 , N(3) – C(6) = 1.335(2), C(4) – N(3) – C(6) = 116.77(15), C(11) – N(4) – C(12) = 115.92(15), N(2) – C(1) – C(2) = 112.42(14), N(1) – C(7) –C(8) = 109.26(13).

There are no strong π-π stacking observed in the packing of this molecule however, weak interactions between different components of the structure (Figure 4.5a) helps to connect it to different molecules giving a 1D polymeric material (Figure 4.5c). The chloride ion serves as connector, joining different molecules through a weak interaction with protons of imidazole, pyridine and the methylene groups (Figure 4.5a) having separations in the range of 2.565 Å – 2.829 Å which is also within the range of the sum of the Cl and H van der Waals radii [22]. In addition the chloride ion also interacts with the π- system of the imidazole at a distance of ca 3.380 Å. Additional interaction involved one end of the pyridine nitrogen having a weak σ interaction with methylene carbon at a separation of 3.327 Å and the imidazole proton is interacting with the π system of the other pyridyl close to the nitrogen end with a distance of 2.611 Å (Figure 4.5b) both distances are within the sum of their respective atom van der Waals radii.[22]

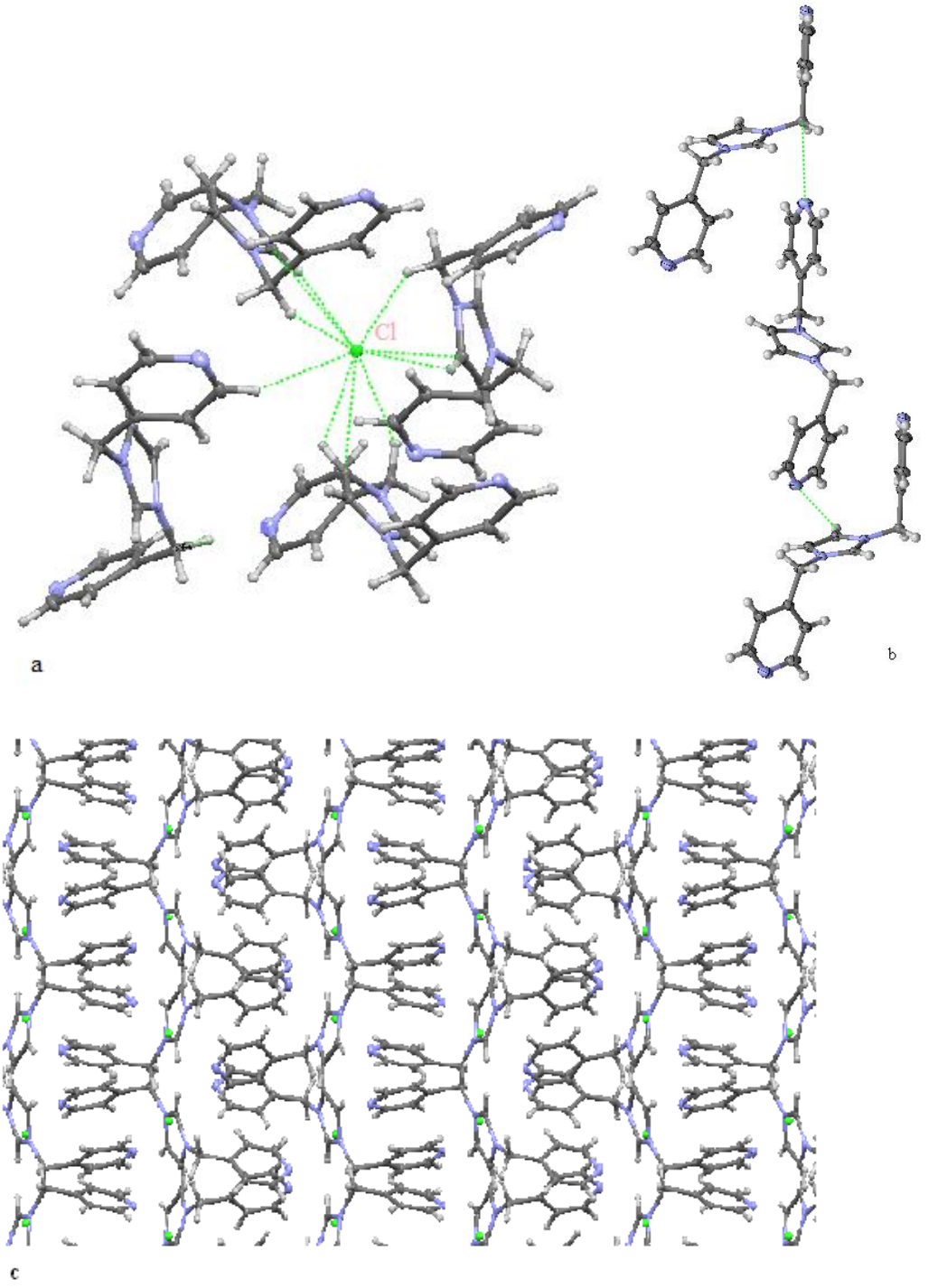
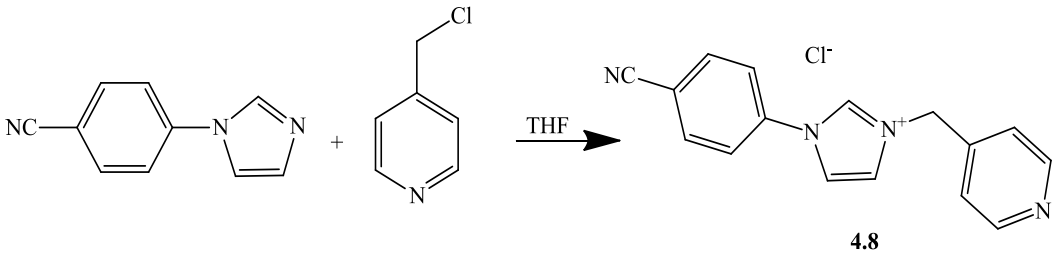


Figure 4.5: Crystal Structure of **4.6** showing a) Cl^- interaction environment b) C-H---N and C-N----C interactions and c) packing viewed along the c axis

4.2.1.4. 1-(4-Cyanophenyl)-3-(4-picolyl)imidazolium salt

A mixed nitrile and pyridyl functionalised imidazolium salt (**4.8**) was prepared by refluxing 4-cyanophenyl imidazole and 4-picolyl chloride in THF for 5 days (Scheme 4.6). The product gradually precipitated during the course of the reaction. Although the precipitated product was confirmed spectroscopically to be our desired compound (**4.8**) the reaction was time consuming and the yield was very low at ca 20%. The solvothermal procedure we employed to synthesised **4.6** was tested and it was also found to work effectively for this system, giving our desired product in a reduced time of 1-2 days, and most importantly improving the yield significantly to about 60%. In this process, the 4-picolyl chloride hydrochloride was deprotonated using a saturated solution of NaOH, the liberated 4-picolyl chloride and 4-cyanophenyl imidazole were dissolved in THF and heated at 45^{o}C for 1-2 days in a sealed pressure tube.



4.8

Scheme 4.6: Synthesis of 1-(4-cyanophenyl)-3-(4-picolyl)imidazolium salts

The product precipitated out and was washed several time with diethyl ether and dried in vacuum. Once more, to improved solubility in a range of solvents, the chloride counter ion was exchanged for hexafluorophosphate. Similarly it also proved to be purer than the chloride counterpart.

The formation of this mixed functionalised imidazolium salt (**4.8**) was confirmed spectroscopically to be our desired compound. In the ^{1}H NMR a new resonance peak absent in the 4-cyanophenyl imidazole, was observed at 5.68 ppm which is attributed to the methylene group protons, being in an almost identical position as in the symmetrical imidazolium salt (**4.6**). There is a significant shift of the -NC(H)N- resonance from 7.95 ppm in 4-cyanophenyl imidazole to 10.40 ppm which is a clear indication of the

formation of **4.8**. The mass spectrum shows a dominant ion peak (M+) at m/z = 261 which is consistent with the calculated value (261) of **4.8**, furthermore the good agreement in microanalysis confirmed the synthesis of this new unsymmetrical imidazolium salt (**4.8**).

Despite the imidazolium chloride product not being completely pure, a single crystal suitable for X-ray analysis was obtained from slow diffusion of diethyl ether into a methanol solution of the ligand (**4.8**). The crystallographic information is presented in Table 4.1. It crystallises in the monoclinic space group $P2_1/c$, and the molecular structure is consistent with formulation of the targeted imidazolium salt (**4.8**) (Figure 4.6). The structure shows the imidazole and cyanophenyl ring in an almost coplanar arrangement with C(1) – N(1) – C(11) – C(16) torsion angle of 3.57° while the pyridine ring are pointed away out of plane to the attached imidazole ring with the C(1) – N(2) – C(4) – C(5) torsion angle of -99.37. The N(1) – C(11) bond length 1.4298(7) Å is less than N(2) – C(4) at 1.4748(8) Å, this might be due to the aromatic nature of the directly attached phenyl ring compared to the methyl linkage.

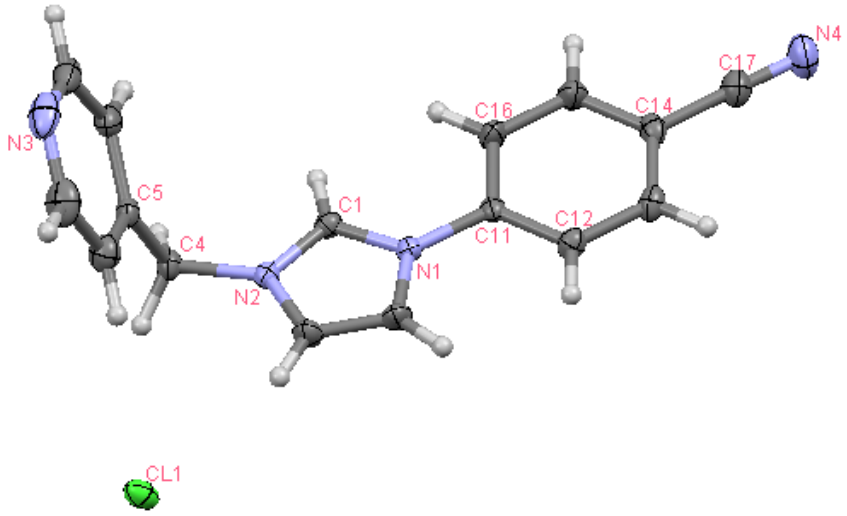


Figure 4.6: Crystal structure of **4.8,** thermal ellipsoids drawn at 50% probability level. some selected bond length (å) and bond angles (°). N(1) – C(11) = 1.4298(7), N(2) – C(4) = 1.4748(8), N(3) – C(7) = 1.3347(5), N(3) – C(9) = 1.3309(3), C(7) – N(3) – C(9) = 116.4(2), N(2) – C(4) – C(5) = 111.0(1). C(1) – N(1) – C(11) = 125.6(1).

Packing of the crystal along b crystallographic axis reveals a 1D polymeric material links through a combination of weak interactive forces. The chloride anion is hydrogen bonded to three molecules through the hydrogen of imidazole, phenyl and the methylene groups (Figure 4.7a) at a distance in the range of 2.382 – 2.794 Å, it also interacts with the imidazole ring through the N(C)N carbon at a distance of ca 3.282 Å (Figure 4.7a). Weak bonding interactions between nitrile nitrogen and phenyl hydrogen on C(13) at separation of 2.497 Å results in the formation of a head to head dimer of molecule **4.8** as shown in Figure 4.7b. Although similar interaction was reported by Pandey et al in 2010[23] it is very rarely observed with similar cyanophenyl groups. There was observed head to tail π-π stacking between adjacent phenyl rings at a distance of 3.392 Å. Additionally there are also head to tail π-π stacking arrangement between the pyridyl rings of adjacent molecule with a separation of 3.250 Å as shown in Figure 4.7a. The nitrogen on the pyridine ring is also interacting with the π system of the imidazole with a separation of 3.016 Å. These combinations of different interactions like in **4.7** connect the molecule in to a 1D polymeric material (Figure 4.7 c)

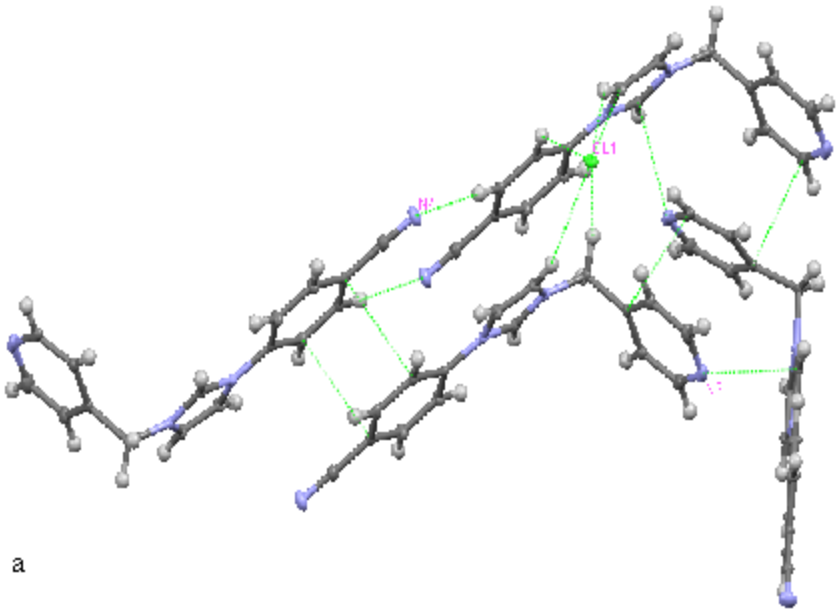
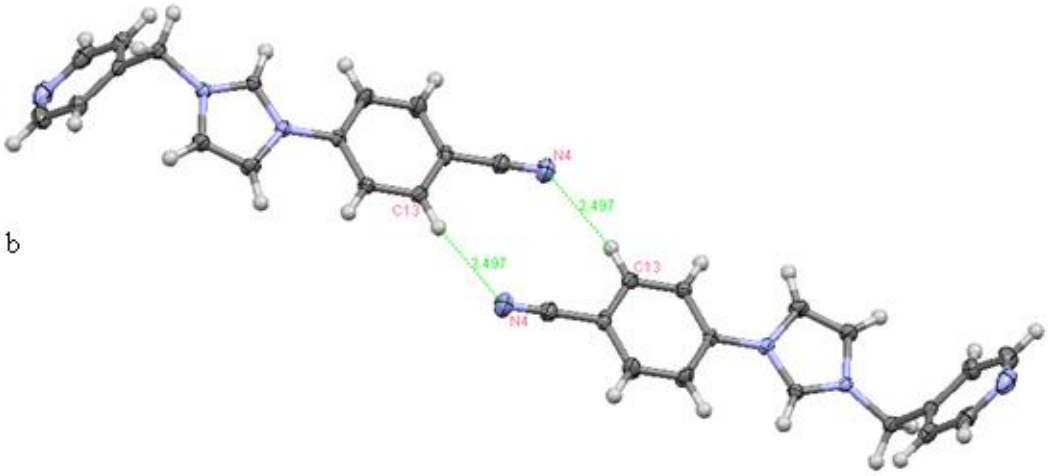


Figure 4.7a: Crystal structure of **4.8** showing intermolecular interactions including Cl---H-C, Cl---C, N---H-C and π---π stacking interactions



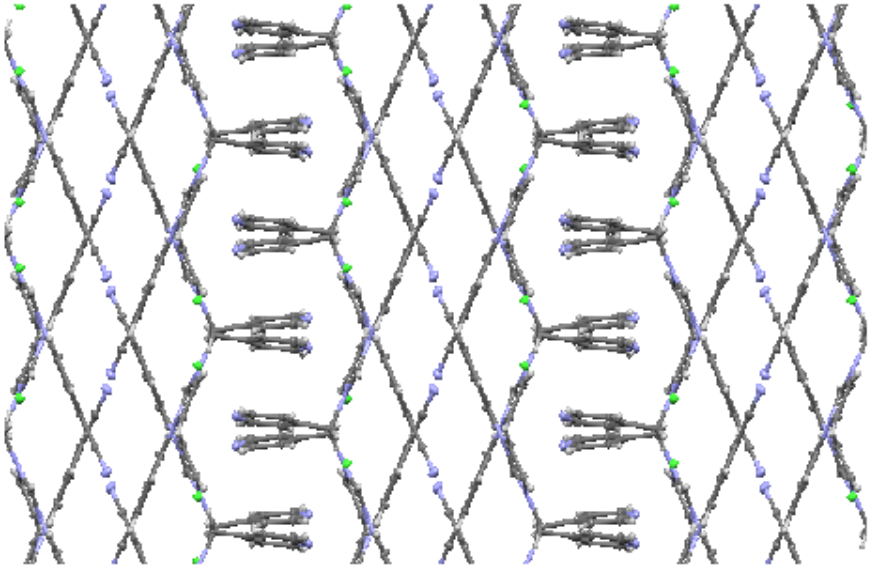


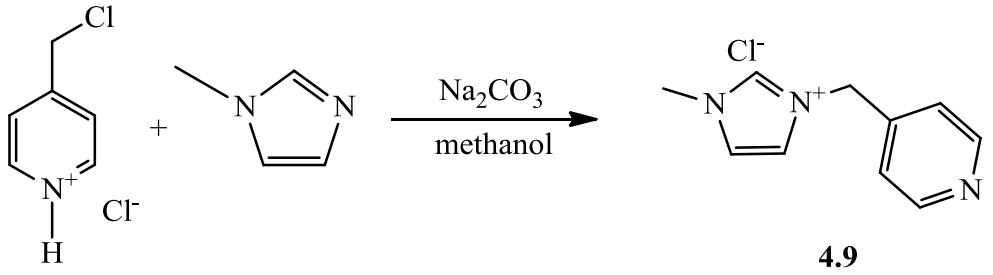
Figure 4.7: Crystal structure of **4.8** showing b) dimeric structure of **4.8** as a results C-H---N. c) extended view along crystallographic a-axis, hydrogen bonding and all other weak intermolecular interactions are omitted for clarity.

4.2.1.5. 1- Methyl -3-(4-picolyl)imidazolium chloride

1-Methyl-3-(4-picolyl)imidazolium chloride (**4.9**), was successfully prepared according to Scheme 4.7. Again, the initial method used to synthesise this compound failed to give

a clean product, rather a mixture of the compound with many side products was observed. The earlier method involved refluxing 1-methyl imidazole with 4-picolyl bromide hydrobromide at reflux in the presence of $NaHCO_3$ as a base. This with the previous problem associated with synthesis of **4.4** and **4.6** made us believe that our desired product could not be isolated due to side reactions of the pyridine at such temperature.

We therefore adopted another approach in which the picolyl bromide was deprotonated with sodium carbonate and extracted at 0^oC, and 1- methyl imidazole in methanol was added at 0^oC and stirred at room temperature. This procedure avoids using a high temperature which may be responsible for the side reaction of the pyridine.



4.9

Scheme 4.7: Synthesis of 1-methyl - 3- (4-picolyl)imidazolium chloride

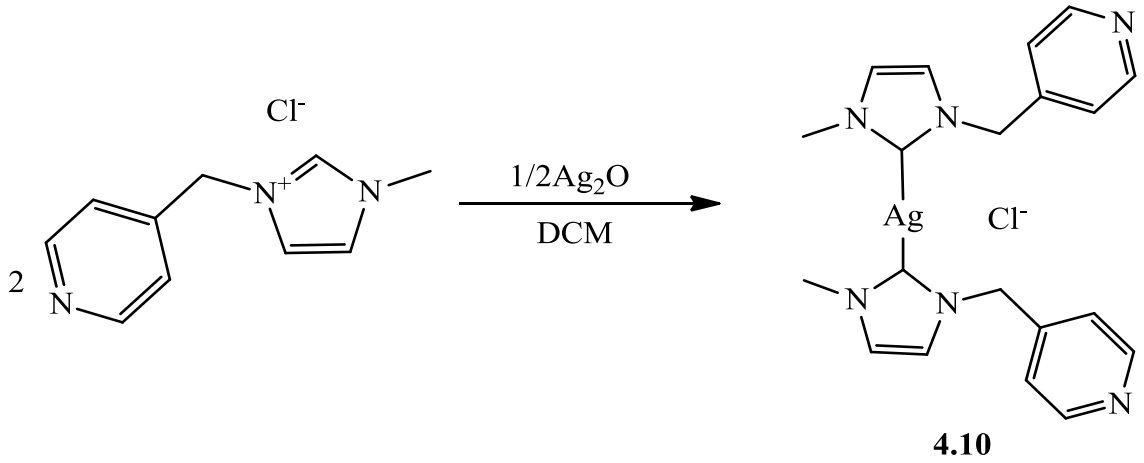
The oil formed was found to be our desired compound (**4.9**) in pure form using ^1H NMR and mass spectral analysis. The ^1H NMR spectrum revealed doublets at 7.19 ppm and 8.23 ppm which may be assigned to the pyridine ring protons. Singlets at 6.79 ppm, 6.85 ppm and 7.37 ppm assigned to the imidazole ring while the peak at 4.40 ppm was assigned to the methylene spacer between the imidazole and pyridine ring. Furthermore the terminal methyl protons on the imidazole were observed to resonate at 3.46 ppm. The mass spectrometry reveals a positive ion peak at m/z = 174 as the only major peak which is consistent with the expected value of our desired product (**4.9**).

Table 4.1. Selected crystallographic data **4.6**, and **4.8**

Compound	**4.6**	**4.8**
Chemical Formula	$C_{15}H_{15}N_4Cl_1$	$C_{16}H_{13}N_4Cl_1$
Formula weight	286.8	296.8
Colour	Colourless	Colourless
Lattice Type	Monoclinic	Monoclinic
Space group	P 2_1/c	P 2_1/c
a/Å	15.2689(5)	16.286(5)
b/ Å	8.1714(2)	7.135(5)
c/ Å	11.8084(5)	13.654(5)
α/°	90	90
β/°	104.523(4)	114.708(5)
γ/°	90	90
V/ Å	1426.24(8)	1441.3(12)
Z	4	4
T/K	293(2)	123(2)
ρ/gcm-3	1.336	1.368
μ/mm^{-1}	0.263	0.263
F000	600	616
No of reflection collected	8677	8111
No of independent reflections/(R_{int})	3500/0.032	3699/0.027
No of observed Reflection (I>2 σ(I))	2667	2922
No of parameters Refined	176	190
R1 (obsd/all)	0.044/0.066	0.04/0.057
wR2 (obsd/all)	0.084/0.094	0.086/0.096
Largest difference in peak and hole e$Å^{-3}$	0.263, -0.237	0.316, -0.245

4.2.1.6. 1-Methyl -3-(4-picolyl)imidazol-2-ylidine silver chloride (4.10)

Bis(1-methyl-3-(4-picolyl)imidazol-2-ylidene) silver(I) chloride (**4.10**), was synthesised by stirring a mixture of **4.9** and silver(I) oxide at room temperature for 5 hours in DCM (Scheme 4.8).



4.10

Scheme 4.8: Synthesis of 1-methy-3-(4-picolyl) silver NHC complex

The product was identified to be the silver complex, **4.10,** initially by using ^{1}H NMR and mass spectral analysis, since attempts made to obtain single crystals for X-ray analysis did not yield an immediate result. From the mass spectrometry peaks it was observed that the silver was linked to two carbene ligands to give a complex of type $[Ag(L)_2]Cl$, rather than [Ag(L)Cl] which are also observed from these type of reactions.[15, 24] Single crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into DCM solution of the silver compound at room temperature. The crystallographic information is given in Table 4.2.

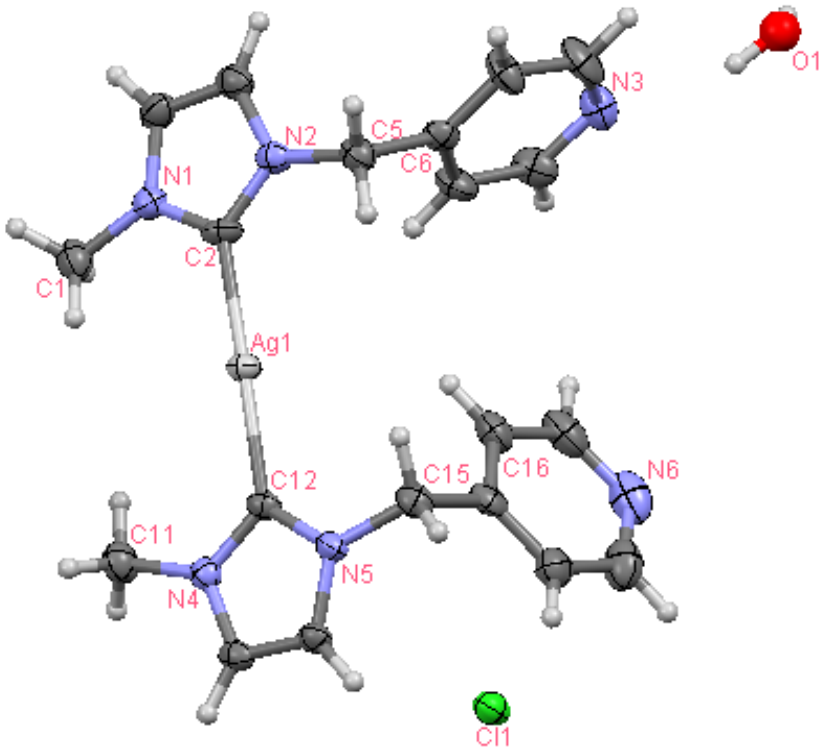


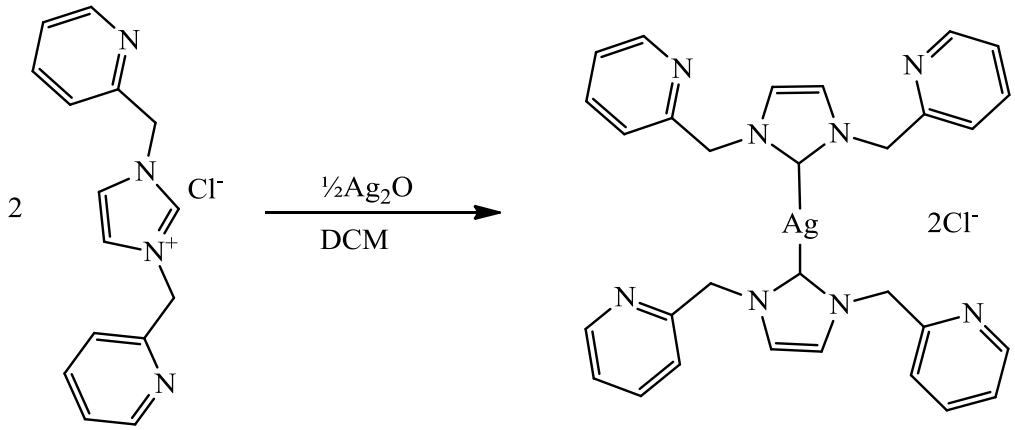
Figure 4.8: Crystal Structure of **4.10,** thermal ellipsoids drawn at 50% probability level. Some selected bond length (Å) and bond angles (°). Ag(1) – C(12) 2.085(4), Ag1 – C2 2.088(4), N(1) – C(1) = 1.463(9), N(2) – C(5) = 1.449(9), C(2) – Ag(1) – C(12) = 175.6(2), C(2) – N(2) – C(5) = 125.7(5), N(2) – C(5) – C(6) = 112.0(5), C(11) – N(4) – C(12) 124.6(5).

4.10 Crystallises in the triclinic space group P-1. The asymmetric unit consists of one Ag(I) attached to two NHC ligands, a chloride counter ion and one water molecule (Figure 4.8). The structure shows an almost linear geometry about silver(I) center with C(2) –Ag(1) – C(12) bond angle of 175.6(2)^{o} which is consistent with the typical $[Ag(NHC)_2]^+$ complexes (between 174^{o} and 177^{o}).[8] The silver - carbene distances were observed to be identical (Ag(1) – C(2) = 2.088(4) Å and Ag(1) – C(12) = 2.085(4) Å) which are also within the expected range of typical $[Ag(NHC)_2]^+$ complexes.[8] It is thought that the two pyridyl rings on the carbene ligand should be directed towards the

methyl group to avoid steric hindrance, but instead they are arranged adjacent to one another as shown in Figure 4.8. Furthermore the pyridyl rings are twisted with respect to imidazole ring which may facilitate the stacking of pyridyl and imidazole ring in crystal lattice.

4.2.1.7. 1, 3-Bis(2-picolyl)imidazol-2-ylidine silver chloride (4.11)

In accordance with the general reaction for the generation of silver-NHC complexes,[9] the ligand (**4.5**), was reacted with slight excess of silver(I) oxide in dichloromethane (Scheme 4.8) in the absence of light. The product was filtered through celite and the solvent removed to give white solid product which was assumed to be compound **4.11**. A similar reaction was reported by Catalano and Malwitz in 2003[18] using acetonitrile as the solvent in place of DCM.



4.11

Scheme 4.9: Synthesis of bis-(2-picolyl) NHC silver (I) complex

The ^{1}H NMR has multiplet peaks at 7.29, 7.72 and 8.58 ppm which may be assigned to the 2-pyridyl protons, while the peak at 5.38 ppm can be attributed to the methylene spacer between the pyridyl and imidazole ring. The downfield signal observed in the imidazolium salt (**4.5**) at 8.94 ppm was absent in the new complex, which indicates the deprotonation of the imidazolium salt and consequently the formation of the carbene. Also, the ^{13}C NMR spectral signals are of the expected compound **4.11**. The positive ion

peak in the mass spectrometry at m/z = 609 further suggest the formation of the silver bis carbene complex (**4.11**).

