Department of Chemistry
Adran Chemeg

Mixed donor carbene pyridyl ligands and their metal complexes

by

Aminu Ahmed

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School of Chemistry
Cardiff University
Wales, UK

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ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

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Abstract

This thesis describes the synthesis of a series of Ag(I), Pd(II), Rh (I) and Ir(I) complexes of quinoline functionalised nucleophilic heterocyclic carbene (NHC) ligands. The transmetallation properties of the Ag(I) complexes were utilised to prepare the corresponding Pd(II), Rh (I) and Ir(I) (NHC) complexes.

A series of quinoline based imidazolium, pyrimidinium salts were prepared and characterised as NHC ligand precursors.

Ag(I)(NHC) complexes were prepared by the reaction of the quinoline functionalised salts with Ag_2O in DCM. All complexes were spectroscopically characterised and the results of single X- ray crystallographic studies are reported for two of the complexes and the geometry around the silver cation was observed to be distorted linear.

Two quinoline based palladium (II) (NHC) complexes were prepared via transmetallation Ag(I)(NHC) complexes is reported.

The synthesis of a series of methylene bridged quinoline functionalised Rh (I) and Ir(I) (NHC) complexes through transmetallation of the Ag(I)(NHC) complexes is reported and the results of single X- ray crystallographic studies are reported for most of the complexes showing consistent pattern in term of bond lengths and angles.

Two of the Ir(I) (NHC) complexes were tested as catalysts in transfer hydrogenation reactions , showing good activity at low Ir loadings.

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Abbreviations used in this Thesis

AcOH	acetic acid
Ar	aryl group
Barf	tetrakis[(3,5-trifluoromethyl)phenyl]borate
BAP	4-bromoacetophenone
^{n}Bu	n-butyl group
^{t}Bu	tert-butyl group
COD or cod	1, 5-cyclooctadiene
DCM	dichloromethane
DMF	N, N-dimethylformide
DMSO	dimethyl sulfoxide
ESMS	electrospray mass spectrometry
Et	ethyl group
Et_2O, ether	diethyl ether
GC	gas-liquid chromatography
GCMS	gas-liquid chromatography/mass spectrometry
HRMS	high resolution mass spectrometry
^{i}Pr	iso-propyl group
^{n}Pr	n-propyl group
IR	infra red spectrometry
LSIMS	liquid secondary ion mass spectrometry
M	metal
Me	methyl group
Mes	mesityl group
MS	mass spectrometry
NBS	N-bromosuccinimide
NHC	nucleophilic heterocyclic carbene
NMR	nuclear magnetic resonance
OAc	acetate ion
OTf	trifluoromethanesulfonate (triflate) anion
Ph	phenyl group
Qiun	qiunolyl group

R	alkyl group
THF, thf	tetrahydrofuran
TON	turnover number ($mol_{product}/mol_{Ir}/hr$)
TMS	tetra methyl saline

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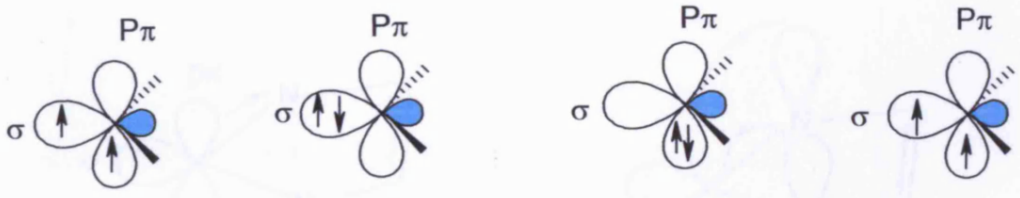
CHAPTER ONE

1.1 Background

Carbenes are neutral compounds featuring a divalent carbon atom with only six electrons in its valence shell [1]. Due to an incomplete octet of electrons, they are generally very reactive species. The carbenic carbon can be either linear or bent, each geometry describable by a certain degree of hybridization. The sp-hybridized carbon carbene adopts a linear geometry with two non bonding degenerate orbital (P_x and P_y). In sp^2- type hybridization where the carbon adopts bent geometry, the degeneracy is broken in which case the P_x is stabilised by acquiring some s character (it is usually called σ while the P_y (usually called P_π) remains almost unchanged. It should be noted that most carbenes are bent (sp^2 hybridized).

As a result of this break in degeneracy, carbenes can exit in two states: triplet state (where two non bonding electrons occur in two different orbital with parallel spins and singlet state (two non bonding electrons can pair in the same σ or P_π orbital). Based on this classification, we can have four possible electronic configurations as depicted in figure 1.1



$\sigma^1P\pi^1$ $\quad$ σ^2 $\quad$ $P\pi^2$ $\quad$ $\sigma^1P\pi^1$

$^3B_1$ $\quad$ $^1A_1$ $\quad$ $^1A_1$ $\quad$ $^1B_1$

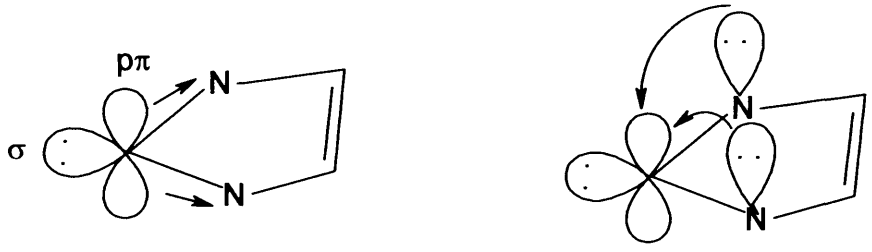
Figure 1.1. Electronic configuration of carbenes.

The ground state spin multiplicity is a fundamental feature of carbenes that dictates their reactivity [2]. A singlet state is favoured by a large σ-Pπ

separation and according to Hoffmann; a value of at least 2 eV is needed to impose this. Anything below 1.5 eV will favour the triplet state [3].

The substituents on the carbene determine whether a singlet or triplet state is formed through a combination of inductive, mesomeric and steric effects. Electron withdrawing groups increase the σ-P_π gap by inductively stabilising the d non bonding orbital by increasing its s character and thus favouring the singlet state. On the other hand an σ-electron donating group will induce small σ-P_π gap and favour the triplet state. For illustration purposes substituents that are electron donating can be termed X, while electron withdrawing groups can be termed Y. XX carbenes are bent singlet, while most of the YY carbenes are predicted to be linear singlet.

N-Heterocyclic carbenes (NHCs) (Figure 1.2, (a)) are the focus of this work and are firmly placed within the singlet state. With two nitrogen substituents next to the carbene carbon atom, the NHCs are predicted to stabilise their singlet state (two paired electrons in the σ-orbital) by push- pull effect (Figure 1.2) [4]. Firstly, the σ- electron withdrawing nitrogen inductively stabilises the σ- non bonding orbital by increasing its s-character. Secondly, the energy of the vacant Pπ-orbital is increased by interaction with the symmetric combination of the nitrogen lone pairs.



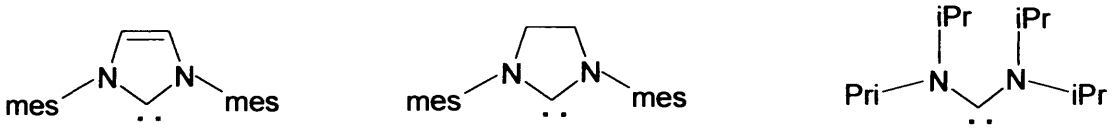
-I Inductive effect +M mesomeric effect

Figure 1.2: Electronic stabilisation of NHCs.

The combination of the two effects increases the σ-Pπ gap and favours therefore the singlet state. Additionally, the sp^2 hybridization adopted by the carbene carbon atom in its singlet state matches the bent geometry of the NHC five membered ring. The interaction of the nitrogen lone pair with the π-orbital of the

carbene is reflected by an N-C carbene bond length of 1.365Å, which is consistent with double bond character. An accurate assessment of the π back bonding was found by analysing dynamic ^{1}H-NMR behaviour of bis (diisopropylamine) carbene **3** [5]. The major process involves rotation about the N-C carbene bonds; the measured barrier to rotation of 53 kJ/mol was mostly attributed to the substantial π- component of these bonds.

Dimerisation of NHCs has been known since the first attempt to isolate them [6]. Alder recently showed that dimerisation is thermodynamically unfavourable for imidazolin-2-ylidenes 1 (singlet/triplet gap of 354 KJ /mol), but very likely to happen for imidazolidin-2-ylidenes **2** due to lack of aromaticity and acyclic NHCs due to loss of conjugation through twisting around N-C carbene bond [7]. The ^{13}C-NMR chemical shifts [1] range from 210-220 ppm downfield from TMS for aromatic imidazolin-2ylidenes **1** and to 235-245 ppm for imidazolidin-2-ylidenes **2** and acyclic NHCs **3** (Figure 1.3).



1 **2** **3**

Figure 1.3: Unsaturated, saturated NHCs and acyclic carbenes

1.2 Brief History of Carbenes

Since the pioneering work of Doering in 1954, carbenes have been recognised as a unique type of intermediate with characteristics distinct from radicals already known in the organic chemistry community [8]. A decade later Wanzlick and co-workers started working on saturated N-heterocyclic system where they explored the dimers of electron rich tetraaminoethylenes to which they proposed

an equilibrium existed between the free carbenes and the dimer and was named the 'Wanzlick Equilibrium' [6, 9-11] (Figure1.4). The Wanzlick equilibrium was recently confirmed following observation of equilibrium mixtures between free carbenes and tetraaminoethylenes for some benzimidazolin-2-ylidenes [11, 12, and 14].

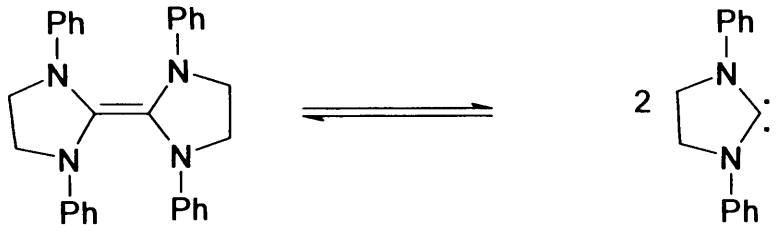
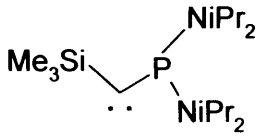


Figure 1.4: The Wanzlick equilibrium.

Wanzlick proposed that the dimer dissociated into two carbenes [13].

Since then research on carbenes has rapidly expanded, but almost no attempts were made to prepare stabilised carbenes until 1980 when Tomoika started to study persisted triplet diarylcarbenes [14].

The first isolable carbenes were reported in 1988 by Bertrand [15] **4** and in 1991 by Arduengo [16] **5**. Phosphinocarbene **4** can be distilled at 80-85 °C/10-2 Torr and N-heterocyclic carbene (NHC) **5** is crystalline solid that melts at above 240-241 °C (Figure 1.5).



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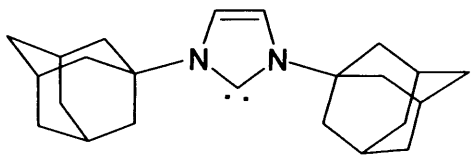

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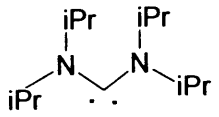
Figure 1.5: The first isolated carbenes

Although NHCs have been known since the pioneering work of Wanzlick, who observed their dimerisation and was able to trap them to form mercury salt carbene complexes [17], three decades went by before the first NHC was isolated. When compound **5** was isolated, the stability of the compound was thought to be due to steric hindrance of the bulky adamantyl sudstituents preventing nucleophilic attack [16]. However in 1995, Arduengo proved using NHC carbene **2** that aromaticity was not needed for stabilisation, [18] and in1996 Alder isolated acyclic NHC **6** [19]. This research area continue to expand with the isolation of four -membered carbene **7** [20] by Grubbs and alkyl carbene **8** by Bertrand in 2004 [21]. Arduengo reported the synthesis of 1,3,4,5-tetramethylimidazolin-2-ylidene **9** and 1, 3-dimethylimidazolin-2-ylidene **10** [22] which are less sterically hindered. Carbenes with only one nitrogen atom have also been isolated as indicated in compounds **8** and **11.** This shows that the presence of one nitrogen atom is adequate enough to stabilise carbenes in certain cases provided the carbene carbon is bound to tertiary alkyl group. The replacements in compound **11** of one of the electronegative nitrogen by a strong σ-donor alkyl group makes the ligand more electronegative than diamino NHCs and therefore behave as strong σ donor towards transition metal centres [21]. Carbenes with more than two heteroatoms (**12** [22]) and those with mixture of heteroatoms have also appeared in the literature (**13** [23] and **14** [24]). Hermann and co-workers reported the synthesis of chiral **15** and bis-imidazol-2-ylidenes **16** [25].



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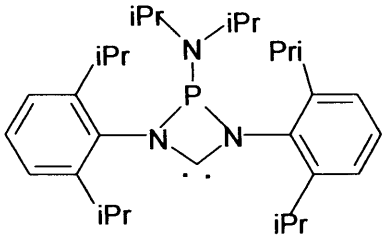

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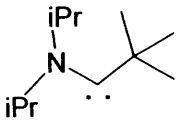

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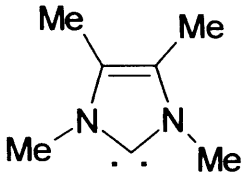

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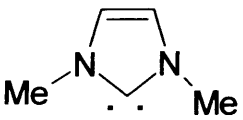

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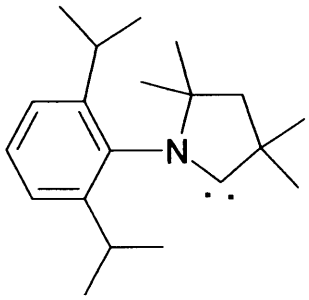

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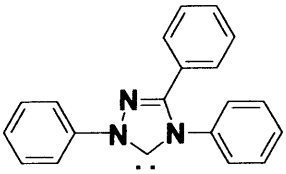

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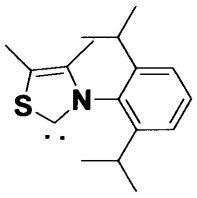

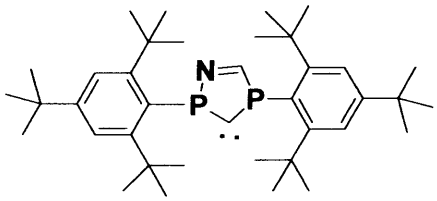

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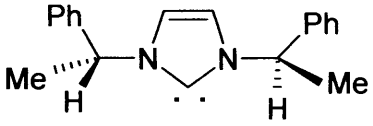

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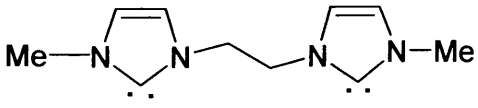

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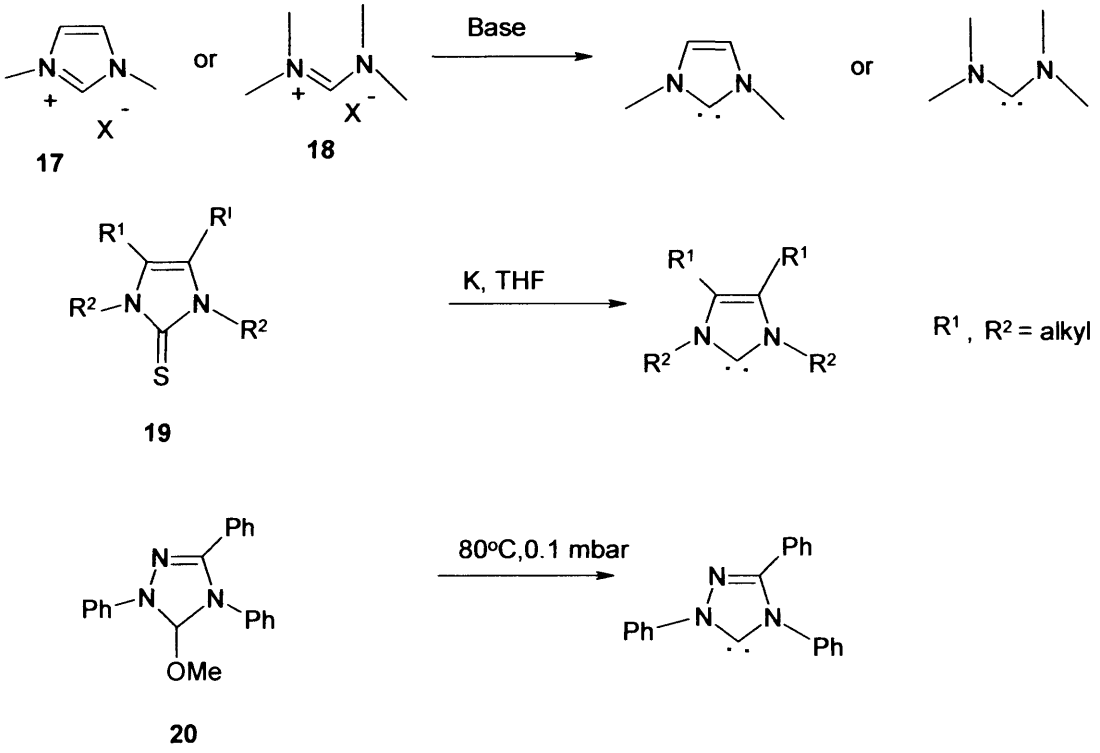
Figure 1.6: Stable carbenes and their derivatives

1.3 Synthesis of diaminocarbenes and pKa

Three principal methods have been used to successfully generate diaminocarbenes:

(i) Deprotonation of imidazolium salt **17** or formamidinium salts **18** with a base [16] (ii) Desulfurisation of thioureas **19** [26](iii) thermolysis of methanol adducts of type **20** [22,95] (Scheme 1.0)



Scheme 1.0: methods of generating NHCs.

The measured pKa value for diisopropylimidazolin-2-ylidenes on the DMSO scale was found to be 24 by Alder [27, 28]. For di-tert-butylimidazolin-2-ylidenes Streitweiser reported a pKa of 20 on the THF scale [29]. It is therefore not surprising that the principal method used in the synthesis of NHCs is by deprotonation of the corresponding imidazolium or formamidinium salts. To synthesize the first NHCs Arduengo used NaH/KH in THF in the presence of KOtBu and DMSO [16].

Herrmann showed that milder conditions such as the use of sodium amide in liquid ammonia and THF at -40°C, were efficient [30]. When the pKa is

increased by 2 to 6 units, formamidinium salts underwent nucleophilic addition of the base rather than deprotonation [28]. Hindered alkali amide bases such as lithium diisopropylamide or potassium hexamethyldisilazide were used to overcome this drawback.

Kuhn and Kratz reported another pathway to imidazolin-2-ylidene by reduction of thioureas using metallic potassium [30]. Though this has been difficult to reproduce [28], it is an interesting discovery because the only other product, potassium sulphide, is insoluble in THF and therefore, can easily be removed.

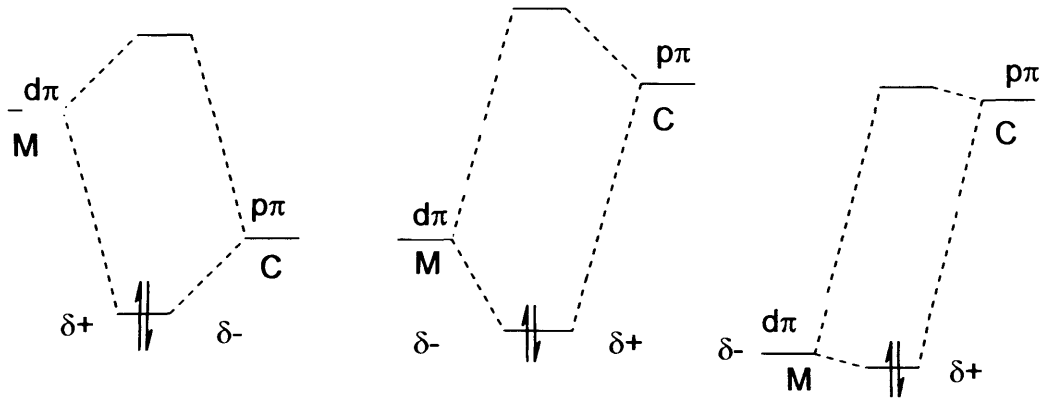
In another method triazol-2-ylidene was synthesised in good yield by Enders by thermolysis of the corresponding methanol adducts [22]. However, this method has some disadvantages due to the extreme sensitivity of the methanol adduct.

I.5 NHC Ligand properties

N-Heterocyclic carbenes (NHCs) are ligands formed by the deprotonation of an N, N-disubstituted imidazolium (or other azolium) salts. Binding of a transition metal to the C2 carbon of the NHC leads to the formation of a very strong bond, the strength deriving from the thermodynamic instability of the free NHC [31]. Unlike metal-carbon bonds in general, those to NHCs do not undergo fast insertion or reductive elimination reactions and so NHCs are generally good spectator ligands. The role of spectator ligand is to act as a placeholder by promoting a desired reaction at the metal, while avoiding dissociation or entering directly into the reaction. NHCs being used as spectator ligands for many decades have risen to prominence, having both steric and electronic tenability and capability to promote catalysis of many useful reactions.

The bonding mode of metal carbene in Schrock and Fischer carbene complexes are both described by double a bond, though they differ by the polarity of the electron density. This difference arises from the difference in energy between the $d\pi$ orbital of the metal and the p_π orbital of the carbene (Figure 1.6). If the $d\pi$ orbital is lower in energy than the $p\pi$ orbital, the metal – carbon is polarised $\delta-$ and $\delta+$ on the carbene and we would have a Fischer carbene complex. On the contrary, if the $d\pi$ orbital is higher in energy than the $p\pi$ orbital, the metal carbon bond is polarised $\delta+$ on the metal and $\delta-$ on the carbene and we would

expect a Shrock carbene complex. NHCs are firmly placed within the Fischer carbenes, their pπ orbital have high energy because multiple bonding between the carbene atom and the two nitrogen atoms. As a result the pπ orbital does not interact well with the dπ thus preventing almost any π- back bonding from the metal to the carbene. In NHC complexes the metal carbon bond is therefore best represented by a single bond.



Schrock nucleophilic carbene | Fischer electrophilic carbene | NHC carbene

Figure 1.7 Partial molecular diagrams for Schrock, Fisher and NHC carbene complexes.

The absence of a requirement for back bonding enable NHCs to form stable metal complexes with a range of metals that do not posses occupied orbitals and so would not be able to participate in back-bonding. Metals such as Li [32, 33], and Be [34, 35] and hexavalent U [36, 37] have been reported to form stable metal complexes with NHCs.

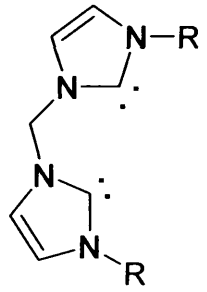
The fundamental difference between a typical Schrock carbene and NHC as ligand is shown in the crystal structure of $[RuCl_2(NHC)_2(=CHC_6H_4Cl)]$ (NHC= 1,3-diisopropylimimidazolin-2-ylidene) where the two types of the carbenes are linked together to the same metal centre [38].The ruthenium-carbon bond of the Schrock carbene, generally written as a double bond, has a bond length of 1.821(3)Å, whereas the Ru-C bond length in NHC (2.107(3)Å and 2.115(3)Å)

which justifies its representation as a single bond (σ- donor and virtually no π-backbonding).

Measurement of IR carbonyl absorption frequencies of NHC carbonyl metal (Fe, Cr, Rh, Mo and Ir) and their phosphine analogues showed significantly donor capacity of NHC relative to phosphines, even to trialkylphosphines [39, 40, and 4]. Furthermore, experimental investigations [42], and calorimetric studies [43, 44] and experimental calculations [45] agree that the ligand dissociation energy of NHC from Ru complexes is higher than for phosphines. Similar results were obtained from calculations with other metals such as Au, Cu, Ag, Pd and Pt [46, 47].

1.6 Chelating, Pincer and Mixed donor Ligands

One of the attractive features of NHCs is the wide variety of steric [48] and asymmetric environments [49] that are available through modification of the substituents attached to the NHC nitrogen atoms. Furthermore, through the use of appropriate donor groups on the NHC substituents, it is possible to make multidentate NHCs [50]. Such variability makes possible the synthesis of NHC analogues of many traditional phosphine ligands. Through this synthetic modification, a wide range of ligands containing two or more NHCs groups are known. In 1994 Dias and Jin isolated bis-carbene **21** and tri-NHC ligand **22** [51] as shown in figure1.8.



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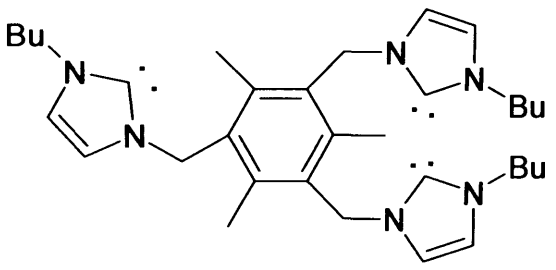

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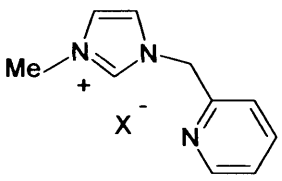
Figure 1.8: Chelating NHCs ligand

Through the use of appropriate donor groups on the NHC substituents, the coordination sphere of the metal can be tailored by chelating ligands incorporating a strongly bound, robust functional group, (NHC), with additional tethers carrying labile donors [52]. The later can temporarily dissociate during catalytic reactions creating electronic coordinative unsaturation, which is important for catalysis. Towards this end Danopoulos et al have synthesised NHC precursors functionalised with pyridine rings. Almost simultaneously, related ligand designs were reported by Cavell [53] and Crabtree [54].

Danopoulos stated that the σ-donating pyridine rings tethered to the NHCs are believed to add versatility to the ligand designs for four reasons:(i)The pyridine function is expected to bind weakly to lower , softer oxidation states of the metal. (ii) This in combination with adjustment of the chelate ring size by using variable length linkers, can promote ligand hemilability with possible implications on the catalytic activity. (iii) The electronic asymmetric of the chelating N-functionalised NHC ligands renders the corresponding trans-sites electronically inequivalent, due to large difference in the trans effect of the chelating ends. (iv) The donor and steric characteristic of the pyridine and NHC functional groups are easily tunable by a variety of substituents [55]. It was along these lines that a number of research groups were able to prepare hemilabile pyridine functionalised ligands [53, 56, and 57]. A number of examples are depicted in Figure 1.8.

In order to test the hypothesis advanced for the choice of the pyridine functionalised ligands, the ligands shown below were used to prepare some carbene complexes and complexes tested in some catalysis. The reaction of the corresponding silver carbene Ag(I)NHC of **23** with PdMeCl(cod) gave PdMeCl (NHC). The catalytic activity of the palladium carbene was tested in Heck coupling reaction of 4-bromoacetophenone/4-chlorobenzaldehyde with n-butyl acrylate and the catalyst was found to have good activity and high stability. The Suzuki coupling of 4-bromoacetophenone with $C_6H_5B(OH)_2$ gave good to satisfactory result as well [53]. Danopoulos reported the synthesis of PdMeCl(NHC) from salts analogous to **23** which gave good activities in Heck and amination reactions [55]. Ligand **28** which is an example pyridinyl carbene (denoted as **pyN^C-R**) was used to prepare iridium (1) carbene complexes as

well as catalytic activities towards the hydrogen transfer reduction of nitroarenes under mild conditions [58].



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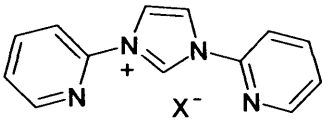

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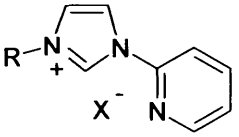
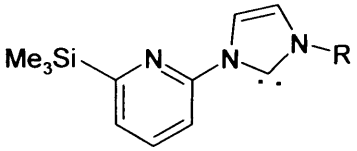
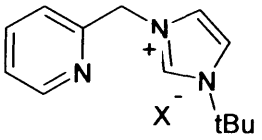


25 R= iPr



26: R = iPr



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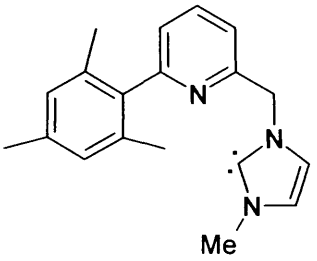
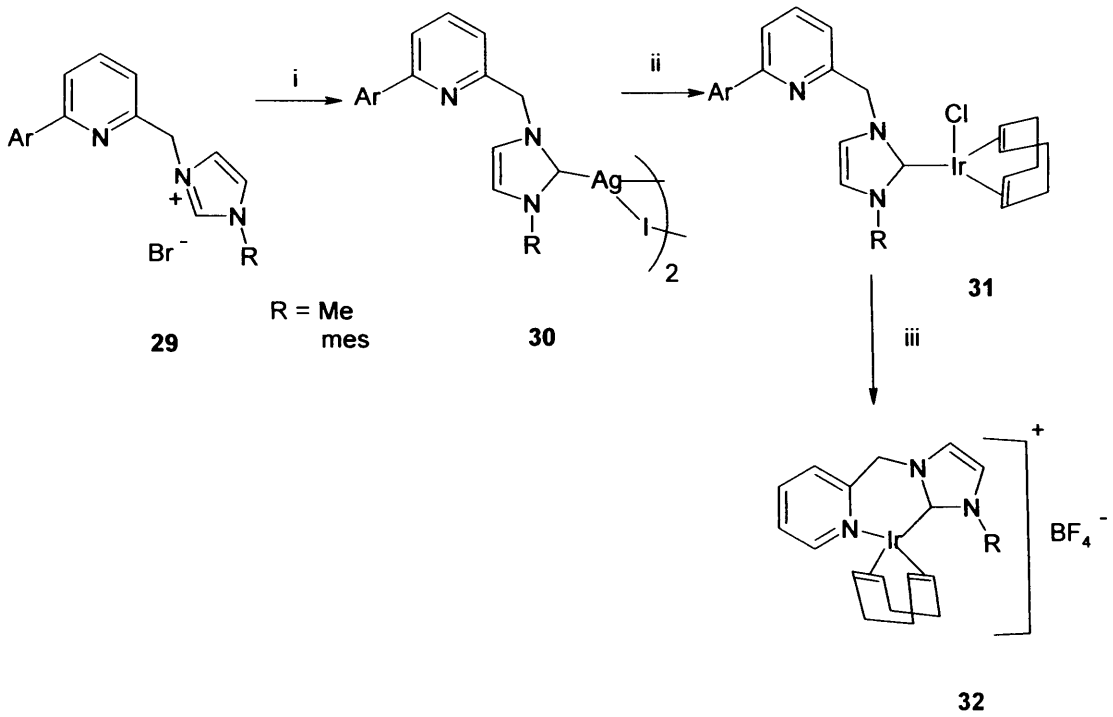


28

Figure 1.9 Pyridyl functionalised Ligands

The reaction of the corresponding silver carbene **30** with $[Ir(COD)Cl]_2$ gave the unchelated compound **31**. Chelation of the **pyN^C-R** toward the iridium centre was achieved by the treatment of **31** with an equimolar amount of $AgBF_4$, leading to the ligand substitution of chloride by the pyridine nitrogen to give compound **32** as shown in Scheme 2.

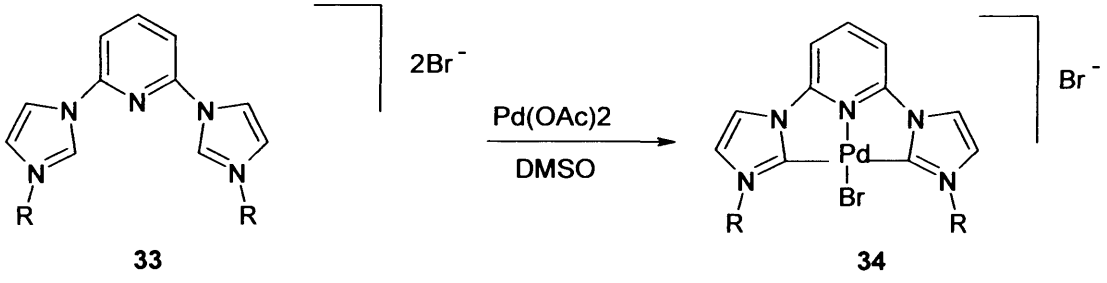


Scheme 2: Reagents and condition (i) Ag_2O, NaI, r.t. 24 hrs. (ii) [Ir (COD) Cl] $_2$, r.t. 3 hrs. (iii) $AgBF_4$

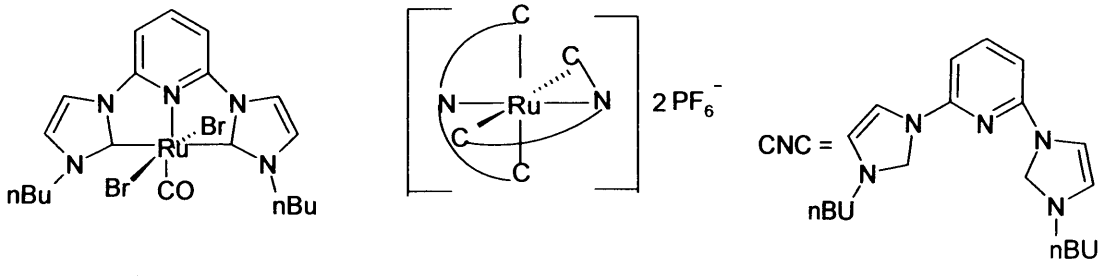
The catalytic activities towards reduction of benzophenone and nitroarenes showed that the ligand binding in a monodentate fashion compound **31** has higher catalytic activity compared to their respective chelation complexes **32.** However, in all the NHC iridium complexes described showed higher catalytic activities relative to when [Ir (COD) Cl] $_2$ were used as catalyst towards reduction of benzophenone and nitroarenes.

The research interest in metal N- Heterocyclic carbene (NHC) is now expanding to the study of new versatile ligand topologies, which have shown promising spectator characteristics with classical functional groups [59]. One of these is the pincer architecture which in the case of pyridyl carbene ligands are mostly tridentate in nature. The pincer ligands provide a preorganised backbone capable of blocking pseudo-meridional coordination sites of metal, leaving the remaining available for catalysis [60]. In line with above principles Crabtree reported the CNC ligand **33** and its corresponding pincer complex of Pd (II) **34** through reaction with Pd (II)$(OAc)_2$. Complex **34** proved to be a robust catalyst for the Heck reaction at 165°C, showing the resistance of the complex to

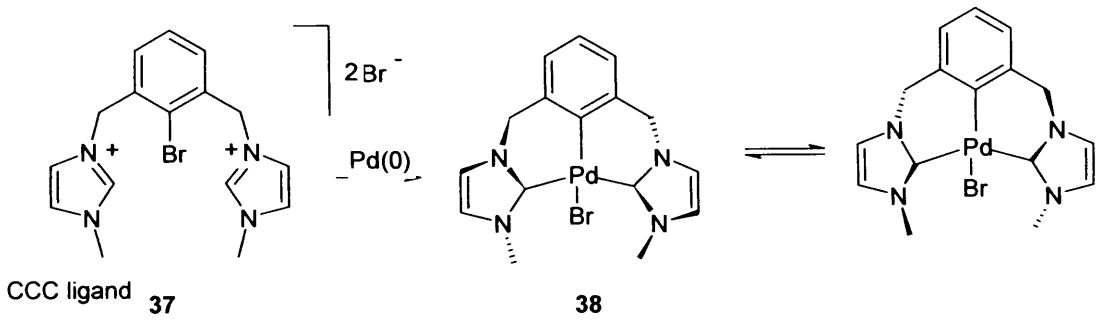
thermal decomposition and in air [61].The planar complex showed low solubility but using R= n-Bu wingtip gave sufficient solubility for convenient study. Introduction of methylene linker result in loss of planarity and greatly improved the solubility. The Ru pincer complexes of the mode CNC have also been reported by the same group (**35, 36**). Catalytic tests showed **35** to be active in both hydrogen transfer and oxidation of olefins while **36** was inactive in both cases [62]. The same group reported CCC pincer ligand **37** and its conversion to Pd (II) complex **38** by using Pd (0) through oxidative addition cyclometallation. The CCC complex was more rigid than CNC pincer but still fluxional enough to give coalescence at elevated temperature. All the species however appeared to be catalytically active in the usual coupling reactions. The Crabtree pincer ligands and complexes are depicted in Scheme 3.



33 **34**



35 **36**



Scheme 3: Synthesis and example of some Crabtree pincer complexes

The Cavell group has also looked at related Pd (II) complexes (**39**, **40**, **and 41**) [63 and 64]. Compound **39** which is a Pd-hydrocarbyl pincer complex was prepared using a one pot transmetallation technique via the Ag^{I}(NHC) complexes [64]. The complexes reported have shown good activity in a model Heck coupling reaction using activated aryl bromides with the complexes bearing bulkier N- substituents outperforming the N-Me substituent in the case of complexes **40** analogues.

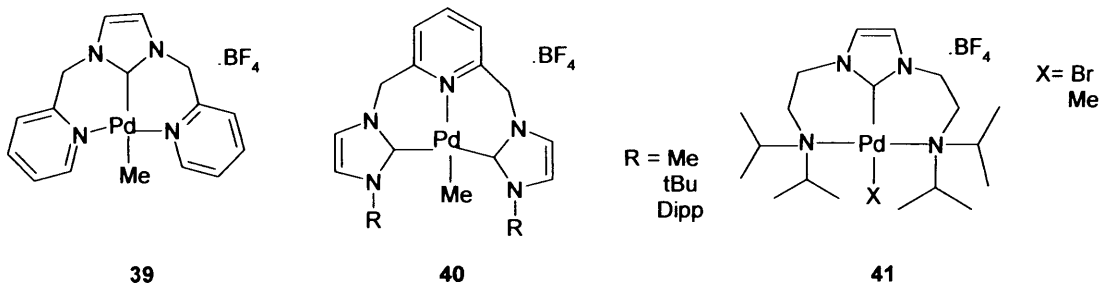
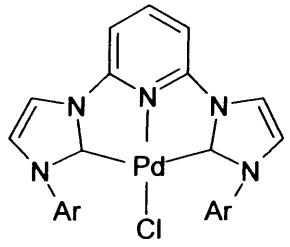


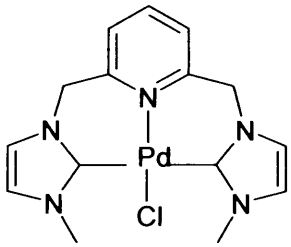
Figure 1.20: Cavell pincer complexes reported.

The Danopoulos group has also reported analogous carbene complexes as part of his contribution to the investigation of the behaviour of these noble metal complexes. Compounds (**42, 43** and **44**) are Pd (II) carbene complexes and their tests in catalysis have showed good stability and activity in the Heck reaction [65].The same group also reported the synthesis of complexes **45** and **46**. Complex **45** was accessed by the reaction of the corresponding imidazolium salt with [Fe(N($SiMe_3$)$_2$]. Complex **46** is the first reported dinitrogen complex

stabilised by NHC [66]. The same synthetic methodology was applied for the synthesis of complex **47** by the reaction of $Co[N(SiMe_3)_2]_2$ with a bis imidazolium salt which on further reaction with Na(Hg) and MeLi gave complexes **48** and **49**. Also reported in the literature by the same group is complex **50** which was prepared by the reaction of 2,6-[(o-dialkyl)phenylimidazolylidene]pyridine with $RuCl_2(PPh_3)_3$ in THF. Catalytic tests of complex **50** in hydrogenation of C=O and C=N groups by hydrogen transfer from isopropyl alcohol in the presence of $KOBu^t$ or $KOPr^i$ showed remarkable activity [67], though the reactions are slow at room temperature but proceed at good rates at 55°C or 80°C.



42: Ar = mesityl



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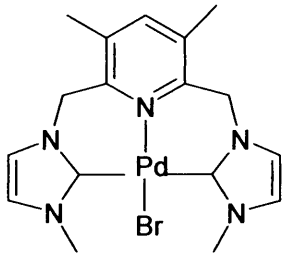

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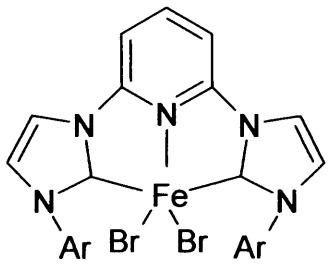
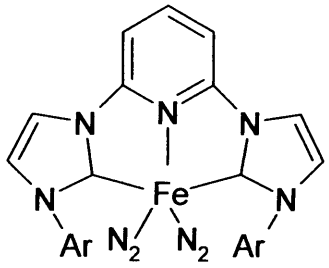
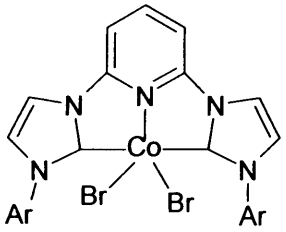


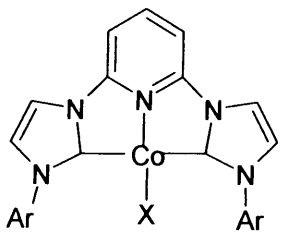
45: Ar = 2, 6-$iPr_2C_6H_3$





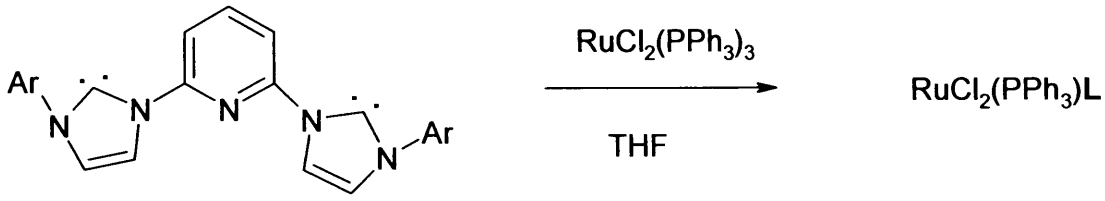
47

Na(Hg) or MeLi



X = Br , Me

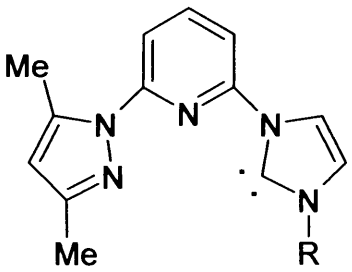
48 / 49



L: Ar = 2, 6-iPrC$_6$H$_3$ **50**

Figure 1.21 Examples of some Danopoulos Pincer carbene complexes

In 2006 Zeng and Yu reported the synthesis of pyridyl-supported pyrazolyl- N-Heterocyclic carbene ligands (**51**, **52**) and their corresponding palladium complexes (**53**, **54**) and tested in Suzuki-Muyaura reactions [68]. A methylene linker was introduced in ligand **52** to release the steric strain encountered on **51**. All the palladium complexes exhibited good to excellent catalytic activity in Suzuki-Miyaura reaction of phenyl or p-tolylboric acid with aryl halide including iodobenzene, aryl bromides, and activated aryl chlorides under mild conditions, revealing that the new ligands are promising for the construction of highly active transition metal catalysts. The ligands and the complexes are depicted in figure 1.22.



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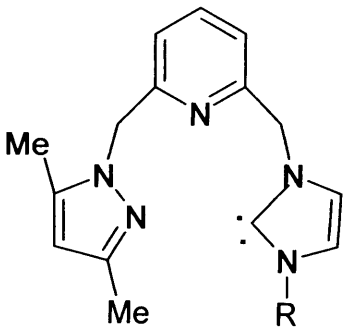

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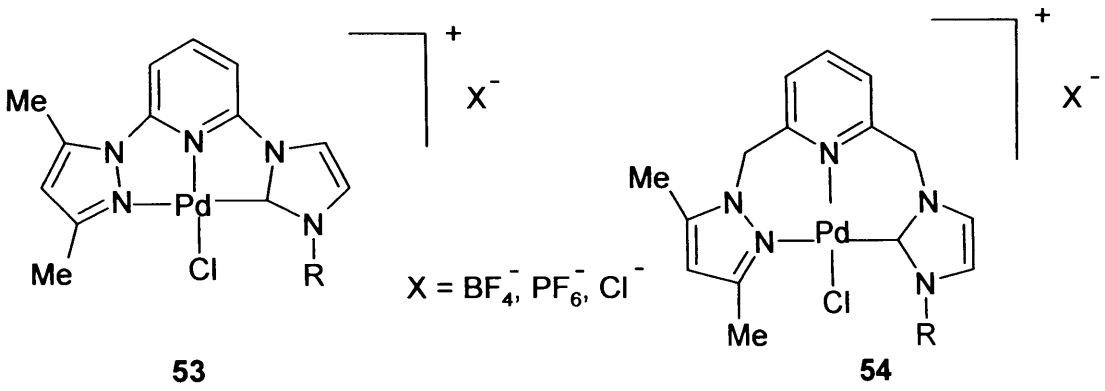
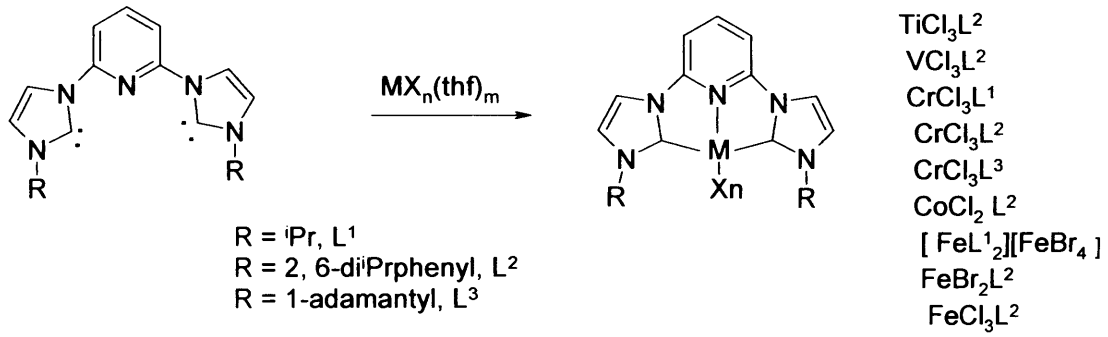


53 54

Figure 1.22 Pyridyl Supported pyrazolyl NHC Ligands

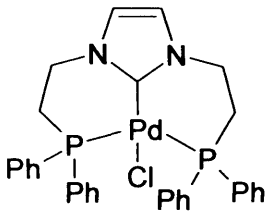
A series of other pyridyl functionalised pincer carbene complexes were reported by Gibson and tested in oligomerisation and polymerisation of ethylene [69] as shown in Scheme 4 below. However, of all the reported complexes (Fe, V, Cr, Ti, Co), only Fe complexes showed evidence of alkyl carbene coupling signifying the importance of the early transition metal complexes in this chemistry[69, 70].



Scheme 4: Examples of Gibson pincer NHCs

Pincer PCP complex **55** [71] and tetradentate pyridine functional ligand **56** and its corresponding Pd(II) **57** and Ni(II) **58** [72] have also appeared in the literature. Compound **55** as can be seen contains three strong σ- donors and its use in Heck and Suzuki reaction was found to be effective. In contrast to carbene complexes with mono, bi-, and tridentate ligands widely used in C-C coupling reactions, tetradentate ligands are rarely employed because of restriction on the available coordination sites for the incoming substrates, though the more robust nature of metal complexes with tetradentate ligands can

provide extra stability to the catalytic species. Few reports exist on the use of NHC nickel as catalyst in Suzuki coupling [73]. However preliminary application of the tetradentate nickel complex $[NiL]^{2+}.2Br^-$ **58** in Suzuki coupling of aryl halides with phenylboronic acid has shown effective catalytic activities including aryl chlorides as substrates. This is particularly important as nickel is cheaper than palladium, thus the use nickel catalyst will give access to large-scale of inexpensive compounds.



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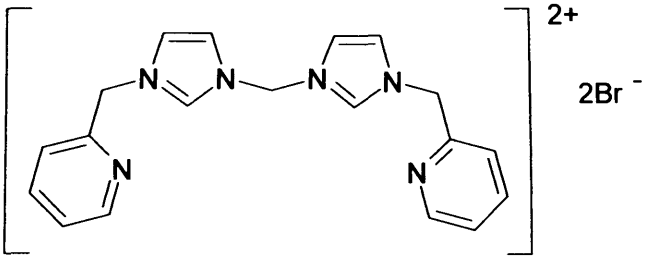
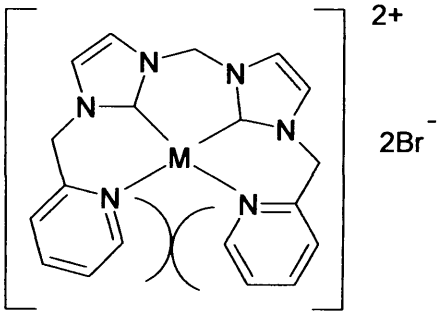


56

DMSO, $M(OAc)_2$



57: M = Pd

58: M = Ni

Scheme 5: Examples of PCP and Tetradentate complexes

1.8 Carbene complexes

Carbene was first introduced into organometallics chemistry in 1964 [74] by Fischer. Fischer complexes exhibited σ- donor/ pπ-acceptor behaviour for the bound carbene, and the metal to carbon bonds were shorter than the usual single bond [75]. Following this discovery it became evidently clear that there were

two distinct types of carbene complexes at that time. Fisher carbene complexes combine weakly donating singlet carbene, which accepts back bonding from low-valent metal [1, 75, 76,], while the already known Schrock carbene complexes combine a covalent triplet carbene and triplet metal fragment. In contrast to NHCs, these carbenes generally contain alkyl substituents and therefore are nucleophilic and coordinate to high oxidation state metals.

With the isolation of free carbene by Arduengo, there were renewed interests in the study of nucleophilic carbene complexes. It was initially thought that Arduengo NHCs carbene would yield Fisher type carbene complexes upon coordination to a metal centre, but the bonding properties showed different characteristics. Due to the back donation from the adjacent nitrogen heteroatoms and their strong capacity as σ-donors to metals, NHCs form only a single σ-bond to metals with negligible π-back donation [1, 76], and therefore these complexes exhibit different reaction chemistry to either Fischer or Schrock carbene complexes.

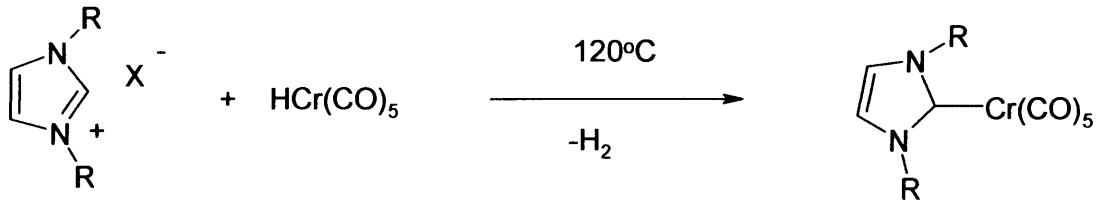
N-heterocyclic carbenes (NHCs) have attracted much attention because their transition metal complexes display rich coordination chemistry and have wide applicability in catalysis [1].Recently research efforts have been devoted to the synthesis of polydentate ligands containing NHC moieties. The combination of pyridine and NHC functionalities leads to diverse polydentate ligands, some of which have shown interesting coordination chemistry [54, 77,78, 79], efficient catalytic applications [53,80,81,] and biological activities [82].The basis of this study was to develop new ligand structure, by substituting pyridine with quinoline substituents, which are expected to provide greater rigidity and hence stability, though these rigid structures also lead to significant steric over crowding. Hopefully, this controlled flexibility/steric crowding parameters will lead to improved catalytic performance in a range of reactions.

1.8.1 Synthesis of N- heterocyclic carbene transition metal complex

What is to be done with the transition metal carbene complexes is probably more important than the complexes themselves and since carbene complexes have found utilization in many industries, scientists have been working to find simple methods to access these very important compounds. A number of routes have been developed, allowing the preparation of complexes bearing carbene ligands with a large variety of electronic and steric properties [83]. This has mainly been achieved as a result of the straight forward methods of synthesis of a range of imidazolium salts thereby allowing for the design of carbene ligands with a variety of electronic and steric properties, ideal for tailoring the properties of the desired complex as catalyst. Of the many synthetic methodologies available in the literature for the preparation of NHC metal complexes, four are more prominent :(i) In- situ deprotonation of azolium salts (ii) complexes via free carbenes (iii) Ligand transfer reactions (iv) Oxidative addition reactions.

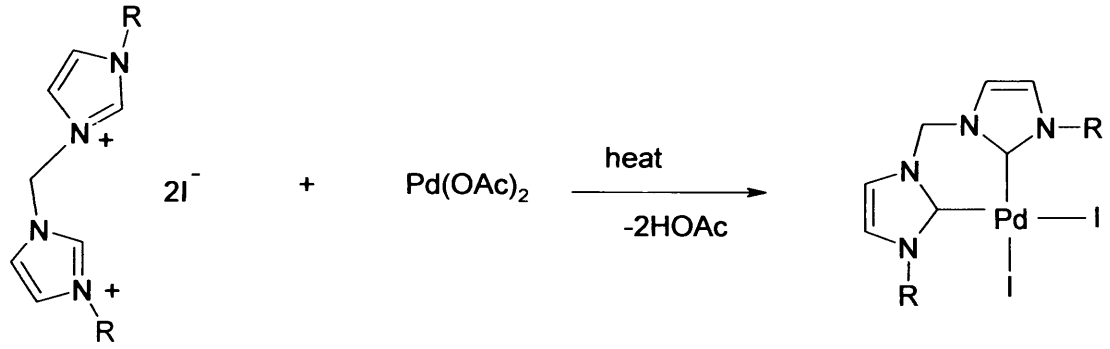
1.8.1.1 In- situ deprotonation of azolium salts

This is the most widely used method of accessing carbene complexes. In this method, the isolation of the free carbene is not necessary. In his original work, Ofele formed NHCs by in situ deprotonation of the corresponding imidazolium salts. The basic metalate ion $[HCr(CO)_5]^-$ serves as base as well as ligand acceptor [84].