Like in Catalano et al[18] the complex crystallised in the triclinic space group P-1, the crystallographic information are given in Table 4.2. The asymmetric unit reveals a twin identical species having two NHC ligand molecules, one silver atom, one chloride ion and a H_2O molecule in each species. The silver ion bridges the two NHC ligands in a near linear arrangement. These molecular structural features are similar to those reported by the Catalano group[18] although the packing and thus the unit cells dimensions are different. In particular, the Ag---Ag interaction was shorter at 3.468 Å than in their report, which was at 3.650 Å.

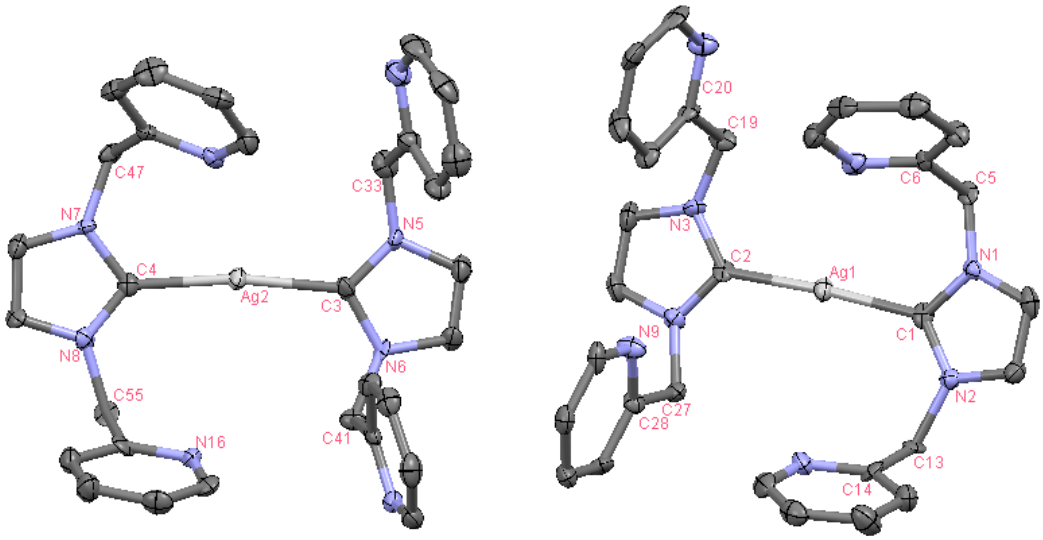


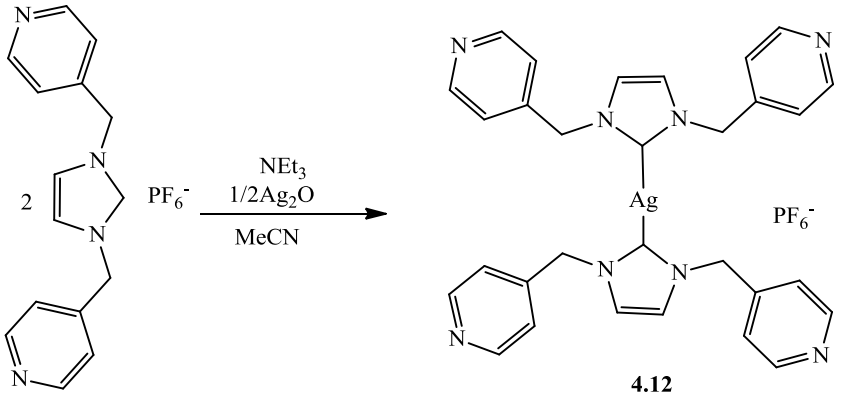
Figure 4.9: Crystal Structure of **4.11,** thermal ellipsoids drawn at 50% probability level. Some selected bond length (Å) and bond angles (°). Hydrogen, Cl^- and H_2O omitted for clarity. Ag(1) – C(1) 2.08(9), Ag(1) – C(2) 2.088(9), Ag(2) – C(3) 2.080(9), Ag(2) – C(4) 2.077(9), C(1) – Ag(1) – C(2) 175.4(4), C(3) – Ag(2) – C(4) 171.2(4), N(1) – C(5) – C(6) 110.6(8), N(2) – C(13) – C(14) 112.6(8),

4.2.1.8. 1,3-Bis(4-picolyl)imidazol-2-ylidine silver hexafluorophosphate

The use of silver(I) oxide in the preparation of silver carbene complexes has become the most commonly used method.[8, 9, 24] This may be due to stability the generated carbene complex has towards air. In accordance with literature method, bis(4-picolyl) imidazolium salt (**4.7**) was reacted with Ag_2O in acetonitrile initially with mild heating and then at reflux. The Ag_2O normally acts as a deprotonating agent, generating the NHC *in situ* and also acting as a silver source which then binds to the NHC forming silver NHC complex. The formation of the carbene is associated with disappearance of imidazolium acidic proton (-NCHN-) in the ^{1}H NMR spectrum but this signal was observed it only slightly shifted from 9.44 ppm in the ligand to 9.40 ppm and also other spectroscopic data shows the non formation of the carbene complex **4.12**.

However repeating the reaction with use of external base (NEt_3) afforded the bis carbene complex **4.12** (Scheme 4.10). The most downfield resonance at 9.44 ppm associated with acidic proton of the ligand (**4.7**) precursor has disappeared indicating the deprotonation of the –NCHN- proton which may leads to the formation of the carbene complex, and all other resonances have shifted upfield as was observed in similar compounds reported.[25] The pyridyl proton peaks have shifted from 8.74 ppm and 7.55 ppm to 8.51 ppm and 7.15 ppm respectively, this shift of the pyridyl protons suggest a further coordination through the pyridine nitrogen; the other imidazolium protons peak also shifted upfield from 7.91 ppm to 7.65 ppm and the methylene proton signal from 5.63 ppm to 5.42 ppm. There are observed five ^{13}C NMR peaks one less than observed in the ligand (**4.7**). This is an indication of the formation of the silver carbene complex as the carbene carbon peak is sometimes not observed in silver carbene complexes due to problems of exchange and long relaxation times.[7] The formation of this carbene complex was further supported by the mass spectrum with its intense peak at m/z = 607 which is in agreement with the targeted bis carbene complex **4.12**. However the presence of a small peak at ca m/z = 715 indicates the coordination of the second silver atom to the complex suggesting the formation of a polymeric pattern of the product, but the monomeric species are apparently more dominant in solution. This gives an indication

that the targeted NHC coordination polymer might be formed. Therefore, from the NMR (^{1}H and ^{13}C) and mass spectrum it become apparent that one of the silver atoms was coordinated to the carbene carbon while the other silver was coordinated to the pyridine nitrogen forming a polymer of **4.6.** This was further supported by the elemental analytical data which gives a good agreement with formulation indicating two silver atoms for one ligand molecule. All attempts to produce single crystals suitable for X-ray diffraction did not yield the expected results, as such crystal structural analysis was not possible, hence the targeted NHC containing polymer of **4.6** cannot be conclusively ascertained.

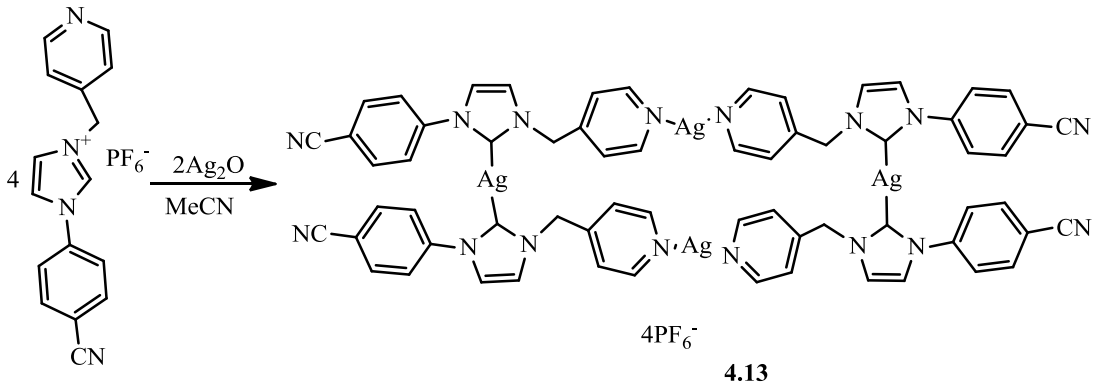


Scheme 4.10: Synthesis of bis-(4-picolyl) NHC silver(I) complex

4.2.1.9. Bis(1-(4-cyanophenyl)-3-(4-picolyl)imidazol-2-ylidine silver hexafluorophosphate

The mixed functionalised silver NHC complex (**4.13**) was prepared in similar manner to **4.12** but in this case external base was not necessary. Ag_2O was reacted with the ligand (**4.8**) in total exclusion of light under reflux overnight (Scheme 4.11). It was filtered through celite to remove any unreacted Ag_2O and compound **4.13** was precipitated using diethyl ether. The product was characterised using ^{1}H and ^{13}C NMR, mass spectrometry, elemental analysis and single crystal X-ray analysis. In the ^{1}H NMR spectrum the downfield signal of –NC(H)N- proton has disappeared, indicating the deprotonation of

the imidazolium salts, and there was no trace of any unconverted imidazolium -NC(H)N- proton peaks observed. The other imidazolium, phenyl and pyridine proton peaks have all shifted upfield similar to **4.12,** and the consistencies of the ^{13}C NMR peaks although like in **4.12** the carbene carbon signal was not observed further confirm the formation of the carbene complex **4.13**. The mass spectrum of the product shows a peak at m/z = 627.07, which is in agreement with the monomeric species of the NHC complex **4.13**, However the presence of a small peak in the mass spectrum at m/z = 734 (z = 2) indicates the formation of **4.13.** The m/z = 627 being the major peak indicates the dominance of the monomeric species over **4.13** in solution. But microanalysis is in good agreement with the formulation of **4.13** which indicates the formation of the dimer of the bis NHC complex bridge with the silver atom as shown in Scheme 4.11. Formation of **4.13** as the main solid product was further confirmed by X-ray crystallographic analysis.



4.13

Scheme 4.11: Synthesis of 1-(4-cyanophenyl)-3-(4-methylpyridine) NHC silver(I) complex

Single crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the silver complex **4.13** at room temperature, and crystallographic information are given in Table 4.2. It crystallised in the monoclinic space group $P2_1/c$, with one asymmetric unit consisting of four NHC molecules, four Ag(I) ions, and four PF_6^- counter ions. Also the asymmetric unit shows two NHC ligands bridged by silver cation (Figure 4.10) in near linear geometry having a C(32) – Ag(1) – C(100) bond angle of 172.69^o which is slightly less than the expected bond

angles of similar $[Ag(NHC)_2]^+$ compounds.[7] The C(32) – Ag(1) and C(100) – Ag(1) bond lengths of 2.07(3) Å and 2.05(3) Å respectively are within the range for silver carbene bond length.[7, 8] The asymmetric unit further shows two pyridine nitrogen from separate biscarbene coordinated to another Ag(I) in near linear geometry hence elongating the molecule to contain four ligand, four silver and four PF_6^- counter ions (Figure 4.11). The Ag(3) – N(12) and Ag(3) – N(15) bond distances are 2.16(18) Å and 2.137(18) Å respectively which are within the range of Ag-N bond distances reported[26] and the N(12)–Ag(3)–N(15) bond angle is 177.9(8) which is higher than that joining the imidazolylidene rings but it also indicates the near linearity around the silver atom. The two imidazolylidene rings bonded to the silver are nearly coplanar, and also the cyanophenyl groups, although slightly twisted, are approximately coplanar with their attached imidazolylidine rings. They were oriented on the same side of the molecule although no evidence of strong π-π interaction was observed between them, as they have separation of ca 4.80 Å (Figure 4.11). The two pyridyl portions are rotated out of plane of their respective imidazolylidine rings, and are also arranged on the same side of the molecule but unlike the phenyl rings they are face to face with separation of ca 3.65 Å suggesting strong intermolecular π – π interaction.

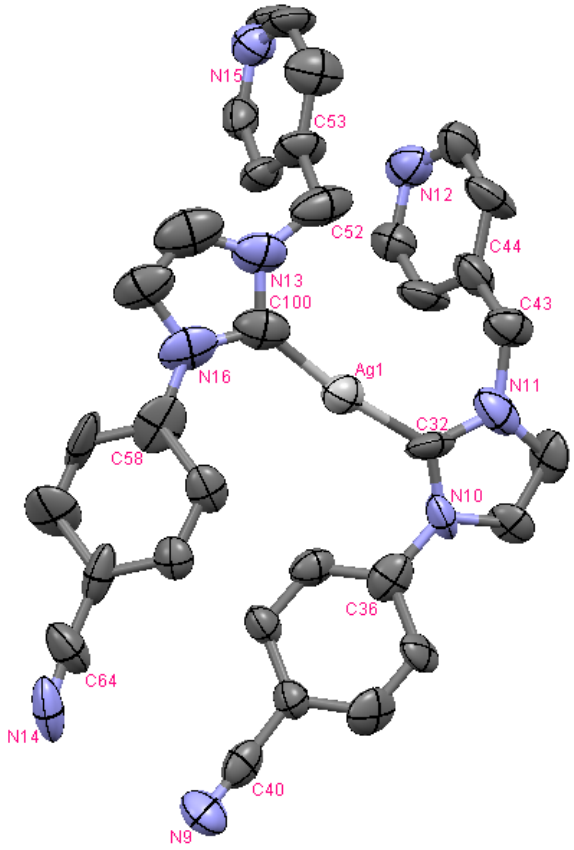


Figure 4.10: Crystal structure of monomeric species of **4.13**

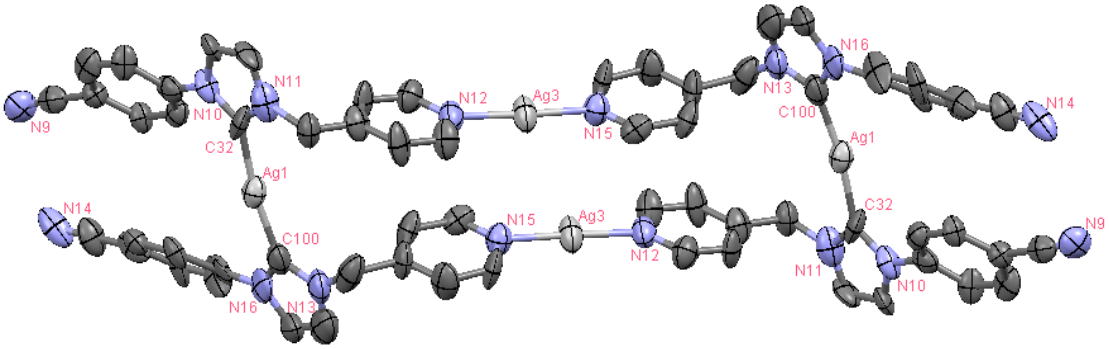
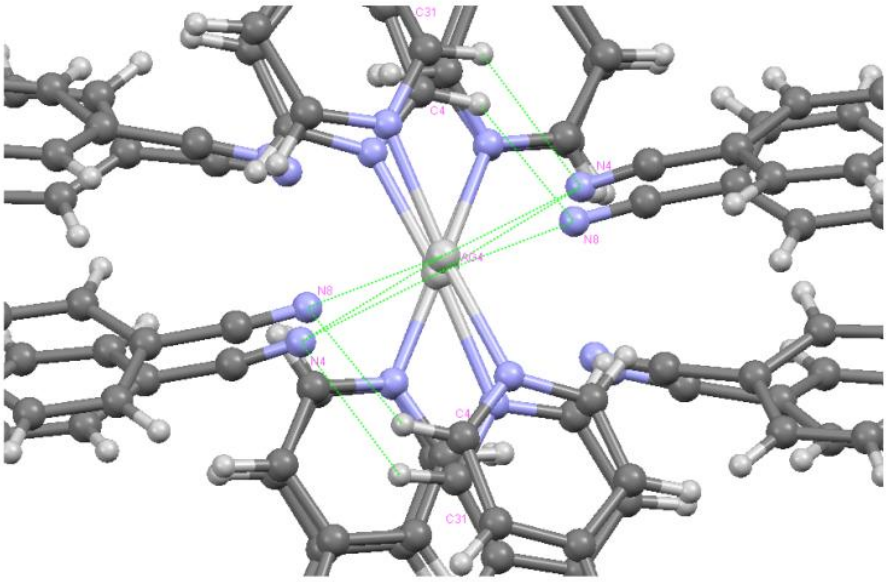


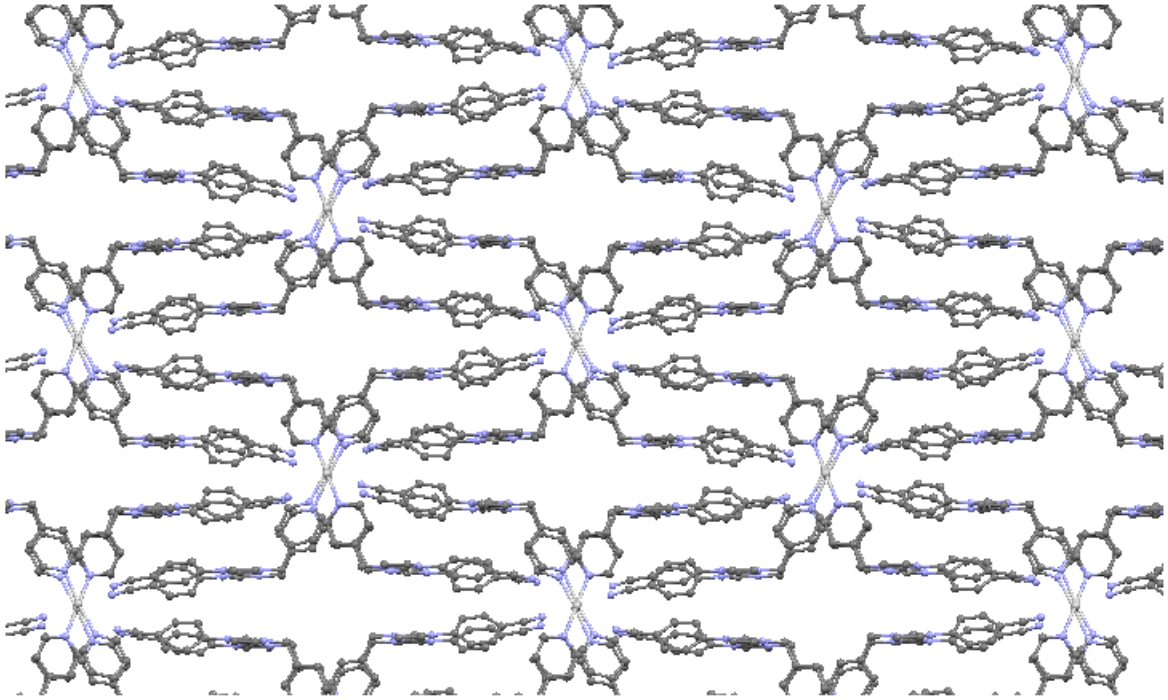
Figure 4.11: Crystal Structure of **4.13,** thermal ellipsoids drawn at 50% probability level. Some selected bond length (Å) and bond angles (°). Ag(1) – C(32) = 2.07(3), Ag(1) – C(100) = 2.05(3), Ag(3) – N(12) = 2.16(18), Ag(3) – N(15) = 2.137(18), C(32) – Ag(1) – C100 = 172.69, N(12) – Ag(3) – N(15) 177.9(8)

Although the nitrile nitrogens are not coordinated to the silver atom, they are weakly interacting with the Ag(I) (bridging the pyridyl group), the N(4)---Ag(4) and N(8)---Ag(4) separations are 3.140 Å and 2.984 Å respectively which are shorter than sum of the van der Waals radii of Ag and N,[22] making the nitrile groups at each end of the molecule to be directed towards the silver coordination environment (Figure 4.12a). Also like **4.11** above this interaction serves as a connection points aiding the formation of a 2D like polymer (Figure 4.12 b and c)

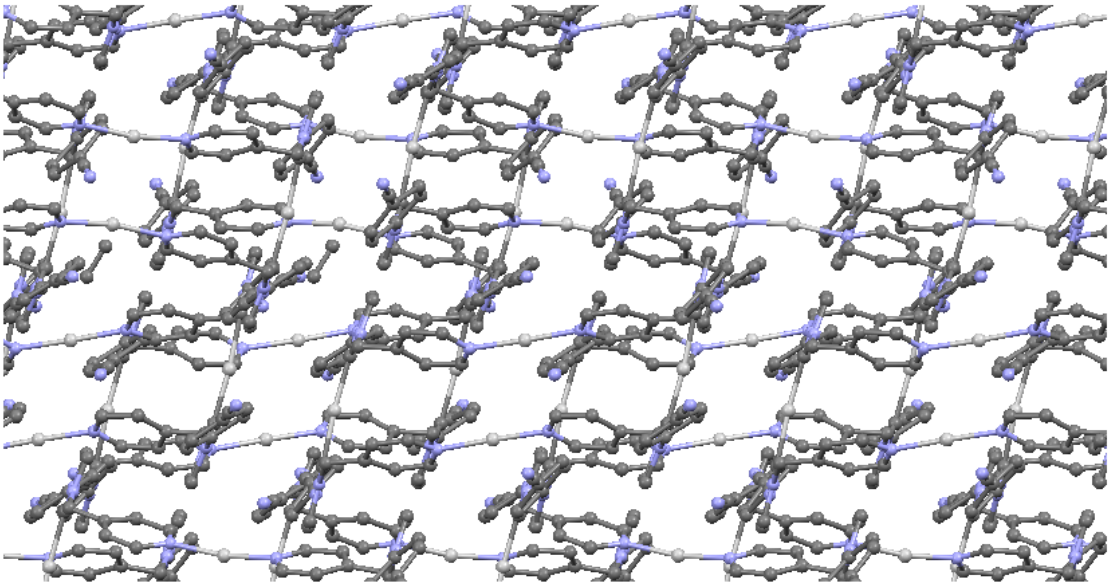


a

Figure 4.12a: Packing diagram in **4.13,** showing N----Ag and N---H- C interactions



b



c

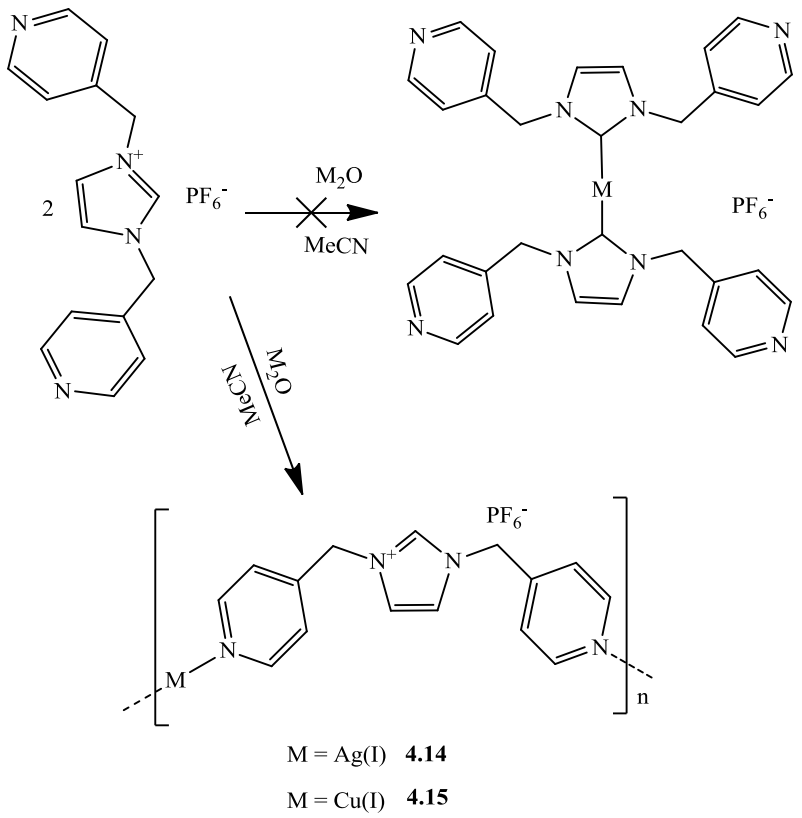
Figure 4.12: Packing diagram in **4.13,** b) view along crystallographic a-axis c) view along b crystallographic axis. Hydrogen atoms, PF_6^- anion, hydrogen bonding omitted for clarity.

Table 4.2. Selected crystallographic data for **4.10**, **4.11** and **4.13**

Compound	**4.10**	**4.11**	**4.13**
Chemical Formula	$C_{20}H_{24}AgClN_6O$	$C_{30}H_{28}AgClN_8$	$Ag_1C_{16}H_{12}N_4P_1F_6$
Formula weight	507.77	679	457
Colour	Colourless	colourless	colourless
Lattice Type	Triclinic	Triclinic	monoclinic
Space group	P-1	P-1	$P2_1/c$
a/Å	10.0958(15)	10.738(5)	15.8824(13)
b/ Å	10.624(2)	10.988(5)	29.383(3)
c/ Å	10.9551(14)	25.655(5)	16.3625(14)
α/°	81.716(13)	102.186(5)	90
β/°	89.005(12)	95.527(5)	108.051(8)
γ/°	66.893(16)	99.735(5)	90
V/ Å	1068.5(3)	2889(2)	7260.1(11)
Z	2	2	16
T/K	123(2)	298(2)	100(2)
ρ/gcm-3	1.578	1.173	1.88
μ/mm^{-1}	1.092	0.721	1.267
F000	516	1040	4032
No of reflection collected	4710	24617	31198
No of independent reflections/(R_{int})	3163/0.045	12587/0.0966	16281/0.1666
No of observed Reflection (I>2 σ(I))	2270	8068	5091
No of parameters Refined	267	748	1027
R1 (obsd/all)	0.0391/0.0634	0.105/0.161	0.138/0.336
wR2 (obsd/all)	0.0769/0.0832	0.218/0.248	0.34/0.481
Largest difference in peak and hole $eÅ^{-3}$	1.121, -0.613	3.975, -1.403	1.683, -1.757

4.2.1.10. 1,3-Bis(4-picolyl)imidazolium cationic polymers

In an attempt to convert the bis 4-picolyl imidazolium salt to carbene complexes of Ag(I) and Cu(I), the imidazolium salt (**4.7**) was reacted with Ag_2O and Cu_2O respectively according to scheme 4.12. Surprisingly the ^1H NMR spectrum of the product in both Ag(I) and Cu(I) targeted carbene shows that the downfield -NCHN- signal did not disappear but only slightly shifted from 9.44 ppm in the ligand to ca 9.40 ppm in the product. This clearly shows the deprotonation of the most acidic -NCHN- proton fails, and also other imidazole protons signals are intact in the spectrum at 7.89 ppm therefore ruling out any possibility of abnormal proton abstraction from the imidazolium salts as such no chances of abnormal carbene formation as is observed in some system [27]. Therefore ^1H NMR analysis rules out any possibility of *in situ* carbene formation, which explain why no traces of silver bis(4-picolyl) carbene complexes were found. But interestingly a careful analysis of the ^1H NMR suggests that the silver preferentially binds to the pyridine nitrogen forming the imidazolium salts polymer (**4.14**) instead of the carbene complex (**4.12**). This is not surprising because silver(I) has shown a preference to coordinate to amine,[5] but what is surprising is the inability of the imidazolium salts to be deprotonated despite using excess of M_2O (M = Ag or Cu).



Scheme 4.12: Synthesis of imidazolium salt silver (I) polymer

The formation of the polymer can be explained by the shift in the signal attributed to the pyridine protons in ^{1}H NMR, those of imidazole are almost identical to the starting ligand. The major difference in ^{1}H NMR between **4.14** and **4.15** was the broadening of pyridine protons signals in the latter. The aromatic -C=N- stretching vibration at ca 1640 cm^{-1} in the IR had shifted to ca 1617 cm^{-1}. Good agreement in elemental analysis of both **4.14** and **4.15** further confirmed the formation of these polymers, but it should be noted that, both corresponding carbene complexes and the polymers may have same elemental compositions as such may not be very precise in confirming whether carbene complexes or polymers were formed. However **4.14** and **4.15** were confirmed by X-ray crystallographic analysis when single crystal suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into acetonitrile solutions of the compounds.

4.14 crystallises in monoclinic space group P 2/c, the crystallographic information are given in Table 4.3, the asymmetric unit contains one Ag(I) ion, one ligand (**4.7**) and one and half hexafluorophosphate anion. The Ag(I) ion coordinates to four imidazolium salt cationic ligands (**4.7**) via the pyridine groups giving an approximately tetrahedral coordination geometry (Figure 4.13). Three of the four pyridyl rings are twisted around the Ag(I) centre assuming non-planar conformation with N(1) – Ag(1) – N(1) – C(7) torsion angle of 117.35^{o}. The Ag(1) – N(1) and Ag(1) – N(2) bond length are 2.314(7) Å and 2.285(5) Å respectively are within the range of Ag – N bond length of similar compounds reported.[28] The N – Ag – N angles are in the range of 108.3(2)° – 111.0(2)° which are also within the range of reported similar pyridine polymers.[29] The N(1) – C(7) and N(1) – C(8) bond length are 1.341(1) Å and 1.352(1) Å respectively. These values were observed to be slightly higher than the corresponding distances in the ligand (**4.7**), which has an average bond length of 1.3337 Å. This may be due to the impact of the nitrogen coordination which increases the distance to its neighboring carbon atom in the pyridine ring. The structure further reveals that each Ag (I) is linking two imidazolium cationic ligand (**4.7**), with two PF_6^- serving as counter ions (figure 4.13). They group together to form a continuous rings of the cationic ligand (**4.7**) connected by the Ag(I), with each charge of the cationic framework balanced by PF_6^- anions. Some of the PF_6^- are encapsulated within the ring and the others located at the side of the ring chain as shown in Figure 4.14.