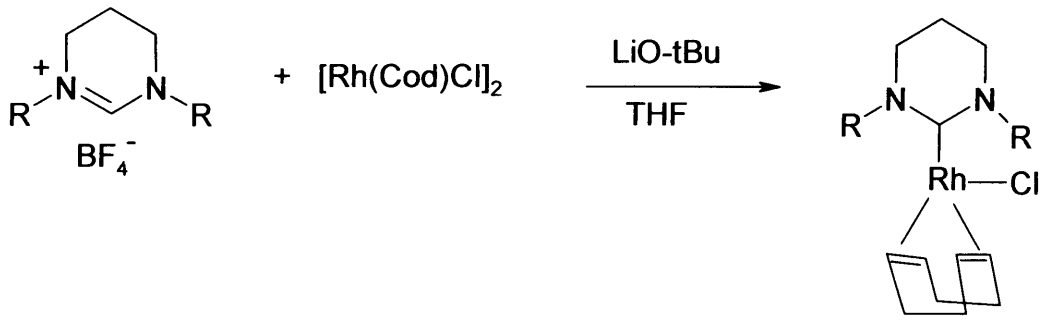
Scheme 6: Carbene complexes through basic metalate anion deprotonation

Basic counter ions of the metal precursors can also act as deprotonating agents. For example, a convenient method to synthesise NHC-Pd (II) is by mixing Pd $(OAc)_2$ with the corresponding imidazolium salt. In a similar way, μ-alkoxo complexes of (η^4-cod) rhodium(I) or iridium(I), formed in situ by adding μ-chloro bridged analogues to a solution of sodium alkoxide in the corresponding alcohol, will deprotonate an imidazolium salt to form the corresponding NHC complex[85]. Despite being relatively simple method, the imidazolium counterion is generally incorporated into the nascent carbene complexes unless non-coordinating anions are used. Good yields require the use of a solvent, such as THF or DMSO, however solvent free reactions have been reported [26, 86].



Scheme 7: Carbene complexes by basic ligand deprotonation

The use of an external base to generate NHCs in the presence of the metal precursor is also an efficient way of accessing carbene complexes. Popular external bases include potassium and lithium tert-butoxide [87, 88], sodium hydride [89], butyl lithium [90, 91], triethylamine [92, 93] and $KN(SiMe_3)_2$ [94]

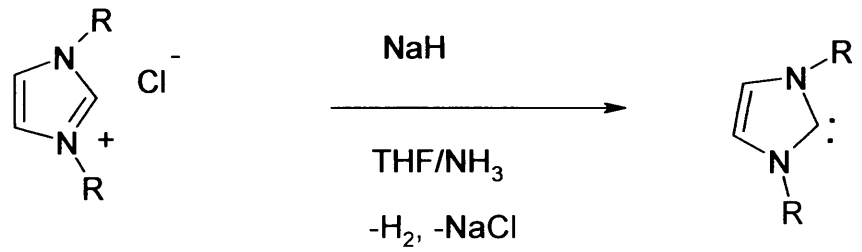


Scheme 8: Synthesis of Carbene Complexes via external base deprotonation

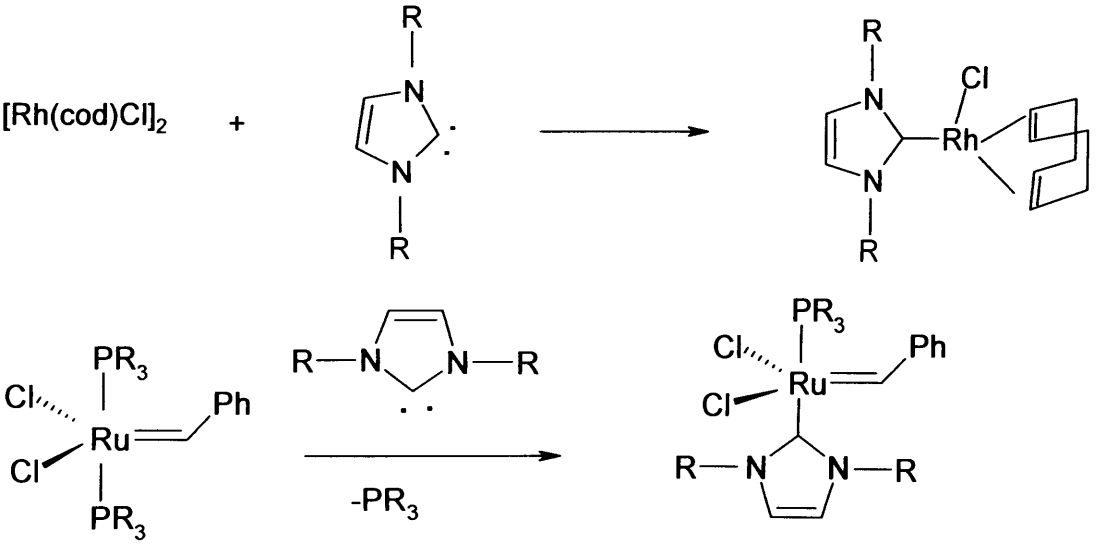
Another method that allows the synthesis of carbene complexes is through the elimination of molecules of methanol and chloroform from the diazaortho-ester [95, 96] and trichloromethyl-substituted relatives of imidazolium salts [97, 98].Thermal elimination of these two substituents gives free carbene which upon reaction by a suitable metal precursor form the appropriate carbene complex.

1.8.1.2 Carbene Complexes through free carbenes

Following the isolation of 1, 3-diadamantylimidazol-2-ylidene by Arduengo, a wide range of new carbene complexes could be synthesised by carefully using the appropriate metal precursor complex. The most popular methods of synthesising free carbenes is by the use of strong bases such as sodium hydride and potassium tert-butoxide in THF [16, 99], or mixture of THF and liquid ammonia [26].



Scheme 9: Synthesis of free carbene

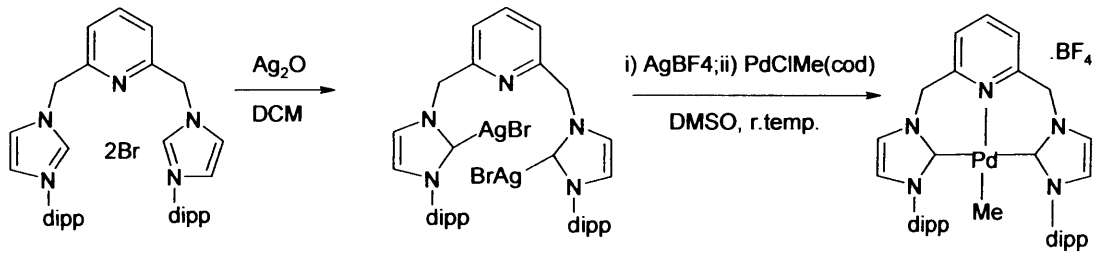


Scheme 10: Carbene complex formation from free carbenes and dimeric cleavage and phosphines exchange

NHCs are very strong σ donors and show dissociation energies higher than phosphines for a large number metals. Therefore, when their free carbene can be isolated, their complexation is achieved in high yield. Free NHCs have been found to be able to cleave dimeric species such as $[(\eta^4\text{-cod})RhCl]_2$ [26] and exchange phosphines [38] and pyridine [100] ligands as depicted above in Scheme 10

1.8.1.3 Carbene complexes through transmetallation

Some NHCs are difficult or not possible to synthesise via the free routes especially in a situation where the NHC precursor contains acidic proton in its linker chain. Gratifyingly it was discovered that Chromium, molybdenum and tungsten complexes could be used for carbene transfer to a variety of metals including rhodium(I), Palladium(II), copper(I), Platinum(II), Silver(I) and gold(I) [101-103]. Recently it has been found that transmetallation reactions using silver carbene have been reported for a wide variety of transition metals: Au(I), Cu(I), Cu(II), Ni(II), Pd(II), Pt(II), Rh(I), Rh(III), Ir(I), Ir(III), Ru(II), Ru(III), and Ru(IV) [104]. The Ag(I) NHC complexes are simply prepared by deprotonation of the imidazolium salt with Ag_2O in a suitable solvent and transmetallation reaction is usually conducted in DMSO or DCM [64].

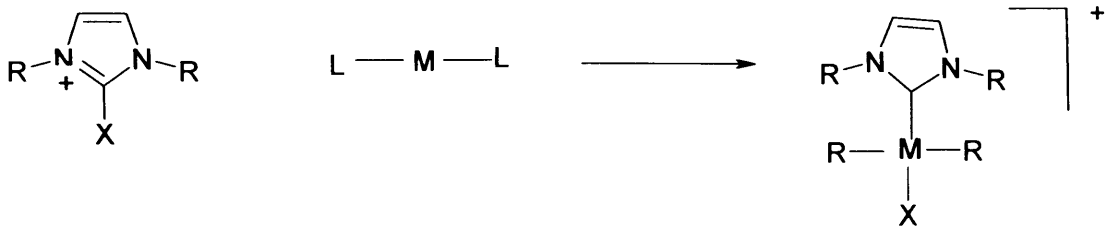


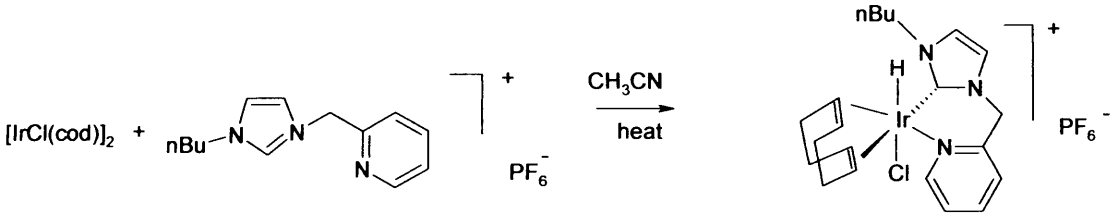
Scheme 11: Carbene complex through silver transfer reactions

1.8.1.4 Carbene complexes through oxidative addition reactions

C-H oxidative addition of an imidazolium salt is another effective alternative method to obtain carbene complexes. The group of Lappert [105] and Stone et al

used oxidative addition method in the 1970's for creating thiazol-2-ylidene complexes from 2-chlorothiazolium salts [106,107]. Cavell group [108, 109] used a similar method to carry out oxidative addition of imidazolium salts to Ni^0, Pd^0 and Pt^0 and recently the method was utilised by Peris et al [110] to synthesize Ir(III) carbene complexes through direct reaction of pyridyl functionalised imidazolium salt with $[IrCl(cod)]_2$ as shown in Scheme 11 below.





Scheme 12: carbene complexes through oxidative addition

Though accessing carbene complexes via this method is generally restricted to nickel, palladium, platinum, rhodium and iridium, these are the commonly used metal in catalysis.

1.9 Abnormal carbene complexes

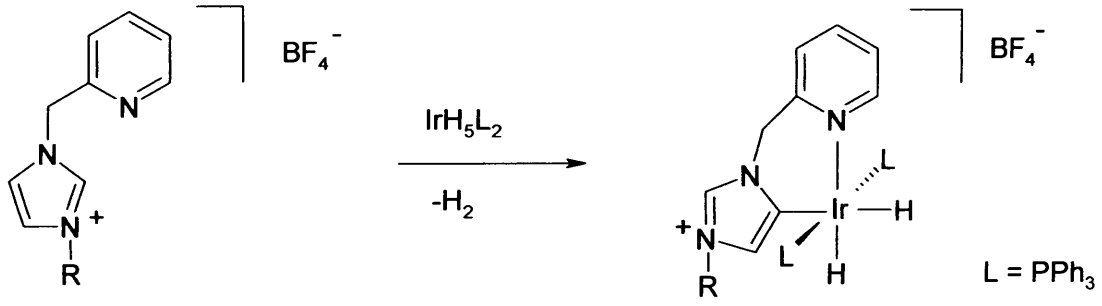
So far all the carbene complexes reported are those in which the coordination took place at the C(2) position of the NHCs. However, in 2001, Crabtree discovered an expected binding mode of NHCs. Instead of having coordination at the usual C(2) position of the NHC, the metal was attached at C(4) or C(5) [111] as shown in figure 1.23.

After this discovery a lot of other publications of NHC have appeared in the literature [112-114].

Normal binding at C(2) Abnormal binding at C(4) or C(5)

Figure 1.23 C(2) and C(4) or C(5) binding mode of the NHCs.

The abnormal carbene complex was initially observed by mixing pyridine-substituted imidazolium salts with $[IrH_5(PPh_3)_2]$ in refluxing benzene. From theoretical calculation [115], binding through C(4) or C(5) positions is less favoured. It was therefore reasoned that steric effects of the bidentate pyridine-NHC around the metal centre and selection of imidazolium salt counter ion controlled the reaction [115]. With many catalytic reactions involving carbene being prepared in situ, care should be taken when designing reactions as slight changes in reaction condition can affect the properties of the catalyst and the overall reaction. The study of the abnormal carbene complexes is still going on.

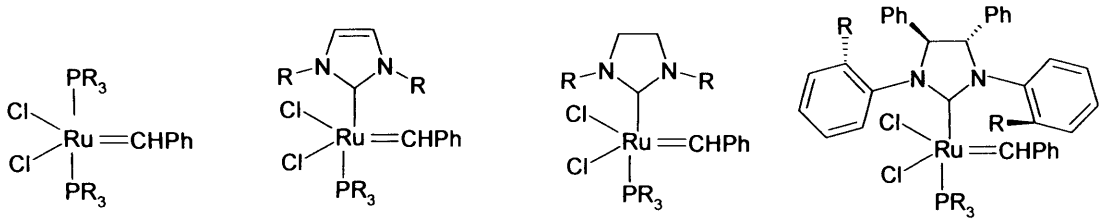


1.2.0 Catalysis involving NHCs

1.2.1 Ruthenium metathesis

The trial of Schrock and Fischer type carbene complexes in catalytic reactions showed that they had the tendency to suffer from M-C cleavage thereby making them catalytically inactive [75]. However, NHCs form stable bond with metals and can accommodate a wide range of oxidation states, making them suitable for

many catalytic transformations. Because of σ-donor ability and their strong metal-carbon bond, NHC ligands have been applied as directing ligands in various catalytic transformations [59]. It is however in ruthenium catalysed olefin metathesis type reactions that NHC ligands have proved their efficiency giving access to unprecedented successful catalytic systems.



59 **60** **61** **62**

Figure 1.24 NHCs in ruthenium metathesis

In his catalysis investigations Herrmann showed that having one imidazolin-2-ylidene in place of a phosphine **60** favours the dissociative substitution of the phosphine ligand with olefinic substrate, giving rise to a more active species [42, 116]. Catalyst **60** was found to have good activities in ring opening metathesis of 1, 5-cyclooctadiene. In a similar fashion Grubbs [117] synthesised and tested catalyst **61** containing more basic NHC and results showed excellent activity in ring opening metathesis. The use of imidazolidin-2-ylidene allowed access to more catalysts by introducing chirality at the C(4) and C(5) positions of the NHC. Towards this end complex **62** was made and its application in desymmetrisation of triolefins yielded the ring closing metathesis products in high enantioselevtivities [118]

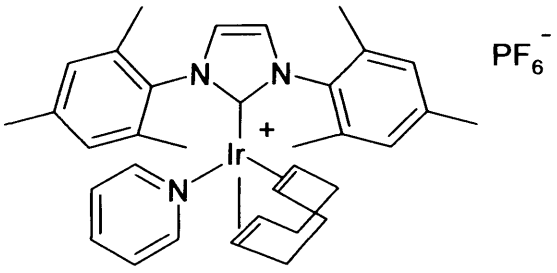
1.2.2 Asymmetric catalysis

Following the success of the use of chiral carbenes in asymmetric catalysis in1996/1997 by Enders [119] and Herrmann [129], chemists have pursued this area leading to many publications on the use of NHCs for asymmetric homogeneous catalysis [121]. Enders applied the NHC and their derivatives in catalysed asymmetric nucleophilic acylation processes with remarkable success.

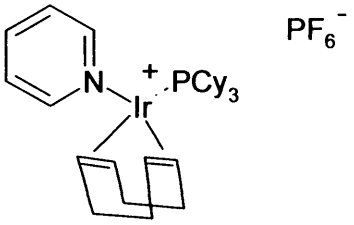
Chiral NHC ligands have found applications in the following catalytic processes: Rh-hydrosilation of ketones [120, 122, 123], olefin metathesis [118, 124], Rh(I) and Ir(I)-transfer hydrogenation of ketones [125] .

1.2.3 Hydrogenation

In his pioneering work Nolan used achiral monodentate NHC iridium complex **63** for the hydrogenation of cyclohexene and 1-methyl cyclohexene (Figure 1.24). Catalyst **63** and Crabtree's catalyst **64** were found to have comparable activity at room temperature [126]. However, catalyst **63** was found to be more robust and efficient at higher temperature probably due to the stability of metal-carbene bond relative to metal –phosphine bond.



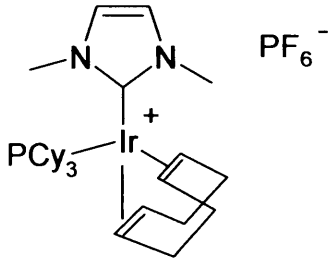
63



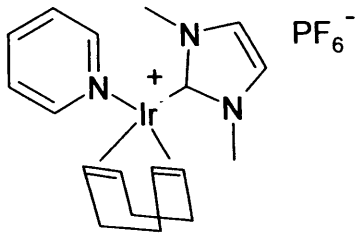
64

Figure 1.25 Achiral monodentate NHC ligand and Crabtree's catalyst

In another investigation, Buriak discovered that combining NHC with phosphine ligands led to efficient systems for the hydrogenation of simple olefins [127]. Comparing complex **65** with its analogue **66** in hydrogenation of 1-methylcylohexene and 2, 3-dimethyl-2-butene showed the superiority of catalyst **65** in activity. While complex **65** fully hydrogenated 2, 3-dimethyl-2-butene in less than an hour at 1 bar H_2 at room temperature, complex **66** gave 19% conversion in 4 hours under the same conditions.



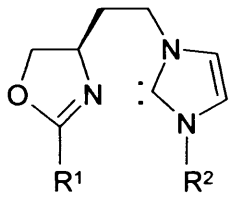
65



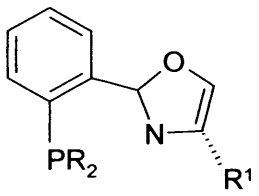
66

Figure 1.**26** Achiral monodentate NHC phosphine and NHC pyridine iridium complexes

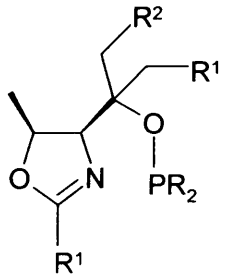
There also exist in the literature some reports on the use of chiral NHCs carbene complexes in asymmetric iridium- catalysed hydrogenation. In particular Burgess chiral bidentate oxazoline-NHC ligand **67** gave high enantioselevtivities for a range of olefins with best results obtained using phosphine-oxazoline (PHOX) **68** and its derivatives **69** [128, 129].



67



68



69

Figure 1.27 Burgess's bidentate oxazoline-NHC ligand, PHOX ligands and its derivatives

NHC carbene complexes are also known to catalyse a wide range of reactions such as hydroformylation [129], hydrosilylation [26, 42, 88, 115, 132,], olefin metathesis [38, 44,130,133-135,136], and polymerisation of alkynes [137 and C-C coupling reactions including Suzuki, Stille and Heck reactions [53, 80, 139, 140].

1.2.4 Catalyst decomposition

NHCs complexes show remarkable stability in many catalytic reactions are often stable to heat, moisture and oxygen. However, McGuiness et al discovered that the carbene catalyst decomposed during the catalytic reaction giving unsatisfactory results [115]. Further investigation indicated that the decomposition was as a result of reductive elimination of *cis* located carbene and alkyl or acyl ligands [141, 142] (Figure 1.28)

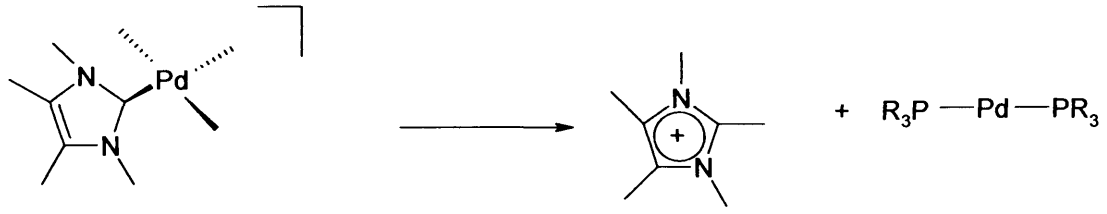


Figure 1.28 Decomposition pathways in carbon monoxide ethylene copolymerisation

It is believed that the reaction is assisted by twist of the carbene with respect to the square planar Pd(II) centre by approximately 60° so that the empty p orbital on the carbene centre is directed towards the alkyl/ acyl group adjacent to it on the metal centre. Since the acyl/ carbene intermediates are necessary intermediates in the CO/ ethylene catalytic cycle, the discovery of the decomposition was quite disturbing, and no reports of success has appeared in the literature of carbene complex catalysis of this reaction since then.

1.2.5 Aims and overview of the thesis

Carbene based ligand systems with functionalised pyridine groups have proved very effective as ligands for catalysis and there has been considerable work on these types of system. The task of this thesis was to develop a new variation on this ligand structure, involving quinoline substituents, which are expected to provide greater rigidity and stability to the complexes. Also as part of this work, the catalytic applications of interesting reactions was explored, primarily the iridium complexes. Ligands of this nature were largely unknown and this opens up an opportunity to develop a whole range of systems with a cross section of properties.

This thesis is composed of chapters which contains introductions, and reviews of relevant literatures to date.

Chapter 2 describes the preparation and characterisation of a range of quinoline functionalised imidazolium salts and a tetrahdropyrimidium salt that were required as precursors to the respective NHC ligands.

Chapter 3 deals with the synthesis and characterisation of a range Ag^{I}(NHC) complexes and few Pd^{II}(NHC) complexes accessed by transmetallation of the corresponding silver carbenes. Some of the Ag^{I} (NHC) complexes were found to be biscarbenes and the nature of the functional group was found to be of no influence to the type of complexes formed.

Chapter 4 presents the synthesis and characterisation of a range Rh^{I} (NHC) and Ir^{I} (NHC) complexes by transmetallation of Ag^{I}(NHC) complexes, with Rh^{I} (NHC) complexes giving higher yields. Attempt to prepare the chelated version was not successful as the complexes were found to insoluble in less polar solvents and decomposed in high polar solvent like DMSO. It also covers the catalytic testing of some the Ir^{I} (NHC) complexes prepare in reduction of 4-bromoacetophenone by hydrogen transfer reactions. The results show that all the complexes were very active giving a conversion of up to 100% with as little as 0.01 mole % of the catalysts.

Chapter 5 deals with conclusions and further work to be carried out as there a lot of research opportunities in this area.

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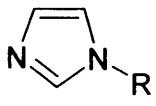
CHAPTER TWO

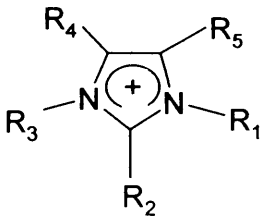
Quinoline functionalised imidazolium and pyrimidinium salts

2.1 Introduction

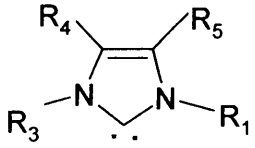
Imidazolium salts can be defined as planar 5 five membered heterocycle with nitrogens at the 1 and 3 positions and a substituents (H, R, Ar, or X) at each position of the ring. The ring members are sp^2 hybridized and the ring bears a single positive charge that is delocalised around the ring [1]. In most cases the imidazole **2a** which does not have substituents on one of the nitrogens serves as a precursor to the many imidazolium salts possible.



2a

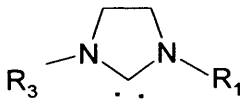


2b

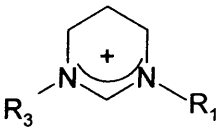


2c

2d



2e



2f

The numbering presented in **2b** is used throughout this research work with $R_2 = R_4 = R_5 = H$ in all the imidazolium salts. The structures are named according to the degree of saturation in the heterocycle of the parent compound. As presented above the imidazole **2a** has two double bonds. The imidazolin-2-ylidene **2c** is derived from **2b** by loss of a proton. In contrast to **2b**, **2d** is a dihydroimidazolium salt and is fully saturated and this does not allow delocalisation of the charge beyond the NCN region, therefore, it has the effect of increasing the donor ability of the derived imidazolidin-2-ylidenes, **2e** [2]. All

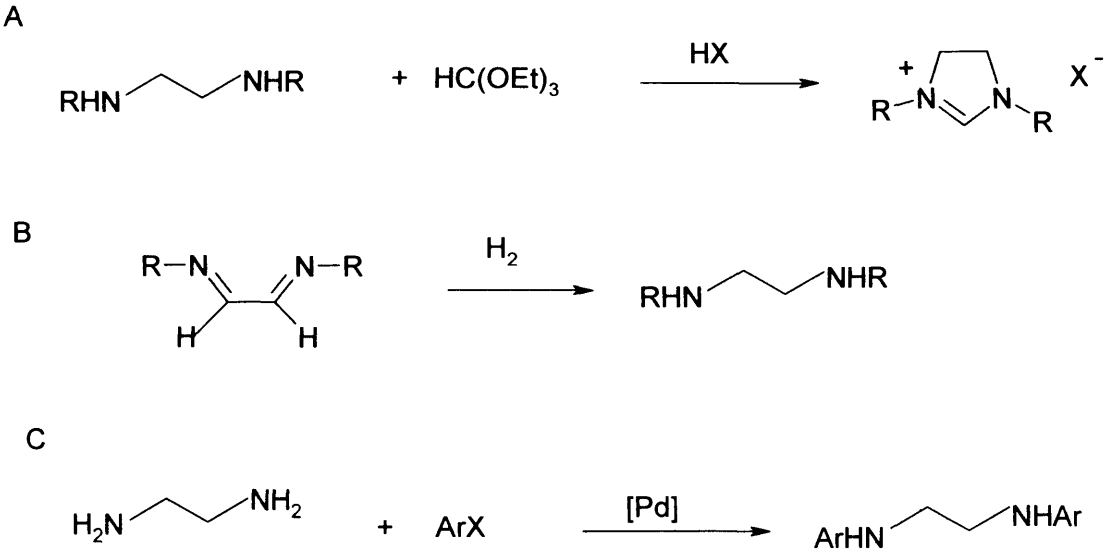
but one of the imidazolium salts described in this thesis are those based on type **2b**. One type **2d** based imidazolium salt is also presented.

Structure **2f** is a typical example of pyrimidinium salt which is a six membered ring with nitrogens at positions 1 and 3. The two nitrogens and C-2 carbon are sp^2 hybridized while C4, C5 and C6 are sp^3 hybridized. The NHC derived from pyrimidinium would be expected to be more basic with high donor capability due to the absence of delocalisation of charge in the NCN region. Though as stated above the NHCs with an unsaturated backbone are generally more stable as free carbenes, since the normally empty pz orbital is part of an aromatic system, conjugated with the C-C double bond in the backbone. There is however little evidence that the aromaticity of an NHC has much bearing on its properties as a ligand for transition metals [3].

The ease of synthesis of imidazolium salts is one of the chief reasons for the popularity of NHCs. Other attractive features of imidazolium based NHCs are the wide variety of steric and asymmetric environments that are available through modification of the substituents on the nitrogen of the heterocycle. Furthermore, through the use of appropriate donor groups on the nitrogen substituents, it is possible to make multidentate NHC ligands [4]. Such variability makes possible the synthesis of numerous ligands. Along these lines Cavell [5], Crabtree [6] and Danopoulos groups [7] have reported wide variety of multidentate pyridyl functionalised ligands. Multidentate ligands especially those that can behave as a chelating ligand having both strong and weak donors (hemilabile ligands) are particularly important in catalysis. The weak hemilabile part of the ligand is capable of reversible dissociation from metal centre, thereby creating vacant coordinating sites during catalytic cycles and stabilising the metal centre by recoordinating when it is catalytically inactive. In addition to the works so far reported on pyridyl ligands, we envisioned the synthesis of an analogue of the quinoline framework. It was our hope that replacing the relatively small pyridine with large quinoline substituents will provide greater rigidity and hence stability to the complexes, though, the rigid structures also lead to steric crowding. Bearing these in mind methylene linker was introduced in some of the imidazolium salts between the imidazole and the quinoline moiety to reduce the steric strain and improve solubility.

2.1.1 Ligand synthesis

Our initial intention was to synthesize a wide range of quinoline based imidazolium salts. However, while we were successful in the synthesis of symmetrically substituted saturated imidazolium salt, the unsymmetrical substituted analogues could not be accessed via traditional approaches [8].



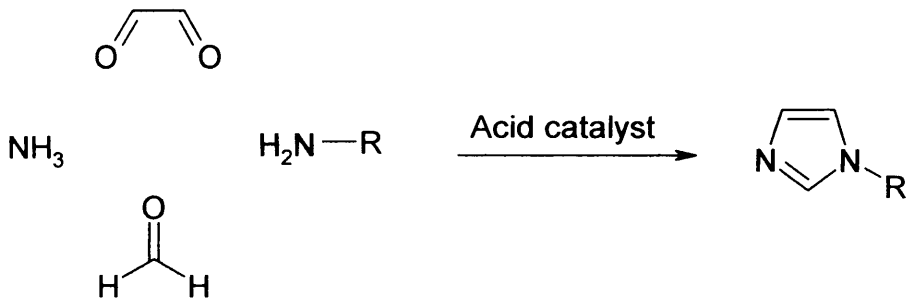
Scheme 2.1: Traditional approach to the synthesis of symmetrical saturated imidazolium salts

Unsymmetrical substituted imidazolium salts have been successfully synthesized via nucleophilic attack of 1-alkylimidazole or 1-aryl imidazole on an alkyl halide [9-12] (Scheme 2.2).Through this direct quartinization, a lot of functional groups have been attached to the imidazolium moiety. Such functional groups include: hydroxyl group [13], carboxylic groups [14], thiol groups [15], alkyne and alkene groups [16, 17].

Scheme 2.2: Synthesis of unsymmetrical imidazolium via nucleophilic attack of imidazole on alkyl halide

However nucleophilic attack on an aryl ring by an imidazole is difficult, making N, N-diaryl substitution unattainable by this approach.

This is a set back because one of our aims was to create as much as possible some steric environment in our target NHCs precursors. Therefore, N, N'-diaryl substituted imidazolium salt with quinoline as one of the substituents was considered an ideal candidate. Fortunately, flexible approaches allowing for the synthesis of bulky N-substituted imidazoles are available in the literature [18, 19] (Scheme 2.3). Synthetic routes to organohalide compounds with donor functionalised groups are also available, though in most cases they can be obtained from commercial sources. Once the N- substituted imidazole is made, a wide range of imidazolium salts can be prepared by reaction with the appropriate alkyl halides as shown in Scheme 2.2 above.



Scheme 2.3: Synthesis of bulky N- substituted imidazoles

In summary, this chapter reports the syntheses of a wide variety of quinoline functionalised imidazolium salts giving access to bidentate and in some cases tridentate ligands. All the reported imidazolium salts were fully characterised by ^{1}H and ^{13}C NMR spectroscopy, mass spectroscopy, micro analysis and in most cases were structurally characterised using single crystal X-ray crystallography.

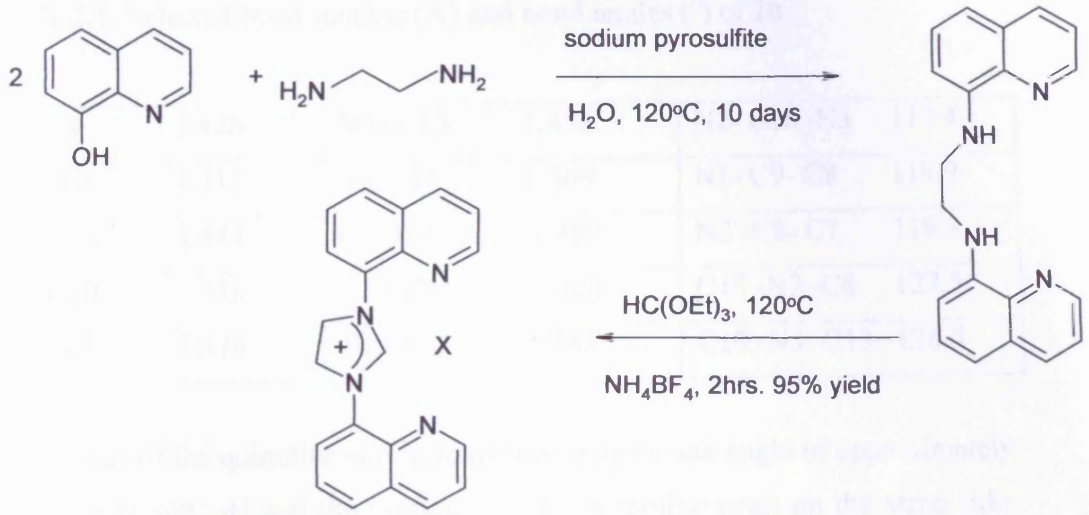
2.2 Results and Discussion

2.2.1 Synthesis and characterisation of symmetrical saturated imidazolium imidazolium salt

Prior to that the start of this work there was no reported synthesis of symmetrical quinoline substituted imidazolium salts and several attempts towards accessing this compound were not successful by the established procedure [20]. However, in 2006 Michon et al almost at the same we synthesised our quinoline based salts reported the synthesis of analogue chiral tetradentate diamine and chiral dihydroimidazolium salts, [21]. In their reaction they utilised Buchwald-Hartwig Palladium –catalysed amination [22] involving 2.1 equivalents of 8-bromoquinoline, 3 equivalents of sodium t-butoxide, 5 mol% of $Pd_2(dba)_3$ and 10mol% of rac-BINAP in toluene at 80 °C under argon affording the chiral amine in 90% (Scheme 2.4). Ring cyclisation of the chiral diamine with triethylortho formate solution at 135°C afforded the desired dihydroimidazolium salts in 60-90% yield.

Previously this type of diamine was synthesised using a Bucherer reaction by refluxing 8-hydroxy quinoline, the desired diamine and sodium pyrosulfite in water for two weeks[23,24], but the yield obtained via this method was low by almost 50% compare to that reported by Michon [21]. This method was also used by T. Okada to make N,N-Di quinolyl-1,3-propanediamine [25].

In our study, we formed our diamine from the considerably cheaper 8-hydroxyquinoline material [23] and the achiral dihydroimidazolium **2** was prepared in 95% yield by reaction with triethyl orthoformate and ammonium tetraflouroborate salt at 120°C in 2 hours as depicted in (Scheme 2.4) above. Compound **1** was characterised by ^{1}H and ^{13}C NMR spectroscopy while imidazolium salt **2a** was characterised by ^{1}H, ^{13}C NMR, mass spectroscopy and microanalysis. The salt is soluble only in high polar solvents such as DMSO or DMF. Of particular importance is the identification of CH unit between the N atoms which appeared at δ value of 11.4 which is higher than the figure reported by Michon [21]. The signal for the C2- carbon in ^{13}C NMR occurs at a δ of 159.21 which is typical of such group [21] (161.90).



2a : X = BF_4^-

2b : X = Barf

In order to carryout any further investigations with the salt there was a need to improve the solubility of the dihydroimidazolium salt. This was achieved by replacing the counter ion tetrafluoroborate with Barf giving access to the imidazolium salt **2b** that is soluble in almost all organic solvents with the exception of petroleum ether and hexane. The characteristic features of **2b** as observed in the ^1H and ^{13}C NMR spectra did not changed significantly in relation to what was observed in **2a**. Diffusion of hexane into the DCM solution of compound **2b** gave crystals suitable for X- ray crystallographic determination, figure 2.1.

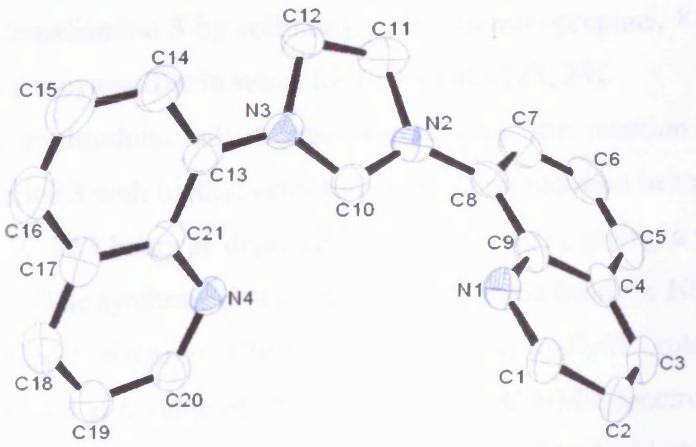


Figure 2.1: ORTEP projection of the cation of **2b.Barf,** excluding hydrogen atoms for clarity, showing labelling of atoms.

Table 2.1: Selected bond lengths (Å) and bond angles (°) of **2b**

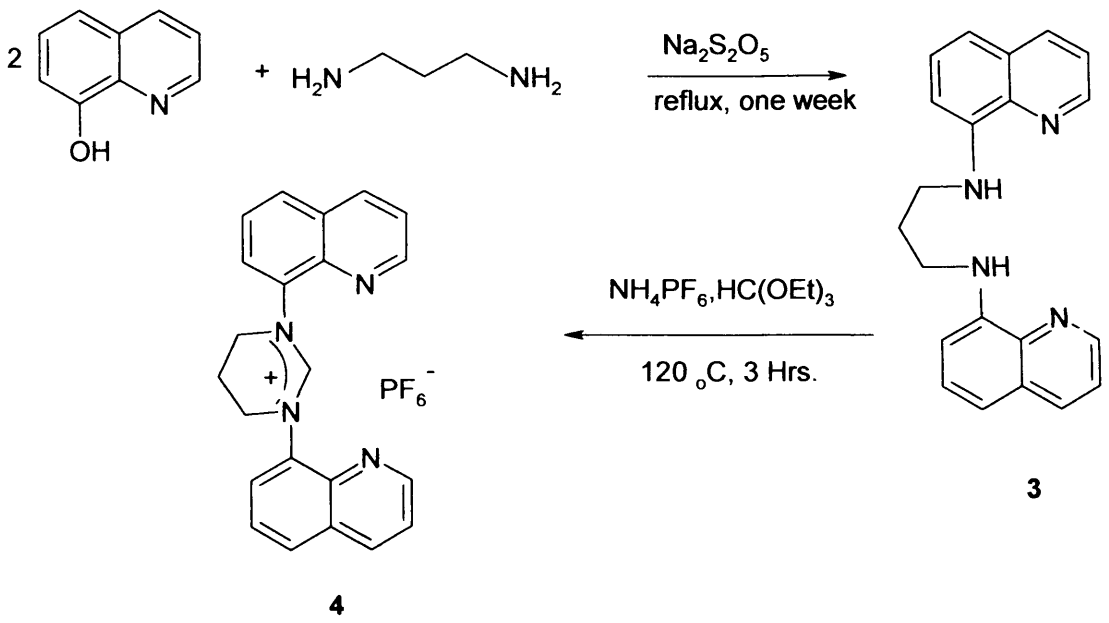
N2 -C8	1.428	N3- C13	1.476	N2- C10 -N3	113.4
N2-C10	1.315	N4-C21	1.369	N1- C9- C8	119.9
N2- C11	1.481	C8- C9	1.480	N2 -C8- C7	119.3
N3- C10	1.316	C13-C21	1.420	C10 -N2 -C8	127.5
N3-C12	1.476	NI-C9	1.363	C10 -N3 -C13	126.4

The planes of the quinoline and imidazolium rings make angle of approximately 36.71° with imC_2-H and the nitrogen on the quinoline rings on the same side. Some selected bond angles and bond length are presented in table 2.1 above. The N2-C10-N3 bond angle of 113.4° obtained is higher than that generally reported for imidazolium salts (108°) [31, 32], but there is no significant difference in bond lengths.

2.2.2 Synthesis and characterisation of bis quinoline pyrimidium salt

Reports on the synthesis of 1, 3- dimesityl and 1, 3-dialkyl tetra hydropyrimidinium salts have appeared in the literature [26]. However, pyrimidium salt **4** is the first six membered ring that is functionalised with quinoline giving a tridentate ligand that may behave as a pincer ligand. The method of Okada was employed to prepare N, N-Di quinolyl-1, 3-propanediamine **3** by refluxing 1, 3 –diaminopropane, 8-hydroxyquinoline and sodium pyrosulfite in water for two weeks [23, 24].

The pyrimidium salt **4** was prepared by the reaction of the corresponding diamine **3** with triethyl orthoformate and ammonium hexafluorophosphate salt at 120°C in 3 hours as depicted in (Scheme 2.5) , giving a white powder in good yield. The synthesis of the salt was confirmed from the NMR data. The ^{1}H NMR showed a signal at 9.3ppm corresponding to C_2-H proton and C_2 carbon was appeared at δ value of 156.72 from the ^{13}C NMR spectrum. The data from the mass spectrum and micro analysis were consistent with the proposed structure.



Scheme 2.5: Synthesis of quinoline functionalised pyrimidium salt

Diffusion of Et_2O into a MeCN of solution of **4** yielded crystals suitable for a single X-ray crystallographic determination, Figure 2.1

Table 2.2: Selected bond lengths (Å) and bond angles (°) of **4**

C1 -N1	1.317(3)	N4-C22	1.372(3)	N1-C1-N2	124.2(3)
C1 -N2	1.317(3)	C5-C6	1.365(3)	C1-N1-C5	120.71(3)
N1 -C5	1.439(3)	C14-C15	1.371(3)	C1-N2-C14	120.32(3)
N2 -C14	1.429(3)	N4-C21	1.323(3)	N1-C5-C15	118.33(3)
C13 -N3	1.370(3)			N1-C2-C3	109.90(3)

The molecular structure of the tetrahydropyrimidium salt **4** in the solid state is depicted in Fig 2.2 being the first structure of a tetrahydropyrimidium salt with nitrogens of the quinoline substituents on the same side with the imC_2-H. The quinoline and imidazolium rings of **4** make an angle of approximately 53.69° which shows a clear divergence from co-planarity. Search of the available literature revealed that X-ray structures of 1,3-disubstituted 3,4,5,6-tetrahydropyrimidinium salts have been reported only for a few symmetrical:

diisopropyl[33], diethyl [34] and dimesityl [35]. The data obtained for compound **4** is very similar to that of the corresponding diisopropyltetrahydropyrimidinium salt reported by Alder [33]. The N1-C1-N2 angle of 124.2(3)° and C1-N2 distance of 1.317(3) Å are nearly identical to the ones published by Alder[33] and Herrmann[35] who reported 124.72(15)° and 1.3147(14)Å respectively.

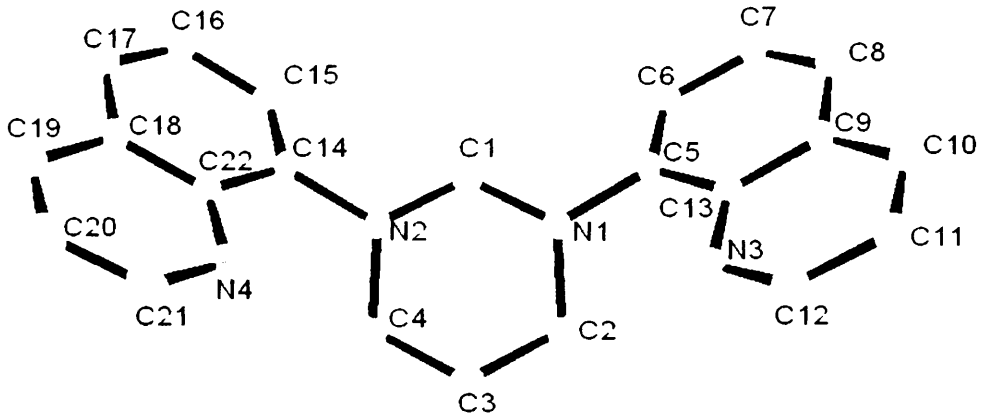
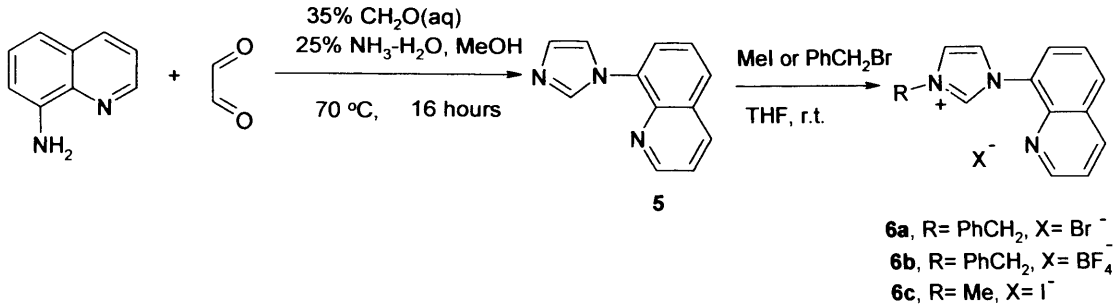


Figure 2.2: ORTEP projection of the cation of **4.PF$_6$** excluding hydrogen atoms for clarity, showing labelling of atoms.

2.2.3 Unsymmetrical substituted Quinoline imidazolium salt

Two quinoline based imidazolium salts are herein reported. 8-imidazol-1-yl-quinoline was synthesised following the Zhang modified procedure for the synthesis of 1-arylimidazole [27].The yield obtained is low (~ 20%) which is a known problem in the literature with most 1-aromatic substituted imidazoles.



Scheme 2.6; Synthesis of quinoline imidazolium salt

The low yield may be connected with the generation of large amounts of unknown by-product during neutralisation. The use of large volume of diethyl ether and vigorous agitation during extraction slightly increased the yield. The use of small scale synthesis is generally more efficient, though the overall yields were not constant. The imidazolium salts were prepared following the standard N-alkylation using methyl iodide or benzyl bromide. The alkylatiom of the quinoline imidazole follows S_N2 behaviour and is difficult to achieve with nucleophile less reactive than a secondary alkyl bromide precluding access to desired bulky N-^{t}Bu, N- Mes and N-dipp substituents on the resulting imidazolium salt via this route [2]. The quinoline imidazole was reacted with either methyl iodide or benzyl bromide in THF overnight to give the desired imidazolium salts (**6a,** and **6c**) as light brown solid in good yield. While imidazolium **6c** is stable towards air and moisture, compound **6a** is hygroscopic and the anion (bromide) was exchanged for tetrafluoroborate anion to obtain compound **6b**. The anion exchange was accomplished by mixing a solution of the halide salt in acetonitrile with a solution of an excess of sodium tetraflouroborate in water which on work gave the BF_4 salt in good yield. The imidazolium salts were fully characterised. The characteristic peak in the ^{1}H NMR is the C_2-H imidazolium proton appearing as singlet between 10.15-10.75ppm. In the ^{13}C NMR the C_2 appeared at a δ value of 150.70ppm. Quality crystals for X-ray crystallography were obtained for the BF_4 version of the imidazolium salt **6b** by vapour diffusion of Et_2O into DCM solution. In the ^{1}H NMR spectra of the BF_4 salt ($CDCl_3$ solvent) the C_2-H imidazolium proton was observed to move upfield while only little of such change could be observed in ^{13}C NMR.

Table 2.3: Selected bond lengths (Å) and bond angles (°) of **6b**

N6-C7	1.391(2)	N9-C8	1.381(2)	N6-C10-N9	108.38(14)
N6-C10	1.3405(19)	C7-C8	1.349(2)	C10-N6-C18	127.40(13)
N6-C18	1.4411(19)	C12-C13	1.389(3)	N9-C11-C12	111.31(14)
N9-C10	1.324(2)	C19-N20	1.367(2)	C18-C19-N20	119.85(14)
N9-C11	1.4846(19)	N20-C21	1.315(2)	N6-C18-C27	118.31(14)

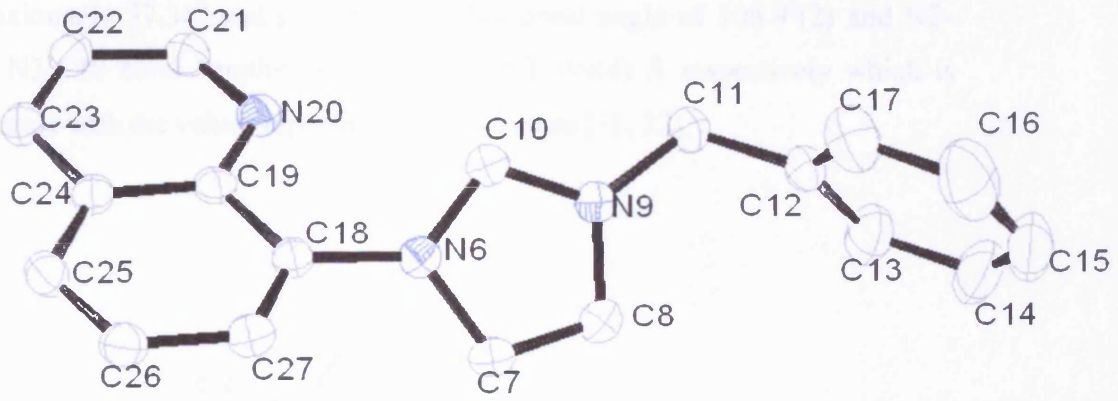


Figure 2.3: ORTEP projection of the cation of **6b.BF_4** excluding hydrogen atoms for clarity showing atom labelling scheme.

The quinoline and imidazolium rings make an angle of approximately 36.16° and both the nitrogen of the quinoline ring and imC_2-H are directed on the same sides of the molecules. The crystal structure of **6b** reveals N6-C10-N9 bond angle of 108.38° and N6-C10, N9-C10 bond lengths of 1.3405(19) Å and 1.324(19) Å respectively which is within the expected values of imidazolium salts reported [31, 32].Crystals suitable for X- ray chromatography was obtained for compound **6c** by diffusion of diethyl ether into the DCM solution of the compound and the crystal structure is depicted in figure 2.4. ^{1}H and ^{13} NMR, MS, and micro analysis data correspond to the proposed structure.

Table 2.4: Selected bond lengths (Å) and bond angles (°) of **6c**

CI-C2	1.367(4)	C10- N2	1.340(4)	N2-C10-N3	108.9(2)
CI-C9	1.442(4)	C10-N3	1.319(4)	C1-N2-C10	127.4(3)
C1-N2	1.439(4)	C13-N3	1.461(4)	C1-C9-N1	119.5(2)
C5-C9	1.423(4)			C9-N1-C8	116.8(2)
C9-NI	1.365(4)			C10-N3-C13	125.3(3)

The planes of the quinoline and imidazolium rings of **6c** make an angle of approximately 37.34° and gave N2-C10-N3 bond angle of 108.9°(2) and N2-C10, N3-C10 bond lengths of 1.340(4) and 1.319(4) Å respectively which is consistent with the values reported in the literature [31, 32].

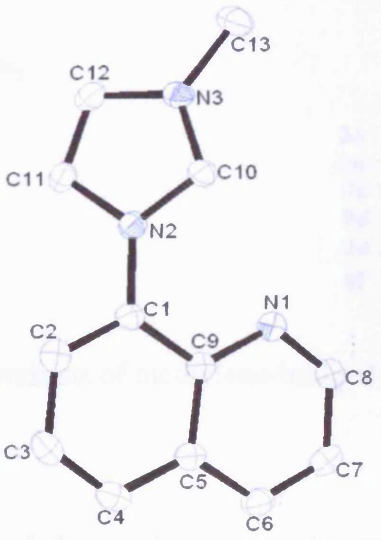
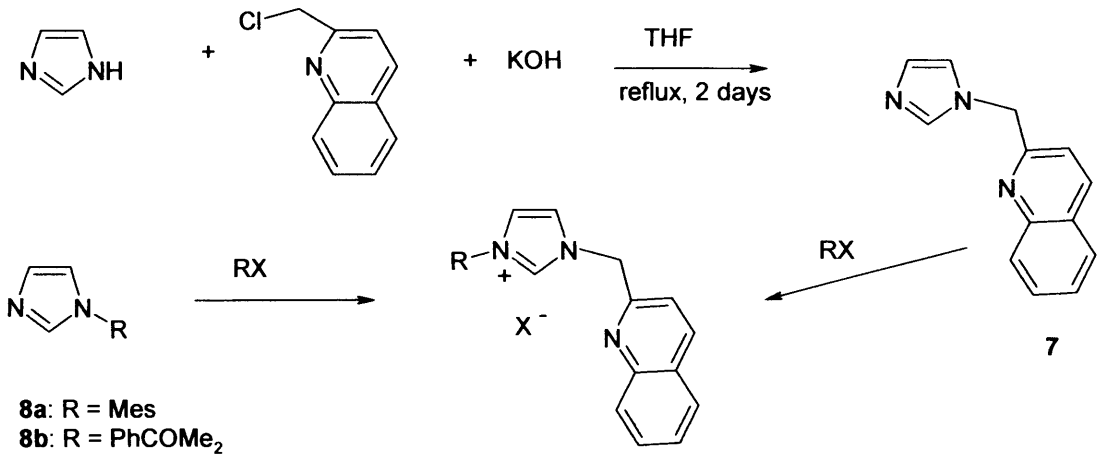


Figure 2.4: ORTEP projection of the cation of **6c.I** excluding hydrogen atoms for clarity showing atom labelling scheme.

2.2.4 Synthesis and characterisation of methylene-bridged quinoline functionalised imidazolium salts

Synthesis of imidazolium salts with the quinoline methylene bridge was desired, as apart from reducing the steric strain, it also improves solubility. The methylene bridged quinoline imidazole was prepared in good yield following the procedure reported in the literature [28] by refluxing a mixture of imidazole, 2-chromethylquinoline monohydrochloride and KOH in THF for 2 days. The direct quarternization of the methylene bridged quinoline imidazole with appropriate alkyl halides gave the desired salts in good yield.



Scheme 2.7: Synthesis of methylene-bridged imidazolium salts

However two of the imidazolium salts reported in this work could not be obtained via this method because of the difficulty associated with synthesising imidazolium salts by alkylating imidazoles with aryl halides or tertiary alkyl halides. Therefore 2-methypropiophenone imidazole and mesityl imidazole were prepared according to the reported literature methods [29] and [30] respectively, which upon alkylation with 2- chromethylquinoline monohydrochloride in the presence of a base gave the desired imidazolium salts.