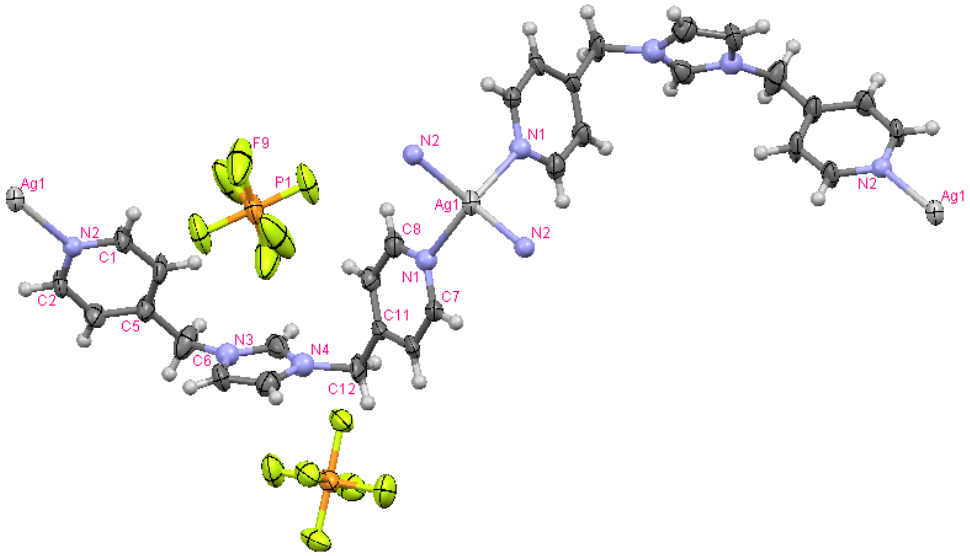


Figure 4.13: Crystal Structure of **4.14** including the asymmetric unit, thermal ellipsoids drawn at 50% probability level. Some selected bond length (Å) and bond angles (°). Ag(1) – N(1) = 2.314(7), Ag(1) – N(2) = 2.285(5), N(1) – C(8) = 1.35(1), N(1) – C(7) 1.34(1), N(1) – Ag(1) – N(2) 108.3(2), N(1) – Ag(1) – N(1) = 111.0(2), N(2) – Ag(1) – N(2) = 112.1(2), C(7) – N(1) – Ag(1) = 121.8(5), C(8) – N(1) – Ag(1) = 122.2(5)

Each of the encapsulated PF_6^- anions forms eight C-H----F hydrogen bonds with the pyridine, having a separation within a range of 2.535 Å – 2.609 Å , further supporting the silver in linking the two imidazolium cationic ligand (**4.7**) (Figure 4.14b).

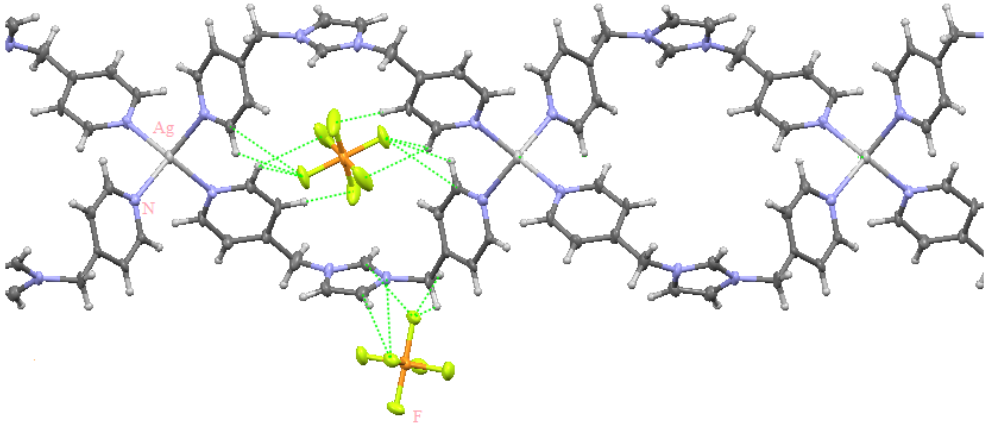
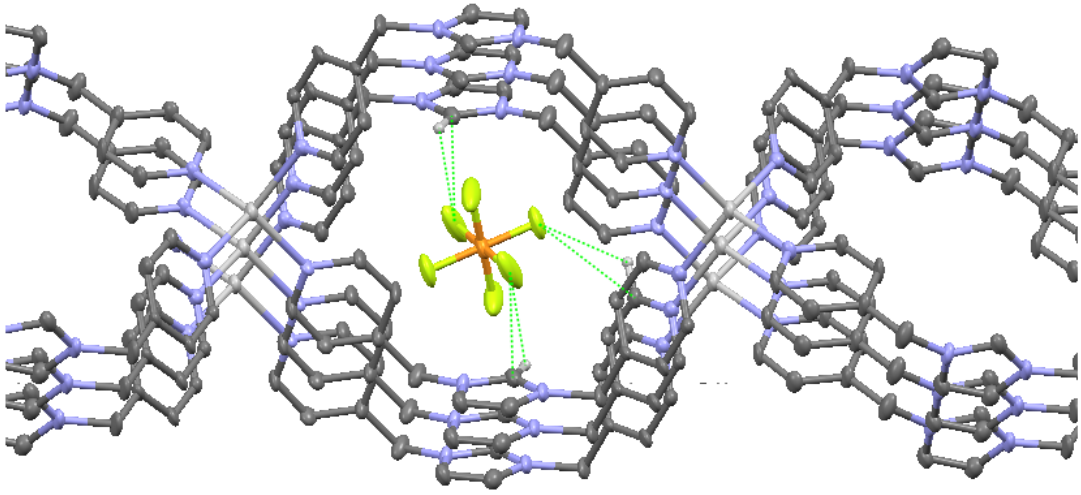
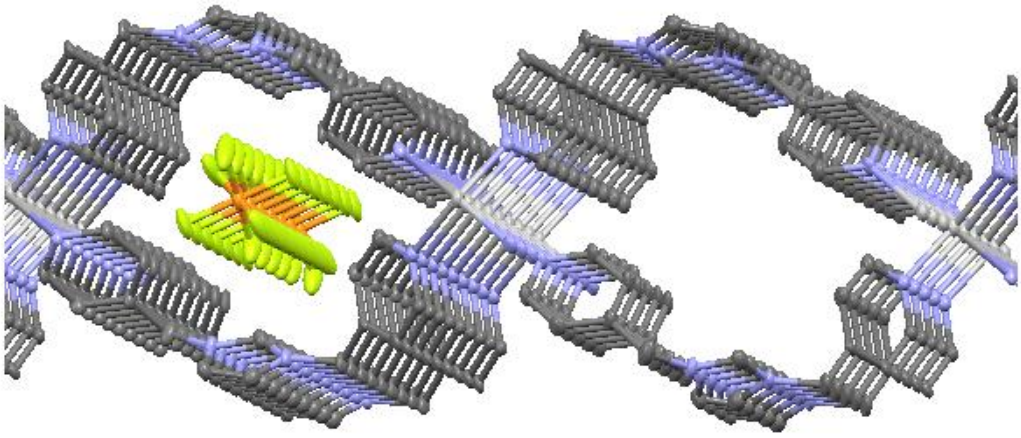


Figure 4.14: The network in **4.14,** showing the interaction environment around PF_6^-

The PF_6^- anion further support the crystal packing of the complex **4.14** by interacting with three different layers of the compound, one at the center one below and the other above through C-H---F hydrogen bond involving both pyridine and imidazolium rings hydrogen with a separation in the same range of 2.535 Å – 2.609 Å. In addition the PF_6 anion also interacts with pyridine and imidazolium ring carbon atoms at a separation 3.168 Å (Figure 4.15 a.).



a



b

Figure 4.15: Parallel stacking of the network in **4.14**, hydrogen atoms, PF_6^- anion, hydrogen bonding omitted for clarity a) the C-H---F hydrogen bonding between PF_6^- anion and the different layers of the network b) view along the channel

These interactions are the major factor that helps to stack the parallel layers onto each other (Figure 4.15), despite the separation between them being 6.34 Å which rules out any stronger π-π stacking between pyridine or imidazolium rings. Ag----Ag interaction are observed in some reported silver complexes,[8] this separation of 6.340 Å between closest Ag (I) suggest a strong interaction was not observed in this system as the distance is higher than the sum of the van der Waals radii for silver atom.

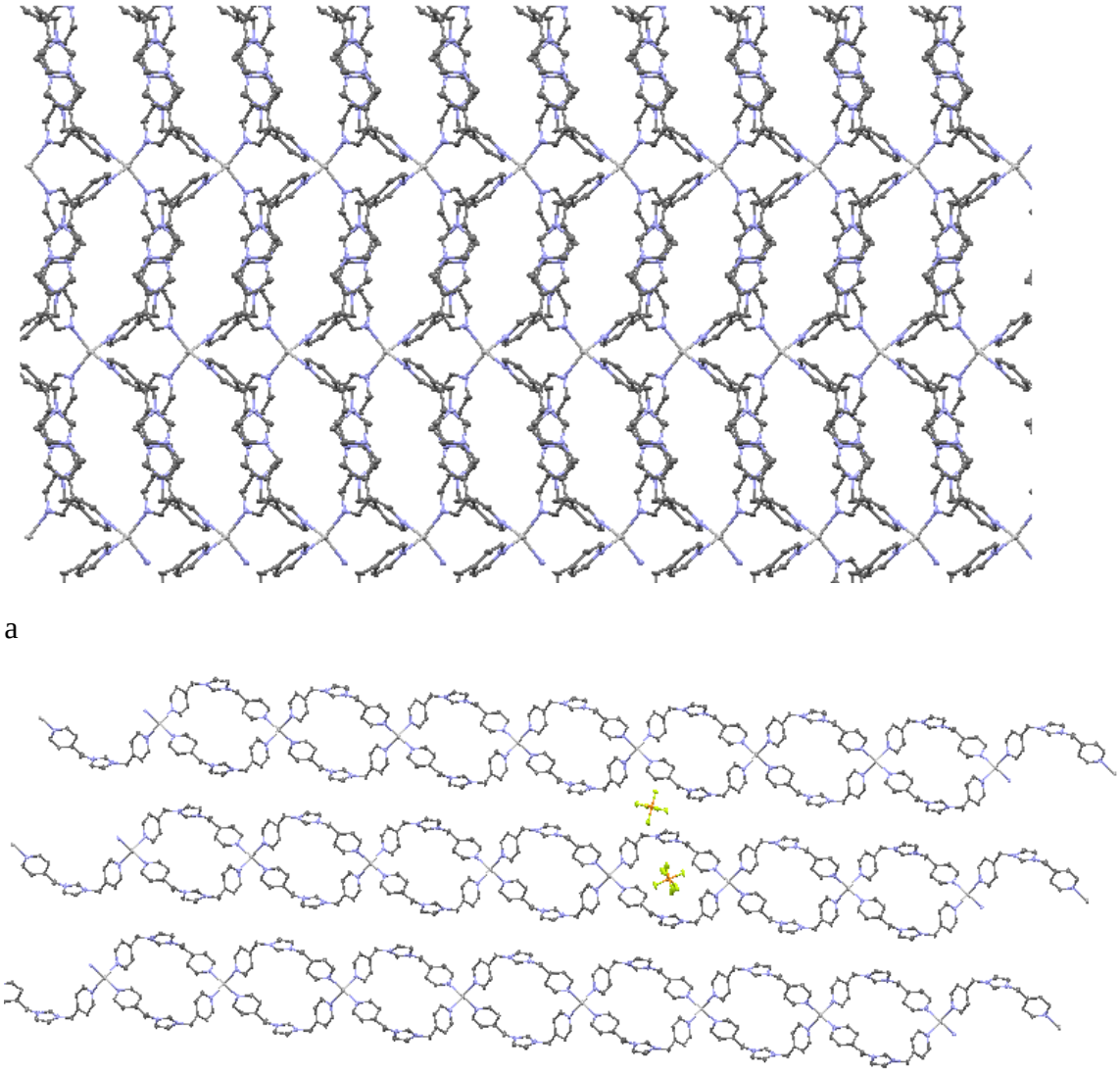


Figure 4.16: Packing diagram in **4.14,** hydrogen atoms, PF_6^- anion, hydrogen bonding omitted for clarity a) along a crystallographic axis and b) along b crystallographic axis.

Table 4.3. Selected crystallographic data for **4.14**, and **4.15**

Compound	**4.14**	**4.15**
Chemical Formula	$Ag_1C_{30}H_{30}N_8P_2F_{12}$	$Cu_1C_{15}H_{15}N_4P_1F_6$
Formula weight	898.4	461
Colour	Colourless	Colourless
Lattice Type	Monoclinic	Monoclinic
Spacegroup	P 2/c	P 2/c
a/Å	13.0640(3)	12.7435(3)
b/ Å	6.3399(12)	6.3113(17)
c/ Å	24.0380(4)	23.8491(7)
α/°	90	90
β/°	99.233(19)	100.687(3)
γ/°	90	90
V/ Å	1965.1(4)	1884.87(4)
Z	4	4
T/K	293(2)	293(2)
ρ/gcm-3	3.03	1.62
μ/mm^{-1}	1.367	1.307
F000	1787.7	923.8
No of reflection collected	9125	11408
No of independent reflections/(R_{int})	4509/0.1145	4651/0.0342
No of observed Reflection (I>2 σ(I))	2208	3624
No of parameters Refined	254	273
R1 (obsd/all)	0.085/0.181	0.0508/0.0712
wR2 (obsd/all)	0.162/0.216	0.1121/0.1243
Largest difference in peak and hole $eÅ^{-3}$	0.794, -1.294	0.855, -0.936

The Cu(I) imidazolium cationic polymer (**4.15**) is isostructural with the Ag(I) polymer (**4.14**), (Figure 4.17 and 4.18) only slight differences exist. The Cu – N bondlengths (Cu(1) – N(1), 2.0414(2) Å and Cu(1) – N(4), 2.071 (3) Å) as expected on the basis of the ion sizes are lower than Ag – N bond length (Ag(1) – N(1), 2.314 (7) Å and Ag(1) – N(2), 2.285(5) Å). All other bond length and angles are similar. The lower values obtained for the Cu – N bond length are within the expected range and are consistence with Cu – N bond reported for other similar compounds.[15]

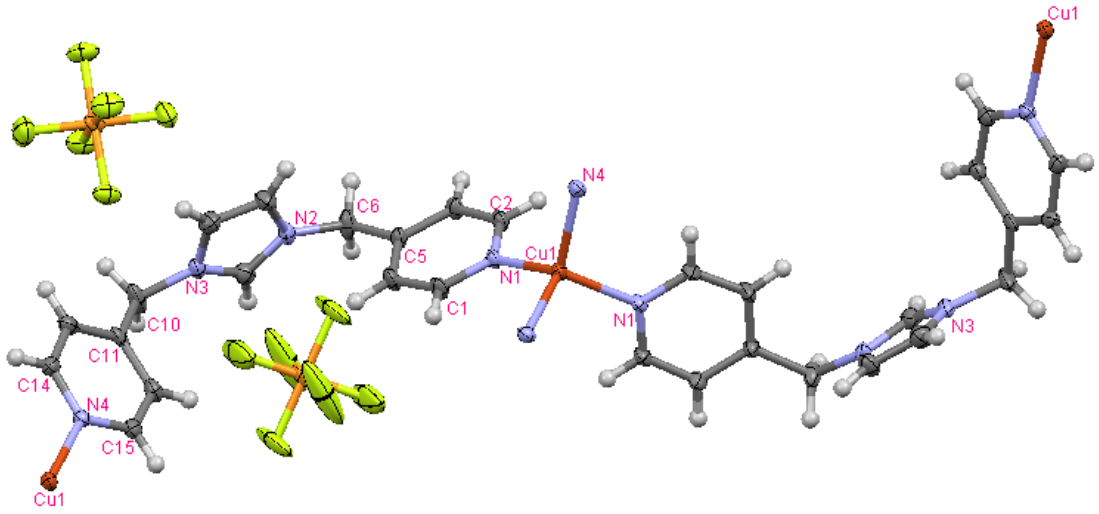


Figure 4.17: Crystal Structure of **4.15,** thermal ellipsoids drawn at 50% probability level. Some selected bond length (Å) and bond angles (°). Cu(1) – N(1) = 2.0414(2), Cu(1) – N(4) 2.071(3), N(4) – C(15) = 1.346(3), N(4) – C(14) = 1.345(3), N(4) – Cu(1) – N(1) = 108.4(1), N(1)– Cu(1) – N(1) = 111.2(1), C(14) – N(4) – Cu(1) = 121.3(2), C(15) – N(4) – Cu(1) = 121.9(2).

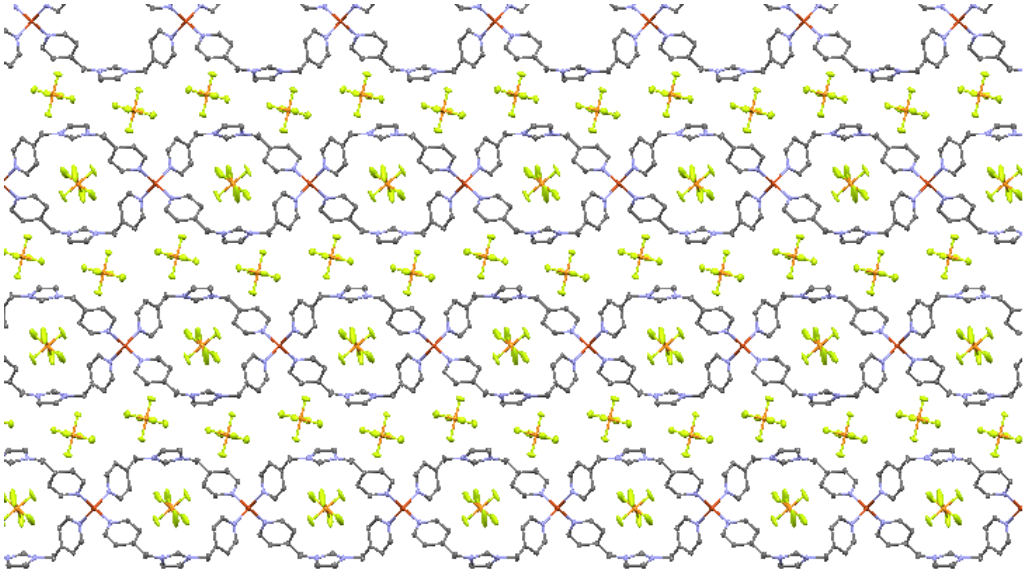


Figure 4.18: Packing diagram in **4.15,** view along b crystallographic axis, hydrogen atoms, hydrogen bonding omitted for clarity.

4.3. Attempted generation of more coordination polymers

Having successfully synthesised these two linear non chelating ligands, **4.7** and **4.8** which shows a huge potential as building block for constructing coordination polymers and building on the successes of the two cationic polymers **4.14** and **4.15**, more polymers were attempted.

Initially these polymers **4.14** and **4.15** were treated with more excesses Ag_2O and Cu_2O respectively with mild heating and then at reflux to obtained the respective NHC containing frameworks, but that did not yield the desired results, in both cases there was no evidence from the ^{1}H and ^{13}C NMR of the NHC complex formation. Steric factors may be part of the reason but the actual reason was not fully ascertained. Also the mixed functionalised silver NHC complex **4.13** was further treated with more Ag_2O in acetonitrile to explore the possibility of extending the molecule through the uncoordinated nitrile end, but that also did not yield the expected product.

An attempt was made to replicate the success of the Ag(I) and Cu(I) in forming the cationic polymers **4.14** and **4.15** respectively by using various M(II) salts in place of the

M(I) ions. Those used were the tetrafluoroborates and halides of Cu(II), Zn(II), Fe(II), Ni(II) and Pd(II). The attempt involves dissolving separately the ligand **4.7** and **4.8** with each of the M(II) salt listed above at room temperature, with mild heating and then at reflux. None of the precipitates or crystals obtained gave satisfactory data to confirm the formation of the target compound. The reaction was also conducted in the presence of base to adjust the pH to favour the formation of the target polymeric compound but all with no success.

However reaction of the $Fe(BF_4)_2$ with ligand **4.7** in acetonitrile and slow evaporation produce a product which was structurally characterised by X-ray crystallographic analysis. It crystallised in monoclinic space group $P2_1/c$. The asymmetric unit contains one cationic bis(4-picolyl)imidazolium salt and three PF_6^- ions. The crystal structure shows the pyridine nitrogen of the ligand not to be coordinated to the Fe(II) but rather it was protonated at both end to form a tricationic species which was balanced by the presence of three PF_6^- counter ion within the molecule (Figure 4.19). This protonation of the pyridyl nitrogen at both ends of the molecule suggest that pH might be the major militating factor against forming the polymer.

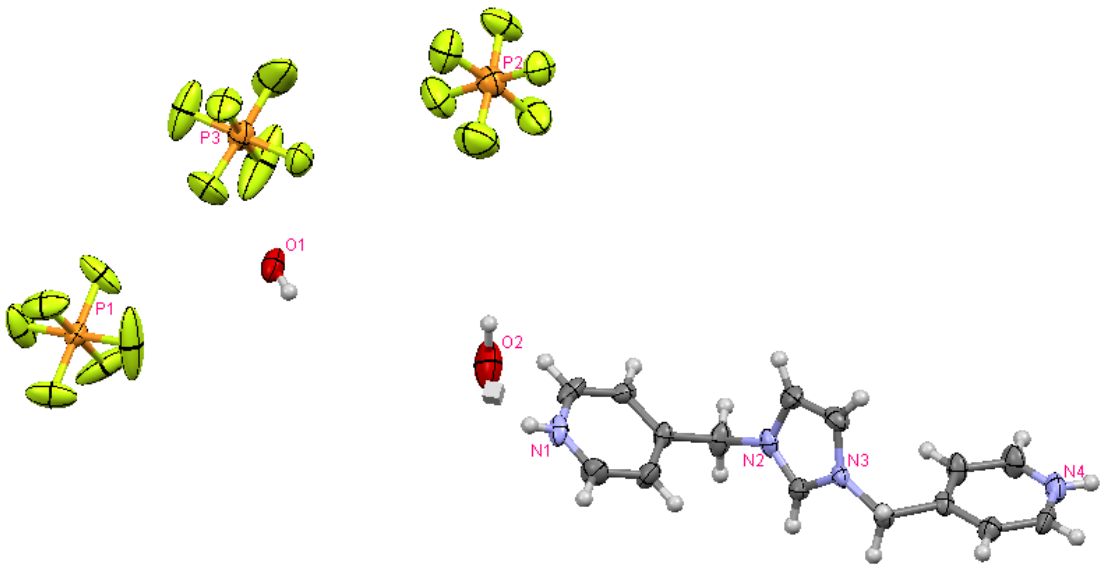


Figure 4.19: Crystal structure obtained from reaction of $Fe(BF_4)_2$ and ligand **7,** thermal ellipsoids drawn at 50% probability level, showing protonation of the pyridine nitrogen

Also reacting $PdCl_2$ and ligand **4.7** in acetonitrile results in the formation of crystals good enough for X-ray diffraction. The compound crystallised in orthorhombic space group Pbcn. The crystal structure shows the ligand to be protonated at one pyridine end through N(3) unlike the previous structure which was protonated at both pyridine end. This protonation makes the ligand to be dicationic and the presence of two PF_6^- in the molecule balanced the cations as shown in Figure 4.20. This further supports the suggestion that pH might a key factor in coordinating behavior of this ligand.

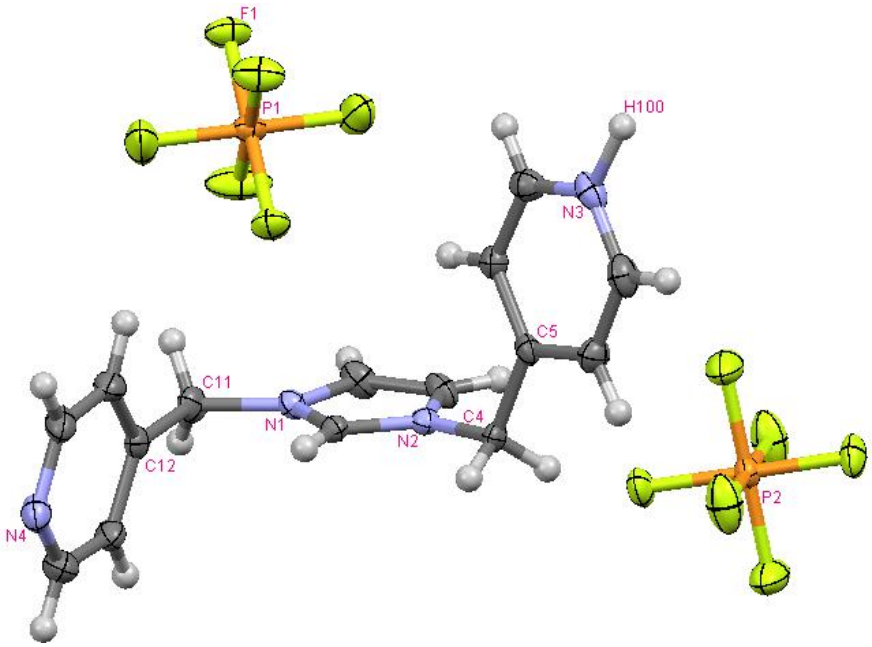


Figure 4.20: Crystal structure obtained from reaction of $PdCl_2$ and ligand **4.7**, thermal ellipsoids drawn at 50% probability level, showing protonation of one of the pyridine nitrogen.

These ligands, the bis picolyl imidazolium and the mixed pyridyl and nitrile imidazolium salts were obtained toward the tail end of the research studies, so there was insufficient time and resources to continue, otherwise with the right pH and other reaction conditions many polymers should be obtainable. In fact the bis picolyl containing ligand has potential to be a huge success in coordination chemistry due to the affinity of the amine towards transition metals. It can serve as a non-linear 4,4-bipyridine replacement, offering a slightly longer ligand with great potential.

4.4. Conclusion

Four pyridine functionalised imidazolium salts were synthesised and characterised. To the best of our knowledge bis(4-picolyl) imidazolium salt (**4.7**), mixed nitrile and pyridine functionalised imidazolium salts (**4.8**) and 1-methyl-3-(4-picolyl) imidazolium salt (**4.9**) were new. All the four ligands were characterised spectroscopically; however **4.6** and **4.8** were additionally analyzed using X-ray crystallography when their single crystals suitable for X-ray diffraction were successfully grown. These four ligands were successfully converted into Ag(I) NHC complexes by reacting each with Ag_2O. These four synthesised silver NHC complexes formed were characterised spectroscopically and by elemental analysis. Additionally **4.10**, **4.11**, and **4.13** were analyzed using X-ray crystallography. They all assume a near linear geometry around the Ag(I) ion assuming $Ag(NHC)_2^+$ type which are common with silver NHC complexes.

Spectroscopic data and elemental analysis of **4.12** confirmed the carbene complex formation, the data further indicates the coordination of another silver to the pyridine nitrogen forming our much targeted NHC complex containing polymer. Although this cannot be conclusive as no crystal structure has been obtained to confirm this.

Two interesting isostructural porous cationic coordination polymers of the imidazolium salts **4.7** with Ag(I) and Cu(I) (**4.14** and **4.15**) were obtained and structurally characterised. They revealed large, uniform, circular cavities with a well characterised structural motif.

4.5. Experimental

4.5.1. General considerations. Unless otherwise stated all reactions were performed under nitrogen using standard Schlenk line techniques. All reagents were unless otherwise stated were purchase from Aldrich and were used without further purification.