Imidazolium salts **9b**, **9c** and **9d** are stable to moisture and air while compounds **9a**, **9e** and **9f** are hygroscopic salts. The characteristic features confirming the synthesis of the salts are appearances of a singlet in ^{1}H NMR between 10.20-11.60 corresponding to the C_2-H proton between the two nitrogens and the ^{13}C NMR spectra showed the value of the C_2 carbon between 152.25-153.60 ppm with the highest value of 153.60ppm being observed in compound **9b** and 152.25 ppm in **9c**. Crystals of compounds **9b** and **9c** suitable for X-ray structures were obtained by diffusion of Et_2O into the acetonitrile solutions of the salts. Crystals of compound **9f** suitable for X-ray crystallography were grown by layering hexane onto a DCM solution of the salt. In order to investigate the effect of counter ion on the crystal structure, the counter ion chloride in salt **9b** was exchanged for tetraflouroborate and crystals suitable for X- ray crystallography of the corresponding salt were obtained by vapour diffusion of Et_2O into the DCM solution of the salt Figure 2.5. The nature of the counter ion, i.e coordinating and non-coordinating, may have little influence on the structure of the cation as the X-ray revealed almost identical data, though peaks in the ^{1}H NMR spectra of the BF_4 version are shifted slightly upfield from the values observed in **9b**. X-ray quality crystals were also obtained for salts **9c** and **9f** by diffusion of diethyl ether into the DCM solutions of the respective salts and the crystal structures are depicted in Figures 2.6 and 2.7 respectively.

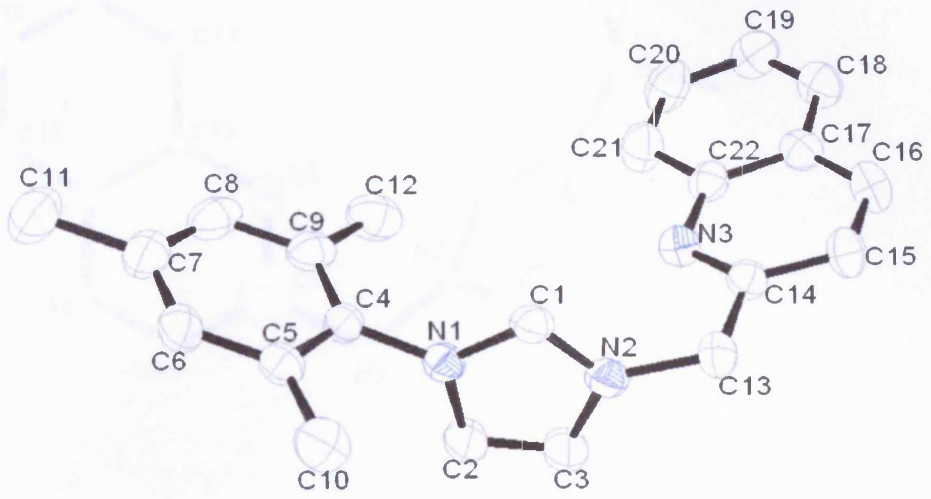


Figure 2.5: ORTEP projection of the cation of **9b.BF_4** excluding hydrogen atoms for clarity showing atom labelling scheme.

Table 2.5: Selected bond lengths (Å) and bond angles (°) of **9.BF_4**

CI- N1 1.340(3)	C4-C9 1.402(3)	N1-C1-N2 108.2(2)
C1-N2 1.323(3)	C9-C12 1.500(3)	C1-N1-C4 126.2(2)
C2-N1 1.374(3)	C13-N2 1.463(3)	C1-N2-C13 125.3(2)
C3- N2 1.370(3)	C13- C14 1.506(3)	N1-C4-C9 117.5(2)
C4-N1 1.446(3)	C14-N3 1.306(3)	N2-C13-C14 112.9(2)

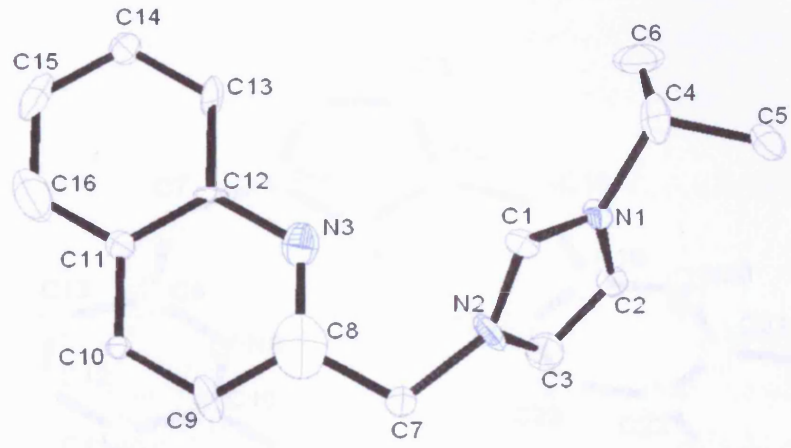


Figure 2.6: ORTEP projection of the cation of **9c.I** excluding hydrogen atoms for clarity showing atom labelling scheme.

Table 2.6: Selected bond lengths (Å) and bond angles (°) of **9c.I**

C1-N1	1.30(2)	C7-C8	1.4888	N1-C1-N2	105.9(12)
C1-N2	1.369(2)	N3-C8	1.3899	C1-N2-C7	129,5(13)
C7-N2	1.515(15)	C8-C9	1.3888	C1-N1-C4	124.4(11)
C4-N1	1.50(2)			C6-C4-C5	109.7(14)
C4-C5	1.53(2)	N2-C7-C8	111.2(5)	N3-C8-C7	119.2

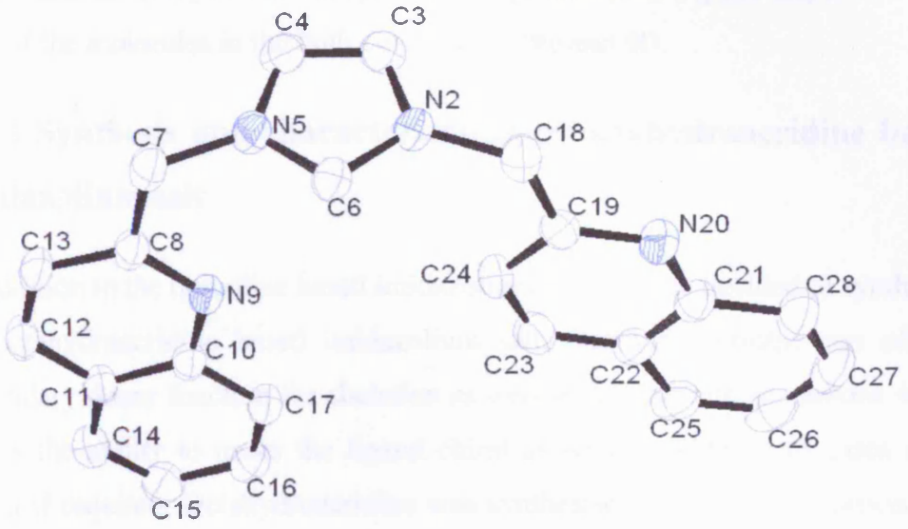


Figure 2.7: ORTEP projection of the cation of **9f.Cl** excluding hydrogen atoms for clarity showing atom labelling scheme.

Table 2.7: Selected bond lengths (Å) and bond angles (°) of **9f.Cl**

N2- C6 1.335(3)	C8-N9 1.316(3)	N2-C6-N5 108.3(2)
N2-C18 1.467(3)	C19-N20 1.323(3)	C6-N5-C7 125.0(2)
N5-C6 1.327(3)	N9-C10 1.371(3)	C6-N2-C18 124.7(2)
N5-C7 1.461(3)		N2-C18-C19 113.0(2)
C7-C8 1.511(3)	C7-C8-N9 117.6(2)	N5-C7-C8 112.07(2)

The imidazolium salts **9b**, **9c** and **9f** for which single X-ray structure determinations were performed show relatively consistent parameters in terms of bond distances and internal angles around the imidazolium rings and are all within the data reported in the literature [31, 32]. Important bond angles and bond distances are tabulated in tables 2.5, 2.6 and 2.7. In **9b** the mesityl and imidazolium rings planes are almost perpendicular to each making an angle of approximately 88.69° and the imC_2-H and the nitrogen on the quinoline ring are disposed to the same side of the molecule. The planes of the methylquinoline

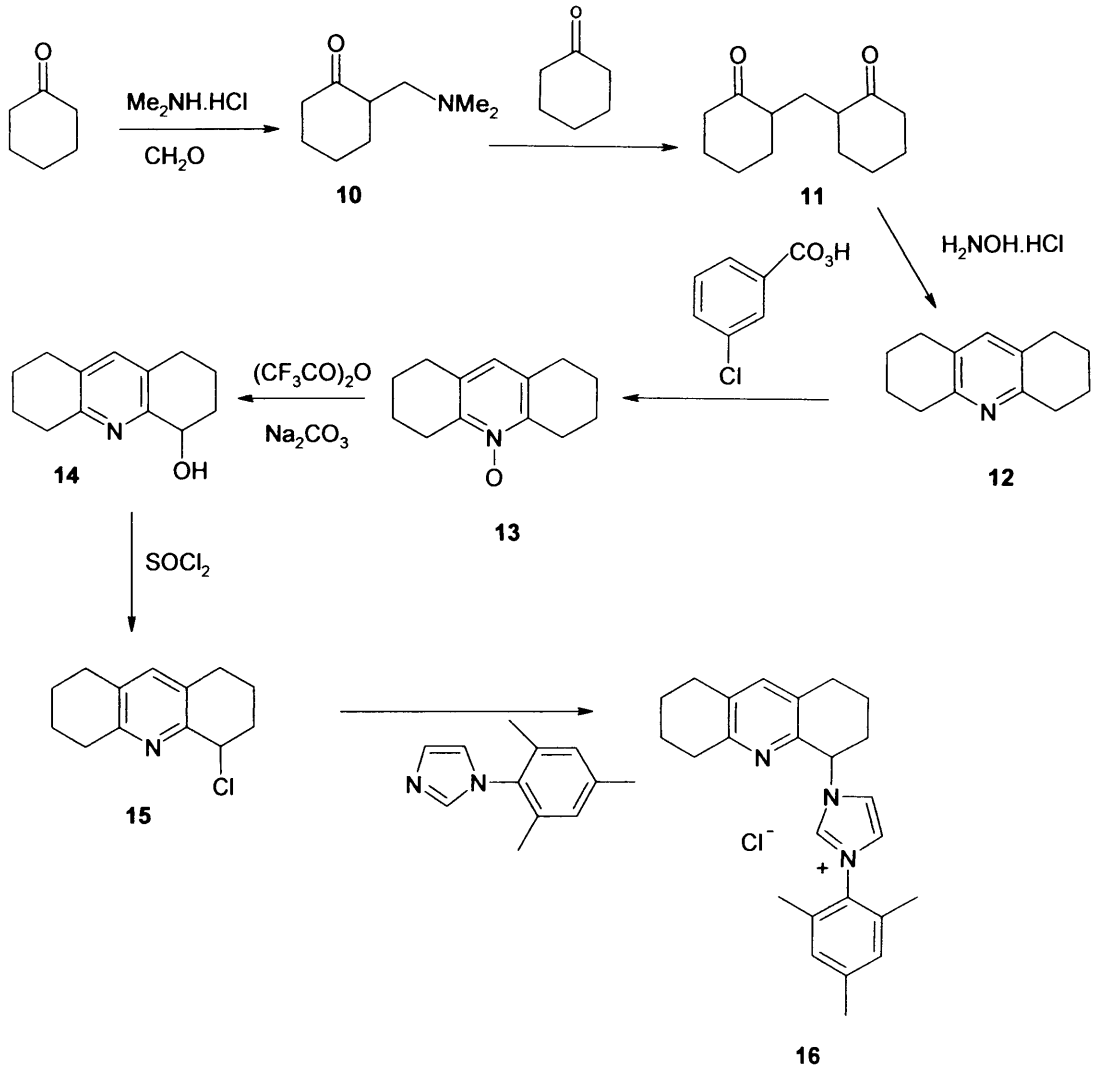
and imidazolium ring of **9c** make an angle of approximately 61.83° while those of **9f** are almost perpendicular to each other forming an angle of approximately 85.65° and the imC_2-H and nitrogen on the quinoline moiety are disposed on the side of the molecules in the both compounds (**9c** and **9f**).

2.2.4 Synthesis and characterisation of octahydroacridine based imidazolium salt

In addition to the quinoline based imidazolium salts, it was decided to synthesise an octahydroacridine based imidazolium salt. Octahydroacridine can offer a secondary donor function for chelation as well as sp3 hybridized carbons which offers the ability to make the ligand chiral as well as addition of extra steric strain if required. Octahydroacridine was synthesised following the procedures of Paine [29] and Bell [30]. Bell's method offers fewer synthetic steps as well less forcing conditions but the yield as stated in the paper (50%) could only be achieved by strict adherence to conditions and deviation from the procedure led to the formation of large quantities of by-products.

Although Paine's method requires the use of many steps and forcing reaction conditions, it was found to be more reliable giving access to cleaner products.

Paine's synthetic procedure as well as steps leading to the synthesis of the desired imidazolium salt is depicted in Scheme 2.8 above. To introduce the chlorine onto position 4 it was necessary to functionalise the octahydroacridine ring with hydroxyl group. Paine's procedure involves the reaction of octahydroacridine with 3-chloroperoxybenzoic to form octahydroacridine N-oxide which upon reaction with an excess of boiling acetic anhydride gave 4-hydroxyl substituted octahydroacridine **14** after work up. However, in our work Fontena's method was employed [31] which requires the use triflouroacetic anhydride instead of large excess of acetic anhydride with the reaction being carried out at room temperature to form the desired 4-hydroxyoctahydroacridine. 4-Chlorooctahydroacridine **15** was prepared by the reaction of 4-hydroxyoctahydroacridine with thionyl chloride which upon work up gave the desired compound as a yellow solid.

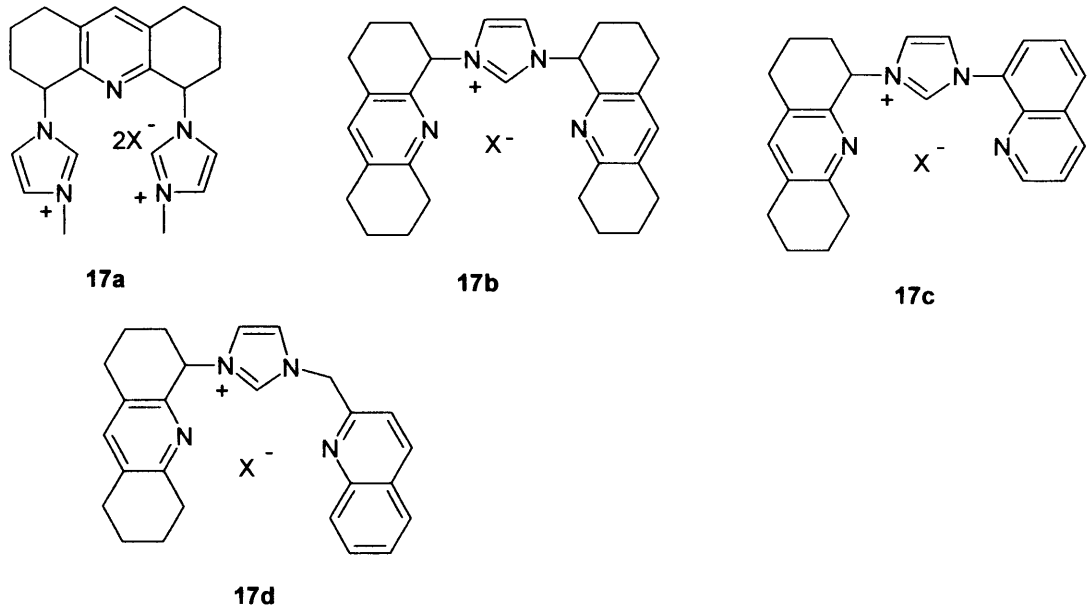


Scheme 2.8: Synthesis of octahydroacridine based imidazolium salt

Finally the acridine based salt was prepared by reaction of 4-chlorooctahydroacridine with 1-mesitylimidazol in THF in a pressure tube at 90 ^{o}C for 14 days. The yield obtained in this reaction was very low because the reaction follows a typical SN_2 pathway, and with secondary alkylchloride, the reaction would be expected to be very slow even under the forcing conditions used. Attempt to prepare a more reactive 4 iodooctahydroacridine was made by the addition of sodium iodide to an acetone solution of 4-chlorooctahydroacridine and stirred overnight and after work up there was no observable effect from the ^{1}H NMR spectra. The imidazolium salt prepared was fully characterised by ^{1}H NMR, mass spectroscopy and micro analysis with the

^{1}H NMR showing C2-H appearing as singlet at a δ value of 10.15pmm. The imidazolium salt **16** returned satisfactory MS and elemental analysis results.

Due to low yield and time constraints large varieties of the acridine based imidazolium could not be prepared using the secondary alkyl chloride **14**. However, it should be noted that, there is a lot of research opportunities in this area that need to be explored. It is envisage that once a more reactive halooctahydroacridine such as bromo or iodooctahydroacridine can be prepared and following the procedure of Steiner et al [29] 1-acridine imidazole can be obtained thereby opening the way to a range of acridine based imidazolium ligands. Some of the interesting acridine based ligands that can possibly be prepared are presented in figure 1.8 below. It will be interesting to compare these potential pincer ligands with the pincer ligands reported by Gibson, Cavell, Danopoulos and Crabtree.



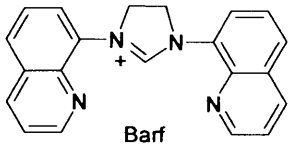
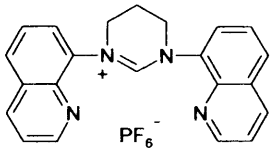
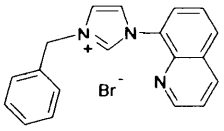
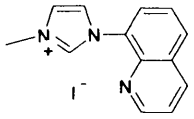
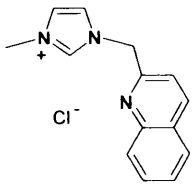
17a **17b** **17c** **17d**

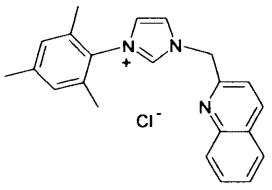
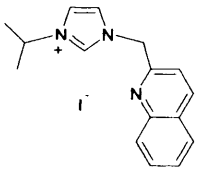
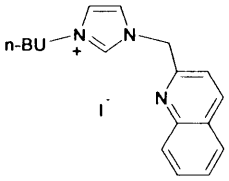
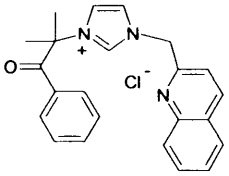
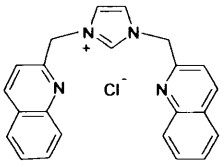
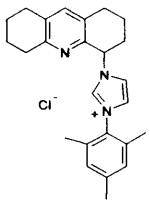
Figure 1.8: Proposed acridine based pincer ligands

2.3 Conclusions

A range of quinoline based imidazolium salts have been synthesised and characterised as precursors to the corresponding NHC ligands. A range of N-substituents give variable steric bulk to the imidazolium rings. The summary of all the imidazolium salts synthesized in this work are presented below in Table 2.8.

Table 2.8: Ligands synthesized in this project

S. NO	Ligand	Structure
1	**2b**	
2	**4**	
3	**6a**	
4	**6c**	
5	**9a**	

6	**9b**	
7	**9c**	
8	**9d**	
9	**9e**	
10	**9f**	
11	**16**	

The previously unreported bis 1, 3-(quinoline) tetrahdropyrimidium salt **4** is the first reported quinoline based salt of this nature. Though in 2006 Michon et al reported chiral bis 1,3-quinolinedihydroimidazolium salts [21], salt **2b** is an achiral analogue and therefore is a new compound. Compounds **6a, 6c** and **16** have earlier been prepared by Cavell group while all the other ligands are new.

Similar ligands functionalised with pyridine have been reported in the literatures [7, 31, 32, and 40]. However in this study, the pyridine moiety has been replaced by quinoline and this change is expected to increase the steric strain of the ligands as well as rigidity which may have important implications in the synthesis of the metal complexes. The acridine based imidazolium salt offers the possibility of accessing chiral ligand as well as varying the steric strain. Synthesis of the acridine based imidazolium salt also open up the opportunity to look into the possibility of synthesising the ligands presented in figure 1.8 above.

2.4 Experimental

2.4.1 General comments

Unless otherwise stated all manipulations were carried out using standard Schlenk techniques under an atmosphere of dry argon or in an MBRAUN M72 glove box (N_2 atmosphere with > 1ppm O_2 and H_2O). Glassware were dried overnight in an oven at 120°C or flame dried prior to use. Tetrahydrofuran (THF), diethyl ether (Et_2O), and hexane were dried and freshly distilled before used. Dichloromethane (DCM), methanol (MeOH) and acetonitrile (MeCN) were dried over calcium hydride. All other anhydrous solvents were obtained by distillation from the appropriate drying agent under dinitrogen. Deoxygenation of solvents and reagents was carried out by freeze- thaw- degassing.

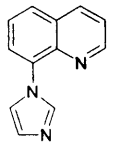
All NMR solvents were purchased from Aldrich and Goss, dried over 3Å molecular sieves and freeze-thaw degassed three times. All reagents were purchased from commercial sources and used without purification, unless otherwise stated.

All NMR data are quoted δ/ppm. ^1H and ^{13}C spectra were recorded on a Bruker 400 MHz DPX Avance, unless otherwise stated, and referenced to $SiMe_4$. Electrospray mass spectrometry (ESMS) was performed on a VG Fisons Platform II instrument by the department of Chemistry, Cardiff University. Micro analysis was performed by Warwick Analytical Service.

2.4.2 N-Substituted imidazoles

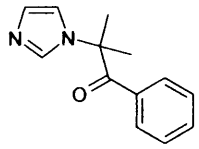
The following imidazoles were prepared by established literature methods. 1-(-2-methylpropiophenone)imidazole [29], mesitylimidazole [19], imidazole-1-yl-quinoline [27] and 1-(2methylquinoline) imidazole [28].

Imidazol-1-yl-quinoline (5):



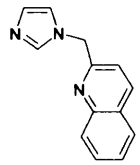
8-aminoquinoline (2.27 g, 8.8 mmol) was mixed with 40% glyoxal (1.22 g, 8.8 mmol) in 30 mL MeOH and stirred overnight at room temperature to give a yellow mixture. NH_4Cl (0.94 g, 17,6 mmol) and 37% aq formaldehyde (1.42 g, 17.6 mmol) were then added to the mixture which was then diluted by further addition of 150 ml MeOH. This was refluxed for an hour and H_3PO_4 (1.6 mL.85 %) was slowly added to the mixture before heating to reflux for 12 hours. After removal of the solvent the dark residue was poured on to ice (100g) and neutralised with aqueous 40% KOH until pH 9. The resulting mixture was then extracted with diethyl ether (4 x 100 mL). The ethereal phase was then washed with water, brine and dried with Na_2SO_4. The solvent was then removed to give a light brown solid product, 0.19 g (10%). ^1H NMR ($CDCl_3$ 400 MHz 298K) : 8.90 (s, 1H, NCHN-H), 8.2 (m, 1H, J = 6.7 H_Z, quin-H), 8,05(s, 1H, CHHC), 7.8 (m,1H, J = 7.9 H_Z, quin-H), 7.6 (m, 1H, J = 1.3 H_Z, quin-H), 7.5 (m, 1H, J = 7.9 H_Z,), 7.4(m, 2H, J = 4.2 H_Z, quin-H), 7.2(s, IH, HCCH-H). ^{13}C NMR ($CDCl_3$ 100.61MHz 298K): 159.0, 140.5, 138.5, 136.0, 135.5, 128.5,127.0, 126.8, 125.0, 123.0, 122.5, 120.5.

1-(-2-methylpropiophenone) imidazole (8b).



A round bottomed flask was charged with imidazole (1.70g, 25mmol), 2-bromo-2-methylpropiophenone (2mL, 11.9mmol) and 40mL of ethanol. The yellow solution was refluxed for 3 days. Aqueous work up yielded yellow oil which crystallized in the freezer. Recystallization from from dichloromethane/n-hexane (1:2) afforded pure colourless product (1.56g. 7.25mmol, 61%).^{1}H NMR ($CDCl_3$ 400 MHz R.T.): 7.60(s, 1H, NCHN), 7.4(m, 1H, J = 2.5 H_Z, arom-H), 7.2(m, J = 1.1 H_Z, 4H, arom-H), 7.05(s, 1H, CHHC), 6.85(s, 1H, CHHC), 1.8(s, 6H, CH_3). ^{13}C NMR ($CDCl_3$ 72.5MHz R.T): 198.45(PhCOC), 134.78,134.48, 130.17, 128.60, 128.50, 117.39, 64.89, 27.14(CH_3).

1-(2methylquinoline)imidazole (7):

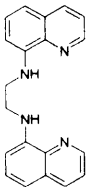


A mixture of imidazole (0.38g, 5.51mmol), 2-(chloromethyl) quinoline and KOH (1.24g, 0.022mol) in THF (20mL) was refluxed for 2 days. The solvent was removed completely under reduced pressure. DCM (20mL) and water (20mL) were added and shaken vigorously in a separatory funnel. The organic layer was extracted and washed thoroughly with 20mL of water. The organic layer was separated and dried with anhydrous $MgSO_4$. The solution was filtered and removal of the solvent under reduced pressure gave an orange solid as the desired product (0.80g, 69%). ^{1}H NMR ($CDCl_3$ 400 MHz 298K):8.1(d, 1H, J = 8.5 H_Z, quin-H), 8.0(d, 1H, J = 8.5 H_Z, quin-H), 7.75(d, 1H, J = 8.2 H_Z, quin-H), 7.65(t, 1H, J = 5.6 H_Z, qiun-H, 7.6(s, 1H, NCHN), 7.45(t, 1H, J = 8.6 H_Z, quin-H), 7.05(s, 1H, CHHC), 7.0(s, 1H, CHHC), 6.95(d, 1H, J = 10.0 H_Z, quin-H), 5.35(s, 2H, NCH_2) ^{13}C NMR ($CDCl_3$ 100.61MHz R.T): 156.13 (NCN),

147.71, 137.80, 137.60, 130.14, 129.18, 127.64, 127.41, 126.93, 119.58, 118.66, 53.25 (NCH_2)

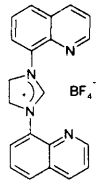
2.4.3 Symmetrical saturated bis(1,3- quinoline) imidazolium salt

N, N-Diquinolinethane -1, 2-diamine (1):



A mixture of 8-hydroxyquinoline (36.25 g, 0.25 mol), 1,2-diaminethane (9.75 g, 0.125 mol), sodium pyrosulfite (47.5 g , 0.25 mol) and water (250mL) was refluxed and stirred for one week. The solution was made strongly alkaline, cooled and filtered. The solid product was extracted several times with hot 0.2N NaOH until removal of 8-quinolinolate was complete and the residue was recrystallised from ethanol to give the desired product as a light yellow solid (6.00g 16 %).^{1}H NMR ($CDCl_3$, 400MHz 298K): 8.6(m, 2H, J = 2.6 H_Z, Quin-H),), 8.0(m, 2H, J = 6.8 H_Z, Quin-H),), 7.3(m, 4H, J = 7.7 H_Z, Quin-H), 7.0(m, 2H, J = 7.5 H_Z, Quin-H), 6.7(m, 2H, J = 8.0 H_Z, Quin-H), 6.35(b, 2H,CNH), 3.7(s,4H,NCH_2), ^{13}C NMR ($CDCl_3$ 72.5MHz R.T): 146.94, 144.68, 138.34, 136.01, 128.73, 127.77, 121.46, 114.23, 104.77(quin-C), 42.79(NCCN).