All infrared spectra (KBr disk, 400-4000 cm^{-1}) were recorded on Nicolet Avatar 360 FTIR spectrometer, spectra of liquids were measured as a neat film between two NaCl plates, those of the solid as KBr discs. Mass spectra were recorded on a thermo Finnigan LCQDUO mass spectrometer using ESI. The data were given in mass unit per charge

and the intensities of the signal were indicated in percent of the base ion. All TLCs were performed on aluminium supported silica plates (obtained commercially) and visualised by immersing the plate in iodine dip (iodine in silica). ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE/DPX 400(400 MHz) and or AVANCE/DRX 500 (500 MHz) in $CDCl_3$ and DMSO-d_6 with tetramethyl silane as external standard. Elemental analyses were carried out at the micro analytical laboratory at the University of Strathclyde, Glasgow. Single crystal measurements were made at 123K with graphite monochromated MoKα1 radiation (wavelength 0.71073 Å) on an Oxford Diffraction Gemini S diffractometer equipped with a CCD detector and a variable temperature device. Data for **4.13** was collected by the EPSRC Crystallographic Service at Southampton University on a Bruker Nonius FR591 rotating anode source using Mo K_α radiation, focussed by a 10cm confocal mirror and detected using an APEX II CCD camera. Crystals were mounted in oil on a fibre loop and data collected at 120 K. Initial atomic sites were located using direct methods. Remaining non-hydrogen atom sites were calculated using difference Fourier maps. Refinement of atomic co-ordinates and thermal parameters was to convergence and by full-least squares methods on F^2 within SHELX-97.[30] Where the quality of the data allowed, H-atoms bound to O or N were refined isotropically, all other H-atoms were placed in calculated positions and in a riding mode. Reported wR2 values are based on F^2 and all reflections, whilst reported R1 values are based on F and on observed reflections with $I>2\sigma(I)$

4.5. 2. 1-(Ethoxycarbonyl)pyridine (4.1)

Conc. Sulphuric acid (10 mL) was added to a suspension of isonicotinic acid (16g, 0.13 mol) in 70 mL of absolute ethanol. The mixture was refluxed for 28h, cooled to room temperature, 60mL of water was then added and excess ethanol removed under vacuum. NaOH was added to adjust the pH of the solution to basic, which gave an oil. The oil obtained was extracted with diethyl ether (5 x 80 mL), the diethyl ether extracts were dried over sodium sulphate, filtered and the solvent removed under vacuum to give a pale yellow oil (8.30 g, yield 42%). ^{1}H NMR (400MHz, Solvent $CDCl_3$) δ ppm: 1.38 (3H, t, $-CH_3$), 4.39 (2H, q, $-CH_2-$), 7.81 (d, -CH- of Py, 2H), 8.70 (d, -CH- of Py, 2H,).

4.5.3. 4-(Hydroxymethyl)pyridine (4.2)

Sodium borohydride (3.80g) was added in one portion to **4.1** (5.00g, 33.08mol) in 180 mL of ethanol. The mixture was refluxed for 3hrs cooled to room temperature and 100 mL of water was added. The ethanol was removed under vacuum and the resulting solution was extracted with diethyl ether (6 x 60 mL). The diethyl ether extracts were dried over sodium sulphate, filtered and the solvent was removed in vacuum to give an oil (3.13g, yield 87%).

^{1}H NMR (400MHz, Solvent $CDCl_3$) δ ppm: 4.51 (s, -CH_2-, 2H,), 7.28 (d, -CH- of Py, 2H), 8.41 (d, -CH- of Py, 2H). MS (ESI, methanol; m/z):110

4.5.4. 4-(Bromomethyl)pyridinium bromide (4.3)

2.50g (22.91 mol) of the alcohol **2** was dissolved in 30 mL of 48% HBr and refluxed for 12hrs. The water formed was removed under vacuum and the residue was treated with 20 mL of absolute ethanol at 5^{o}C and then filtered. White crystals were obtained, washed with 5 mL cold absolute ethanol to afford 3.82g, yield 70%.

^{1}H NMR (400 MHz, Solvent $CDCl_3$) δ ppm: 4.62 (2H, s, -CH_2-), 8.07 (d, -CH- of Py, 2H), 8.67 (d, -CH- of Py, 2H). MS (ESI, methanol; m/z):174.

4.5.5. Attempted synthesis of 1-(4-picolyl)imidazole (4.4)

NaH (0.085g, 1.89 mmol) and imidazole (0.129g, 1.89 mmol) were dissolved in 10 mL DMF and heated at 50^{o}C for 1 hr to give deprotonated imidazole. Separately 1g (46.89mmol) of 4-picolyl bromide hydrobromide and 1.15g (10.85mmol) of Na_2CO_3 were suspended in 10 mL water. The suspension formed was filtered and the filtrate extracted with diethyl ether. The diethyl ether extract was added drop wise to the deprotonated imidazole above on hot plate and the temperature raise to 100^{o}C. It was allowed to stay overnight and the solvent removed in vacuum. A dark coloured oil was obtained.

4.5.6. Synthesis of 1,3-bis(2-picolyl)imidazolium chloride (4.5)

2-Picolyl chloride hydrochloride (2.03g, 12.38 mmol), imidazole (0.27g, 4.03 mmol) and $NaHCO_3$ (1.01g) were taken up in 20 mL ethanol. The mixture was refluxed for 2

days under nitrogen atmosphere. The solution was cooled and the solvent removed under vacuum. The residue was taken up in DCM and dried over sodium sulphate, it was filtered and the DCM was removed to give a dark oil. The oil was triturated with THF to give a white precipitate. Yield 1.36g, (76.70%)

^{1}H NMR (400 MHz, Solvent $CDCl_3$) δ ppm: 5.69 (4H, s, -CH_2-), 7.29 (m, CH of Py, 2H), 7.56 (d, -CH- of imid. 2H), 7.77 (m, -CH- of Py, 4H), 8.85 (d, -CH- of Py, 2H), 11.09 (s, -NCHN- of imid. 1H). $^{13}C\{^{1}H\}$ NMR (400 MHz, Solvent $CDCl_3$) δ ppm : 151.90 (C_{Py}), 149.38 (C_{Py}), 137.95 (NCN), 137.34 (C_{Py}), 123.87 (C_{Py}), 123.64 (C_{Py}), 121.65 ppm (C_{imid}), 53.75 (C of CH_2). MS (ESI, methanol; m/z): 251 $[M]^+$. Anal. Calculated for $C_{15}H_{14}N_4Cl_1.H_2O$: C, 59.10; H, 5.62; N, 18.39. Found: C, 59.27; H, 4.86; N, 18.52.

4.5.7. Attempted synthesis of 1,3-bis(4-picolyl)imidazolium bromide (4.6)

4-picolyl bromide hydrobromide (2.03g, 8.03 mmol), imidazole (0.27g, 4.03 mmol) and $NaHCO_3$ (1.01g) were taken up in 20 mL ethanol. The mixture was refluxed for 2 days under a nitrogen atmosphere. The solution was cooled and the solvent evaporated under vacuum. The residue was taken up in DCM and dried over sodium sulphate. The DCM was removed and the product treated with THF to form a dark brown oil.

4.5.8. Synthesis of bis 1,3-(4-picolyl)imidazolium chloride (4.6)

A solution of 4- picolyl chloride hydrochloride (2.00g, 12.00 mmol) was neutralized with a saturated solution of sodium hydroxide. The liberated 4-picolyl chloride was extracted into diethyl ether (20 x 3), separated and the ether layer dried using sodium sulphate and filtered. The filtrate was concentrated to 20 mL and 5ml DMF was added and the ether removed under reduced pressure. The solution was transferred to a 20 mL pressure tube and imidazole (0.40g, 5.89 mmol) and sodium hydride 60% (0.24g, 6.00mmol) were added, the mixture was heated at 110^{o}C for 48 hours. A dark brown oily product was obtained by addition of diethyl ether. It was recrystallised by diffusion of diethyl ether into a methanol solution. Yield (0.97g, 56%). ^{1}H NMR (DMSO-d6) δ ppm: 9.44 (s -NCHN- of imid., 1H), 8.74 (d, -CH- of Py 4H), 7.91 (d, -CH- of imid.,

2H), 7.55 (d, -CH- of Py, 4H), 5.63 (s, -CH_2- of imid,. 4H). $^{13}C\{^1H\}$ NMR (DMSO-d6) δ ppm: 147.98 (C_{Py}), 146.44 (C_{Py}), 137.88 (C_{imid}) 123.47 (C_{imid}), 123.41 (C_{Py}), 50.41 (C of –CH_2-) MS (ESI, methanol; m/z): 251 $[M]^+$.

4.5.9. Synthesis of bis 1,3-bis(4-picolyl)imidazolium hexafluorophosphate (4.7)

4.6 (1.00g, 3.50 mmol) was dissolved in the minimum amount water and a saturated solution of NH_4PF_6 was added to give a brownish precipitate. The mixture was stirred for 2 hours, filtered, washed with diethyl ether and dried under vacuum. Yield 1.30g (93.80%)

Anal. Calculated for $C_{15}H_{15}N_4Cl_1.1½$ (PF_6): C, 38.41; H, 3.23; N, 11.95. Found: C, 38.32; H, 3.43; N, 11.04.

4.5.10. Synthesis of 1-(4-cyanophenyl)-3-(4-picolyl)imidazolium chloride (4.8)

A solution of 4-picolyl chloride hydrochloride (2.00g, 12.00 mmol) was neutralized using saturated solution of sodium hydroxide. The liberated 4 – picolyl chloride was extracted into diethyl ether (20 x 3). The ether layer was separated, dried with sodium sulphate and filtered. The solution was concentrated to about 10 mL, THF 10 mL was added, then ether was removed under reduced pressure and the 4-cyano phenyl imidazole (2.03g, 12.00 mmol) in 5 mL THF was added. The solution was transferred to a 20ml pressure tube and heated at 100^oC for 48 hours. The dark brown precipitate formed was filtered, washed with ether and dried. It was recrystallised from methanol – diethyl ether diffusion method. Yield 1.5g (42.15%)

^1H NMR (DMSO-d6) δ ppm: 10.41 (s –NCN- of imid., 1H), 8.69 (d, -CH- of Py 2H), 8.53 (s, -CH- of imid., 1H), 8.22 (d, -CH- of Ph, 2H), 8.14 (s, -CH- of imid,. 1H), 8.09 (d, -CH- of Ph, 2H), 7.58 (d, -CH-, of Py, 2H), 5.68 (s, - CH_2-, 2H). $^{13}C\{^1H\}$ NMR (DMSO-d6) δ ppm: 149.09 (C_{Py}), 144.34 (C_{Py}), 137.99 ($C_{imid.}$), 137.10 (C_{Ph}), 134.33 (C_{Ph}), 123.72 (C_{Py}), 123.21 (C_{Py}), 122.66 (C), 121.51 (C), 117.76 (C), 112.30 (C), 51.14 (C of CH_2). MS (ESI, methanol; m/z): 261 $[M]^+$. IR (KBr, cm^{-1}) 2238 (νCN).

4.5.11. Synthesis of 1-(4-cyanophenyl)-3-(4-picolyl)imidazolium hexafluorophosphate

1-(4-Cyanophenyl)-3-(4-picolyl)imidazolium chloride (1.5g, 5.07 mmol) was dissolved in the minimum amount water and concentrated solution of NH_4PF_6 was added to give a brown precipitate. The mixture was stirred for 2 more hours, filtered, washed with diethyl ether and dried under vacuum. Yield 1.9g (92.30%)

Anal. Calculated for $C_{16}H_{13}N_4.1½PF_6$: C, 40.12; H, 2.74; N, 11.70%. Found: C, 40.83; H, 2.89; N, 10.35%.

4.5.12. Synthesis of 1-methyl-3-(4-picolyl)imidazolium chloride (4.9)

4-Picolyl chloride hydrochloride (1.30g, 7.93 mmol) was neutralized using a saturated solution of sodium carbonate. The liberated 4-picolyl chloride was extracted into diethyl ether (3 x 40 mL) at 0^oC, dried with anhydrous sodium sulphate and filtered. The filtrate was concentrated to 80 mL, 1- Methyl imidazole (0.656g, 8 mmol) in methanol (80 mL) at 0^oC was added. Diethyl ether was removed under pressure and the solution stirred at room temperature overnight. The solvent was taken off under reduce pressure to give a dark oil (1.13g, 73% yield)

^1H NMR (400 MHz, Solvent $CDCl_3$) δ ppm: 3.46 (s, $-CH_3$, 3H), 4.41 (s, $-CH_2-$ 2H), 7.19 (d, -CH- of Py 2H,), 8.23 (d, -CH- of Py 2H), 7.37 (s, -NCHN- of imid. 1H), 6.79 (s, -CH- of imid. 1H), 6.85 (s, -CH- of imid. 1H). MS (ESI, methanol; m/z) = 174$[M]^+$.

4.5.13. Synthesis of [Ag (3-methyl-1-picolylimidazol-2-ylidine)$_2$]chloride. (4.10)

A mixture of **4.9** (1.03g, 4.93 mmol) and silver (I) oxide (0.395g, 1.70 mmol) was taken up in 50 mL DCM and the mixture stirred at room temperature for 5hrs. The solution was filtered through celite to give a dark brown solution. The solvent was removed under vacuum to yield 0.82g. It was recrystallised from DCM – diethyl ether by vapour diffusion. ^1H NMR (400 MHz, Solvent $CDCl_3$) δ ppm: 5.34 (s, $-CH_2-$ 4H), 7.85 (d, -CH- of Py 4H), 8.63 (d, -CH- of Py 4H), 6.88 (s, -CH- of imid. 2H), 7.45 (s, -CH- of imid. 4H). MS (ESI, methanol; m/z): 489 $[M]^+$

4.5.14. Synthesis of [Ag-((2–picolyl)$_2$ imidazol-2-yledene)$_2$ chloride (4.11)

A mixture of **4.5 (**1.255g, 4.35 mmol) and silver (I) oxide (0.505g, 2.19 mmol) was taken up in 25mL DCM and the mixture stirred for 5 hrs at room temperature. The solution was filtered through celite, reduced in volume and precipitated by diethyl ether to give white crystals, which were recrystallised from DCM – diethyl ether by vapour diffusion. (0.33g, 23% yield).

^{1}H NMR (400 MHz, Solvent $CDCl_3$) δ ppm: 5.39 (s, -CH_2- 4H), 7.22 (s, -CH- of imid 2H), 7.29 (m, -CH- of Py, 4H), 7.72 (m, -CH- of Py 2H), 8.58 (m, -CH- of Py 2H). ^{13}C{^{1}H} NMR (400 MHz, Solvent $CDCl_3$) δ ppm : 154.32 (C_{Py}), 149.47 (C_{Py}), 138.98 (C_{Py}), 123.05 (C_{Py}), 123.12 (C_{Py}), 121.63 (C_{imid}), 56.83 (C of CH_2). MS (ESI, methanol; m/z): 609 $[M]^+$. Anal. Calculated for $Ag_2C_{30}H_{28}N_8Cl_5$: C, 40.30; H, 3.16; N, 12.54%. Found: C, 40.30; H, 2.73; N, 12.55%.

4.5.15. Synthesis of [Ag-((4-picolyl)$_2$imidazol-2-yledene)$_2$ hexafluorophosphate (4.12)

4.7 (0.91g 2.23 mmol) and NEt_3 (0.22g, 2.23 mmol) were dissolved in 20 mL acetonitrile and Ag_2O (0.52g, 2.23mmol) was added. The mixture was refluxed for 2 days. It was filtered through celite to remove unreacted silver oxide. The solvent was removed to give a white precipitate which was recrystallised from acetonitrile - diethyl ether by vapour diffusion. The crystals were not of suitable quality for X-ray diffraction Yield, 0.52g (59.90%)

^{1}H NMR (DMSO-d_6) δ ppm: 8.51 (d, -CH- of Py 4H), 7.65 (d, -CH- of imid., 2H), 7.15 (d, -CH- of Py, 4H), 5.42 (s, -CH_2- of imid,. 4H). ^{13}C{^{1}H} NMR (DMSO-d6) δ ppm: 150.14 (C_{Py}), 146.43 (C_{Py}), 123.21 (C_{imid}), 122.03 (C_{Py}), 52.84 (C of –CH_2-) MS (ESI, methanol; m/z): 607 $[M]^+$, 715$[M]^+$ Anal. Calculated for $Ag_2C_{15}H_{14}N_4.PF_6$: C, 29.47; H, 2.31; N, 9.17%. Found: C, 28.80; H, 2.17; N, 9.34%.

4.5.16. Synthesis of [Ag-bis-(1-(4-Cyanophenyl)-3-(4-picolyl)imidazol-2-yledene)$_2$] hexafluorophosphate (4.13)

1-(4-Cyanophenyl)-3-(4-methylpyridine)imidazolium hexafluorophosphate (**4.8**) (1g, 2.46 mmol) was dissolved in 20 mL acetonitrile, Ag_2O (0.57g, 2.46 mmol) was added and the mixture refluxed overnight. It was filtered through celite to remove any unreacted silver oxide. The solvent was removed to yield a white precipitate which was recrystallised from acetonitrile - diethyl ether by vapour diffusion. Yield, 0.52g (63.41%)

^{1}H NMR (DMSO-d6) δ ppm: 8.54 (d, -CH- of Py 4H), 8.04 (s, -CH- of imid., 2H), 7.95 (br, -CH- of Ph, 8H), 7.83 (s, -CH- of imid,. 2H), 7.18 (d, -CH- of Ph, 4H), 5.48 (s, -CH_2- 4H). MS (ESI, methanol; m/z): 627 $[M]^+$, 734 $[M]^{2+}$. IR (KBr, cm^{-1}) 2228 (νCN). Anal. Calculated for $Ag_4C_{64}H_{48}N_{16}.4PF_6$; C 37.43; H 2.36; N 10.92%. Found C 37.61, H 2.59, N 11.10%.

4.5.17. Synthesis of [Ag-((4–picolyl)$_2$ imidazolium)$_2$] hexafluorophosphate (4.14)

4.7 (1g, 2.26 mmol) was dissolved in 20 mL acetonitrile, Ag_2O (0.52g, 2.26 mmol) was added and the mixture refluxed overnight. It was filtered through celite to remove unreacted silver oxide. The solvent was removed under vacuum to yield a white precipitate which was recrystallised from acetonitrile - diethyl ether by vapour diffusion. Yield 0.28g (62.22%)

^{1}H NMR (DMSO-d_6) δ ppm: 9.40 (s -NCHN- of imid., 1H), 8.65 (d, -CH- of Py 4H), 7.89 (d, -CH- of imid., 2H), 7.35 (d, -CH- of Py, 4H), 5.53 (s, -CH_2- of imid,. 4H). MS (ESI, methanol; m/z): 251 $[M]^+$.

4.5.18. Synthesis of [Cu-((4–picolyl)$_2$ imidazolium)$_2$] hexafluorophosphate (4.15)

4.7 (1g, 2.26 mmol) was dissolved in 20 mL acetonitrile, Cu_2O (0.28g, 2.26 mmol) was added and the mixture refluxed overnight. It was filtered through celite to remove unreacted copper(I) oxide. The solvent was removed in vacuum which gave a light green

precipitate which was recrystallised from acetonitrile - diethyl ether by vapour diffusion. Yield 0.31g, (68.89%)

^{1}H NMR (DMSO-d^{6}) δ ppm: 9.39 (s -NCHN- of imid., 1H), 9.20 (br, -CH- of Py 4H), 7.89 (d, -CH- of imid., 2H), 7.49 (d, -CH- of Py, 4H), 5.49 (s, -CH_2- of imid,. 4H). MS (ESI, methanol; m/z): 251 $[M]^{+}$. Anal. Calculated for $Cu_1C_{30}H_{30}N_8.3PF_6$: C, 35.97; H, 3.02; N, 11.19. Found: C, 35.87; H, 2.86; N, 11.29.

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CHAPTER 5

Carboxylate Functionalised Imidazolium Salts, N-Heterocyclic Carbenes and Coordination Polymers

5.1. Introduction

As explained in Chapter 2, metal organic frameworks are coordination polymers containing organic ligands connected by metal ions or their clusters resulting in crystalline coordination compounds. They have attracted a large amount of interest in recent years,[1, 2] due to their outstanding properties in a range of applications including gas storage, gas purification, catalysis, drug delivery, sensing and luminescence.[3, 4] These are due to their exceptional porosity and large internal surface area, their stability and their ability to be tuned chemically.[4] The majority of the MOFs reported utilise organic linkers with N[5] and O[6] donor groups, among which the carboxylates give more robust frameworks.

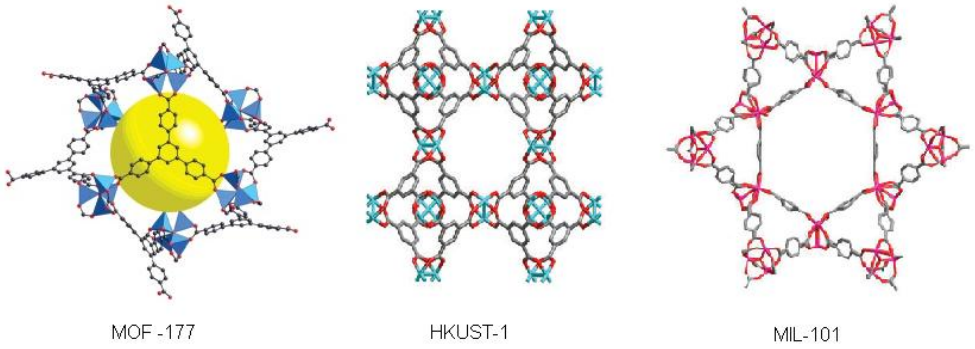


Figure 5.1: Examples of some popular MOFs[7]

Huge amounts of research have been reported on the synthesis and potential applications of these carboxylate containing MOFs.[6, 8, 9] In fact most of the MOFs reported with some exceptional qualities (like good stability, high porosity, wider surface area) e.g MOF-5,[10] MOF-177 ,[11] HKUST-1,[12] MIL-101[13] (Figure 5.1) are of the carboxylate systems. This might be due to the ability of carboxylates to combine with metals having a wide range of coordination tendencies to provide frameworks with a wide range of topologies. In addition the M - O bond in the carboxylate MOFs are strong therefore making them more robust and stable enough in some cases to withstand solvent removal without the frameworks collapsing. Carboxylate MOFs utilise a wide range of transition metals with

varying number of functional site as connectors, but d- block metals ions such as Cu(II), Zn(II), Co(II), Cr(III) are more common.

Another set of metals that have found a wide range of applications as connectors in MOF synthesis are the lanthanides, despite the concern about their high coordination numbers being a hindrance to controlling their coordination geometry. Many lanthanide carboxylate MOFs have been reported[14, 15] and this area is still receiving significant attention.[16-19] This might be due to their special coordination properties and good chemical and physical properties, which lead them to have promising applications in luminescence, catalysis, gas storage and separations, and magnetic applications.[17, 20]

In 2003 Wong et al[20] reported the synthesis and characterisation of two isostructural lanthanide containing MOFs. They were prepared from the reaction of $Ln(NO_3)_3$ (Ln = La or Er) and 1,4-phenylenediacetic acid, using a hydrothermal synthetic method, and were observed to be a good materials for CO_2 adsorption. Qiu et al[21] synthesised and characterised a series of lanthanide carboxylate MOFs of the general formula $[Ln(BTC)(DMF)_2.H_2O]$ (BTC = benzene tricarboxylate, Ln = Tb, Dy, Ho, Er, Tm, Yb) from reaction of the corresponding hydrated lanthanides nitrates and H_3BTC under mild conditions. They were reported to have both luminescence and magnetic properties. A more detailed overview of lanthanide MOFs and their luminescence applications is given in a recent review by Chen et al.[19]

One of the major features of MOFs are their tunable abilities. Therefore MOF frameworks topologies can be designed and synthesised by using specific types of starting organic linkers and metal connectors. To achieve this many organic ligands with pre-determined features suitable for specific frameworks have been prepared, and more recently their synthesis and their corresponding MOFs have been reviewed.[22] One such example is the design of imidazolium salts and their use as building block for MOF synthesis. Not many reports exist in the literature on the use of imidazolium salts in MOF construction most probably due to their cationic nature. Only a few lanthanide containing MOFs utilising imidazolium salt as organic linkers exist. One such example

is the report by Zhang et al.[23] They reported the synthesis and characterisation of 1,3-(dicarboxymethyl)-imidazolium bromides (Figure 5.2) and their corresponding lanthanide frameworks.

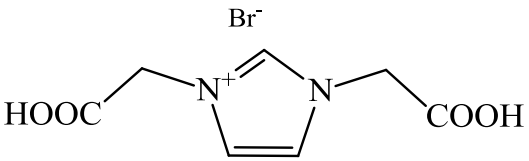


Figure 5.2: Dicarboxylic acid functionalised imidazolium salt

MOFs can also be tuned by modifying the existing framework, for instance by post synthetic modification,[24] affording the tendencies to convert the already prepared imidazolium incorporated MOFs into carbene complex containing MOFs. This may produce carbene containing materials with potential to be an exciting MOF with a wide range of applications from the luminescence, gas storage to heterogeneous catalysis.

Our interest is to synthesise new carboxylate functionalised imidazolium salts, to assemble them into MOFs using a range of transition metals and explore the possibilities of deprotonating the imidazolium salts and treating them with metal sources to form NHC complexes. The conversion of the formed NHC into MOFs will be attempted, and if successful will afford a new class of NHC containing MOFs. Alternatively, the synthesised imidazolium salt will be used to construct MOFs, then post synthetic modification will be attempted to allow its conversion into NHC complex containing MOFs. Here we report the synthesis and characterisation of some bis and mono carboxylic imidazolium salts, and an attempt to assemble them into MOFs by pre- or post-synthetic modifications. Reaction of 1,3-bis(4-carboxyphenyl) imidazolium salts with hydrated lanthanide chloride result in isostructural lanthanides MOFs which were explored for possible conversion to NHC containing materials. We also report synthesis and characterisation of a rhodium bis-NHC complex with one of the mono carboxylate imidazolium salts without protecting the carboxylic acid group, which is very rare.

5.2. Results and discussion

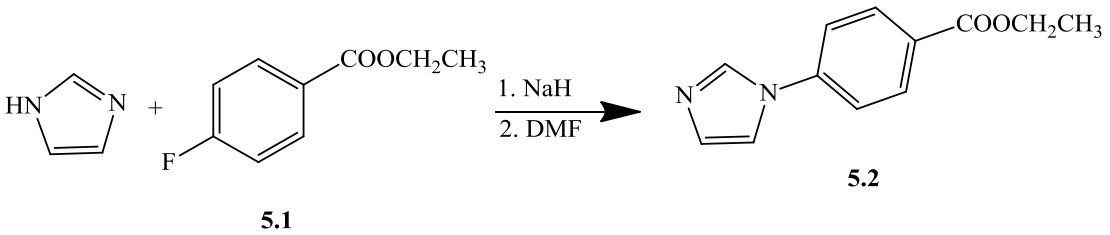
5.2.1. Ligand synthesis

5.2.1.1. Biscarboxylate bisimidazolium salts

An initial attempt to prepare carboxylic acid functionalised imidazolium salts by direct treatment of fluorobenzoic acid with imidazole in the presence of a base proved very challenging, although this method works easily for nitrile functionalised salts as described in Chapter 2. This might be due to the preference of the fluorobenzoic acid to react through the carboxylate end of the molecule rather than expected N-arylation through fluorine substitution. However, they are easily prepared from hydrolysis of ester or nitrile functionalised imidazolium salts which are easier and more straightforward to synthesise.

The biscarboxy bisimidazolium salt (**5.5**) was synthesised following a lengthy synthetic procedure which requires esterification and then hydrolysis in multiple steps; Step 1 involves conversion of 4-fluorobenzoic acid to 4-fluoro ethylbenzoate (**5.1**) according to a procedure used by Ferri *et al*[25] and described in Chapter 4. The disappearance of the carboxylate proton signal in the ^{1}H NMR, and the subsequent appearance of ethyl signals indicates the total conversion to the ester (**5.1**), which was further supported by good agreement in mass spectroscopic data.

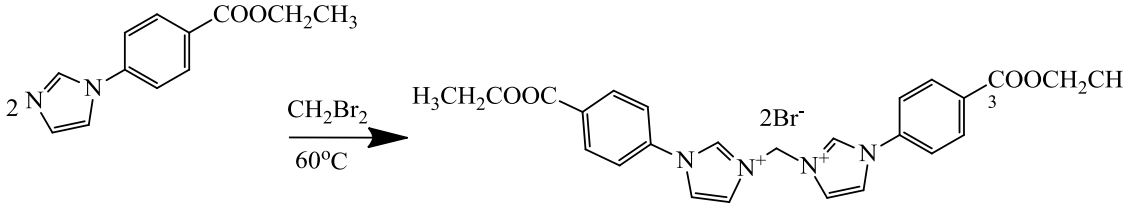
In step 2, the 4-fluoroethyl benzoate was treated with imidazole in DMF using sodium hydride as deprotonating agent, according to Scheme 5.1. The reaction refluxed for five hours and stirred at room temperature over night to afford 1-(4-ethylbenzoate) imidazole, **5.2,** in high yield. This was also characterised using NMR and mass spectrometry, seven expected peaks in the ^{1}H NMR were observed, which were attributed to the seven different proton environments of the imidazole, phenyl and ethyl groups, and was also supported by the presence of a dominant ion in the mass spectrum at m/z = 217.



5.1 **5.2**

Scheme 5.1: Synthesis of ethyl 4-(1*H*-imidazol-1-yl)benzoate

The third step involves the coupling of the ethyl 4-(1*H*-imidazol-1-yl) benzoate, **5.2**, using dibromomethane as the source of a methylene bridge yielding the 3,3'-methylenebis(1-(4-(ethoxycarbonyl)phenyl)-1H-imidazol-3-ium) salt (**5.3**). It was prepared by heating the ethylbenzoate imidazole in excess dibromomethane for 2 days at 60^{o}C (Scheme 5.2). This was characterised spectroscopically and by elemental analysis.



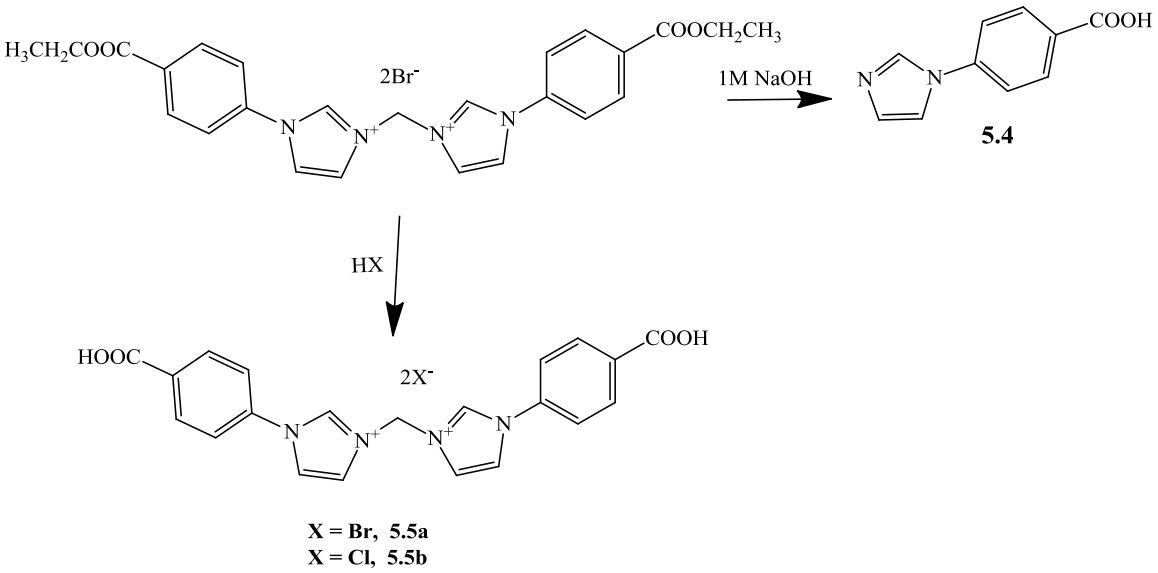
5.3

Scheme 5.2: Synthesis of 3,3'-methylenebis(1-(4-(ethoxycarbonyl)phenyl)-1H-imidazol-3-ium) salts (**5.3**)

In the ^{1}H NMR spectrum a new peak was observed at 6.92 ppm in addition to those observed in **5.2**. This new peak was attributed to the two methylene protons between the imidazolium rings, furthermore the NC(H)N peak of the imidazole has shifted significantly downfield to 10.39 ppm indicating the formation of **5.3**. Also the number and position of ^{13}C NMR signals is as expected for our targeted compound with the new methylelene carbon appearing at 59 ppm. The mass spectrum shows the presence of dominant ion peak at m/z = 445. It was further confirmed by good agreement between expected and observed values of the elemental analysis.

In the final step, the bisimidazolium ester (**5.3**) was refluxed overnight in 37% HCl or 48% HBr, to give a white powder of 3,3'-methylenebis(1-(4-carboxyphenyl)-1H-

imidazol-3-ium) salt, **5.5**, in high yield (Scheme 5.3). This was also confirmed spectroscopically and by elemental analysis.



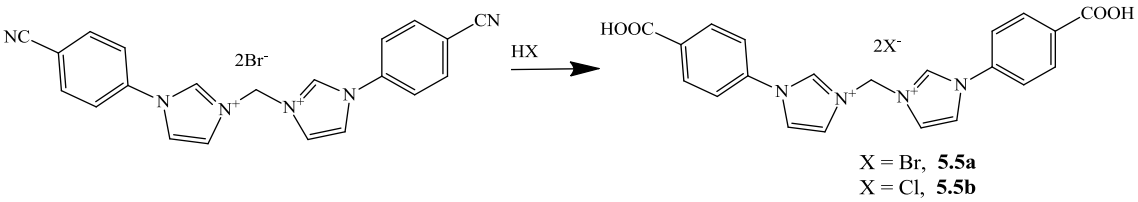
Scheme 5.3: Synthesis of 3,3'-methylenebis(1-(4-carboxyphenyl)-imidazolium) salt

The disappearance of the peaks at 1.36 ppm and 4.40 ppm in the ^{1}H NMR spectra assigned to the ethyl protons and the appearance of the carboxylic proton signal at ca 13.46 ppm in addition to other peaks in **5.3** indicates the complete conversion of the ester to our desired biscarboxy bisimidazolium salt (**5.5**). This was also supported by the disappearance of peaks at 14.60 ppm and 61.88 ppm from the ^{13}C spectrum of **5.3**, attributed to the loss of the ethyl carbons. The appearance of a dominant ion at m/z = 389 is also consistent with the formulation of our targeted biscarboxy bisimidazolium salt (**5.5**). Furthermore, the IR spectra of **5.5** displays the strong carboxylic acid stretching vibration peaks at 1710 cm^{-1} and 1726 cm^{-1}. Elemental analysis shows a very good agreement between observed and expected values for **5.5**, confirming its synthesis.

While the acid hydrolysis was effective, when basic hydrolysis was attempted using 1M NaOH, it was observed that the bisimidazolium bridge is cleaved to re-generate the monocarboxylic monoimidazole (**5.4**). This indicates that the methylene bridge is

sensitive towards bases, and consequently mild basic conditions may be necessary. Spectroscopically, the peaks attributed to the methyl spacer between the imidazolium rings have disappeared and the NC(H)N peak has shifted back up-field to 8.01 ppm. The conversion of the ester to the carboxylic acid was confirmed by removal of the ethyl peaks at 1.36 ppm and 4.40 ppm.

Alternatively, the biscarboxy bisimidazolium salt (**5.5**) was prepared according to Scheme 5.4, by acid hydrolysis of biscyanophenyl bisimidazolium salt (**3.2**) prepared and reported in Chapter 3. The bisnitrile bisimidazolium salt was refluxed in 48% HBr to give a white precipitate of the biscarboxy bisimidazolium bromide, in good yield. When 37% HCl was used in place of HBr the chloride salt was obtained. This is a quicker and more efficient route than the ester route described above.



Scheme 5.4: Hydrolysis of the bisnitrile imidazolium salt to biscarboxylate bisimidazolium salts

The anion was easily exchanged for BF_4^- or PF_6^- by dropwise addition of HBF_4 or a solution of NH_4PF_6 respectively to the imidazolium salt solution in water with mild heating. The exchange was to improve solubility, giving more scope to use other solvents which may not dissolve the bromide or chloride salts, in particular acetonitrile. The conversion of the nitrile to the carboxylic functionality was also confirmed spectroscopically, using elemental analysis and in addition by X-ray crystallographic analysis. The spectroscopic data and the elemental analysis results were the same as reported above for samples obtained by hydrolysis of the corresponding ester. Single crystals suitable for X-ray diffraction were obtained when a hot solution of **5.5a** in water

was allowed to slowly cool to room temperature. It crystallised in triclinic space group P-1, and the crystallographic data are presented in Table 5.1.

Table 5.1: Selected crystallographic data for **5.5a** and **5.5b**

Compound	**5.5a**	**5.5b**
Chemical Formula	$C_{21}H_{17}N_4O_5Br_1$	$C_{21}H_{18}N_4O_4Cl_2$
Formula weight	487.31	461
Colour	colourless	Colourless
Lattice Type	Triclinic	monoclinic
Spacegroup	P -1	C2/c
a/Å	7.6829(4)	11.5000(5)
b/ Å	8.4326(3)	8.1850(5)
c/ Å	16.2098(6)	22.826(5)
α/°	82.114(3)	90
β/°	79.489(4)	99.141(5)
γ/°	77.010(4)	90
V/ Å	1001.05(7)	2121.3(17)
Z	2	4
T/K	123(2)	293(2)
μ/mm^{-1}	2.097	0.099
F000	496	832
No of reflections collected	10993	4432
No of independent reflections/(R_{int})	4855/0.0311	2062/0.028
No of observed Reflection (I>2 σ(I))	4063	1849
No of parameters Refined	284	158
R1 (obsd/all)	0.038/0.051	0.07/0.082
wR2 (obsd/all)	0.083/0.089	0.218/0.223
Largest difference in peak and hole $eÅ^{-3}$	1.035, -0.419	0.978, -0.472

The asymmetric unit was found to contain one cationic biscarboxyphenyl bisimidazolium salt (**5.5a**), one Br^- ion and one H_2O molecule as shown in Figure 5.3. The carboxylate imidazolium cations assume an almost linear geometry, unlike its nitrile starting material which is more bent or V-shaped (discused in Chapter 3).

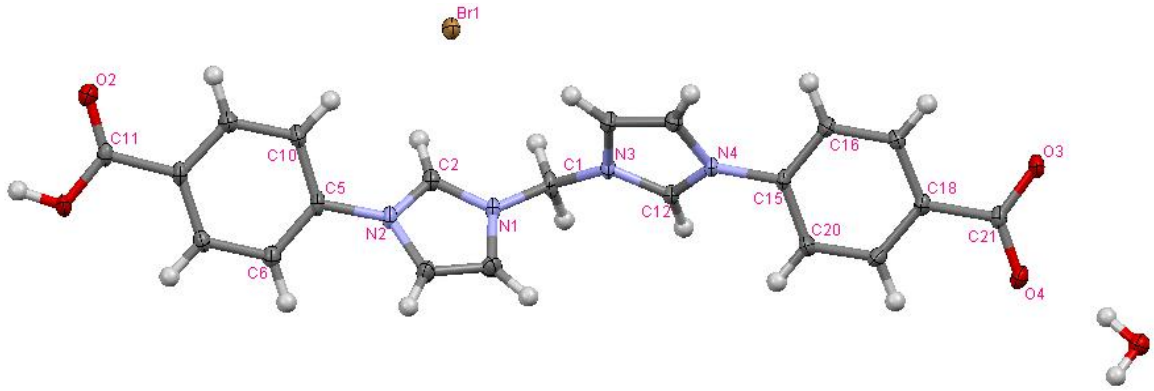


Figure 5.3: X-ray crystal structure of **5.5a,** thermal ellipsoids drawn at 50% probability level. Some selected bond lengths (Å) and bond angles (°). N(1) – C(1) 1.460(3), N(3) – C(1) 1.457(3), N(2) – C(5) 1.442(3), C(11) – O1 1.298(3), C(11) – O(2) 1.221(3), C(21) – O(4) 1.251(3), C(21) – O(3) 1.266(3), C(11) – C(8) 1.508(3), C(2) – N(2) – C(5) 124.400(2), N(1) – C(1) – N(3) 110.100(2), O(1) – C(11) – O(2) 125.100(2).

Each carboxyphenyl ring is slightly twisted in respect to their respective imidazolium ring with torsion angles in the region of -35.49 to -37.60^o. Surprisingly the structure shows one of the the carboxylic acid groups to be deprotonated (Figure 5.3) despite the use of concentrated acid (48% HBr) in the hydrolysis, and this explains why only one Br^- anion was present in the structure. The cationic ligand molecules are packed in an almost parallel arrangement when viewed along the crystallographic axis a, as shown in Figure 5.4a. There is a phenyl – phenyl separation of 3.313 Å between neighbouring molecules suggesting a significant $\pi - \pi$ interaction.

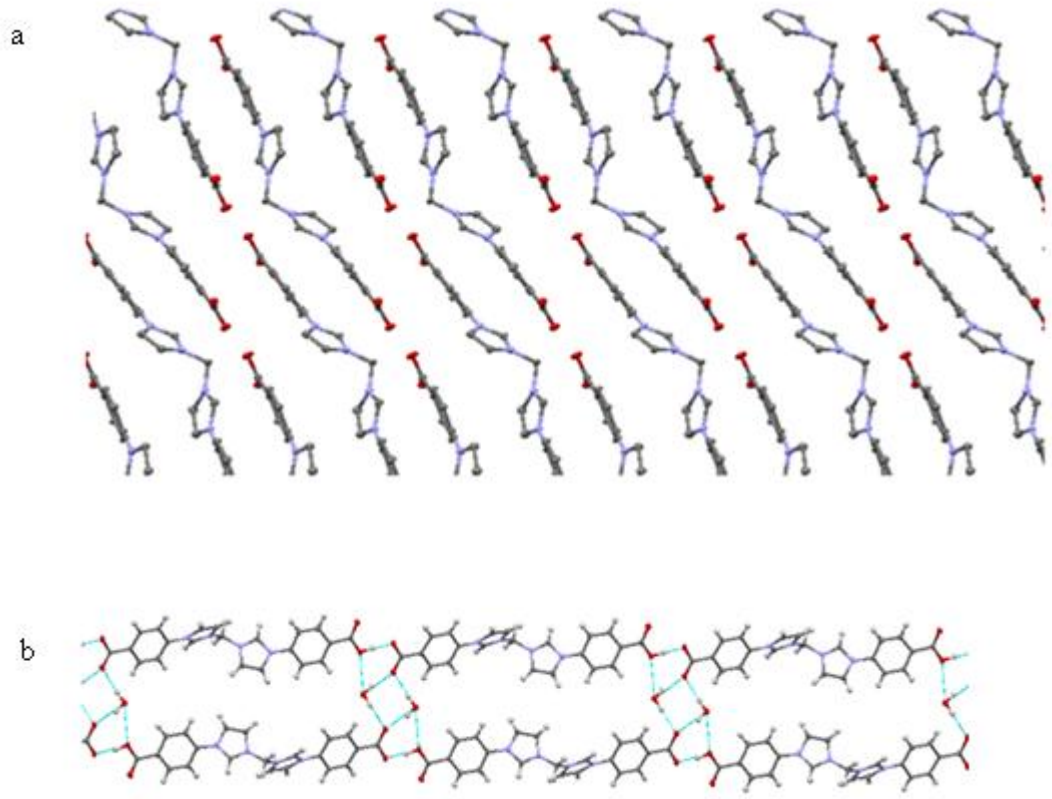


Figure 5.4: Extended crystal structure of **5.5a**, a) viewed along the crystallographic a-axis b) showing hydrogen bonding of the water molecule and acid groups

The water molecule present in the crystal structure interacts with three different cationic molecules, which results in the formation of an extended polymeric structure (Figure 5.4b). The two H_2O molecules serve as a bridge, and as a result the structure assumed a 2D network, having an average O----H bond distance of 1.992 Å.

There are also significant contacts between the bromide and hydrogens of three different molecules as shown in Figure 5.3. These molecules are held by an interaction between hydrogens of C(3), C(12) and C(20) from the first molecule, on the second molecule the bromine is in contact with the hydrogen on C(13) and C(10) while the third molecule is in contact through C(4) hydrogen (Figure 5.5). The Br----H distances are in the range of 2.706 – 2.988 Å which are within the van der Waals radius for Br and H.[26] Furthermore

an interaction was observed between the bromine and the imidazolium π- system with an average distance of 3.4075 Å.

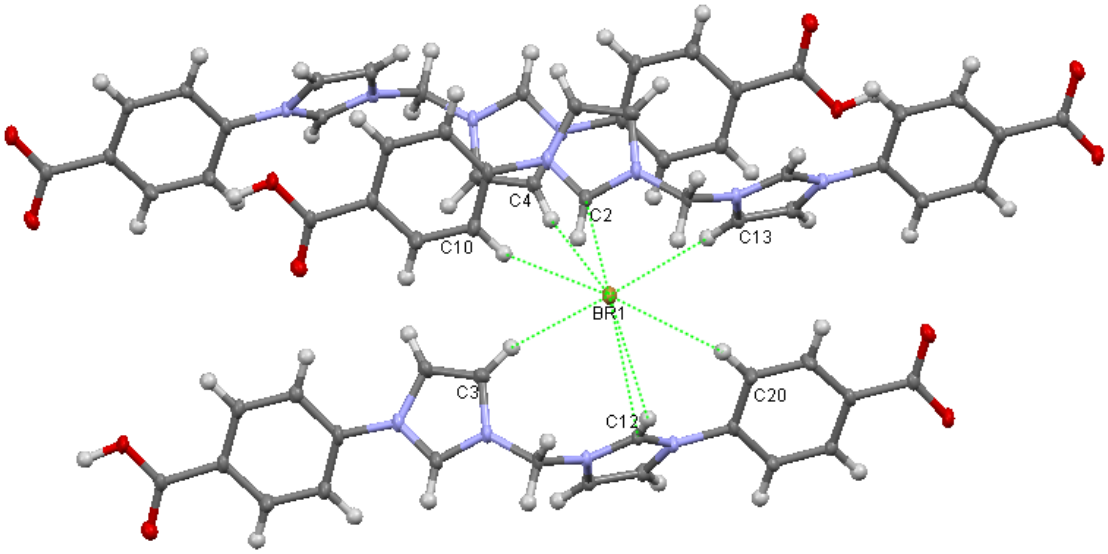
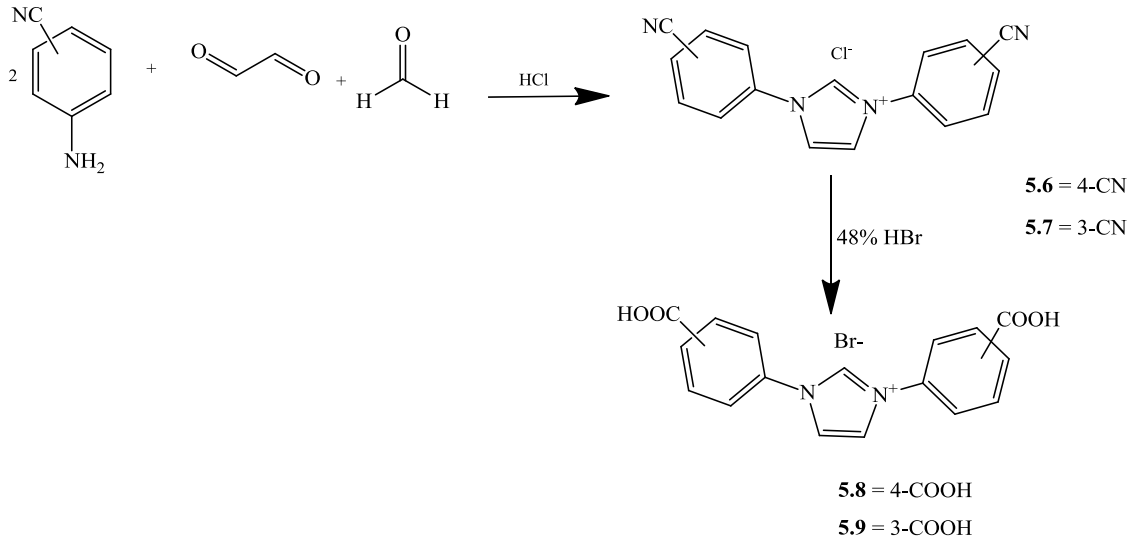


Figure 5.5: Crystal structure of **5.5a,** showing the coordination environment of Br^- ion.

5.2.1.2. Dicarboxylic monoimidazolium salts

The synthesis of the dicarboxylic acid functionalised mono imidazolium salts were also conducted in two stages similar to the bisimidazolium salts explained above. The first stage was the synthesis of bisnitrile imidazolium salts and the second stage involves conversion of the nitrile functionalities into carboxylic acid functionality by acid hydrolysis.

In the first stage, the bisnitrile functionalised imidazolium salt **5.6** was synthesised using one pot synthetic method according to Scheme 5.5. 4-Cyanoaniline, glyoxal and paraformaldehyde were suspended in toluene in the presence of hydrochloric acid and refluxed overnight. The Water produced was removed using a Dean-Stark apparatus. An oil was obtained, which was triturated with acetonitrile to yield **5.6** as a dark brown powder in good yield. The bis 3-cyanophenyl imidazolium salt (**5.7**) was prepared by a similar method, from 3-cyanoaniline. Both compounds were characterised spectroscopically.



Scheme 5.5: Step wise synthesis of biscarboxyphenyl imidazolium salts

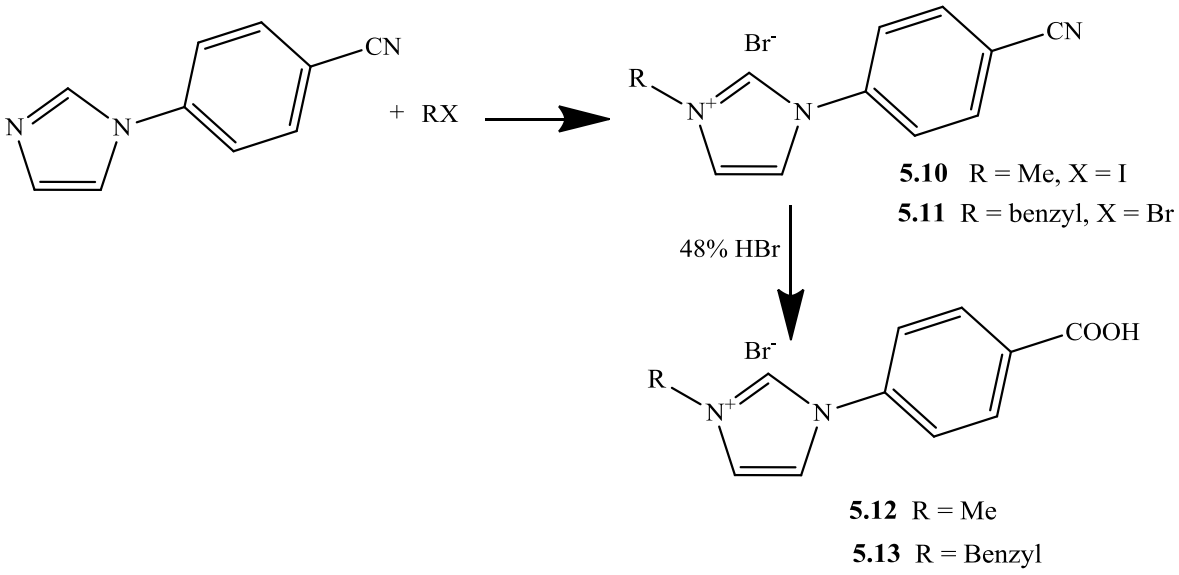
^{1}H NMR indicates the appearance of imidazolium NC(H)N proton at 10.74 ppm and 10.89 ppm for **5.6** and **5.7** respectively which is within expected region for this type of proton in imidazolium salts. As expected the other signals are in agreement with the expected positions and number of protons for both **5.6** and **5.7**. Furthermore in the ^{13}C NMR the seven peaks for **5.6** and the ten peaks for **5.7** are in good agreement with the expected values for these compounds. The ions in the mass spectrum (M^+) at m/z = 271 for both **5.6** and **5.7** further supported the synthesis of these imidazolium salt precursors. An IR spectrum indicates characteristic peaks for CN stretching at 2223 cm^{-1} and 2233 cm^{-1} for **5.6** and **5.7** respectively. These characterisation data were enough to convince us that the product may be good enough for the next stage of the synthesis.

In the second stage the synthesised imidazolium salts **5.6** and **5.7** were converted to bis carboxylic acid functionalised imidazolium salts **5.8** and **5.9** respectively by refluxing them in 48% HBr overnight. This resulted in the formation of **5.8** and **5.9** in good yield as brown powders according to Scheme 5.5. The powder was filtered washed several times with ethyl acetate and then with diethyl ether, they were confirmed to be the targeted imidazolium salts **5.8** and **5.9** spectroscopically. The appearance of a new broad peak in the ^{1}H NMR at 13.44 ppm indicates the conversion of the nitrile functionality to carboxylic acid group, also the nitrile (CN) carbon signals in the ^{13}C NMR spectrum

have significantly shifted downfield to ca 166 ppm in both salts indicating the CN groups have been completely converted to COOH. The conversion was further confirmed by complete disappearance of the CN stretching peak around 2230 cm^{-1} in the IR spectra, suggesting that there are no traces of the nitrile left, and the appearance of a new strong peak at around 1716 cm^{-1} and 1726 cm^{-1} for **5.8** and **5.9** respectively arising from the carboxylate groups. Although elemental analysis did not give a good agreement between expected and observed values there is an indication of the target compound.

5.2.1.3. Monocarboxylate functionalised imidazolium salts

Two additional mono-imidazolium carboxylates, **5.12** and **5.13**, were synthesised, also through hydrolysis of nitrile functionalised imidazolium salts **5.10** and **5.11** respectively. The nitriles functionalised were first synthesised through alkylation of cyanophenyl imidazole with methyl iodide and benzyl bromide to give **5.10** and **5.11** respectively (Scheme 5.6).



Scheme 5.6: Step wise synthesis of mono carboxylate imidazolium salts

Cyanophenyl imidazole and an equivalent amount of methyl iodide were refluxed in DCM for five hours according to Scheme 5.6 to give **5.10** in high yield while changing

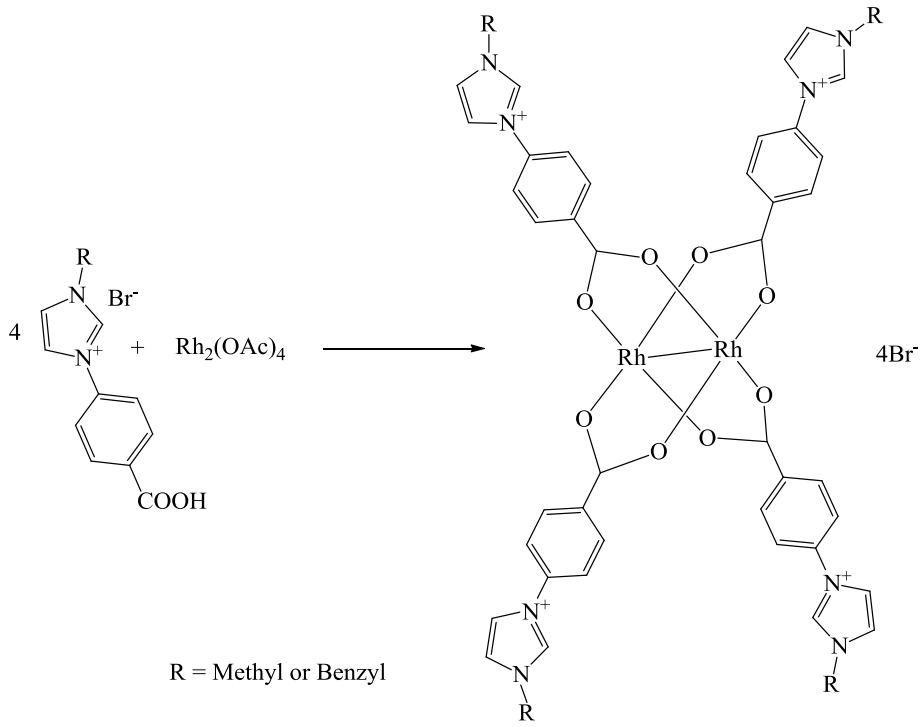
methyl iodide with benzyl bromide under the same reaction conditions afforded **5.11** in good yield. The appearance of the expected six signals in the ^{1}H NMR indicates the formation of **5.10** while the signals obtained for **5.11** are in agreement with its expected formulation. Furthermore the mass spectra for both compounds are in agreement with the expected results.

These synthesised imidazolium salts (**5.10** and **5.11**) were reflux in 48% HBr overnight to give **5.12** and **5.13** respectively in good yield. These conversions were confirmed by combinations of spectroscopic and elemental analytical data. A new peak in the ^{1}H NMR spectra at 13.39 ppm for both **5.12** and **5.13** was attributed to COO(H) proton , also the peaks attributed to the nitrile carbon in the ^{13}C NMR have shifted significantly to 166 ppm which is a region for carboxylate carbon atoms observed for other compounds[27] including those explained in this chapter. The IR peaks for CN have completely disappeared and are being replaced by carboxylic acid peaks at around 1720 cm^{-1} for both **5.12** and **5.13**.

5.2.2. Synthesis of metal complexes

5.2.2.1. Rhodium NHC complex

Having successfully synthesised these monocarboxylate imidazolium salts (**5.12** and **5.13**), we attempted to prepare dirhodium species of the type $[Rh_2L_4]^{4+}$ (where L is **5.12** or **5.13**) by reaction with $[Rh_2(OAc)_4]$ according to Scheme 5.7. Compounds of this type have, in recent years, attracted significant interest due to their application in homogenous catalysis and also their biological applications.[28, 29] They are commonly prepared from dirhodium(II) tetraacetate, by replacing the acetate with the corresponding carboxylic ligands. Our targeted compounds were intended to be prepared by reacting four equivalents of the ligand (**5.12** or **5.13**) with the dirhodium(II) tetraacetate, hoping all the acetate will be replace with the ligand (Scheme 5.7).



Scheme 5.7: Attempted synthesis of the dirhodium species of **5.12** and **5.13**

In addition we also attempted to prepare three more compounds of the type $[Rh_2(OOCCH_3)_3L_1]^+$, $[Rh_2(OOCCH_3)_2L_2]^{2+}$ and $[Rh_2(OOCCH_3)_1L_3]^{3+}$ by substituting one, two and three acetates respectively. The reaction was carried out in methanol at reflux temperature, but the desired four substituted was not obtained. However, there is some evidence for the formation of the mono substituted ($[Rh_2(OOCCH_3)_3L_1]^+$) for the methyl substituted ligand **5.12** (Figure 5.6), this was indicated by the appearance of a significant peak at m/z = 584 and this was consistent with the formulation and isotope pattern for $[Rh_2(OOCCH_3)_3L_1]^+$. But this was only observed in solution as the elemental analysis did not give a good agreement and growing single crystal suitable for X-ray diffraction was not successful.