Synthesis of 1, 3-diquinolin-4, 5-dihydroimidazoluim tetraflouroborate (2):

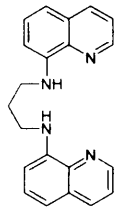


N, N'-diquinolinethane-1, 2-diamine (0.3g 0.58mmol) and NH_4BF_4 (0.095g, 0.58mmol) in triethyl orthoformate were heated at 120°C for 24 hours. The precipitate which was isolated was washed several times with diethyl ether and recrystallised from $CHCl_3$/Diethyl ether to afford the desired product 0.3g (85%). Anal. Calcd. for $C_{21}H_{17}N_4BF_4$: C, 61.19; H, 4.13; N, 13.60; F, 18.46%.

Found: C, 59.06; H, 4.01; N, 13.48; F, 19.04%. HRMS: Calculated for $C_{21}H_{17}N_4BF_4$: 325.1453. Found: 325.1437. ^1H NMR (DMSO-d_6, 400MHz R.T):11.40(s, 1H, NCHN), 9.20(m, 2H, J = 2.6 Hz, Quin-H), 8.70(m, 2H, J = 1.2 Hz, Quin-H), 8.20(m, 2H, J = 8.2 Hz, Quin-H), 8.10(m, 2H, J = 8.0 Hz, Quin-H), 7.90(m, 2H, J = 8.0 Hz, 7.8(m, 2H, J = 4.2 Hz, Quin-H), 4.95(s, 4H, NCH_2CH_2N). ^{13}C NMR (DMSO-d6, 72.5MHz R.T.): 158.91(NCN), 150.95(quin-C), 139.98(quin-C), 137.35(quin-C), 132.52(quin-C), 128.97(quin-C), 127.87(quin-C), 126.60(quin-C), 122.81(quin-C), 49.99(im-C).

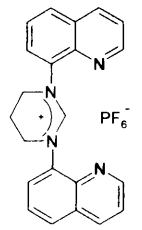
2.4.4 Bis(1,3-quinoline)pyrimidium hexaflouro phosphate salt

N, N-diquinolinepropane-1, 3-diamine (3):



Following the procedure for preparation of **1**, 7.32g of compound **3** was obtained from 8-hydroxyquinoline (18.13g, 0,125moles), 1,3-diamonopropane (4.64g, 0.125moles), sodiumpyrosulfite (23.77g, .125moles) and 125mL of water as a yellow solid. ^1H NMR ($CDCl_3$, 400MHz 298K): 8.60(m, 2H, J = 2.7 Hz, quin-H), 8.00(m, 2H, J = 6.7 Hz, quin-H),), 7.30(m, 4H, J = 4.4 Hz, quin-H), 7.00(m, 2H, J = 8.3 Hz, quin-H), 6.65(m, 2H, J = 7.7 Hz, quin-H), 6.20(broad, 2H,CNH), 3.50(m,4H, J = 7.0 Hz, NCH_2), 2.20(m, 2H, J = 6.8 Hz, CCH_2C). ^{13}C NMR ($CDCl_3$ 72.5MHz R.T): 146.84, 144.80, 138.25, 136.04, 128.70, 127.84, 121.41, 113.85, 104.72(quin-C), 41.30(NCC), 29.01(CCH2C).

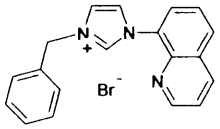
1, 3-diquinoline-3, 4, 5, 6-tetrahydropyrimidinium hexaflouro phosphate (4):



Following the procedure for the synthesis of **2**, the desired pyrimidinium salt **4** was synthesised from N,N-diquinolinepropane-1,3-diamine(3.59g,0.011moles) NH_4PF_6(1.78g, 0.011moles) and triethyl orthoformate(30mL) as a light brown solid (Yield= 5.00g, 94.34%). Anal. Calcd. for $C_{22}H_{19}N_4PF_6$: C, 54.35; H, 3.93; N, 11.57%. Found: 53.74; H, 3.84; N, 11.37%.HRMS: Calculated for $C_{22}H_{19}N_4PF_6$: 339.1610. Found: 339.1618. ^1H NMR (DMSO-d6, 400MHz 298K): 9.30 (s, 1H, NCHN), 9.20(m, 2H, J = 4.2 H_Z, quin-H), 8.70(m, 2H, J = 4.1 H_Z, quin-H), 8.30(m, 2H, J = 8.3 H_Z, quin-H), 8.25(m, 2H, J = 7.4 H_Z, quin-H), 7.90(m, 2H, J = 7.8 H_Z, quin-H), 7.80(m, 2H, J = 4.1 H_Z, quin-H), 4.30(m, 4H, J = 5.4 H_Z, NCH_2C), 2.70(m, 2H, J = 5.1 H_Z, CH2C). ^{13}C NMR (DMSO-d6, 72.5MHz R.T.): 156.72 (NCN), 151.57, 141.82, 138.10, 136.93, 129.64, 128.97, 126.65, 126.51, 122.72, 48.03, 19.54.

2.4.5 Unsymmetrical substituted quinoline imidazolium salts

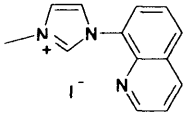
Synthesis of 1-benzyl-3-quinolinimidazolium bromide (6a):



Benzyl bromide (1.41g, 8.25 mmol) was added to a solution 8-imidazol-1-yl-quinoline (0.70 g, 3.59 mmol) in 20 mL THF.The resulting mixture was allowed to stir overnight at r.t. The resulting yellow/brown precipitate was filtered using filter stick and washed with fresh THF to afford a brown powder. This was then recrystallised from DCM/Hexane to give the desired imidazolium salt (light brown solid).^1H NMR($CDCL_3$:250MHz 298K):10.80(s, 1H, NCHN), 8.90(m,1H, J = 4.1 H_Z, Quin-H), 8.25(m, 1H, J = 8.7 H_Z, Quin-H), 8.00(m, 1H, J = 8.3 H_Z, Quin-H), 7.90(s, 1H, CHHC), 7.70(m, 1H, J = 5.7 H_Z, Quin-H), 7.60(m, 2H, J = 6.2 H_Z, Quin-H , CHHC), 7.50(broad 2H, Quin-H), 7.30(m, 3H, J = 7.3 H_Z, Ar-H), 5.85(s, 2H, CH_2). ^{13}C NMR ($CDCl_3$ 100MHz R.T): 152.07(NCN),140.79, 137.30, 137.10,133.60, 131.40, 131.03, 129.86, 129.75, 129.70, 129.55, 126.90, 126.00, 124.72, 123.23, 121.95, 53.76(NCH2).

1-benzyl-3-quinolinimidazoliumtetraflouroborate (6b): The counter ion bromide in **6a** was exchanged for tetraflouroborate ion by mixing one equivalent of 1-benzyl-3-quinolineimidazolium bromide (0.5g, 1.75 mmol) in acetonitrile with 1.5equivalent of $NaBF_4$(0.28g, 2.63mmol) in water. The acetonitrile was removed under reduced pressure and product was washed twice with water. The residue was then dissolved in DCM and the organic and aqueous layer separated. The DCM solution was dried over $MgSO_4$ and solution concentrated under reduced pressure. Addition of Et_2O precipitates out the product which was filtered and dried in vacuum to give the desired product as brown solid. Crystals suitable for X-ray crystallography were obtained by vapour diffusion of Et2O into DCM solution of the product. Anal. Calcd. for $C_{19}H_{16}N_3BF_4$: C, 61.29; H, 4.29; N, 11.27%. Found: C, 60.96; H, 4.31; N, 11.12%.^{1}H NMR ($CDCl_3$, 250MHz R.T.): 9.40(s, 1H, NCHN), 8.85(d, 1H, J = 4.2 H_Z, quin-H), 8.35(d, 1H, J = 7.5 H_Z, quin-H), 8.20(d, 1H, J = 8.4 H_Z, quin-H), 8.00(d, 1H, J = 8.3 H_Z, quin-H), 7.85(s, 1H, CHHC), 7.70(t, 1H, J = 4.2 H_Z, quin-H), 7,50(m, 3H, arom-H), 7.60(s, 1H, CHHC), 7.50(m, 3H, J = 7.0 H_Z, arom and quin-H), 5.50(s, 2H, CH_2). ^{13}C NMR ($CDCl_3$ 72.5MHz R.T): 150.70(NCN), 139.31, 135.92, 135.69, 131.97, 129.96, 129.68, 128.46, 128.41, 128.26, 128.16, 125.42, 124.21, 123.35, 121.85, 120.77, 52.68(NCH2).

1-methyl-3-quinolineimidazolium iodide (6c):

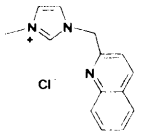


Methyl iodide (1g, 7mmol) was added to a solution of 8-imidazol-1-yl-quinoline (0.5g, 2.7mmol) in 20Ml of THF. The resulting mixture was stirred at room temperature for 48 hrs. The resulting brown precipitate was filtered using filter stick and washed with further amount of THF to afford a brown powder. This was then recrystallised from DCM/Hexane to give the desired imidazolium salt (0.6g, 70%).Crystals suitable for X-ray were obtained by vapour diffusion of Et2O into the DCM solution of the compound. Anal. Calcd. for $C_{13}H_{12}N_3I$: C, 46.30; H, 3.56; N, 12.47%. Found: C, 46.09; H, 3.60; N, 12.16%. ^{1}H NMR(DMSO-d6:250MHz R.T): 9.80(s, 1H, NCHN), 8.90(d, 1H, J = 1.7 H_Z, quin-H), 8.30(d, 2H, J = 1.6 H_Z, quin-H), 8.00(d,1H, J = 7.4 H_Z, quin-H), 7.80(s,

1H, CHHC), 7.70(d, 1H, J = 7.9 H_Z, quin-H), 7.50(m, 1H, J = 4.2 H_Z, quin-H), 7.40 (s, 1H, CHHC), 4.30(s, 3H, CH_3). ^{13}C NMR (DMSO-d6, 72.5MHz R.T.): 152.02(NCN), 140.62, 138.48, 136.95, 131.39, 130.69, 128.77, 126.38, 126.27, 124.41, 123.29, 123.06, 67.00(CH_3)

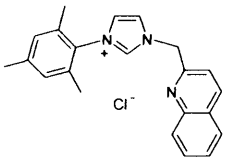
2.4.6 methylene-bridged quinoline Functionalised imidazolium salts

1-methyl -3-(2-methylquinoline) imidazolium chloride 9a:



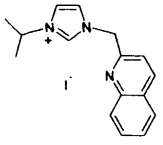
A mixture of methyl imidazole (0.58g, 7mmol), 2-chloromethyl quinoline monohydrochloride (1.5g, 7.00 mmol) and K_2CO_3 (0.50g, 3.50 mmol) in acetonitrile was refluxed for 24 hours. The solvent was removed and the remaining residue was dissolved in dichloromethane. The solution was filtered to remove the KCl formed and unreacted K_2CO_3 and the filtrate were concentrated to few millilitres. Addition of THF to the solution precipitated out the product which was repeatedly to give the product as a pale yellow solid (1.20g, 81%). Required: For $C_{13}H_{14}N_3Cl$: C, 60.12; H, 5.41; N, 15.80; Cl, 13.68%. Found: C, 64.14; H, 5.42; N, 16.00; Cl, 13.93%.HRMS: Anal.Calcd. for $C_{13}H_{14}N_3Cl$: 224.1188. Found: 224.1193. ^1H NMR ($CDCl_3$. 400MHZ, R.T.) : 10.67 (s,1H, NCHN) , 8.10 (m, 1H, J = 8.4 H_Z, Quin-H), 7.90 (d, 1H, J = 8.4 H_Z, Quin-H), 7.65 (m, 3H, J = 8.1 Hz Quin-H, CHHC), 7.60 (s, 1H, CHHC), 7.40 (t, 1H, J = 7.1 H_Z, Quin-H), 5.90 (s, 2H, CH_2), 4.00 (s, 3H, CH_3). ^{13}C NMR ($CDCL_3$, 100.61MH_Z, R.T): 153.14 (NCN), 147.86, 138.32, 138.14, 130.47, 129.06, 127.92, 127.57, 123.61, 123.25, 120.71, 54.57(NCH2), 36.92(CH_3).

Synthesis of 1-mesityl 3-(-2-methylquinoline)imidazolium chloride 9b :



A mixture of mesityl imidazole (0.87g, 4.67mmol), 2-chloromethylquinoline monohydrogen chloride (1.0g, 4.67mmol) and K_2CO_3 (0.33g, 2.39mmol) in acetonitrile was refluxed for 24 hours. The solvent was removed and the residue dissolved in dichloromethane. The solution was filtered to remove the KCl formed and unreacted K_2CO_3 and the filtrate were concentrated to few millilitres. Addition of THF to the solution precipitated the product which was repeatedly to give a white product (1.25g, 73.5%). Anal. Calcd. for $C_{22}H_{22}N_3Cl$: C, 72.63; H, 6.05; N, 11.55; Cl, 9.77%. Found: C, 69.41; H, 6.03; N, 10.98; Cl, 9.57%. HRMS: Calculated for $C_{22}H_{22}N_3Cl$: 328.1814. Found: 328.1807. ^1H NMR ($CDCl_3$. 400MH_Z, R.T.) : 10.50 (s,1H, NCHN) , 8.20 (m, 1H, J = 8.4 H_Z, Quin-H), 8.00 (s, 1H, aromatic-H), 7.85 (m,2H, J = 8.4 H_Z, Quin-H), 7.75(d, 1H, J = 8.1 H_Z, Quin-H), 7,65 (t, 1H, J = 7.0 H_Z, Quin-H) , 7.50 (t, 1H, J = 7.1 H_Z, Quin-H),7.05 (S, 1H, aromatic-H) , 6.95 (s,2H, CHHC), 6.30 (s, 2H , CH_2), 2.30 (s, 3H, P-CH3), 2.00 (s, 6H, O-CH_3). ^{13}C NMR ($CDCL_3$, 100MH_Z, 298K): 153.60, 147.77, 141.56, 139.17, 138.36, 134.71, 131.17, 130.48, 130.14, 129.16, 128.23, 128.15, 127.53, 124.43, 123.04, 121.18, 54.57, 21.47, 17.94.

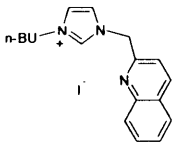
Synthesis of 1-isopropyl -3-(2-methylquinoline) imidazolium iodide (9c)



A mixture 2-iodopropane (1.63g, 9.57mmol) and 1-(2-methylquinolin) imidazole (1g, 4.8mmol) in 50ml of ethyl acetate was refluxed for 3 days. The reaction solution was allowed to cool to room temperature, after which the crystals were filtered off and washed with ethyl acetate and dried in vacuum to give the desired product, (1.25g, 68.68%). Anal. Calcd. for $C_{16}H_{18}N_3I$: C, 50.67; H, 4.75; N, 11.08; I, 33.49%. Found: C, 50.17; H, 4.64; N, 10.89; I, 33.13%. HRMS: Calculated for $C_{16}H_{18}N_3I$: 252.1501. Found: 252.1491. ^1H

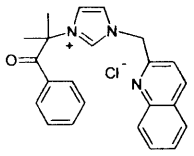
NMR (CDCL3, 400MHz, R.T): 10.35 (s, 1H, NCHN), 8.15 (d, 1H, J = 8.4 H_Z, quin-H), 7.90 (d, 1H, J = 3.5 H_Z, quin-H), 7.90 (t, 2H, J = 8.4 H_Z, quin-H), 7.80 (m, 2H, quin-H), 7.70 (m,2H, J = 6.5 H_Z, CHHC, Quin-H), 7.50 (m, 2H, J = 9.0 H_Z, quin-H, CHHC), 6.90 (s, 2H, NCH_2C), 4.80 (m, 1H, J = 7.8 H_Z, $NCHC_2$, 1.60 (d, 6H, J = 7.0 H_Z, CH_3). ^{13}C NMR ($CDCL_3$, 100MH_Z, 298K):152.25 (NCN), 147.93, 138.43, 136.07, 130.63, 129.45, 128.25, 128.15, 127.74, 123.63, 121.28, 120.29, 54.72, 23.59.

1-n-butyl-3-(-2-methylquinolin) imidazolium iodide (9d):



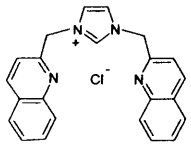
A mixture of 1-(2-methylquinoline) imidazole (1.00g, 4.80mmol) and 1-iodobutane (1.76g, 9.60mmol) was refluxed in 50mL of ethyl acetate for two days. The reaction solution was allowed to cool to room temperature and the ethyl acetate decanted off. The residue was dissolved in minimum amount of DCM and the product precipitated out by the addition of hexane. The desired product was filtered and dried in vacuum. (1.20g, 63.83%). MS (ESMS, Da): M/Z 266.16 $[M-I]^+$ (100%). Anal. Calcd. for $C_{17}H_{20}N_3I$: C, 51.92; H, 5.09; N, 10.69; I, 32.30%. Found: C, 52.58; H, 4.99; N, 10.57; I, 31.94%. ^1H NMR (CDCL3, 400MHz, R.T):10.2(s, 1H, NCHN), 8.15(d,1H, J = 8.4 H_Z, quin-H), 7.90(d,1H, J = 6.6 H_Z, quin-H), 7.85(m, 2H, J = 8.3 H_Z, quin-H, CHHC), 7.65(t,2H, J = 5.9 H_Z, quin-H), 7.50(t, 1H, J = 7.4 H_Z, quin-H),7.40(s,1H, CHHC), 5.90(s,2H, NCH_2), 4.20(t, 2H, J = 7.2 H_Z, NCH), 1.85(m, 2H, J = 7.5 H_Z, CH_2), 1.30(m, 2H, J = 7.4 H_Z, CH_2), 0.90(t, 3H, J = 7.1 H_Z, CH_3). ^{13}C NMR ($CDCL_3$, 100MH_Z, 298K): 152.78(NCN), 147.92, 138.29, 137.02, 130.58, 129.44, 128.21, 128.07, 127.68, 123.64, 122.36, 120.93, 54.65(NCC), 50.43, 32.41, 19.79, 13.88(CH_3).

1-(-2-methylpropiophenone)-3-(-2-methylquinolin) imidazolium chloride (9e)



2(chloromethylquinoline)monohydrochloride(1.50g,7.0mmol),1(2methylpropio phenone) imidazole (1.50g, 7.0mmol) and K_2CO_3 (0.55g, 3.98mmol) in 30mL of acetonitrile was refluxed for 2 days. The solvent was removed and the residue dissolved in dichloromethane. The solution was then filtered to remove KCl and unreacted K_2CO_3 and the dichloromethane completely removed. The residue was repeatedly was washed with diethyl ether and dried in a vacuum to afford the desired product. MS (ESMS): M/Z 366.16 $[M\text{-}Cl]^+$ (100%). ^1H NMR ($CDCL_3$, 400MHz, 298K): 11.60(s, 1H, NCHN), 8.10(d, 1H, J = 8.40 H_Z, quin-H),7.90(m, 2H, J = 3.6 H_Z, quin-H, aromatic-H), 7.80(d, 1H, J = 8.3 H_Z, quin-H), 7.65(t, 1H, J = 1.5 H_Z, Quin-H), 7.60(s,1H, CHHC), 7.50 -7.40(m, 4H, J = 7.7 H_Z, arom-H), 7.20(m, 2H, J = 1.8 H_Z, quin-H),7.25(s,1H, CHHC), 7.00(s, 1H, CHHC). ^{13}C NMR ($CDCL_3$, 100MH_Z, R.T):197.30(CO), 153.45(NCN), 147.91, 138.33, 134.06, 133.75, 130.44, 129.43, 129.26129.08, 128.83, 128.22, 128.13, 127.62, 123.78, 121.40, 120.87, 70.08, 54.79, 27.31(CH_3).

Bis-1, 3- (2-methylquinolin) imidazolium chloride (9f)



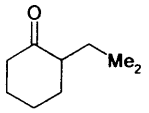
A mixture of 1-(2-methylquinolin) imidazole (1.00g, 4.79mmol), 2-(chloromethylquinoline) monohydrogen chloride (1.02g, 4.79mmol) and K_2CO_3 (0.50g, 3.62mmol) in 50mL acetonitrile was refluxed for 24 hours. The solvent was removed and the residue dissolved in dichloromethane. The solution was filtered to remove the KCl formed and unreacted K_2CO_3 and the filtrates were concentrated to few millilitres. Addition of THF to the solution precipitated the product which was washed repeatedly with THF to give a pale yellow product. (Yield, 0.98g; 72%). Anal. Calcd. for $C_{23}H_{19}N_4Cl$: C, 71.41; H, 4.92; N, 14.48%. Found: C, 71.08; H, 5.00; N, 14.07%. HRMS: Calculated for

$C_{23}H_{19}N_4Cl$: 351.1610. Found: 351.1606. ^1H NMR ($CDCL_3$, 400MHz, 298K): 11.20(NCHN), 8.10(d, 2H, J = 8.4 H_Z, quin-H), 7.85(d, 2H, J = 8.4 H_Z, quin-H), 7.70(m, 4H, J = 8.3 H_Z, quin-H,), 7.65(m, 4H, quin-H, CHHC), 7.45(t, 2H, J = 6.7 H_Z, quin-H), 5.80(s, 4H, NCH2C). ^{13}C NMR ($CDCL_3$, 100MH_Z, R.T):152.79, 147.58, 138. 44, 137.98, 130.12, 129.13, 127.76, 127.69, 127.57, 120.67, 54.57.

2.4.7 Acridine based imidazolium salt

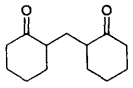
To prepare the desired imidazolium salt, 4-chlorooctahydroacridine was prepared following Paine multi step synthesis [29] and then coupled with mesitylimidazole.

2-Dimethylaminomethylcyclohexanone (10):



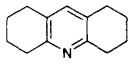
A mixture of cyclohexanone (22.30g, 0.23 mol), dimethylamine hydrochloride (9.9 g, 0.12 mol), and formaldehyde (36.90 g of 37% solution in water) was refluxed (oil bath at 130 °C, 30 min) and then cooled to room temperature. Sodium chloride (4.25g) was added, and the mixture was stirred at 23 °C (20 min). The mixture was transferred to a separatory funnel, and the organic and aqueous phases were separated. The aqueous phase was extracted with Et_2O (4 X 10 mL) to further remove unreacted cyclohexanone, and adjusted to pH= 13.5 by addition of 9.50 g of KOH in 22.5 mL of water. The mannich base was separated as yellow oil, which exhibited a strong amine odour. The aqueous phase was extracted with Et_2O (3 x 20 mL), and the yellow oil and the ether extracts were combined and then dried over anhydrous sodium sulphate. After removal of the ether at 23 °C under reduced pressure, the remaining oil was distilled under vacuum (42-43 °C/100 mTorr): yield 16.00 g (90%).^1H NMR ($CDCL_3$-d3:400 MHz 298K): δ = 2.65(m, 1H, J = 6.0 Hz), 2.40-2.20(m,3H, J = 3.4 Hz), 2.10(m, 8H, J = 6.2 H_Z), 1.9(m, 1H, J = 2.7 H_Z,), 1.8(m, 1H, J = 4.8 H_Z,), 1.6(m, 2H. J = 3.0 H_Z), 1.3(m, 1H, J = 11.1 H_Z,) ^{13}C NMR (DCM, 400MHz R.T.): 24.30, 27, 80, 32.23, 41.69, 45.57, 48.73, 58.80, 212.27.

2, 2'-Dicyclohexanoylmethane (11):



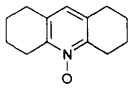
2-Dimethylaminomethylcyclohexanone (19.5 g, 0.125 mol) and cyclohexanone (37 g, 0.38 mol) were mixed and refluxed (oil bath at 205 °C, 1.5 h), and the resulting mixture was distilled under vacuum. The fraction collected at 90-100 °C/ 100 mToor was colourless oil (20.75g). Hexane (25mL) was added to the oil and mixture was cooled to -30 °C overnight. A white solid was collected and washed with cold hexane (3 x 15 mL). The colourless solid product was obtained: yield 14.63 (56.2%).^{1}H NMR ($CDCL_3$:400 MHz 209K): δ = 1.0-2.4(m, 20H): ^{13}C NMR (DCM, 400MHz R.T.): 24.37, 24.60, 27.56, 29.11, 29.88, 33.88, 34.68, 41.44, 41.77, 47.18, 48.33, 212.33, 212.83.

Sym-Octahydroacridine (12):



Hydroxylamine hydrochloride (7.63 g, 0.11 mol) was added with stirring to a boiling solution of 2, 2-Dicyclomethane (14.13g, 0.068mol) in EtOH (100 Ml). The mixture was refluxed (20 min), after cooling, the ethanol was removed under reduced pressure, and 25 mL of water was added to dissolve the residue. A solution of NaOH (5.00g) in water (25mL) was added at 0 °C to bring the pH of the solution to 13.5. The solid that appeared was collected, washed with water and dried. Yield 11.7 g (92. 2%).^{1}H NMR ($CDCL_3$-d3:400 MHz R.T): δ = 7.00 (s 1H, aromatic-H), 2.80(m, 4H, J = 6.2 Hz), 2.6(m, 4H, J = 6.3 Hz), 1.8(m, 4H J = 6.2 Hz), 1.6(m, J = 6.2 Hz), ^{13}C NMR (DCM, 400MHz R.T.): 22.53, 22.95, 27.98, 31.75, 128.85, 137.14, 153.51.

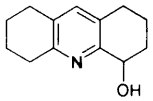
Sym-Octahydroacridine N-Oxide (13):



A mixture of sym-Octahydroacridine (11.50 g, 0.062 mol) and 3-chloroperoxybenzoic acid (17.75 g, 77% max) in $CHCl_3$ (100ml) was stirred (17h) at 23 °C. The resulting reaction mixture was extracted with $NaHCO_3$ (32.50 g) and Na_2CO_3 (15 g) in water (350 mL). The aqueous phase (pH = 8.5)

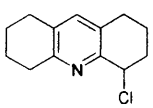
was washed with CH_2Cl_2 (2 x 75 mL), and the chloroform and dichloromethane solutions were combined and dried with anhydrous sodium sulphate. After removal of the solvent at 23 °C under reduced pressure, the product sym-octahydroacridine N-oxide was obtained as a light yellow solid: yield 12.0 g (96.3%).^{1}H NMR ($CDCL_3$-d3: 400 MHz R.T): 6.7(s, 1H), 2.80(m 4H, J = 6.5 H_Z), 2.6(m, 4H, J = 6.2 H_Z), 1.8(m, 4H, J = 6.4 H_Z), 1.6(m, 4H, J = 2.4 H_Z,): ^{13}C NMR ($CDCl_3$, 100MHz R.T.): 21.19, 21.44, 24.11, 27.58, 125.58, 131.10.