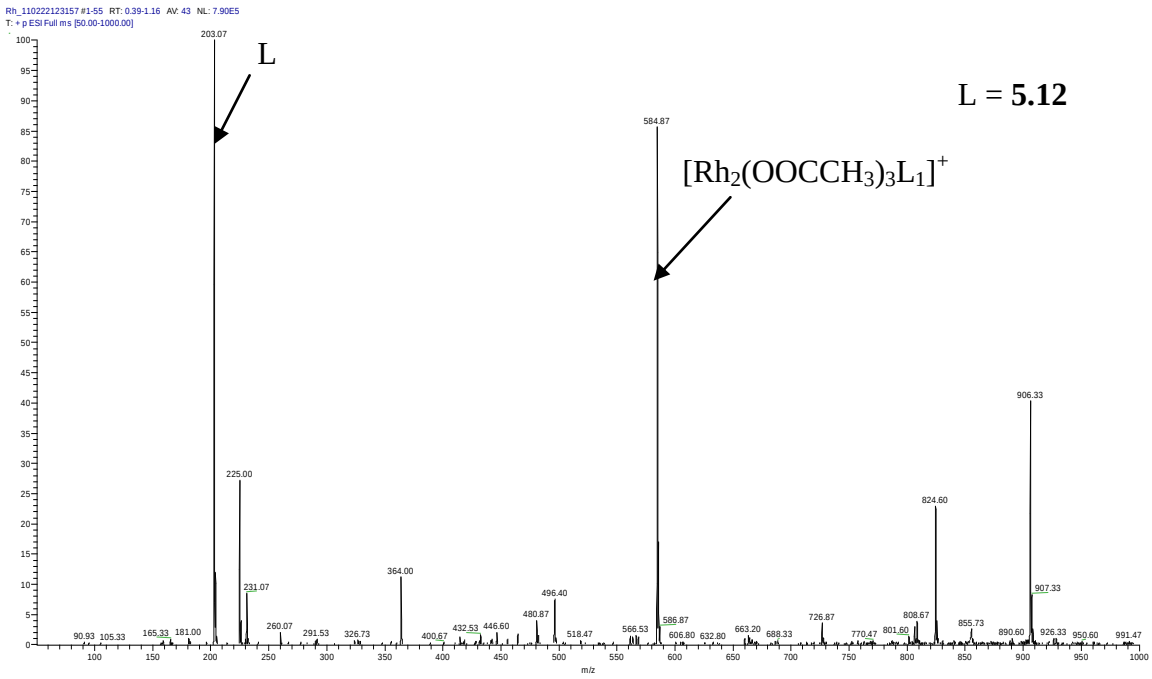


Figure 5.6: Mass spectrum of dirhodium complexes of **5.12**

Reaction of the benzyl substituted imidazolium carboxylate with the dirhodium tetracetate shows evidence for the formation of three species, the mono, di and tri substituted dimers in the mass spectrum (Figure 5.7). The peak at $[M]^+$ m/z = 660 is consistent with the formulation and isotope pattern for $[Rh_2(OOCCH_3)_3L_1]^+$ (L = **5.12**). The ion (M^{2+}) at m/z = 440 is in agreement with the formulation and isotope pattern of the di-substituted $[Rh_2(OOCCH_3)_2L_2]^{2+}$ while the ion (M^{3+}) m/z = 366 is in agreement with the tri-substituted $[Rh_2(OOCCH_3)_1L_3]^{3+}$. All these species are only observed in solution as evident from the mass spectral peaks, but the elemental analysis of solids obtained from the reaction fails to represent any of the three. This is probably due to the presence of these species as impure product. Attempts to grow crystals also was not successful as such the characterisation of these complexes were not conclusive.

Changing the solvent to acetonitrile or a mixture of both also did not improve the process, and once more the targeted tetra-substituted $[Rh_2L_4]^{4+}$ (where L is **5.12** or **5.13**) was not satisfactorily obtained, as there was no evidence from the mass spectrum or NMR to suggest its formation. This might be due to problem of non attainment of the

required temperature to push the reaction to completion or the cationic nature of the ligand which makes the carboxylate less basic.

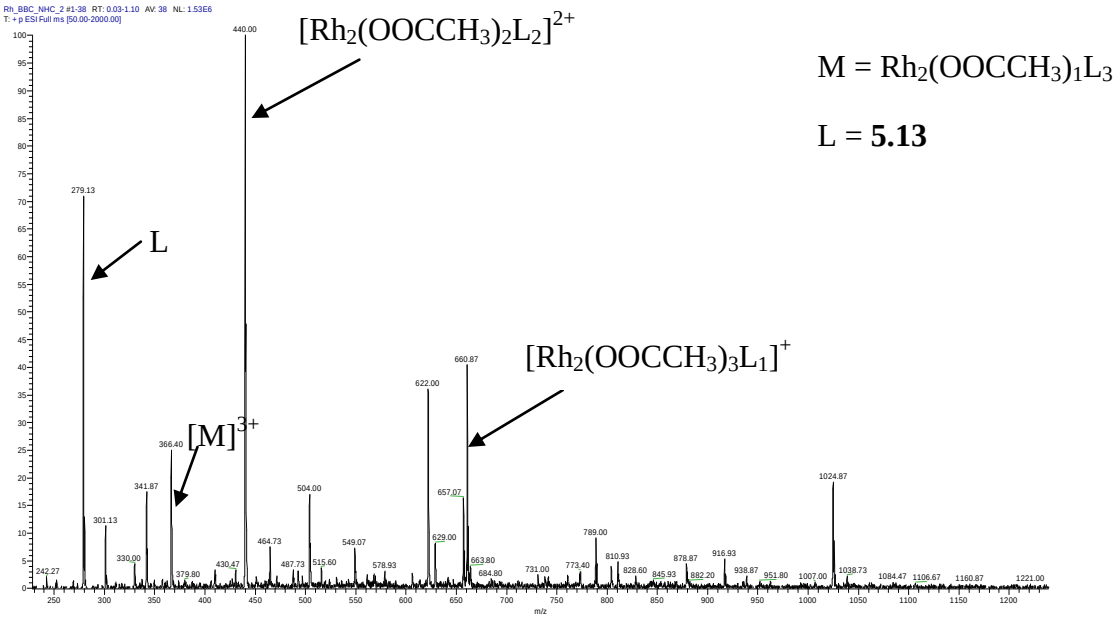
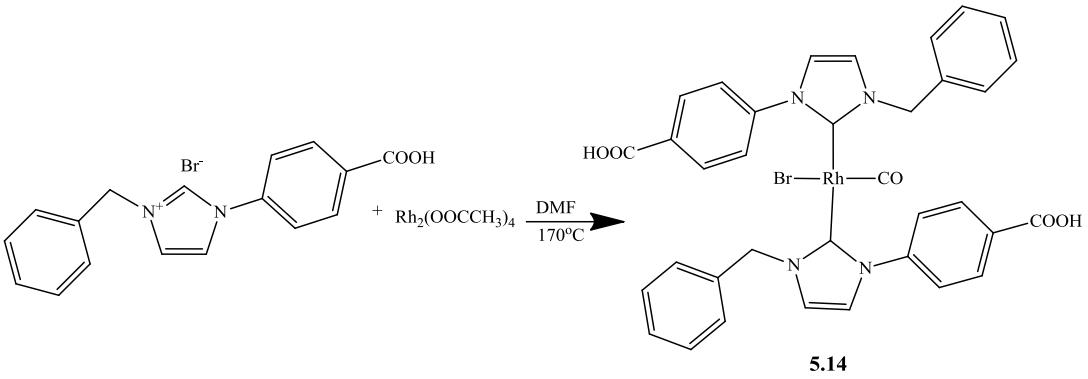


Figure 5.7: Mass spectrum of dirhodium complexes of **5.13**

However adopting a solvothermal synthetic method with ligand **5.13** afforded a rather different and interesting carbene complex **5.14** (Scheme 5.8). The process involves taking dirhodium(II) tetraacetate, 3-benzyl-1-(4-carboxyphenyl)-1H-imidazol-3-ium bromide (**5.13**), in a 20 mL pressure tube with Teflon cap using DMF as a solvent and heating at 170^{o}C in an oven overnight. The reaction was cooled to room temperature and the solvent was allowed to evaporate yielding yellow needle like crystals of **5.14**. Although ^{1}H and ^{13}C NMR spectra did not give a clear view of the structure formed, surprisingly a strong peak in the IR at 1950 cm^{-1} indicates the presence of carbonyl stretching frequency. This suggests the product may contain carbonyl bonded to the rhodium cation. In addition the new compound, **5.14** was also characterised by mass spectrometry, elemental and X-ray crystallographic analysis.



5.14

Scheme 5.8: Synthesis rhodium(I) bis NHC complex, **5.14**

The actual mechanism of the reaction is not known, but it is clearly a very complex sequence of events precipitated by the harsh reaction conditions (170 °C, sealed tube). The formally Rh(II) centres in the dimer are reduced to Rh(I), and it is likely that the DMF is oxidised and thus acts as the source of the carbonyl ligand. It is probable that the acetate anions released from the dimer are able to deprotonate the imidazolium salt *in situ* to afford the carbene complex. Similar types of carbonyl carbene complexes were previous reported although with non carboxylate imidazolium precursors.[30-32]

The presence of carbonyl in the new compound **5.14**, was further supported by ion in the mass spectrum at m/z = 687, which represent two ligand molecule one Rhodium atom and one carbonyl molecule. Furthermore the appearance of a new peak downfield at around 162 ppm in the ^{13}C NMR further supports the presence of the carbonyl. As is common with carbene complexes, the NC(H)N signal in the ^{1}H NMR spectra was lost indicating the formation of the carbene ligand and it subsequently became coordinated to rhodium atom present in the reaction medium to give the NHC complex, **5.14**. In addition, the methylene protons which were a singlet in the imidazolium salt were observed to be diastereotopic in the new complex, splitting into doublet of doublets at ca 5.59 ppm and 5.98 ppm which is common with these types of compounds,[33] in this case suggesting hindered rotation of the benzyl groups. Surprisingly the signal attributed to the COO(H) is still intact in the ^{1}H NMR spectra, although it shifted upfield from 13.40 ppm in the ligand to 12.92 ppm in the new carbene complex, indicating that the carboxylic acid group have not been coordinated to rhodium despite the harsh reaction

condition of the solvothermal process. Furthermore the presence of carboxylate stretching vibration at 1710 cm^{-1} in addition to the carbonyl stretching frequency at 1950 cm^{-1} in the IR spectrum also confirmed non coordination of the carboxylate group. Agreement between the expected and observed values in the elemental analysis also re-affirms the formation of **5.14.** This is an exciting development, because most carboxylic acid functionalised NHC complexes are synthesised by protecting the carboxylic acid group prior to synthesis, for instance, by converting them to esters which are later hydrolysed back to the acid. This was demonstrated by reports of Yaghi et al[34] and Wang et al.[35] They are mainly protected to avoid the formation of other unwanted side reactions due to their strong coordinating abilities. This proposal was confirmed by X-ray structural analysis.

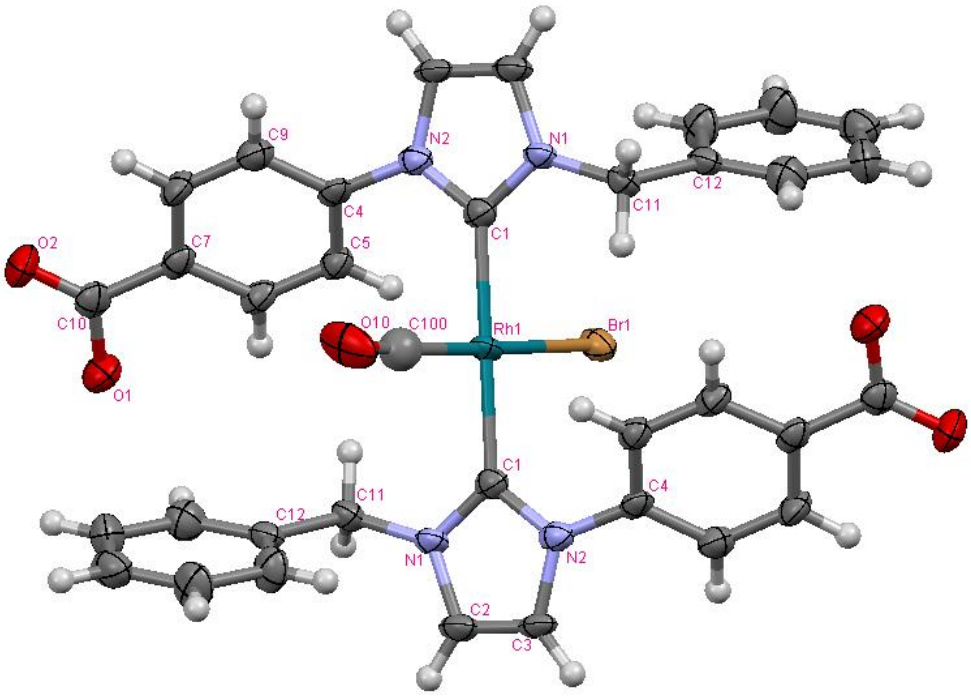


Figure 5.8: X-ray crystal structure of **5.14,** thermal ellipsoids drawn at 50% probability level. Some selected bond lengths (Å) and bond angles (°). Rh(1) – C(1) 2.052(4), Rh(1) – Br(1) 2.4210(19), Rh(1) – C(100) 1.873(17), C(100) – O(10) 1.167(18), C(1) – Rh(1) – C(1) 180.0, Br(1) – Rh(1) – C(100) 178.9(5), C(1) – Rh(1) – Br(1) 90.16(13), C(1) – Rh(1) – C(100) 90.7(5).

The compound was further analysed by X-ray crystallography when single crystals suitable for X-ray diffraction were obtained from evaporation of the DMF solution of **5.14** in a fume hood. The compound crystallised in triclinic space group P-1 and the crystallographic information is given in Table 5.2. The molecular structure shows **5.14** to have two carbene ligands coordinated trans across the rhodium atom, in addition the rhodium is also bonded to one bromine atom and one carbonyl group also coordinated in mutally trans-positions around a square planar rhodium centre as shown in Figure 5.8. The rhodium carbene carbon bond length (Rh(1) – C(1)) is 2.052(4) Å, this bond distance is within the range for similar rhodium carbene complexes reported.[36] The C(1)–Rh(1)–C(1) bond angle is crystallographically imposed at 180° indicating the linearity of the carbene-rhodium-carbene bond as expected for $[M(NHC)_2]^+$ complexes.[36] The bromine and the carbonyl bonded to the rhodium atom are disordered over two sites and are also arranged trans to each other with a Br – Rh – CO bond angle of 178.9(5)°. The Rh(1) – Br(1) bond length of 2.4210(19) Å and the Rh(1) – C(100) bond length is 1.873(17) Å, this rhodium carbonyl bond length is consistent with similar NHC carbonyl complexes.[36, 37] The benzyl rings on the carbene ligand are directed on opposite direction towards their corresponding carboxyphenyl rings, this might be to avoid steric hindrance. The carboxyphenyl rings were observed to be twisted with respect to their corresponding imidazolium rings with a torsion angle of C(1) – N(2) – C(4) – C(5) at 43.2(7)°.

Table 5.2: Selected crystallographic data for **5.14**, **LaMOF** and **CeMOF**

Compound	**5.14**	**LaMOF**	**CeMOF**
Chemical Formula	$Rh_1C_{41}H_{28}N_6O_7Br_1$	$La_1C_{34}H_{22}N_4O_{10}Br_2$	$Ce_1C_{34}H_{22}N_4O_8Br_2$
Formula weight	897.5	865.38	866
Colour	yellow	colourless	Pale yellow
Lattice Type	Triclinic	monoclinic	Monoclinic
Space group	P -1	P 2_1/n	P 2_1/n
a/Å	7.4004(8)	8.839 (5)	8.8096 (2)
b/ Å	10.6279(10)	20.566 (5)	20.5311(3)
c/ Å	12.8316(16)	17.201 (5)	17.1752(3)
α/°	84.325(9)	90	90
β/°	76.832(10)	97.299(5)	97.161(2)
γ/°	88.514(8)	90	90
V/ Å	977.86(19)	3102 (2)	3082.26 (10)
Z	1	4	4
T/K	293(2)	293(2)	293(2)
μ/mm^{-1}	1.516	2.735	4.363
F000	450	1704	1944
No of reflns collected	8926	14718	17043
No of independent reflections/ (R_{int})	4451/0.0611	6636/0.04	6911/0.0257
No of Reflection observed (I>2 σ(I))	3092	5384	6253
No of parameters	281	434	454
R1 (obsd/all)	0.066/0.105	0.072/0.091	0.061/0.068
wR2 (obsd/all)	0.127/0.1486	0.178/0.191	0.16/0.164
Largest difference in peak and hole $eÅ^{-3}$	0.924, -0.679	3.641, -4.773	3.1174, -5.567

The molecules were packed with no identifiable short range packing pattern observed, however there were hydrogen bond formed between the carboxylate oxygen and hydrogens from the imidazole ring through C(3), benzyl ring through C(15) and carboxyphenyl ring through C(9) as shown in Figure 5.9.

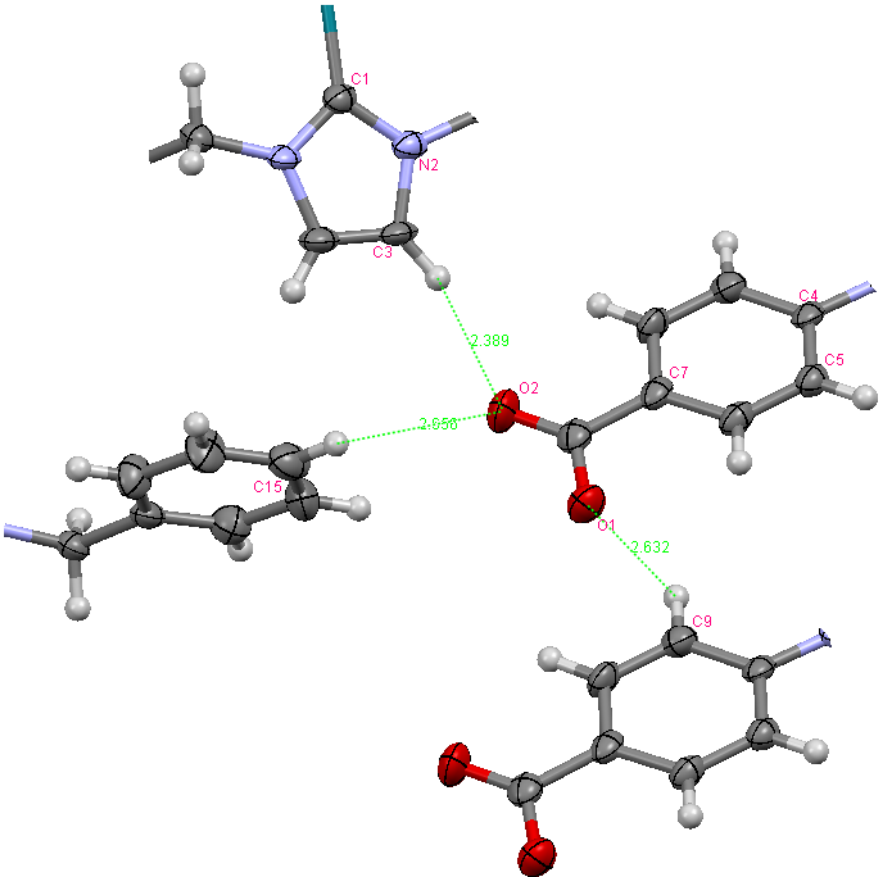


Figure 5.9: Crystal structure of **5.14,** thermal ellipsoids drawn at 50% probability level, showing hydrogen bonding (C-O---H)

5.2.2.2. Lanthanide metal organic framework synthesis

Many methods are available for metal organic framework synthesis as highlighted in Chapter 2, but the most common for carboxylate functionalised linkers is the solvothermal synthetic method (also known as hydrothermal when water is used as a solvent). Reaction of the hydrated lanthanide(III) chloride with 0.3M NaOH and each of the three bicarboxylate imidazolium salts (**5.5**, **5.8** and **5.9**) using solvothermal process utilising DMF as a solvent results in the precipitation of the corresponding products. The

products obtained were insoluble in DMF, water or any common organic solvent, and as such crystallisation became impossible. Although IR spectroscopy shows the absence of the v(COOH) absorption band around 1700 cm^{-1} indicating the possibility of the formation of our targeted lanthanide carboxylate MOFs, unfortunately further characterisation proved to be very challenging as such we were unable to fully ascertain the formation or otherwise of the targeted MOFs. Changing the method to hydrothermal synthesis gave similar results for ligand **5.5** and **5.9**. However reacting the hydrated lanthanide(III) chloride (Ln = La, Ce) with imidazolium salt **5.8** utilising same hydrothermal synthesis using a mixed water – ethanol solvent resulted in the formation of shiny looking needle-like crystals for both La(III) and Ce(III), which were also insoluble in common solvents. These crystals were characterised by IR, elemental analysis and by X-ray crystallographic analysis.

The IR absorption patterns for these two compounds were similar and both show the absence of the strong band around 1700 cm^{-1}, indicating the absence of free carboxylate. They also show an absorption band around 1550 cm^{-1} which is characteristic of coordinated carboxylate, further supporting the coordination of the lanthanide to this ligand. Single crystals suitable for X-ray diffraction were directly obtained as the product of the reaction. The diffraction results show the two compounds to be isostructral and crystallographically isomorphous, and the La(III) complex will be discussed in more detailed as representative of both. It crystallises in monoclinic space group P $2_1/n$, and the crystal data are given in Table 5.2.

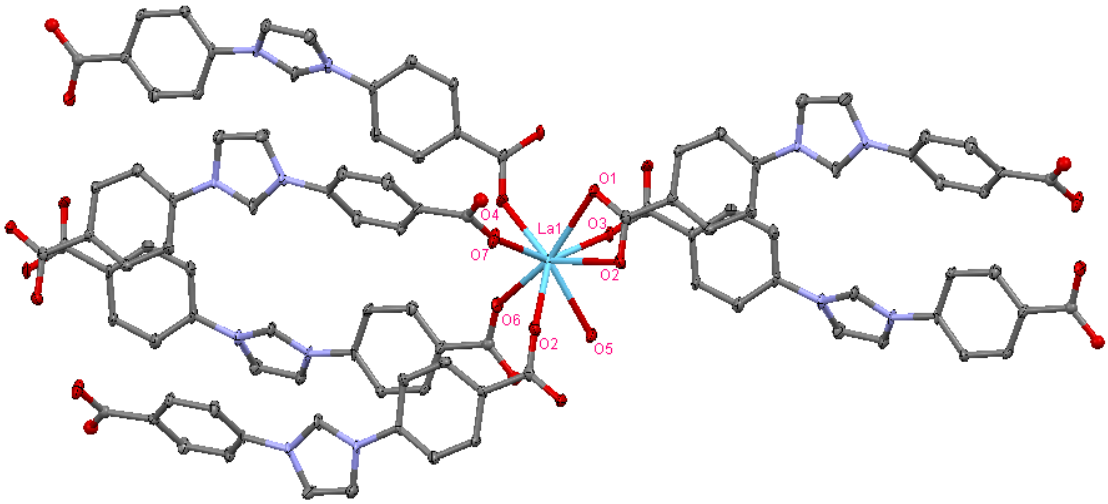
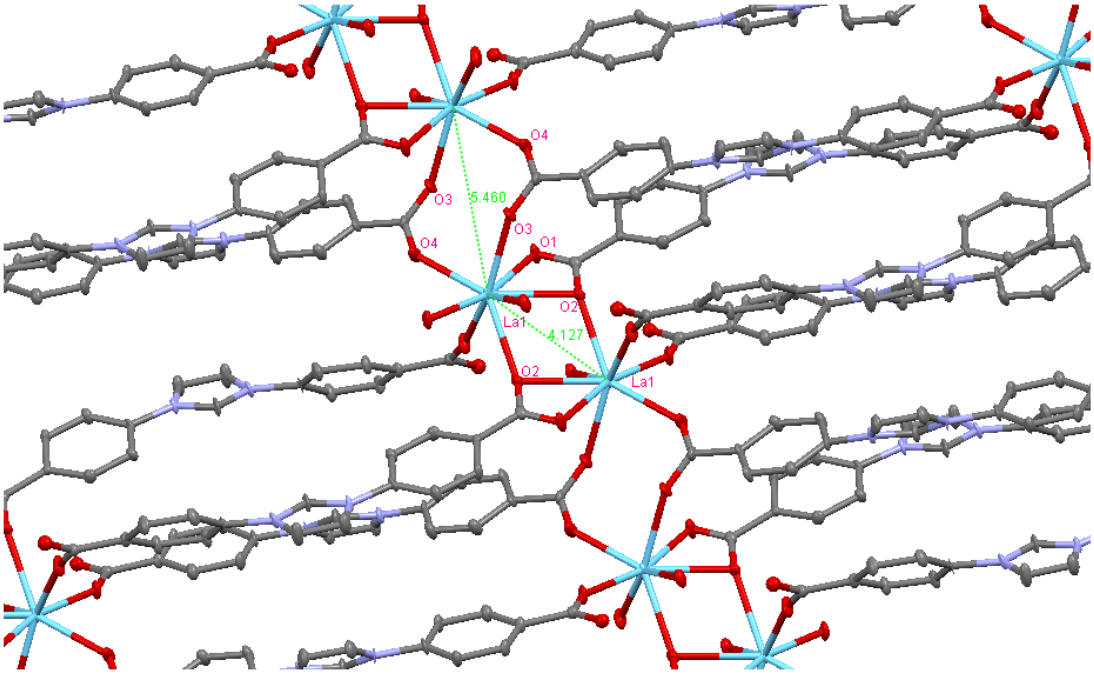


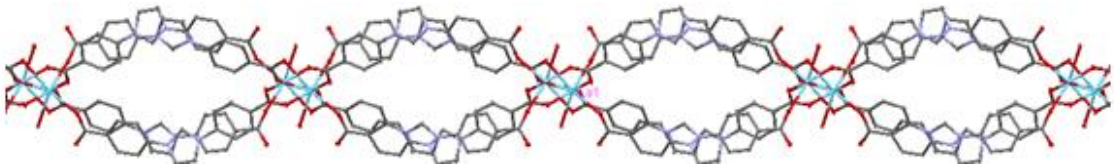
Figure 5.10: Crystal structure of **LaMOF,** thermal ellipsoids drawn at 50% probability level, showing the coordination environment around the La(III) ion.

The asymmetric unit contains one La(III) ion, two ligand molecules, one coordinated water molecule, one Br^- anion and a crystallographically disordered Br^-/Cl^- ion. An expanded structure shows the La^{3+} ion to be coordinated to eight oxygen atoms from six carboxylate ions and one water molecule (Figure 5.10). One of the ligands is coordinated in a bidentate mode via its two O (O(1) and O(2)) atoms while the other five ligands are monodentate, coordinated by only one of their COO^- oxygen atoms. The La – O bond lengths are in the range of 2.365(6) Å – 2.671(6) Å which are within the range of reported La – O bond length of similar lanthanide carboxylate complexes.[14, 15, 38] It is observed that the La - O carboxylate bond length of the bidentate chelating ligand are at the high end of the range (2.671(5) and 2.5943(6)) while the non chelating carboxylate ligands are at the lower end. The lanthanide atoms are interconnected through two different types of COO^- bridging as shown in Figure 5.11a giving an infinite chain having two La ---- La non bonding distances, a shorter distance of 4.127 Å between the La ions bridging through the bidentate chelating COO^- to give a four-membered La_2O_2 ring, and a longer La----La distance of 5.460 Å for the monodentate COO^- bridging of the La(III) ions to give an 8-membered ring as shown in Figure 5.11a. These distances are within the range of similar lanthanide – lanthanide bond distance of similar carboxylate complexes.[20, 39] The framework when viewed along crystallographic a-axis,

has continuous uniform large channels, which are elliptical in shape (Figure 5.11b), and this bridging of the of the La(III) by the carboxylates resulted in a 3D network when viewed along the crystallographic b-axis (Figure 5.12)

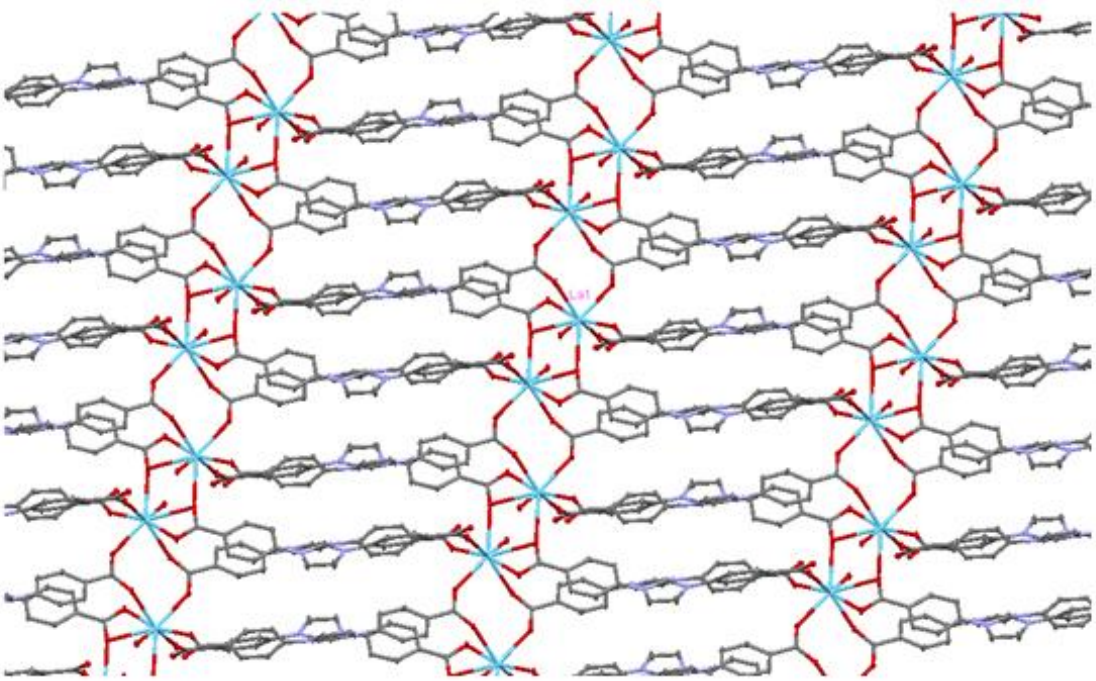


a



b

Figure 5.11: Extended crystal structure of **LaMOF**, a) showing the bridging of La(III) ions, b) viewed along crystallographic a-axis



c

Figure 5.12: Extended crystal structure of **LaMOF**, viewed along b crystallographic axis.

The Br^- ions are encapsulated as shown in Figure 5.13, this encapsulated Br^- ions are involved in significant hydrogen bonding with all the four cationic ligand molecules through both imidazole and the phenyl ring hydrogen atoms, with an average contact distance in the range of 2.333 – 3.027 Å. Similarly, the disordered Br^-/Cl^- was also encapsulated and makes similar hydrogen bonding with its neighbouring ligand molecules.

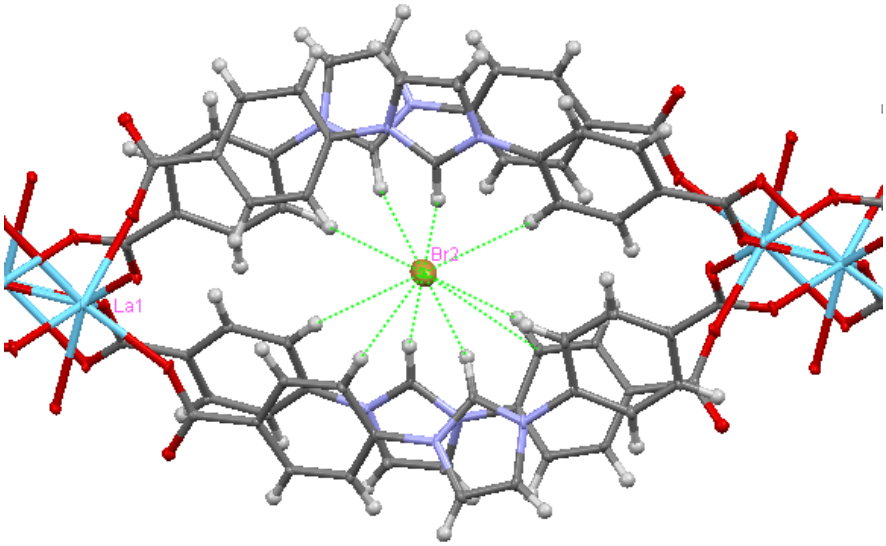


Figure 5.13: Crystal structure of **LaMOF**, showing the coordination environment of Br^- ion.

As mentioned earlier, the Ce(III) complex was also isostructural with the La(III) complex as shown in Figure 5.14, however, the two non bonding Ce(1) ---- Ce(1) distances at 4.098 and 5.458 formed as a results of the two bridging modes of the COO^- are slightly less, compared with their corresponding La(1) --- La(1) distances at 4.127 Å and 5.460 Å in La(III) complex . This slight decrease in the length is expected as the Ce(III) ion is slightly smaller than La(III) ion.

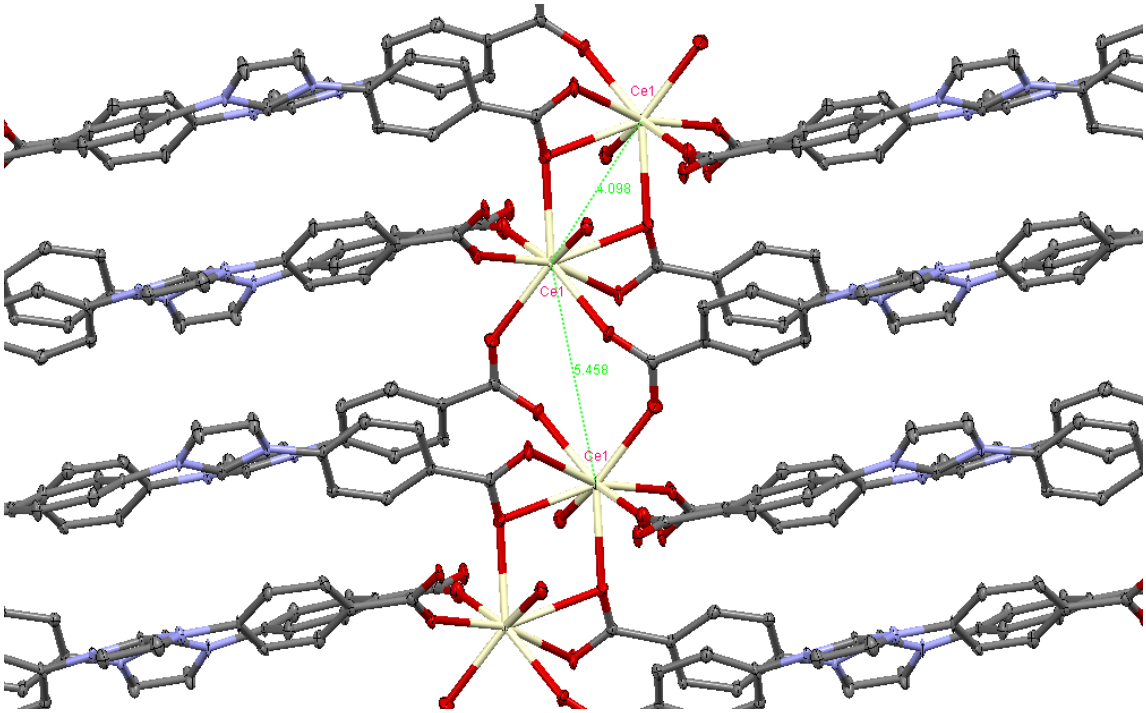


Figure 5.14: Crystal structure of **CeMOF,** thermal ellipsoids drawn at 50% probability level, hydrogen, Br^- and H_2O molecule omitted for clarity, showing the COO^- bridging the Ce (III) ions.

5.2.2.3. Attempts to synthesise more cationic MOFs

Three of the carboxylate functionalised ligands formed, **5.5**, **5.8** and **5.9**, were screened for possible MOF and NHC MOF formation due to their potential tridentate, non-chelating bonding mode. Initial attempts involved dissolving the ligands with first series transition metals involving Cu(II) and Zn(II) ions in water or methanol at room temperature hoping they will assemble into polymeric species as the solvent slowly evaporate. But these attempts were unsuccessful, the spectroscopic data (NMR and mass spectra) of the product obtained shows no changes with the starting ligand also the carboxylic acid peak in the IR at around ca 1700 cm^{-1} remain unchanged indicating non coordination of the metal to the ligand. Raising the temperature up to reflux did not improve the process and similar results were obtained. Another attempt involved the use of diffusion methods. The tetrafluoroborate salt was dissolved in acetonitrile and

allowed to diffuse into Cu(II) or Zn(II) tetrafluoroborate in methanol. This method, as discuss in Chapter 2 has been use to prepare MOFs, but it was unsuccessful for this system as no crystals were obtained. The reason may be similar to the nitrile functionanlised system, i.e the cationic nature of the ligands makes the terminal carboxylates less basic, and also cation repulsion of the metal ion hinders the complexation. In fact this cationic repulsion may be the reasons for the lower number of MOFs based on cationic ligands, compared to the neutral or anionic counterparts.

Considering the cationic effect, harsher reaction conditions were applied by adopting a solvothermal synthetic method which has proved to be a huge success in MOFs synthetic chemistry. **5.5** and $Zn(NO_3)_2$ were dissolved in DMF, the solution in 20mL pressure tube was heated to 170^oC for initial three days, when no crystals were obtained, the heating was sustained for five days. A similar method was repeated with **5.8** and **5.9** but no single crystals were obtained, in each case a powdery product which is insoluble in water or any other common organic solvent were obtained. The metal salt was changed to tetrafluoroborate and corresponding ligand salts were also used. Cu(II) ion was used but similar results were obtained. To adjust the pH of the solution a mild base was added, but also a powdery product was obtained in each case. This solubility issue makes NMR and mass spectrometry almost impossible, but IR spectrum shows disappearance of the carboxylic acid peak at around 1700 cm^{-1}, while elemental analytical data is suggestive that the corresponding metal complexes have formed. These are indications that polymeric materials are formed, but since single crystals were not obtained, which makes single crystal X-ray analysis impossible, it is therefore impossible to unequivocally ascertain their formation or otherwise, it also makes characterisation of the products impossible.

In another attempt to form group I and group II metal MOFs, the biscarboxy bisimidazolium chloride salt **5.5** was dissolved with various group I and II metal salts (the metal ions used include K^+, Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) in water and allowed to evaporate. Where the ligand was insoluble in the solvent at room temperature, it was gently heated until dissolved and allowed to cool slowly to room temperature. The

results obtained also did not indicate the complex formation, rather the uncoordinated ligands were obtained, as evidenced from the spectroscopic data (NMR and mass spectra) and where crystals were obtained suitable for X-ray crystallography, the cell dimensions measured were found to be identical to that of the starting ligand, confirming non complexation.

In one example, when $CaCl_2$ was heated with ligand **5.5b**, and allowed to slowly cool to room temperature, upon slow evaporation, a crystals suitable for X-ray diffraction were obtained, the measured unit cells dimension where found to be different to those of the bromide salt of the ligand **5.5a**, but the crystal structure indicates only the undeprotonated ligand (Figure 5.15) also without any metal coordination as such no coordinated cationic polymeric framework was obtained. It crystallises in monoclinic space group C 2/c, crystal information are in Table 5.1. The asymmetric unit contains half of the cationic molecule, one Cl^- anion and one water molecule. The only major difference between this structure and **5.5a**, is the proton of the carboxylates of this chloride ligand are intact on both ends, it is not deprotonated while the structure of **5.5a** (Figure 5.3) discussed earlier was mono deprotonated, all other features are basically the same.

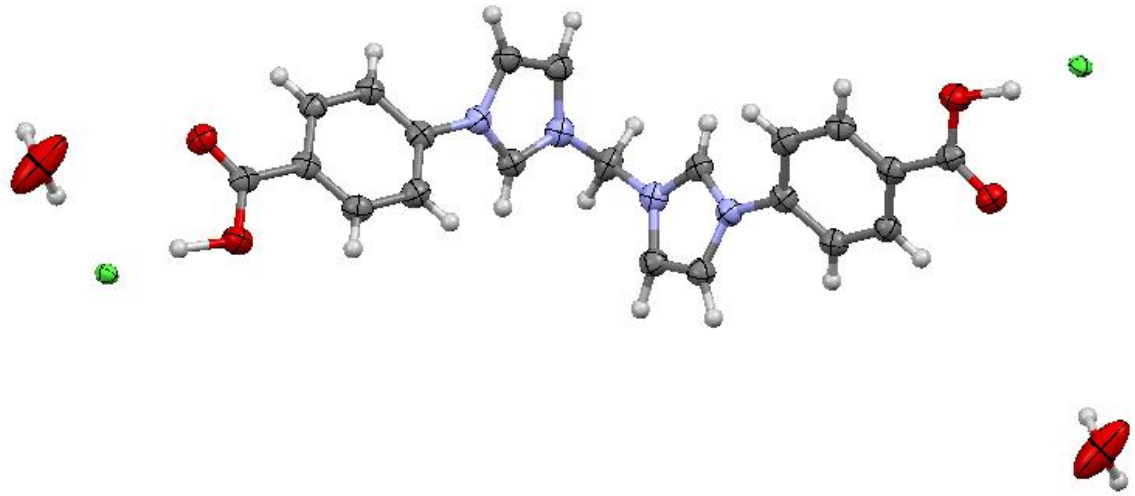


Figure 5.15: X-ray crystal structure of **5.5b,** thermal ellipsoids drawn at 50% probability level

In another attempt using a more basic metal source, the chloride bisimidazolium ligand **5.5a**, was added to water and KOH was added until the ligand, **5.5a**, just dissolved. It resulted in the cleavage of the methylene spacer, reverting the dicationic diimidazolium salts to the monoimidazole compound. However, the newly formed 4-(1H-imidazol-1-yl) benzoic acid, reacted with the K^+ ion to form a polymeric species by coordinating through the nitrogen and carboxylate ends of the compound as shown in the crystal structure (Figure 5.16). It crystallises in monoclinic space group $P2_1/c$, the asymmetric unit contains one carboxy imidazole molecule, one potassium ion and three coordinated water molecules. Each potassium is seven coordinate, bonded to two imidazole molecule through the carboxylate and the nitrogen of the molecule, in addition also it is coordinated to five water molecules. The K(1) – N(1) bond length = 3.3326(6) Å and the K(1) – O(2) = 2.7358(2) Å, while the bond length between K and the O(from H_2O) is within the range of 2.7413(2) Å – 2.9290(2) Å.

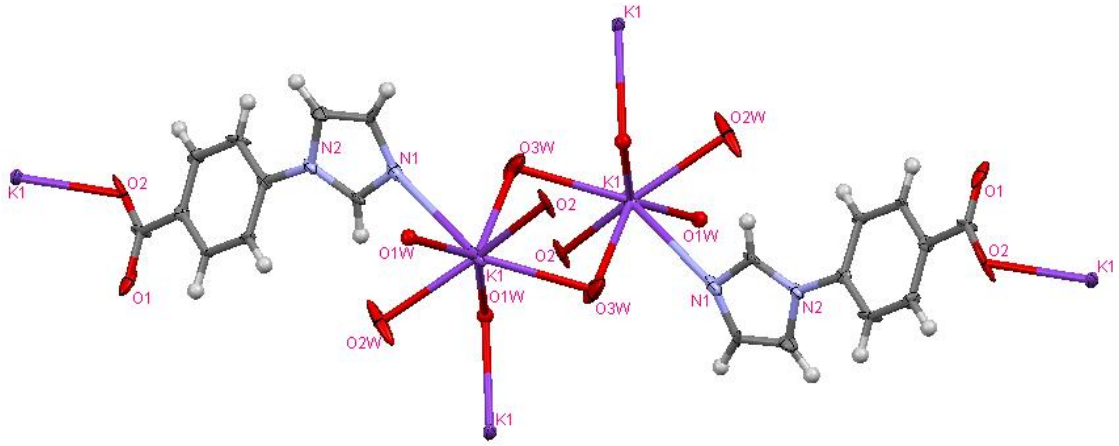


Figure 5.16: X-ray crystal structure of potassium MOF**,** thermal ellipsoids drawn at 50% probability level. K(1) – N(1) 3.3326(6), K(1) – O (2) 2.7358(2), K(1) – O(W1) 2.7976(2), K(1) – O(W2) 2.8055, K(1) – O(W3) 2.9290.

The K(1) has two different oxygen bridges, through O(3)W and O(1)W giving a K(1)--- K(1) non bonding distances of 4.412 Å and 4.522 Å respectively**.** The other carboxylate oxygen is interacting with the imidazole proton and the bridging oxygen O(1), there was also a significant interaction between the π-system of the imidazole and

the potassium ion. This builds up into a layered 3D polymeric network given a uniform features as shown in Figure 5.17.

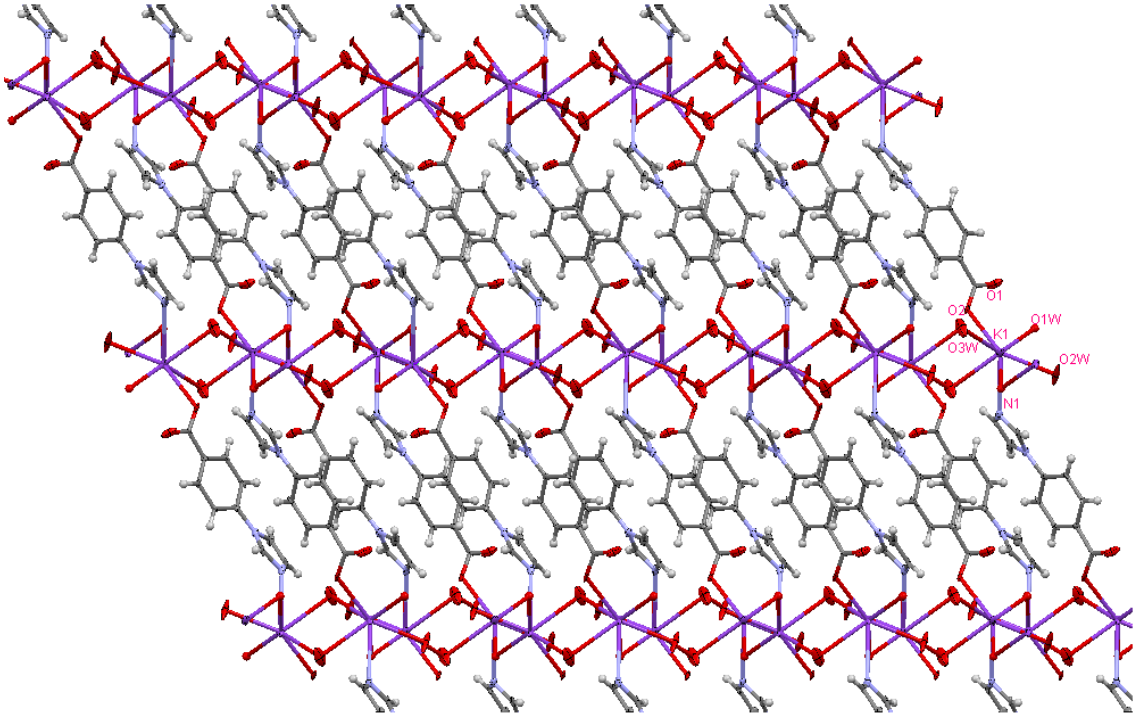


Figure 5.17: X-ray crystal structure of potassium MOF**,** thermal ellipsoids drawn at 50% probability level viewed down the crystallographic b-axis.

5.3. Conclusions

A series of five carboxylate functionalised imidazolium salts were synthesised and characterised. The synthesis involves preparing nitrile functionalised imidazolium salts as intermediates which were subsequently hydrolysed to give the corresponding carboxylate functionalised imidazolium salts. Three were biscarboxylates and as such have the potential to be assembled into MOFs and be post synthetically modified into NHC containing materials. Reaction of **5.8** with hydrated lanthanide chloride afforded two isostructural MOFs of La(III) and Ce(III). They were characterised spectroscopically, by elemental and X-ray crystallographic analysis. In our attempt to synthesise a carboxylate rhodium supramolecule we formed a bis-NHC rhodium complex **5.14** without protecting the carboxylate group. This is rather interesting,

considering the fact that, the few carboxylate NHC reported[34, 35] have their carboxylate group protected prior to carbene complex synthesis. In an attempt to form group I metal MOFs using bisimidazolium bis carboxy ligand, **5.5b**, the methylene spacer cleaved, which resulted in the formation of a potassium imidazole carboxylate MOFs.

Although no more MOFs were unequivocally characterised, we believed these ligands have all the potentials to acts as a precursors to many robust MOFs. With a more complete optimisation they will be able to offer many cationic and NHC based MOFs with exciting qualities and applications.

5.4. Experimental

5.4.1. General considerations. Unless otherwise stated all reactions were performed under nitrogen using standard Schlenk line techniques. $[Rh_2(OOCCH_3)_4]$ was synthesised as reported in the literature.[40] All other reagents were purchased from Aldrich and were used without further purification.

All infrared spectra (KBr disk, 400-4000 cm^{-1}) were recorded on Nicolet Avatar 360 FTIR spectrometer. Mass spectra were recorded on a thermo Finnigan LCQDUO mass spectrometer using ESI. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE/DPX 400(400 MHz) or AVANCE/DRX 500 (500 MHz) in $CDCl_3$ or d_6-DMSO with tetramethyl silane as standard. Elemental analyses were carried out at the micro analytical laboratory at the University of Strathclyde, Glasgow. Single crystal measurements were made at 123K with graphite monochromated MoKα1 radiation (wavelength 0.71073 Å) on an Oxford Diffraction Gemini S diffractometer equipped with a CCD detector and a variable temperature device. Initial atomic sites were located using direct methods. Remaining non-hydrogen atom sites were calculated using difference Fourier maps. Refinement of atomic co-ordinates and thermal parameters was to convergence and by full-least squares methods on F^2 within SHELX-97.[41] Where the quality of the data allowed, H-atoms bound to O were refined isotropically, all other H-atoms were placed in calculated positions using a riding mode. Reported wR2 values

are based on F^2 and all reflections, whilst reported R1 values are based on F and on observed reflections with $I>2\sigma(I)$

5.4.2. Ethyl 4-(1*H*-imidazol-1-yl)benzoate (5.2)

Ethyl 4-fluorobenzoate (2g, 11.90 mmol) was dissolved in DMF (50 mL), imidazole (1.20g, 17.65 mmol) and 60% sodium hydride in oil immersion (0.72g, 18.00 mmol) were added. The mixture was refluxed with vigorous stirring at 110^{o}C for 5 hours and then stirred at room temperature overnight. The resulting mixture was poured on cold water and the white precipitate obtained was filtered, washed with more cold water and dried in vacuum. Yield 1.85g, 70%. ^{1}H NMR ($CDCl_3$, δ): 8.20 (d, -CH- of Ph. 2H), 8.01 (s, -NCHN- of imid. 1H), 7.50 (d, -CH- of Ph. 2H), 7.38(s, -CH- of imid. 1H), 7.28 (d, -CH- of imid.1H), 4.42 (q, $-CH_2-$ 2H), 1.44 (t, $-CH_3$, 3H). ^{13}C ^{42} NMR ($CDCl_3$, δ): 166.07 (-COO-), 140.11 (C_{Ph}), 134.89 ($NCN_{imid.}$), 131.01(C_{Ph}), 130.98 ($C_{imid.}$), 130.46 (C_{Ph}), 128.96 ($C_{imid.}$), 120.10 (C_{Ph}), 68.84(CH_2), 13.81(CH_3). MS (ESI, methanol/water; m/z): 217$[M]^+$

5.4.3. Synthesis of 3,3'-methylenebis(1-(4-(ethoxycarbonyl)phenyl)-1H-imidazol-3-ium) dibromide (5.3)

Ethyl 4-(1*H*-imidazol-1-yl) benzoate (1.5g, 6.91 mmol) was dissolved in excess dibromomethane (5 mL) and stirred for 3 days at 65^{o}C. A white solid formed was filtered, washed with THF and dried to give the bisimidazolium salt **5.3**. Yield 1.6g, 76%. ^{1}H NMR (DMSO-d6 δ): 10.39 (s, -NCHN- of imid. 2H), 8.54 (s, -CH- of imid. 2H), 8.39 (s, -CH- of imid. 2H), 8.27 (d, -CH- of Ph. 4H), 8.00 (d, -CH- of Ph. 4H), 6.92 (s, $-CH_2-$ 4H), 4.39 (q, $-CH_2-$ 4H), 1.36 (t, $-CH_3$, 6H). ^{13}C {^{1}H} NMR (DMSO-d6, δ): 165.07 (-COO-), 138.26 ($C_{imid.}$), 131.65 ($C_{Ph.}$), 123.76 ($C_{imid.}$), 122.76 (C_{Ph}), 122.03 ($C_{Ph.}$), 61.88 (C_{Ph}), 59.24 (CH_2), 14.60 (CH_3). MS (ESI, methanol/water; m/z): 445$[M]^+$

5.4.4. Synthesis of 3,3'-methylenebis(1-(4-(ethoxycarbonyl)phenyl)-1H-imidazol-3-ium) dihexafluorophosphate

5.3 (1g, 1.65 mmol) was dissolve in water and saturated solution of NH_4PF_6 was added in drops which gave a white precipitate. Yield 1.42g, 96%

Anal. Calculated for $C_{25}H_{26}N_4O_4.PF_6$; C, 40.75; H, 3.56; N, 7.61%. Found C, 40.55; H, 3.57; N, 7.71%.

5.4.5. Synthesis of 3,3'-methylenebis(1-(4-carboxyphenyl)-1H-imidazol-3-ium) dichloride (5.5)

5.3 (1g, 1.65 mmol) was dissolved in HCl 37% (20 mL) and refluxed overnight. A white precipitate formed, was filtered, washed with ethyl acetate and then with diethyl ether and dried. Yield 0.59, 78%. ^{1}H NMR (DMSO-d_6, δ): 13.46 (br, COOH, 2H), 10.22 (s, 2-CH of imid. 2H), 8.52 (s, 4-CH of imid. 2H), 8.34 (s, 5-CH of imid. 2H), 8.25(d, 2-CH of Ph. 4H), 7.95 (d, 4-CH of Ph. 4H), 6.89 (s, CH_2 of methyl 2H). ^{13}C {^{1}H} NMR (DMSO-d6, δ): 166.07 (COOH), 137.78 (C_{Ph}), 137.49 ($NCN_{imid.}$), 132.23(C_{Ph}), 131.26 ($C_{imid.}$), 123.24 (C_{Ph}), 122.12 ($C_{imid.}$), 121.53 (C_{Ph}), 58.70(CH_2). IR(KBr, cm^{-1}): 1726, 1710 (ν(COOH)). MS (ESI, methanol/water; m/z): 389.13$[M]^+$. Anal. Calculated for $C_{21}H_{17}N_4O_4Br_2$; C, 45.91; H, 3.12; N, 10.20 %. Found C, 45.33; H, 2.88; N, 10.16 %.

5.4.6. Synthesis of 3,3'-methylenebis(1-(4-carboxyphenyl)-1H-imidazol-3-ium) dibromide.

3,3'-methylenebis(1-(4-cyanophenyl)-1H-imidazol-3-ium) dibromide (2g, 3.90 mmol) was refluxed in 48% HBr overnight. A white precipitate formed, was filtered, washed with ethyl acetate and then diethyl ether, and dried in vacuum. Crystals were obtained by slow cooling its hot solution in water. Yield 1.89g, 88%. Anal. Calculated for $C_{21}H_{17}N_4O_4Cl_2.2H_2O$; C, 50.70; H, 4.46; N, 11.27 %. Found C, 51.34; H, 4.55; N, 11.44%.

5.4.7. Synthesis of 3,3'-methylenebis(1-(4-carboxyphenyl)-1H-imidazol-3-ium) ditetrafluoroborate.

5.5 (1.5g, 1.82 mmol) was added to 20 mL H_2O and heated mildly until it dissolved, HBF_4 was added dropwise and allowed to cool to room temperature overnight. The precipitate formed was filtered, washed with diethyl ether and dried in vacuum. Yield 0.96g, 94%

Anal. Calculated for $C_{21}H_{17}N_4O_4BF_4$; C, 44.61; H, 3.22; N, 9.93 %. Found C, 44.61; H, 3.11; N, 10.23 %.

5.4.8. Synthesis of 1,3-bis(4-cyanophenyl)-1H-imidazol-3-ium chloride (5.6)

Paraformaldehyde (0.49g, 16.50 mmol) was stirred vigorously in toluene (40 mL), 4-amino benzonitrile (3.91g, 33 mmol) and 40% glyoxal (2.37g, 16.30 mmol) were added, and finally 37% HCl (1.86g, 16.30 mmol) was added dropwise. The mixture was refluxed overnight and the water produced was removed using a Dean-Stark apparatus. The solvent was removed and the product was triturated with acetonitrile to yield a brown powder. Yield 4.25g, 84%.

^{1}H NMR (DMSO-d_6 δ): 10.74 (s, -NCHN- of imid. 1H), 8.74 (s, -CH- of imid. 2H), 8.29 (d, -CH- of Ph. 4H), 8.20 (d, -CH- of Ph. 4H), IR(KBr, cm^{-1}): 2223 (ν(CN)). MS (ESI, methanol/water; m/z): 271$[M]^+$.

5.4.9. Synthesis of 1,3-bis(3-cyanophenyl)-1H-imidazol-3-ium chloride (5.7)

Paraformaldehyde (0.49g, 16.50 mmol) was stirred vigorously in toluene (40 mL), 3-aminobenzonitrile (3.91g, 33 mmol) and glyoxal, 40% v/v (2.37g, 16.30 mmol) were added, and 37% HCl (1.86g, 16.30 mmol) was added dropwise. The mixture was refluxed overnight, and the water produced was removed using a Dean-Stark apparatus. The solvent was removed and the product was triturated with acetonitrile to yield a brown powder. Yield 3.75g, 74%.

^{1}H NMR (DMSO-d6 δ): 10.89 (s, -NCHN- of imid. 1H), 8.74 (s, -CH- of imid. 2H), 8.63 (s, -CH- of imid.. 4H), 8.42 (d, -CH- of Ph. 2H), 8.12 (d, -CH- of Ph. 2H), 7.94 (d, -CH- of Ph. 2H). ^{13}C {^{1}H}NMR (DMSO-d_6, δ): 135.86 (C_{Ph}), 135.09 ($C_{imid.}$), 133.60 ($NCN_{imid.}$), 131.50(C_{Ph}), 130.30 (C_{Ph}), 126.71 (C_{Ph}) 125.68(C_{Ph}), 121.80 ($C_{imid.}$), 117.48(CN), 112.21(-C_{Ph}). IR(KBr, cm^{-1}): 2233 (ν(CN)). MS (ESI, methanol/water; m/z): 271$[M]^+$.