1, 2, 3, 4, 5, 6, 7, 8-octahydroacridin-4-ol (14):



Triflouroacetic anhydride (10.2mL, 0.072mol, 2.5 equivalent) was slowly added to a stirred solution of octahydroacridine N-oxide (5.85g, 0.029mol) in dry DCM (50Ml) causing a slight increase in temperature of the solution. The solution was allowed to stir for a further hour at room temperature. The volatiles were then removed under reduced pressure to leave a yellow viscous residue, which was taken up in 20ml DCM. This was then saponified by the addition of a 2M solution of sodium carbonate, the biphasic mixture being vigorously stirred for 3 hours. The organic phase was then separated and the aqueous phase washed twice with DCM. The combined organic extract extracts were then washed with water and brine and then dried over magnesium sulphate. The solvent was removed to give octahydroacridine-4-ol (4.98g, 85%). ^{1}H NMR ($CDCl_3$, 400MMH_Z, δ): 7.05(s, IH, ArH), 4.55(m, 1H, J = 5.5 Hz CHOH), 4.05(broad, 1H, CHOH), 2.8(m, 2H, J = 6.3 Hz CH_2), 2.7(m, 4H, J = 5.9 Hz CH_2), 2.2(m, 1H, J = 3.2 Hz CH_2), 1.6-2.0(m,7H, J = 4.8 Hz CH_2). ^{13}CNMR ($CDCl_3$, 100MH_Z, δ): 154.86, 154.35, 137.5, 130.97, 128.55, 68.36, 31.88, 31.15, 28.42, 27.99, 23.16, 22.79, 19.39.

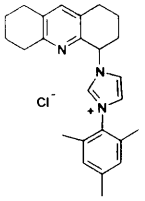
4-chlorooctahydroacridine (15):



Thionyl chloride (15mL) in $CHCl_3$ (15mL) was added to a solution of octahydroacrin-4-ol (7g, 0.0345mol) in 25mL DCM. The mixture was stirred at

room temperature for 10 minutes, and then refluxed for an hour at 80 °C. The excess thionyl chloride and volatile by-products were then removed under reduced pressure and the residue dissolved in DCM (75mL). The solution was then extracted with Na_2CO_3 (7.5g) in water (125mL) and the aqueous phase (pH 8.5) was washed with DCM (2x100mL). The DCM extract was then dried with Na_2CO_3 and the solvent removed under reduced pressure to give a yellow solid of 4-chlorooctahydroacridine (4.90g, 64%). ^{1}H NMR ($CDCl_3$, 400MMH$_Z$, 298K): 7.05 (s, 1H, ArH), 5.20 (m, 1H, J = 2.8 Hz CHCl), 2.55-2.95(m, 6H, J = 4.7 Hz, CH_2), 2.05-2.35(m, 3H, J = 2.9 Hz CH_2), 1.65-1.85 (m, 5H, J = 4.3 Hz CH_2). ^{13}CNMR ($CDCl_3$, 100MH$_Z$, δ): 155.53, 151.22, 137.96, 132.35, 128.97, 59.44, 32.65, 32.24, 28.60, 27.54, 23.15, 22.65, 17.42.

1-mesityl-3-octahydroacridinimidazolium chloride (16):



4-chlorooctahydroacridine (1.00g, 4.5mmol) and mesityl imidazole (0.84g, 4.5mmol) were placed in an ACE pressure tube with 10 mL THF. The mixture was refluxed at 90 °C for 10 days as a dark precipitate formed. The precipitate was filtered and washed with Et_2O (4x10mL) to give the imidazolium salt as an off-white solid (0.15g, 8%). The filtrate was placed back under reflux where it continued to react further over time. Anal. Calcd. for $C_{25}H_{29}N_3Cl$: C, 73.80; H, 7.13; N, 10.33%. Found: C, 65.65; H, 7.11; N, 8.98%. ^{1}H NMR ($CDCl_3$, 400MMH$_Z$, 298K): 10.15 (s, 1H, NCHN), 8.18(s, 1H, CHHC), 7.65(s, 1H, CHHC), 7.20(s, 1H, ArH), 6.95 (s, 2H, ArH), 6.55 (d, 1H, J = 9.7 Hz CHN), 1.80-3.40 (m, 23H, CH_2, CH_3). **MS** (ES) m/z (%): 372.3(29) $[M-Cl]^+$; **MS** (ESI) m/z (%): found 372.3424 $[M-Cl]^+$; expected: 372.5333.

2.4.8 Crystal structure solution

All single crystal X-ray chromatographic determinations presented in this study were kindly performed by Dr. Dirk Beetstra and Dr. Benson Kariuki at the Cardiff University.

X-ray data collection was carried out at 150K on a Bruker/Nonius Kappa CCD diffractometer using graphite monochromated Mo-Ka radiation, equipped with an Oxford Cryostream cooling apparatus. The data was corrected for Lorentz and polarization effects and for absorption using SORTAV [36]. Structure solution was achieved by direct methods [37] and refined by full matrix least – square on F2 with all non- hydrogen atoms assigned anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were placed in idealised positions and allowed to ride on the relevant carbon atom. In the final cycles of refinement a weighting scheme that gave a relatively flat analysis of variance was introduced and refinement continued until convergence was reached. Structure refinement and final geometrical calculations were carried out with the SHELXL-97 [38] program implemented in the WinGX and the diagrams were generated using the ORTEP-3 for windows [39] program.

Table 2.9: Crystal data and structure refinement for 4

Empirical formula	$C_{22}H_{19}F_6N_4P$	
Formula weight	484.38	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.8550(3) Å	α =75.6640(10)°
	b = 8.300(3) Å	β = 82.7570(10)°
	c = 16.4760(8) Å	γ = 80.586(2)°
Volume	1022.59(7) $Å^3$	
Z	2	
Density (calculated)	1.573Mg/m^3	
Absorption coefficient	0.208mm-1]	

F000	496
Crystal size	0.30 x 0.10 x 0.10 mm^3
Theta range for data collection	2.56 to 35.01 o
Index ranges	-12<=h<=12, -13<=k<=13, -26<=l<=26
Reflections collected	12823
Independent reflection	8815 [R_{int} = 0.745]
Completeness of theta = 35.01°	97.7%
Absorption correction	Semi-empirical from equivalents
Max and min. transmission	.9795 and 0.9403
Refinement method	Full matrix least square on F^2
Data/restraints/parameters	8815/0/298
Goodness of fit on F^2	1.029
Final R indices [I>2 sigma(I)]	R1 = 0.0802, wR2 = 0.1579
R indices (all data)	R1 = 0.1888, wR2 = 0.1992
Largest diff. peak hole	0.364 and-0.573e $Å^{-3}$

Table 2.10: Crystal data and structure refinement for 6b

Empirical formula	$C_{19}H_{16}BN_3F_4$	
Formula weight	373.16	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.1833(2) Å	α =82.4233(9)°
	b = 7.9742(2) Å	β = 79.9094(10)°
	c = 16.0924(4) Å	γ = 76.9424(11)°
Volume	879.97(4) $Å^3$	
Z	2	
Density (calculated)	1.408Mg/m^3	
Absorption coefficient	0.114mm-1	
F000	384	
Crystal size	0.08 x 0.25 x 0.35 mm^3	

Theta range for data collection	2.945 to 27.506 °
Index ranges	-9<=h<=9, -10<=k<=10, -20<=l<=20
Reflections collected	14794
Independent reflection	3998 [R_{int} = 0.120]
Completeness of theta = 26.13°	99.50%
Absorption correction	Semi-empirical from equivalents
Max and min. transmission	0.9900 and 0.9700
Refinement method	Full matrix least square on F^2
Data/restraints/parameters	3998/0/245
Goodness of fit on F^2	1.2019
Final R indices [I>2 sigma(I)]	R1 = 0.0793, wR2 = 0.1677
R indices (all data)	R1 = 0.0578, wR2 = 0.1560
Largest diff. peak hole	0.400 and-0.370e $Å^{-3}$

Table 2.11: Crystal data and structure refinement for 6C

Empirical formula	$C_{13}H_{12}IN_3$	
Formula weight	337.16	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/C	
Unit cell dimensions	a = 7.2140(10) Å	α =90.00°
	b = 19.3630(3) Å	β = 126.8350(10)°
	c = 11.5400(2) Å	γ = 90.00°
Volume	1290.16(3) $Å^3$	
Z	4	
Density (calculated)	1.736Mg/m^3	
Absorption coefficient	2.464mm-1	
F000	656	
Crystal size	0.68 x 0.25 x 0.25 mm^3	
Theta range for data collection	3.01 to 27.50 °	

Index ranges	-9<=h<=9, -25<=k<=25, -14<=l<=14
Reflections collected	18959
Independent reflection	2943 [R_{int} = 0.1107]
Completeness of theta = 27.50°	99.50%
Absorption correction	Semi-empirical from equivalents
Max and min. transmission	0.5779 and 0.2851
Refinement method	Full matrix least square on F^2
Data/restraints/parameters	2943/0/153
Goodness of fit on F^2	1.071
Final R indices [I>2 sigma(I)]	R1 = 0.0360, wR2 = 0.0737
R indices (all data)	R1 = 0.0305, wR2 = 0.0702
Largest diff. peak hole	0.643 and-1.089e $Å^{-3}$

Table 2.12: Crystal data and structure refinement for 9b

Empirical formula	$C_{22}H_{22}BF_4N_3$	
Formula weight	415.24	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/C	
Unit cell dimensions	a = 9.8460(4) Å	α =90.00°
	b = 12.5190(6) Å	β = 93.507(3)°
	c = 17.2380(7) Å	γ = 90.00°
Volume	2120.81(16) $Å^3$	
Z	4	
Density (calculated)	1.300Mg/m^3	
Absorption coefficient	0.01mm-1	
F000	864	
Crystal size	0.30 x 0.30 x 0.20 mm^3	
Theta range for data collection	2.663 to 27.47 °	
Index ranges	-12<=h<=12, -14<=k<=16, -22<=l<=22	
Reflections collected	8027	

Independent reflection	4825 [R_{int} = 0.559]
Completeness of theta = 27.47°	99.30%
Absorption correction	Semi-empirical from equivalents
Max and min. transmission	0.9800 and 0.9702
Refinement method	Full matrix least square on F^2
Data/restraints/parameters	4825/267/302
Goodness of fit on F^2	1.028
Final R indices [I>2 sigma(I)]	R1 = 0.1366, wR2 = 0.1814
R indices (all data)	R1 = 0.0650, wR2 = 0.1476
Largest diff. peak hole	0.263 and-0.320e $Å^{-3}$

Table 2.13: Crystal data and structure refinement for 9c

Empirical formula	$C_{16}H_{18}IN_3$	
Formula weight	379.23	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P C	
Unit cell dimensions	a = 11.2770(4) Å	α =90.00°
	b = 12.300(5) Å	β = 90.100(5)°
	c = 11.5370(4) Å	γ = 90.00°
Volume	1600.26(10) $Å^3$	
Z	4	
Density (calculated)	1.574Mg/m^3	
Absorption coefficient	1.996mm-1	
F000	752	
Crystal size	0.30 x 0.22 x 0.15 mm^3	
Theta range for data collection	3.02 to 27.42 °	
Index ranges	-14<=h<=11, -10<=k<=15, -14<=l<=14	
Reflections collected	8017	
Independent reflection	5779 [R_{int} = 0.287]	
Completeness of theta = 27.42°	92.30%	
Absorption correction	Semi-empirical from equivalents	

Max and min. transmission	0.7339 and 0.5859
Refinement method	Full matrix least square on F^2
Data/restraints/parameters	5779/50/306
Goodness of fit on F^2	1.055
Final R indices [I>2 sigma(I)]	R1 = 0.0627, wR2 = 0.1040
R indices (all data)	R1 = 0.0434, wR2 = 0.0939
Largest diff. peak hole	1.046 and-0.934e $Å^{-3}$

Table 2.14: Crystal data and structure refinement for 9f

Empirical formula	$C_{23}H_{10}ClN_4$	
Formula weight	386.86	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.34480(10) Å	α =90.00°
	b = 20.0690(4) Å	β = 95.5741(8)°
	c = 11.4953(2) Å	γ = 90.00°
Volume	1916.04(6) $Å^3$	
Z	4	
Density (calculated)	1.341Mg/m^3	
Absorption coefficient	0.216mm-1	
F000	808	
Crystal size	0.20 x 0.25 x 0.25 mm^3	
Theta range for data collection	2.030 to 27.422 °	
Index ranges	-10<=h<=10, -24<=k<=26, -14<=l<=14	
Reflections collected	30860	
Independent reflection	4358 [R_{int} = 0.189]	
Completeness of theta = 27.442°	99.70%	
Absorption correction	Semi-empirical from equivalents	
Max and min. transmission	0.9600 and 0.9500	
Refinement method	Full matrix least square on F^2	

Data/restraints/parameters	2307/0/254
Goodness of fit on F^2	0.9465
Final R indices [I>2 sigma(I)]	R1 = 0.0422, wR2 = 0.1019
R indices (all data)	R1 = 0.0792, wR2 = 0.1145
Largest diff. peak hole	0.29 and-0.29e $Å^{-3}$

2.5 References

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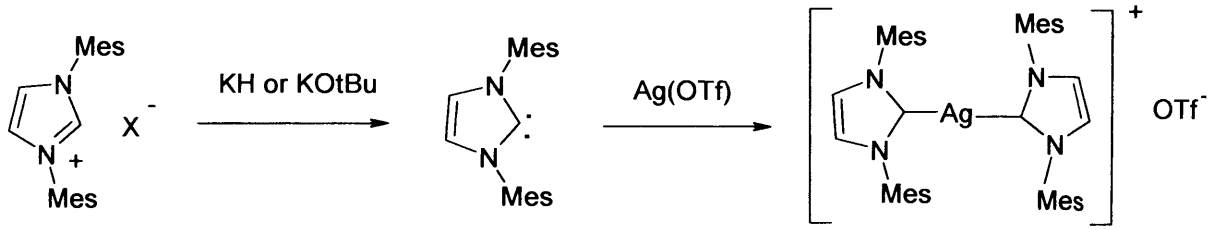
CHAPTER THREE

Siver(I) and Palladium(II) complexes of quinoline functionalised Heterocyclic Carbene ligands.

3.1 Silver(I) (NHC) complexes

3.1.1 Introduction

The synthesis of Ag^{I}(NHC) was first reported by Arduengo in 1993 using the free carbene route [1]. This was accomplished by deprotonation of the imidazolium salt **3.01** to make the free carbene (1, 3-dimesitylimidazolin-2-ylidene) **3.02** and subsequent reaction of **3.02** with silver triflate to yield the desired homoleptic Ag^{I}(NHC) **3.03**. Several other Ag^{I}(NHCs) have been synthesised using this method [1, 2, 3,4,5,]. However, this method has been applied to the synthesis of only a limited number Ag^{I}(NHC) due to the difficulty of generating most free carbenes , which have other acidic protons especially azolium salts with methylene linkers [6].



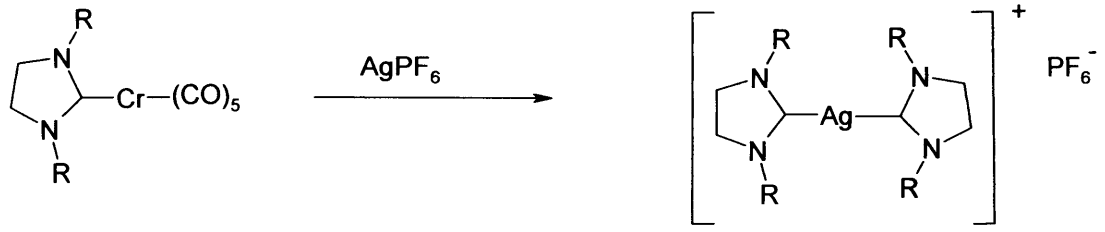
3.01 **3.02** **3.03**

Scheme 3.0: Synthesis of Arduengo homoleptic Ag carbene complex

Ag^{I}(NHC) can also be accessed by transmetallation. Transmetallation of the NHC ligands to $AgPF_6$ yielding homoleptic imidazolindin-2-ylidene complexes **3.04-3.06** was also reported [7].

The *in situ* deprotonation of imidazolium salts with basic silver precursors is the most commonly used method to synthesise Ag^{I}(NHC) complexes. In their reaction Bertrand et al demonstrated that Ag(OAc) reacts with 1,2,4-triazolium

salts producing polymeric Ag^{I}(1,2,4-triazolin-3,5-diylidene) complexes with alternating Ag^{I} and 1,2,4-triazolin-3,5-diylidene units [8]. The use of Ag(OAc) protocol has not been widely utilised with the reports of Ag^{I}(NHC) complexes being restricted to a few examples with symmetrically alkyl substituted NHCs.



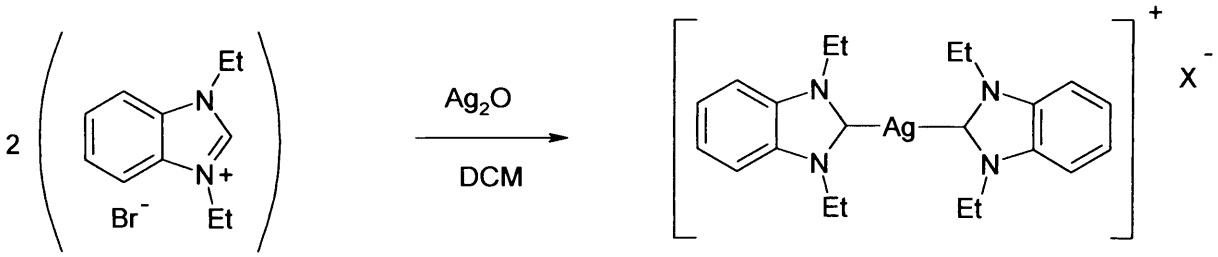
3.04: R = Et

3.05: R = allyl

3.06: R = benzyl

Scheme 3.2: Synthesis of Ag^{I}(NHC) via transmetallation

The most commonly used base is silver (I) oxide, pioneered by Lin and Wang [9]. These workers reported that stirring 1, 3-diethylbenzimidazolium bromide with Ag_2O in DCM, or with AgBr and NaOH under phase transfer conditions gave the Ag^{I}(benzimidazollin-2-ylidene)$_2$ complexes **3.07** and **3.08** in high yield, Scheme 3.3.



3.07: X = $AgBr_2^-$

3.08: X = PF_6^-

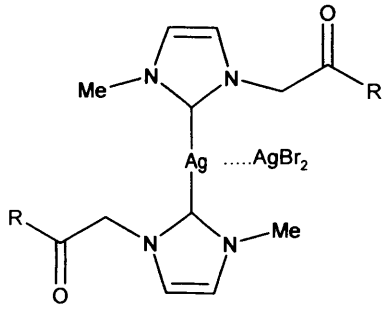
Scheme 3.3: Wang and Lin's preparation of Ag^{I}(benzimidazolin-2-ylidene)$_2$ complexes via silver(I) oxide.

The principle advantage of the Ag_2O protocol is its tolerance to oxygen and moisture, indeed water is the by-product of the reaction. There are in fact reports

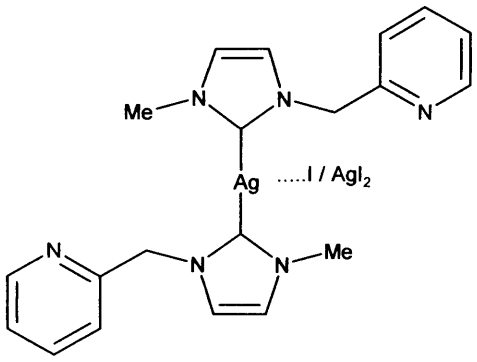
of the reactions being carried out at ambient temperature, in a variety of solvents including water [10-12]. The formation of silver complexes in water suggests that the deprotonation of the imidazolium salt and coordination to metal centre is a concerted process because free carbenes are water sensitive [13]. Several groups have successfully prepared a variety Ag^{I}(NHC) complexes through the application of the Ag_2O method of Wang and Lin with different kinds of imidazolium salts [14-21]. Modification of Wang and Lin's original method used dichloroethane as solvent [17], thereby allowing the reaction to be carried out at elevated temperatures for less reactive imidazolium salts.

In the cases where the imidazolium salts are insoluble in DCM, the use of solvent mixtures such as DCM-MeCN [22] and DCM – EtOH [23] has been found to be useful. The reaction can also be performed in DMSO at 55°C as reported recently [24]. Furthermore, addition of molecular sieves to the reaction has also been reported to facilitate the formation of Ag^{I}(NHC) complexes by removing the water generated in the reaction as shown in Scheme 3 above [17]. Silver(I) carbonate was also reported to have been used in the synthesis of Ag^{I}(NHC), though less effective than the Ag_2O protocol as a longer reaction time is required for the reaction to reach completion [17]

McGuinness and Cavell reported the synthesis of a series of mono donor-functionalised Pd^{II}(NHC) by the use of Ag_2O protocol via the transmetallation Ag^{I}(NHC) complexes **3.09 – 3.10** with appropriate palladium precursors [16].



3.09



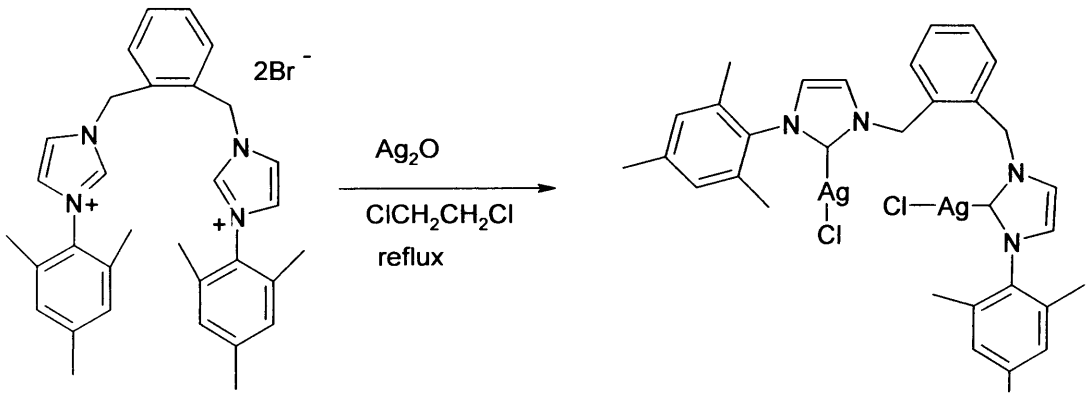
3.10

Figure 3.10: Cavell carbonyl and pyridyl functionalised Ag^{I}(NHC) used to prepare Pd^{II}(NHC) complexes

The Cavell group also reported the application of the Ag_2O protocol to synthesise phenoxy- functionalised [25], pyridyl-functionalised [26] and thiophene and furan-functionalised [27)Ag^{I}(NHC) complexes. A range of imidazolium salts bearing a diverse variety of functionalised groups have been shown to be compatible with the formation of Ag^{I}(NHC) complexes via Ag_2O. Thus, Ag^{I}(NHC) complexes with amine [18], ferrocenyl [15], imines[17], amide [17] and alkoxy functionalised bis-NHC have been prepared through the Ag_2O route. Other Ag^{I}(NHC) prepared were not isolated but used directly as transmetallation reagents [18].

The wide applicability and ease of preparation of stable Ag^{I}(NHC) complexes via the Ag_2O route and the good transmetallation properties of these complexes promised ready access to donor-functionalised NHC complexes of catalytically interesting transition metals [28]. The ability to obtain Ag^{I}(NHC) complexes from the reaction of Ag_2O with imidazolium, saturated imidazolidinium and benzimidazolium salts indicates that their formation is relatively unaffected by the electronics of the heterocyclic ring [28].The reaction is also tolerant of steric group and a wide range functional groups on the NHC N-substituents.

Halogen exchange reactions have been found to occur when NHC complexes are synthesised in chlorinated solvents. Danopoulos and co-workers reported halide exchange reactions when synthesising Ag^{I}(NHC) in 1,2-dichloroethane or dichloromethane [17]. An example of the halide exchange is depicted in Scheme3. 4. Similarly Lin and co-workers reported the salt metathesis of imidazolium iodide salts with chloride from methylene chloride during the synthesis of Ag^{I}(NHC) complexes [22].



Scheme 3.4: Halide exchange in Ag^{I}(NHC) complex synthesis

Mixtures of halogeno and halide anions of silver NHCs have been reported [18, 29]. To reduce the complications due to inorganic halogeno complexes and cluster formation, anion exchange of the imidazolium halide salt for a noncoordinating anion has been widely employed. After the anion exchange, the synthesis of the Ag^{I}(NHC) proceeds cleanly to one product. Anion exchange of the halide after the synthesis of the Ag^{I}(NHC) has also been performed using reagents such as $AgBF_4$, to obtain clean products without the complexities of the halide [26,29,30,31].

Theoretical calculations of group 11 NHC carbenes showed that the metal-carbene bond strengths follow the pattern Au > Cu > Ag [13]. While the bond strength of Ag^{I}(NHC) complexes were shown to be relatively the weakest, the overall strength of 56. 5 Kcal/mol was considered strong enough to stabilise the Ag^{I}(NHC) [32].

3.1.2 Structural diversity in Ag^{I}(NHC) complexes

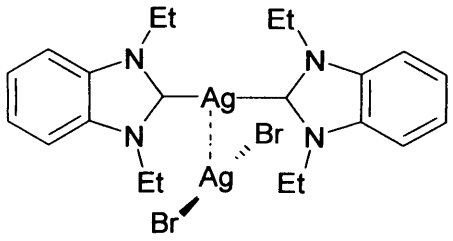
The structural characterisation of N-heterocyclic carbene complexes of silver has led to very complex bonding motifs in the solid state, especially in complexes with halide anions. The ability of silver to form complex anions of the formula $[AgX_2]^-$ (X = halogen), coordinate to either one or two NHC moieties and engage in Ag(I)....Ag(I) interactions in the solid state appear to account for most of this structural diversity. The interactions between Ag(I) and functional groups present on the NHC ligand are weak compared to most of the Ag(I)....Ag(I) interactions observed in Ag(I)NHCs.

Ag^{I}(NHC) complexes with non coordinating anions exist as biscarbene salts with the cationic silver bound by two carbene moieties and the noncoordinating anion balancing out the charge (C2- Ag).

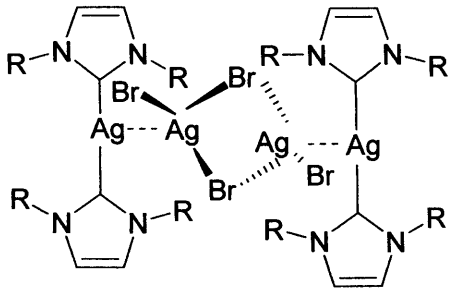
Studying the crystal structure of their non functionalised Ag^{I}(NHC) complex **3.07** Wang and Lin [9] reported a mononuclear complex with two NHC ligands coordinated to Ag(I) and the counter ion $[AgBr_2]$ coordinating through a Ag(I).....Ag(2) interaction above the plane of the cation. The Ag(I).....Ag(2) distance of 2. 954 Å was found to be significantly shorter than the van Waals contact distance of 3. 44 Å. and relatively short for an unsupported Ag(I).....Ag(I) interaction [9].