5.4.10. Synthesis of 1,3-bis(4-carboxyphenyl)-1H-imidazol-3-ium bromide (5.8)

5.6 (4g, 13.05 mmol) was dissolved in 48% HBr (50 mL) and refluxed with stirring overnight. The solution was allowed to cool and the brown precipitate was filtered washed with ethyl acetate and dried. Yield 3.43g, 68%. ^{1}H NMR (DMSO-d_6 δ): 13.44(br, COOH, 2H), 10.56 (s, -NCHN- of imid. 1H), 8.69 (s, -CH- of imid. 2H),

8.25 (d, -CH- of Ph. 4H), 8.08 (d, -CH- of Ph. 4H). ^{13}C {^{1}H}NMR (DMSO-d_6, δ): 166.04 (COOH), 137.69 (C_{Ph}), 135.49 ($NCN_{imid.}$), 131.99(C_{Ph}), 131.12 ($C_{imid.}$), 122.14 (C_{Ph}), 121.98 ($C_{imid.}$), IR(KBr, cm^{-1}): 1716 (ν(COOH)). MS (ESI, methanol/water; m/z): 309$[M]^+$. Anal. Calculated for C 52.44, H 3.37, N 7.20% Found: 50.99, H 2.95, N 7.65%

5.4.11. Synthesis of 1,3-bis(3-carboxyphenyl)-1H-imidazol-3-ium bromide (5.9)

5.7 (3g, 9.79 mmol) was dissolved in 48% HBr (40 mL) and refluxed with stirring overnight. The solution was allowed to cool and the dark brown precipitate was filtered washed with ethyl acetate and dried. Yield 2.12g, 56%. ^{1}H NMR (DMSO-d_6 δ): 13.44(br, COOH, 2H), 10.58 (s, -NCHN- of imid. 1H), 8.69 (s, -CH- of imid. 2H), 8.48 (s, -CH- of imid.. 4H), 8.22 (d, -CH- of Ph. 2H), 8.14 (d, -CH- of Ph. 2H), 7.86 (t, -CH- of Ph. 2H) ^{13}C {^{1}H}NMR (DMSO-d_6, δ): 166.06 (COOH), 135.53 (C_{Ph}), 134.95 ($NCN_{imid.}$), 132.76(C_{Ph}), 130.56 ($C_{imid.}$), 130.50 (C_{Ph}) 126.49(C_{Ph}), 122.98 ($C_{imid.}$), 122.09(C_{Ph}). IR(KBr, cm^{-1}): 1726 (ν(COOH)). MS (ESI, methanol/water; m/z): 309$[M]^+$.

5.4.12. 3-(4-Cyanophenyl)-1-methyl-1H-imidazol-3-ium Iodide (5.10)

1-(4-Cyanophenyl) imidazole (2g, 11.83 mmol) was dissolved in DCM (50 mL), excess iodomethane (5 mL) was added and the solution reflux for 4 hours. The white precipitate obtained was filtered washed with ether and dried under vacuum. Yield 3.35g, 91%
^{1}H NMR (DMSO-d_6 δ): 9.91 (s, -NCHN- of imid. 1H), 8.40 (s, -CH- of imid. 1H), 8.23(d, -CH- of Ph. 2H), 8.03 (d, -CH- of Ph. 2H),8.00 (s, -CH- of imid.. 1H), 3.96 (s, -CH_2- 3H) ^{13}C {^{1}H}NMR (DMSO-d_6, δ): 137.95 (C_{Ph}), 136.58 (NCN_{imid}) 134.43 (C_{Ph}), 124.64 ($C_{imid.}$),122.50(C_{Ph}), 120.71(C_{imid}), 117.76 ($CN_{.}$), 112.21(-C_{Ph}), 36.32 (-CH_3)

5.4.13. 1-Benzyl-3-(4-cyanophenyl)-1H-imidazol-3-ium bromide (5.11)

4-(1H-imidazol-1-yl)benzonitrile (2g, 11.83 mmol) was dissolved in DCM (50 mL), excess benzyl bromide (4 mL) was added and the solution refluxed for 4 hours. The white precipitate obtained was filtered, washed with ether and dried under vacuum. Yield 3.87g, 96%. ^{1}H NMR (DMSO-d_6 δ): 10.13 (s, -NCHN- of imid. 1H), 8.43 (s, -CH-

of imid. 1H), 8.20 (d, -CH- of Ph. 2H), 8.07 (s, -CH- of imid.. 1H), 8.04 (d, -CH- of Ph. 2H), 7.52 (d, -CH- of Ph. 2H), 7.44 (m, -CH- of Ph. 3H). $^{13}C\{^{1}H\}$NMR (DMSO-d_6, δ): 138.49 (C_{Ph}), 136.75 (C_{Ph}), 134.82 (C_{Ph}) 134.70 (NCN_{imid}.), 129.46(C_{Ph}), 129.38 (C_{imid}.), 129.01 (C_{Ph}) 123.96(C_{Ph}), 123.21 (C_{imid}.), 121.99(C_{Ph}), 118.27 (CN), 112.78(C_{Ph}). 53.06 (-CH_2-) IR(KBr, cm^{-1}): 2233 (ν(CN)). MS (ESI, methanol/water; m/z): 260$[M]^+$.

5.4.14. 3-(4-Carboxyphenyl)-1-methyl-1H-imidazol-3-ium bromide (5.12)

5.10 (2.50g, 8.06 mmol) was dissolve in HBr (50 mL) and reflux overnight. The solution was allowed to cool and washed with ethyl acetate to which gave a white crystalline product which was filtered and further washed with diethyl ether and dried under vacuum. Yield 1.56g, 68%. ^{1}H NMR (DMSO-d_6 δ): 13.39 (s, -COOH, 1H), 9.85 (s, -NCHN- of imid. 1H), 8.37 (s, -CH- of imid. 1H), 8.19 (d, -CH- of Ph. 2H), 7.97 (s, -CH- of imid.. 1H), 7.89 (d, -CH- of Ph. 2H), 3.96 (s, -CH_2- 2H) ^{13}C $\{^{1}H\}$NMR (DMSO-d_6, δ): 166.13 (COOH), 137.81 (C_{Ph}), 136.34 (NCN_{imid}) 131.74 (C_{Ph}), 131.16(C_{Ph}), 124.64 (C_{imid}.), 121.80(C_{Ph}), 120.81 ($C_{imid.}$), 36.23 (-CH_3) IR(KBr, cm^{-1}): 1716 (ν(COOH)). MS (ESI, methanol/water; m/z): 203$[M]^+$.

5.4.15. 1-Benzyl-3-(4-carboxyphenyl)-1H-imidazol-3-ium bromide (5.13)

5.11 (3.5g, 10.29 mmol) was dissolved in 48% HBr (60 mL) and refluxed overnight. The solution was allowed to cool to room temperature and the white crystalline product precipitated. Filtered, washed with ethyl acetate and dried under vacuum. Yield 3.46g, 94%. ^{1}H NMR (DMSO-d_6 δ): 13.39 (s, -COOH, 1H), 10.10 (s, -NCHN- of imid. 1H), 8.42 (s, -CH- of imid. 1H), 8.20 (d, -CH- of Ph. 2H), 8.07 (s, -CH- of imid.. 1H), 7.94 (d, -CH- of Ph. 2H), 7.52 (d, -CH- of Ph. 2H), 7.44 (m, -CH- of Ph. 3H), 5.52 (s, -CH_2- 2H) ^{13}C $\{^{1}H\}$NMR (DMSO-d_6, δ): 166.12 (COOH), 137.79 (C_{Ph}), 135.95 (C_{Ph}), 134.35 (NCN_{imid}) 131.69 (C_{Ph}), 131.01(C_{Ph}), 128.91 (C_{imid}.), 128.82 (C_{Ph}) 128.60(C_{Ph}), 123.40 (C_{imid}.), 121.91(C_{Ph}), 121.41 (C_{Ph}), 52.34 (-CH_2-) IR(KBr, cm^{-1}): 1721 (ν(COOH)). MS (ESI, methanol/water; m/z): 279$[M]^+$. Anal. Calculated for $C_{17}H_{15}N_2O_2Br_1$ C 56.84, H 4.21, N 7.80 %. Found C 56.49, H 3.91, N 7.44 %.

5.4.16. Synthesis of a Rhodium bisNHC complex (5.14)

5.13 (0.1g, 0.29 mmol) and [$Rh_2(OOCCH_3)_4$] (0.03g, 0.07 mmol) were dissolved in DMF (10 mL). The solution was transferred to a 20 mL pressure tube and heated at 150^oC for 2 days. It was allowed to cool to room temperature and the solvent evaporated to give yellow crystals of **5.14.** Yield 0.07g, 58%.

^1H NMR (DMSO-d_6 δ): 12.92 (s, -COOH, 1H), 8. 29 (d, -CH- of Ph. 4H), 7.96 (s, -CH- of imid.. 2H), 7.80 (d, -CH- of Ph. 4H), 7.50 (s, -CH- of Ph. 2H), 7.37 (m, -CH- of Ph. 8H), 5.98 (d, -CH_2- 2H) 5.59(d, -CH_2- 2H) ^{13}C {^1H}MR (DMSO-d_6, δ): 166.45 (COOH), 162.27 ($CO_.$), 129.77 (C_{imid}.), 129.44 (C_{Ph}) 128.32(C_{Ph}), 127.72 (C_{Ph}), 124.72(C_{imid}), 122.44 (C_{Ph}), 53.85 (-CH_2-) IR(KBr, cm^{-1}): 1710 (ν(COOH)). 1950 (ν(CO)). MS (ESI, methanol/water; m/z): 687$[M]^+$. Anal. Calculated for $C_{35}H_{24}N_4O_5Br_1$ .2DMF C 52.14, H 4.60, N 9.13 %. Found C 53.88, H 4.64, N 9.20%.

5.4.17. Synthesis of LaMOF

5.8 (0.1g, 0.26 mmol), $LaCl_3.7H_2O$ (0.1g, 0.27 mmol) and a solution of NaOH (1mL, 0.3M) were added to water - ethanol (3 mL : 7 mL) mixed solvent. The mixture was heated in a 20 mL pressure tube with a Teflon cap at 170^oC in an oven for 3 days. It was cooled to room temperature and the shiny, pale yellow crystals were filtered and washed with water. IR(KBr, cm^{-1}): 3119.20, 2776.10, 1603.41, 1541.96, 1398.58, 1168.14, 784. Anal. Calculated for $La_1C_{34}H_{22}N_4O_8Br_2$: C 44.69, H 2.43, N 6.14 %. Found C 44.25, H 1.81, N 6.72 %.

5.4.18. Synthesis of CeMOF

5.8 (0.1g, 0.26 mmol), $CeCl_3.7H_2O$ (0.1g, 26 mmol) and a solution of NaOH (1mL, 0.3M) were added to water - ethanol (3 mL : 7 mL) mixed solvent. The mixture was heated in a 20 mL pressure tube with a Teflon cap at 170^oC in an oven for 3 days. It was cooled to room temperature and the shiny, pale yellow crystals were filtered and washed with water. IR(KBr, cm^{-1}): 3477.67, 2909.25, 1613.66, 1552.20, 1398.58, 1250.07, 778.95. Anal. Calculated for $Ce_1C_{34}H_{22}N_4O_8Cl_2.2H_2O$; C 47.34, H 3.04, N 6.50, Found C 47.34, H 2.88, N 6.72

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CHAPTER 6

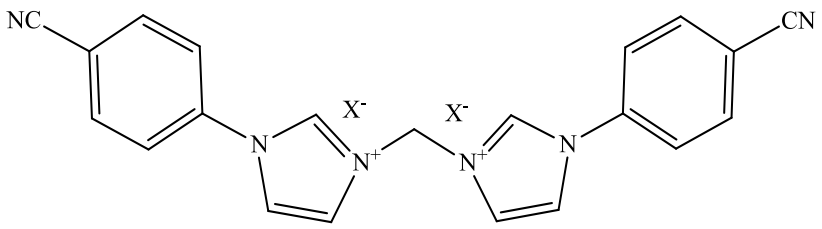
General Conclusion and Suggestions for Future Work

6.1. General conclusion

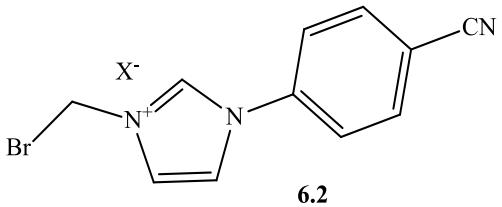
The main aims of this study were to synthesise a series of new imidazolium salts with pendant donor groups, and to screen them for their possible use as building blocks for cationic coordination polymers. In addition it was intended to convert these imidazolium salts into their corresponding NHC complexes, either prior to conversion into coordination polymers, or to be generated by post synthetic modifications of the cationic coordination polymers obtained.

Therefore, the initial aim involved synthesis of the imidazolium salts, which have the potential to be assembled into cationic coordination polymers. The imidazolium salts need to be functionalised with appropriate donor groups with high affinity for the metal centres to be use as connectors (this might be necessary to reduce the effects the cation may have on the positive metal centres). In addition, for the ligand systems to be able to form metal-organic frameworks, they need to be capable of forming one or more bridges. Therefore the imidazolium salts have to be functionalised with at least two donor groups. To achieve this, various donor groups capable of bonding to metal centres, were considered for use as the substituents on the imidazolium ring, particularly nitrile, pyridine and carboxylate.

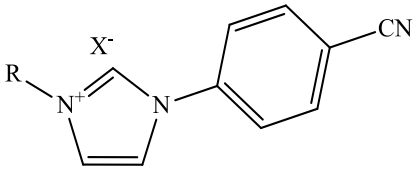
A series of nitrile functionalised imidazolium salts were synthesised (Figure 6.1). Initially, 4-cyanophenyl imidazole was prepared and used to synthesise two promising nitrile functionalised species, namely the 3,3'-methylenebis(4-cyanophenyl)imidazolium (**6.1**) and 1-(4-cyanophenyl)-3-bromomethyl) imidazolium (**6.2**) salts. They were all characterised spectroscopically and their structures confirmed by single X-ray crystallographic analysis as discussed in Chapter 3.



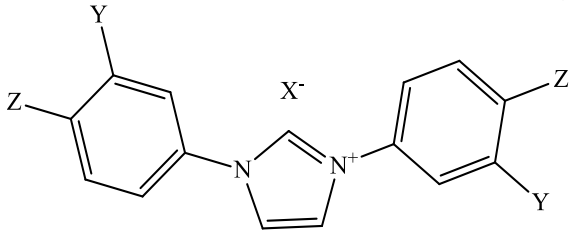
6.1



6.2



6.3, R = Me
6.4, R = Benzyl

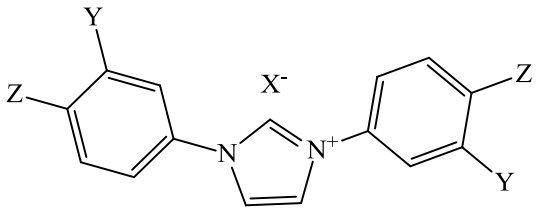


6.5, Y = H, Z = CN
6.6, Y = CN, Z = H

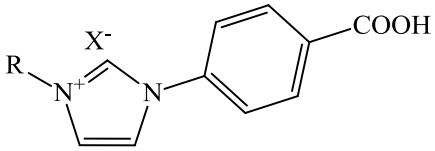
Figure 6.1: Nitrile substituted imidazolium salts synthesised in this work.

Also in the process of synthesising carboxylate functionalised imidazolium salts, further nitrile substituted imidazolium salts were obtained. Two mono-imidazolium nitriles, the 1-(4-cyanophenyl)-3-methyl (**6.3**) and 1-(4-cyanophenyl)-3-benzyl imidazolium (**6.4**) salts were prepared by N-alkylation of the 4-cyanophenyl imidazole. Two additional bisnitrile functionalised imidazolium salts, 1,3-bis(4-cyanophenyl)imidazolium (**6.5**) and 1,3-bis(3-cyanophenyl)imidazolium (**6.6**) salts were synthesised from a one pot synthetic method involving 4-cyanoaniline or 3-cyanoaniline, glyoxal and paraformaldehyde as described in Chapter 5. All these four additional imidazolium salts (**6.3**–**6.6**) were characterised spectroscopically.

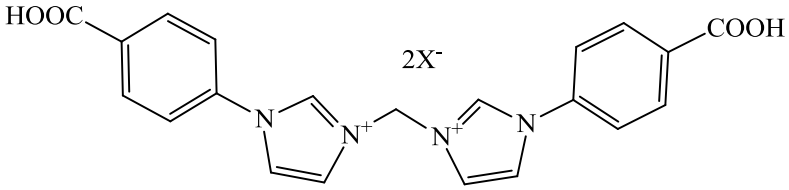
These four novel imidazolium salts were hydrolysed to give the corresponding carboxylates by refluxing them in hydrochloric or hydrobromic acids, resulting in 1,3-bis(4-carboxyphenyl) imidazolium (**6.7**), 1,3-bis(3-carboxyphenyl) imidazolium (**6.8**), 1-(4-carboxyphenyl)-3-methyl imidazolium (**6.9**) and 1-(4-carboxyphenyl)-3-benzyl imidazolium (**6.10**) salts. In addition the 3,3'-methylenebis(1-(4-cyanophenyl)-1H-imidazol-3-ium) salt, **6.1**, synthesised in Chapter 3 was converted to the bis(4-carboxylate) bisimidazolium salt, **6.11**. All these five carboxylate pro-ligands were characterised spectroscopically and by elemental analysis, and the biscarboxylate bisimidazolium salt, **6.11**, was additionally characterised by single X-ray structural analysis as described in Chapter 5.



6.7, Y = H, Z = COOH
6.8, Y = COOH, Z = H



6.9, R = Me
6.10, R = Benzyl



6.11

Figure 6.2: Carboxylate functionalised imidazolium salts synthesised in this work.

Four picolyl substituted imidazolium salts were synthesised; two bispicolyl (**6.12** and **6.13**), one mixed picolyl nitrile (**6.14**) and one monopicolyl (**6.15**) imidazolium salt (Figure 6.3). The new bis(4-picolyl) imidazolium salts bear some resemblance to the 4,4,-bipyridyl ligand and was easily synthesised through solvothermal synthetic process involving 4-picolyl chloride, imidazole and DMF as solvent. The mixed picolyl/nitrile

functionalised imidazolium salt was also synthesised by solvothermal synthesis from 4-cyanophenyl imidazole and 4-picolyl chloride. All the four picolyl functionalised imidazolium salts were characterised by spectroscopic (NMR and mass spectra) and elemental analysis, the bis(4-picolyl) and mixed nitrile picolyl imidazolium salts were in addition characterised by X-ray crystallographic analysis, which as expected reveals a near linear shaped structure of the molecules.

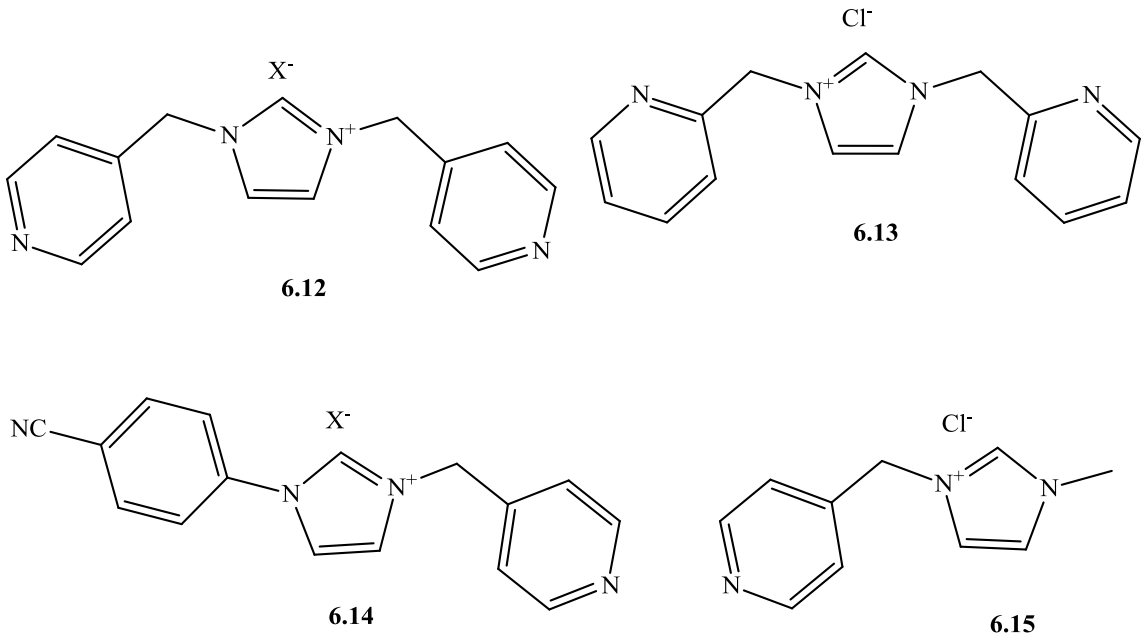


Figure 6.3: Pyridine functionalised imidazolium salts synthesised in this work

In total, fifteen novel imidazolium salt types were synthesised and characterised. Nine of these were bisfunctionalised with nitrile, carboxylate or pyridine pendant groups. The functionalities are spatially disposed to prevent the chance of formation of chelates or pincer-type complexes which may in turn prevent the formation of the frameworks intended in this work. Clearly, some of the imidazolium salts synthesised were monofunctionalised and as such do not have good credentials for forming polymeric frameworks but nevertheless they were good candidates for NHC complex formation. In addition some were intended to be used as precursors to form some interesting

supramolecular compounds which may then be converted into NHC supramolecular complexes or even be extended to polymeric materials.

The second major aim of the study was the conversion of these synthesised imidazolium salts to NHC complexes. A number of silver NHC complexes with various nitrile and picolyl functionalised imidazolium salts were synthesised and characterised. Silver was choosen as one of the preferred metals due to its relatively straightforward carbene complex formation and its ability to serve as a gateway to many other transition metal complexes through transmetallation reactions. One example of such a reaction is between the dimeric silver NHC complexes synthesised from bisnitrile bisimidazolium salts and $[Ru(p\text{-}cy)Cl_2]_2$ which results in transmetallation and the formation of the NHC complex $[Ru(\mathbf{L})Cl]BF_4$ (**L** = 3,3'-methylenebis(1-(4-cyanophenyl)imidazol-2-ylidene). Therefore, this work has further demonstrated that transmetallation is an efficient way of forming transition metal NHC complexes. Also using same pro-ligand as the bromide salt and $[Pt(COD)Cl_2]$, a platinum bisNHC complex $[Pt(\mathbf{L})Br_2]$ was synthesised and characterised and its structure ascertained by single crystal X-ray analysis. We also managed to synthesise a carboxylate functionalised bisNHC complex $[Rh(\mathbf{L_2})BrCO]$ (**L** = 1,3-bis(4-carboxyphenyl) imidazolium bromide), via solvothermal synthesis which demonstrated the unexpected formation of CO by decomposition of the DMF used as a solvent, presumably by a metal-mediated expulsion of Me_2NH.

The third major aim of the studies was the development of cationic polymers from the synthesised imidazolium salts. It is clear that not all of the imidazolium salts synthesised have the capability of forming polymeric materials, so only those with at least two coordination sites were screened. Four cationic polymers were synthesised from the picolyl and the carboxylate ligands. The bis 4-picolyl ligand forms two isostructural cationic framework with Ag(I) and Cu(I) from the reaction of the picolyl ligand with Ag(I) or Cu(I) oxides in acetonitrile. The metal ions are coordinated to the picolyl ligand through the pyridine nitrogen in tetrahedral geometry forming an extended uniform framework with large elliptically shaped pores in which the anions reside. Although the two polymers were structurally found to be isostructural the cell parameters, volume and

bonding distances in the Cu(I) polymer are slightly less in line with the smaller size of its ionic radii compared to Ag(I). Similar trends were observed with the two isostructural lanthanide (Ln = La, Ce) cationic MOFs formed from the bis 4-carboxylate imidazolium salts. The Ce(III) framework has some parameters slightly less than the La(III) since the cerium ionic radii is smaller. The X-ray crystal structures reveal them to be a 3D network with a uniform framework of extended large elliptically shaped channels.

Attempts to construct more cationic polymers using various other metal ions e.g Cu(II), Zn(II), and Fe(II), with the various bisfunctionalised imidazolium salts did not yield the desired results. Although some evidence for the formation of the polymers were observed in some, especially the carboxylates, the lack of single crystals suitable for X-ray analysis hampered our work. Also attempts using the picolyl functionalised imidazolium salts resulted in the protonation of the pyridyl nitrogen atoms suggesting pH may have played a role. When the bis carboxylate bisimidazolium salt was treated with more basic solutions of group (I) and (II) metal ions in an attempt to form group (I) and (II) metal MOFs, cleavage of the methylene linker between the two imidazolium rings were observed which in one example results in the formation of one more additional coordination polymer linked by K(I) ions. This was characterised by single X-ray crystallographic analysis revealing a 3D polymeric network.

Evidence from spectroscopic and elemental analysis suggested that an NHC complex containing polymer was obtained from the reaction of Ag_2O and bis(4-picolyl) imidazolium salts in the presence of a base using acetonitrile as solvent, but this was inconclusive as single crystal was not obtained which makes structure confirmation impossible.

Although only a few cationic porous coordination polymers were obtained, this work has succeeded in adding a series of promising cationic linkers with various functionalities as precursors for metal organic frameworks and also for NHC complexes. This is an interesting development because not many of the linkers currently in use are cationic in nature.

The work also successfully added some new NHC complexes into their large families which were already established to be a replacement for phosphines in catalysis. Some of these exciting imidazolium salts were obtained towards the end of the PhD studies, and consequently limited time was available to fully study them and solve some of problems associated with the complex formation highlighted throughout the thesis. These challenges we believed to be associated with their cationic nature which alters the base strength of the donor atoms and also repels the incoming metal centers. With more work the full potential of these imidazolium salts will be achieved and more interesting NHC complexes and metal organic frameworks will be obtained with wide range of applications.

6.2. Possible future work

Research is an ongoing process, and many areas have not been explored in the work described in this thesis, and even within those described, there are areas for refinement. Some of those new areas will be highlighted below.

Although this research has successfully added new NHC complexes into the carbene library, it has not studied their catalytic application which is a well established area of organometallic chemistry. Therefore future work should study the catalytic applications of these newly formed NHC complexes in different reaction systems. Furthermore, there could be many more NHC complexes with different metal ions that can be generated from the series of the imidazolium salts synthesised in this work, most especially the nitrile functionalised imidazolium salts which shows an excellent NHC complex forming ability. That could be an area to consider which may give a pool of NHC complexes to be screened for a wide range of catalytic applications.

Also the NHC complexes formed offer some potential for use in construction of metal organic frameworks. Our initial attempts have shown promise, but have not yielded the volume of results expected, and due to time constraints we cannot continue to work on that direction. As such this will be a perfect area to explore in future and with proper

optimisation some of these NHCs can be assembled into coordination polymers giving potentially exciting materials in organometallic or organic synthetic chemistry.

The biscarboxylate ($L(H)_4^{2+}$ or $L(H)_3^{+}$) and the bisnitrile ligands ($L(H)_2^{2+}$ or LH^{+}) are promising materials as linkers in metal organic frameworks. The cationic nature of the imidazolium group is thought to reduce the basic character of their donor atoms and is believed to be a significant factor in our difficulties in forming their MOFs with different metal ions, although some evidence of their formation was observed. As such this can be an excellent area for future work, to improve the synthetic procedure, and produce more types of MOFs with different metal ions and fully characterise them using single X-ray crystallographic analysis. This work has great promise considering that not many cationic spacer ligands have been used to form MOFs. Although we were able to form some of these MOFs using lanthanide ions, the yields were not optimised and our attempts to convert the imidazolium salts into NHCs were not successful. Therefore, in future, alternative synthetic methodologies, such as solvothermal synthesis needs to be improved by optimisation of the reaction conditions to give better yields and various other MOFs. Post-synthetic modification may be attempted for their conversion into NHC complex containing MOFs. Furthermore, the applications of these synthesised materials may be explored in areas such as catalysis, gas adsorption and gas purification. The lanthanide MOFs should also be tested for their photo-physical and magnetic properties. Ligand sensitised emission from lanthanide complexes is of great interest in the electronics industry, while a great deal of interest has been shown in the magnetic properties of lanthanide containing MOFs.

The bis 4-picolyl imidazolium salts have given us two isostructural Ag(I) and Cu(I) cationic polymers, but attempts to form more polymers with metal (II) ions failed. Instead, protonated pyridinium salts were formed which suggests the pH may be a key factor in addition to the cation effect. As such if pKa studies can be conducted it will offer some explanation and a possible solution to mitigate the effect of the pH and then a series of cationic polymers can be obtained. In fact not only the picolyl, all the other bis

functionalised imidazolium salts prepared may need their pKa studied to ascertain the basic strength of their coordinating groups.

Another area that may form future work is the improvement on the use of the monoimidazolium salts as precursor in forming supramolecular compounds. With appropriate bases and metal sources the imidazolium salts can then be converted into NHC complexes containing supramolecular compounds, and with a bridging ligand which may even involve some of the ligands synthesised in this work (like the bis N-functionalised imidazolium salts) they can be extended into a large NHC complexes polymeric materials with a huge potential in catalysis and some other applications.