Another study of non functionalised Ag^{I}(NHC) complex **3.11** revealed a linear NHC-Ag(I)-NHC motif with coordinated $[AgBr_2]$- counterion almost perpendicularly aligned [22]. Other structural studies of Ag^{I}(NHC) complexes revealed mono NHC complexes with coordination anions or uncoordination anions. For example, in **3.12** the C2-Ag-X strings deviate from linearity [5, 21]. **3. 13** [19] and **3.14** [22] may therefore be considered to be aggregated **3.12** motifs formed due to Ag...X and weak Ag...Ag interactions between adjacent molecules. As a result of alternating Ag-Br and Br-Ag units in the solid state, the bond length around Ag_2Br_2 rhomboids in **3.14** are unequal.

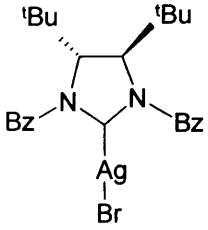
Ag^{I}(NHC) complexes that have donor functionalised group feature most of the structural diversities observed in the non functionalised counter parts. In **3.15** the $[AgBr_2]$- counter ion is coordinated to the pyridine functionality of one of the NHC ligands that make up the linear NHC-Ag(I)-NHC unit [17]. Other reported examples are shown in structures **3.16** and **3.17** where they exhibited rhomboid Ag_2Br_2 and linear NHC-Ag(I)-X geometries respectively [17]. Also reported is a dinuclear Ag^{I}(NHC) complex **3.16** with Ag_2L_2 formulation [3]. The structure of **3.18** is that of double helical unit with the C_2-Ag-C_2 strings distorted by 14.5° from the linear orientation because of relatively rigid ligands Ag...Ag' bonding interaction is present and brings the these atoms to within 3.158Å.The pyridyl group of each ligand is equidistant to Ag, Ag' at a distance of 3.02Å. Structure **3.19** is a trinuclear pyridyl functionalised Ag^{I}(NHC) complex obtained by the reaction of 3-methyl-1-picolylimidazolium iodide with 2.5 eq mole of Ag_2O in DCM[33]. The geometry at the silver centre is planar, with every Ag coordinated by two carbene atom and one triply bridging iodine. The three Ag(I) cations are linked by the bridging I(1) anion symmetrically with an Ag(1)-I(1) distance of 3.04 Å which is more longer than those of the Ag-I(bridging) bonds 2.83 and 2.78 Å [37], and the net charge of 2+ is balanced by two non interacting iodide ions [33].



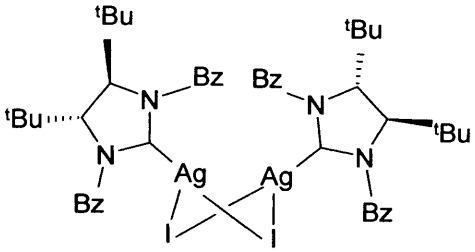
3.07



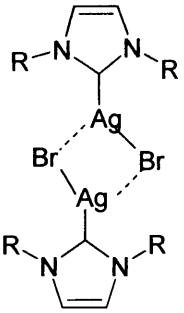
3.11



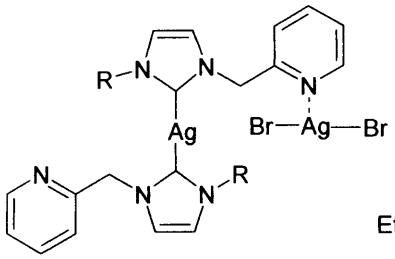
3.12



3.13



3.14



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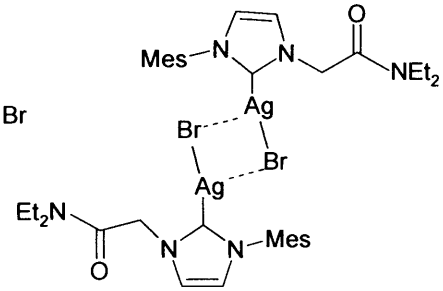
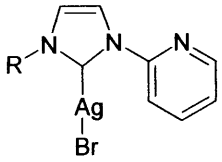
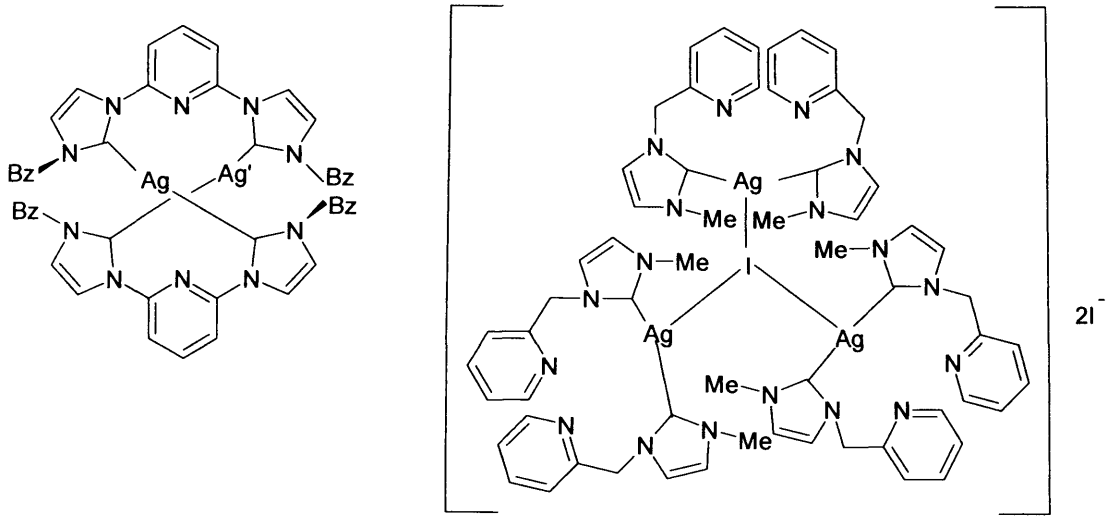


3.16



3.17



3.18 **3.19**

Figure 3.11: Bonding motifs in Ag^{I}(NHC) complexes

Ag...Ag interactions have not been observed in Ag^{I}(NHC) complexes that have been prepared in the absence of coordinating halide anions. In Ag^{I}(NHC) complexes with triflate [1,3,8], barf[15], nitrate[22], and carborane [4] anions, homoleptic $[Ag^{I}(NHC)_2]X$ complexes are formed with quasi-linear C_2-Ag-C_2 strings.

3.1.3 Ag^{I}(NHC) complexes as transmetallation reagents

The use of Ag^{I}(NHC) in homogenous catalysis has recently appeared in the literature: such as in the preparation of 1,2-bis(borane) esters [34], ring opening polymerization of lactides [35 , 36] and olefin polymerization [37]. However, the increased interest in the chemistry of Ag^{I}(NHC) complexes has been mainly due to their role as transfer agents in the development of many important metal-NHCs.The fact that active hydrogen atoms other than C_2-H can be protected effectively by this method solved difficulties encountered in the synthesis of metal- NHCs by other methods [16,18, 26,38]. NHC ligands have thus been transferred from Ag^{I}(NHC) complexes to a variety of metals including Cr^{III}, Fe^{III}, Co^{II}, Ni^{II} [38], Cu^{I} [1], Cu^{II} [39], Pd^{II} [9,14, 16,18,39,40,], Au^{I} [9,23],Rh^{I} and Ir^{I} [41].

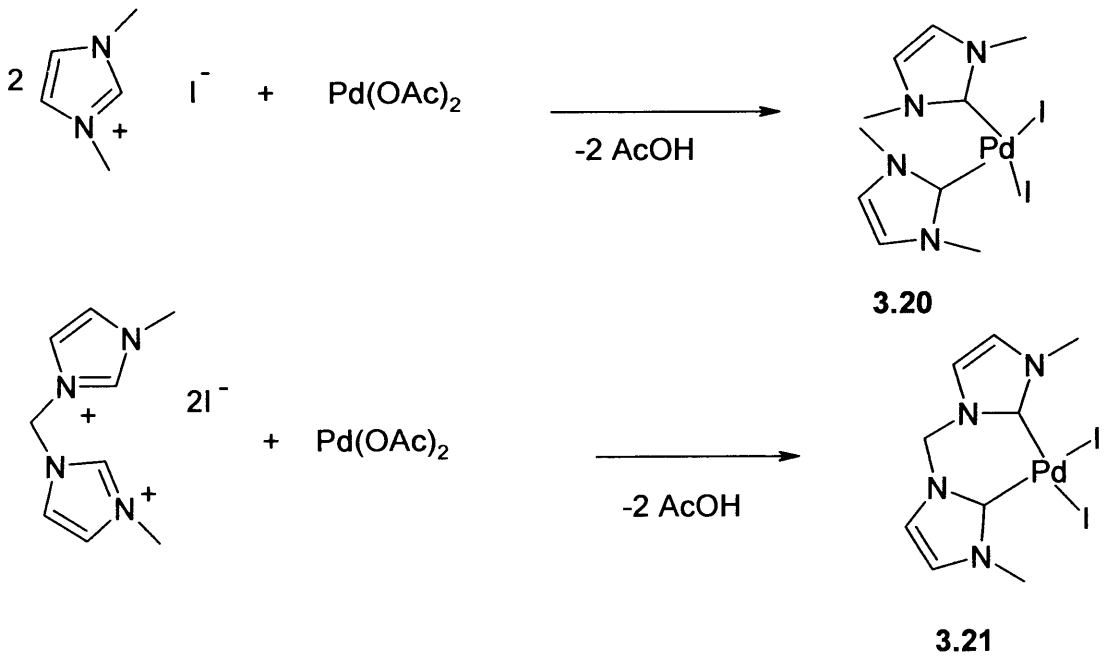
Transmetallation may be carried out using isolated Ag^{I}(NHC) complexes or conveniently performed in a one pot protocol where the Ag^{I}(NHC) complex is

generated from an imidazolium salt and Ag_2O and then reacted in situ with a precursor of the desired metal. The transfer of NHC depends on the nature of Ag^{I}(NHC), the receiving metal precursors and the reaction conditions.

3.2.0 Palladium (II) complexes of quinoline functionalised heterocyclic carbene ligands

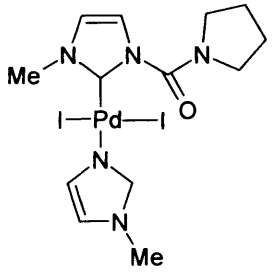
Pd^{II}(NHC) carbene complexes were first reported in 1995 by Herrmann [42] by the reaction of $Pd(OAC)_2$ with 1,3,-dimethylimidazolium iodide to give **3.20** and 3, 3-dimethyl-1,1-methylenediimidazolium diiodide to give **3.21** as shown in scheme 3.5. It was discovered that these new palladium complexes were stable to heat, air and moisture. In addition to this, these complexes were found to be excellent catalysts in Heck reactions.

As enumerated in chapter 1 NHCs exhibit properties that are complimentary to their application as ligands in catalysis. They are more strongly bonded to transition metals such as Pd than the widely used phosphine ligands [42, 43], and thus required only in stoichiometric amounts, and in general Pd^{II}(NHC) complexes are less toxic, easier to handle and exhibit better thermal stability than typical phosphine ligands.

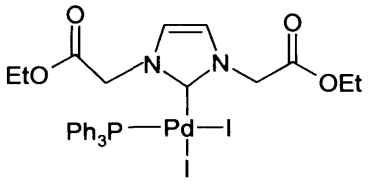


Scheme 3.5: Herrmann's synthesis of **3.20** and **3.21.**

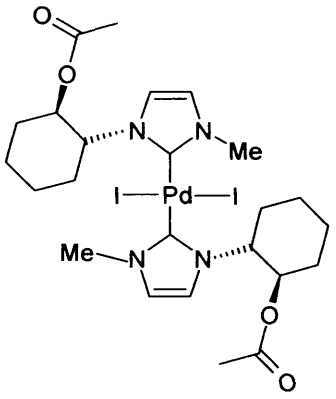
Following the discovery of the qualities of complexes **3.20** and **3.21**, there was renewed interest to explore catalytic applications of the Pd^{II}(NHC) system through modification of the NHC ligands. Among the important ligand design was the combination of the strongly bound NHC moiety with more weakly nucleophilic functional groups allowing access to ligands with hemilabile donor groups, as these can increase catalytic activities by stabilising the low- valent metal centres formed during catalysis. Along this line several Pd^{II}(NHC) complexes were reported bearing one or two functionalised substituents with carbamoyl (**3.22** [44,45]), ester (**3.23**[46] and **3.24**[47]), ethers (**3.25**[48]), hydroxyl(**3.26** [42], **3.27** [48]), oxazoline(**3.28**[49]), picolyl(**3.29** [50]), pyridyl (**3.30** and **3.31** [51], **3.32** [52]),imine **3.33** [53] groups Figure 3.12.



3.22



3.23



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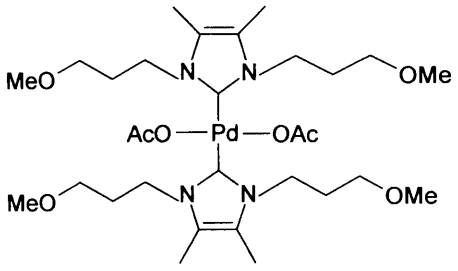

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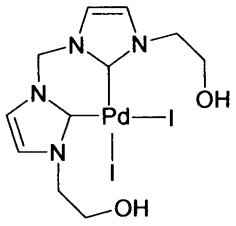

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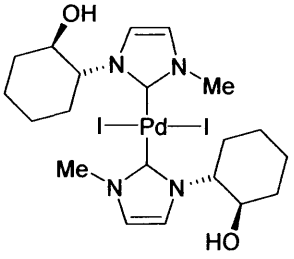

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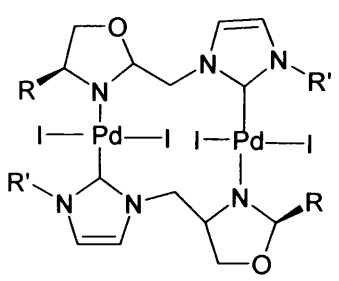

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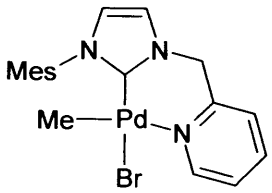

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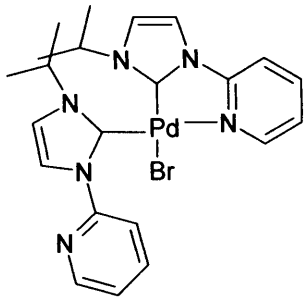

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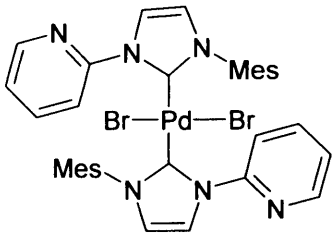

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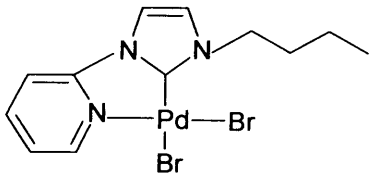

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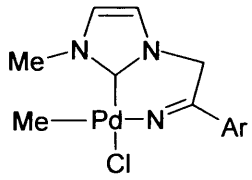


3.33

Figure 3.12: Structurally characterised examples of some reported Pd(II) complexes bearing functionalised NHC ligands.

Many synthetic routes have been employed to synthesise Pd^{II}(NHC) complexes and these have been outlined in chapter one. The routes to be used depend on the nature of available imidazolium salts. The $Pd(OAc)_2$ route is among the many routes available and is suitably for simple mono and bis imidazolium salts as shown by Herrmann in Scheme 3.5 above but does not give access to catalytically important Pd- hydrocarbyl species. Pd^{II}(NHC) complexes can also be prepared via the free carbene route by the use of strong bases such as NaH with catalytic amounts of KOtBu and amides ($K[N(SiMe_3)_2]$). Once the free carbene is formed, it can be reacted with appropriate metal source such as $PdCl_2(COD)$ to produce the desired Pd^{II}(NHC) complexes. However free carbenes are known to be unstable especially in the absence of bulky aryl or alkyl groups on the 1 and 3 positions of the ring thereby making the route unsuitable in the synthesis of some Pd^{II}(NHC) complexes. The use of strong bases have been found to be unsuitable in accessing functionalised carbenes because of acidic protons commonly associated with functional group and any methylene linkers.

The chapter also reports the synthesis and characterisation of quinoline functionalised Ag^{I}(NHC) complexes. X- ray crystallographic studies have been

carried on two of the Ag^{I}(NHC) complexes prepared in this work and the data obtained compared with the published examples. The reported Ag^{I}(NHC) complexes were synthesised primarily as transmetallation reagents to access the catalytically important quinoline functionalised Pd^{II}(NHC) complexes and Ir^{I} and Rh^{I}(NHC) complexes.

Also described in this chapter are the Pd^{II}(NHC) complexes synthesised via transmetallation of the desired Ag^{I}(NHC) complexes and the complexes were characterised spectroscopically and by micro analysis.

3.3 Results and Discussion

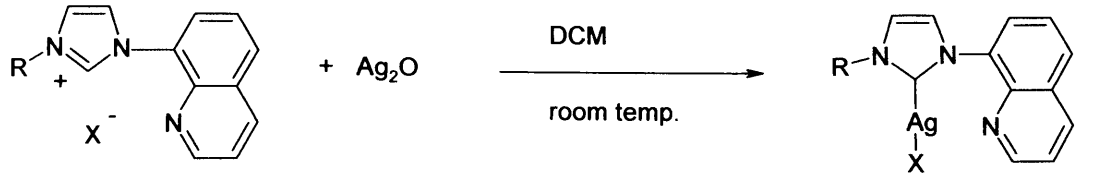
3.3.1 Silver (I) complexes of quinoline functionalised NHC ligands

General comments

Quinoline functionalised imidazolium salts described in chapter two were reacted with Ag_2O to give stable complexes with the general formula $[Ag^{I}(NHC)_2][AgX_2]$ or $Ag^{I}(NHC)X$ based on the two x-ray structures of the complexes obtained. No attempt was made to abstract halide to isolate the Ag^{I}(NHC) complexes as salts of non coordinating anions such as tetraflouroborate, hexaflourophophate or triflate to improve solubility or purity of the complexes. For the purpose of clarity the quinoline based Ag^{I}(NHC) complexes described below are divided into two: the methylene bridged and the rigid quinoline Ag^{I}(NHC) complexes.

3.3.1.1 Silver(I) complexes of rigid quinoline functionalised NHC ligands

Two quinoline functionalised imidazolium salts (**6b** and **6c**) were reacted with Ag_2O to give the corresponding Ag^{I}(NHC) complexes. Two equivalent of the imidazolium salt **6b** was reacted in DCM with one equivalent of Ag_2O overnight at room temperature until the black suspension of Ag_2O disappeared. The reaction was performed free of light as most Ag^{I}(NHC) complexes are light sensitive . After work up , the Ag^{I}(NHC) complex **3.34** was obtained as a light brown powder. The room temperature ^{1}H NMR of complex **3.34** was consistent with the proposed structure with no evidence of residual imC_2-H resonance.



6b: R = $PhCH_2$, X = Br

6c: R = Me, X = I

3.34:R = $PhCH_2$, X = Br

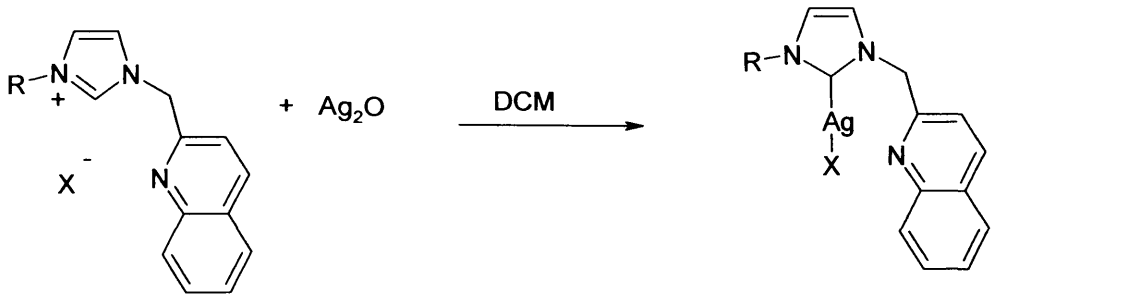
3.35: R = Me, X = I

Scheme 3.6: Synthesis of rigid quinoline functionalised Ag^{I}(NHC) complexes

The proton peak of the methylene linker of the benzyl moiety was shifted upfield (5.35 ppm) relative to those of the corresponding imidazolium salt (5.85 ppm). The carbenic carbon could not be observed in the ^{13} NMR spectra and this is consistent with some of the reports that appeared in the literature as a significant number of silver^{I}(NHC) complexes were reported with no observable carbene resonances [8]. Elemental analysis returned a satisfactory result for complex **3.34**. Crystals suitable for X-ray chromatography were not obtained but the analytical data as well spectroscopic data are consistent with the proposed structure. Complex **3.35** was characterised by ^{1}H NMR, mass spectroscopy and micro analysis. The characteristic feature confirming the formation of the silver^{I}(NHC) complex is the disappearance of C_2-H in the ^{1} H NMR spectra.

3.3.1.2 Silver(I) complexes of methylene-bridged quinoline functionalised NHC ligands

The methylene-bridged quinoline functionalised Ag^{I}(NHC) complexes were prepared following the method reported by Wang and Lin [9], i.e. by interaction of the imidazolium salts with Ag_2O as shown in scheme 3.7.



9a : R = Me, X = Cl
9b : R = Mes, X = Cl
9c : R = ipp, X = I
9d : R = n-Bu, X = I
9e : R = $PhCOC(Me)_2$, X = Cl
9f : R = $QuinCH_2$, X = Cl

3.36 : R = Me, X = Cl
3.37 : R = Mes, X = Cl
3.38 : R = ipp, X = I
3.39 : R = n-Bu, X = I
3.40 : R = $PhCOC(Me)_2$, X = Cl
3.41 : R = $QuinCH_2$, X = Cl

Scheme 3.7: Synthesis of methylene bridged quinoline functionalised Ag^{I}(NHC) complexes

It was found that: (i) with the relatively unreactive sterically hindered imidazolium salts (**9e** and **9f**) the reaction was carried out in refluxing dichloromethane, whereas for all other imidazolium salts the reaction occurred at room temperature ; (ii) synthesis in refluxing dichloromethane increases the formation of by-product (iii) the purity of the product is improved by addition of activated molecular sieves to the reaction medium.

Compound **3.36** was characterised by ^{1}H NMR, ^{13} NMR, microanalysis and X-ray crystallography. The room temperature ^{1}H NMR of Complex **3.36** was consistent with the proposed structure showing complete disappearance of imC_2-H resonance and the protons of the methylene linker was observed to move up field. In the ^{13}C NMR there was sharp singlet peak at 181.18 ppm which is assignable to the carbene carbon of the Ag^{I}(NHC) complex. Microanalysis returned satisfactory results for complex **3.36.**

Crystals suitable for X- ray structural determination were obtained by diffusing Et_2O into a DCM solution of the complex. The crystal structure is depicted in figure 3.13 below.

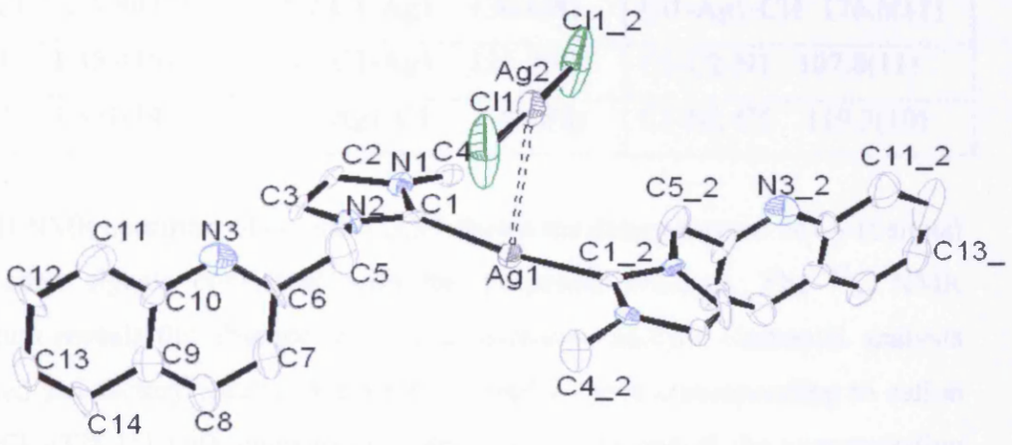


Figure 3.13: ORTEP projection of complex **3.36** excluding hydrogen atoms for clarity showing atom labelling scheme.

Complex **3.36** as shown in the above figure consists of a linear $[Ag(NHC)_2]^+$ cation and a linear $[AgCl_2]^-$ with the two ions associating through Ag^1- Ag^1 interaction. The Ag-C bond distance (Ag(1)-C(1) = 2.106(12) are comparable to those reported by Wang and Lin (2.073 Å) [8]. The geometry of C(1)-Ag(1)-C(1_2) is close to linear (170.8°(8) though it is lower than what was obtained by Wang and Lin (175.6°) [8]. The Ag(1)-Ag(2) separation of 3.201 Å is smaller than the contact van de Waals distance of 3.44Å and is at upper range of the ligand-unsupported Ag-Ag bond lengths (range 2.80-3.30 Å) [54]. The Cl(1)-Ag-Cl(1) angle of 176.6° deviates only slightly from that of the coordinated linear species. Some selected bond lengths (A) and angles (o) are presented in table 3.1 below.

Table 3.1: Selected bond lengths (Å) and bond angles (°) of **3.36**

Ag1- Ag2 3.201(4)	N2-C5 1.48(2)	C1-Ag1-Ag2 94.6(4)
Ag2-Cl1 2.290(5)	N2-C1-N1 104.0(10)	C1-Ag1-Ag2 85.4(4)
Ag1-C1 2.106(12)	N2-C1-Ag1 130.6(8)	Cl1-Ag1-Cl1 176.6(11)
C1-N1 1.353(16)	N1-C1-Ag1 125.2(9)	C3-C2-N1 107.8(11)
C1-N2 1.351(14)	C1-Ag1-C1 170.8(8)	C1-N2-C5 119.3(10)

The ^{1}H NMR spectrum of complex **3.37** shows the disappearance of C_2-H signal with other signals consistent with the proposed structure. The ^{13}C NMR spectrum reveals the absence of $C_{carbene}$ resonance and the elemental analysis returned satisfactory results. A ES-MS showed a peak corresponding to cation [M^{+}-Cl =328.15] with intensity of 100% similar to that of the corresponding imidazolium salt indicating that under these conditions the silver complex undergoes decomposition .This decomposition of silver(NHC) complexes and the observation of the corresponding of the corresponding salts has been reported using ES-MS [55]. Crystals suitable for X-ray chromatography were obtained by diffusion of Et_2O into a saturated DCM solution of the complex and the crystal structure is depicted in Figure 3.14 below. The geometry of the silver in the carbene complex is that of distorted linear with C13- Ag1-Cl2 bond angle of 169.03° (10) which is similar to the silver carbene complex reported by Cesar and Gade

(169.4° (1)) [56] and lower than those reported by Danopoulos et al (176.1°(2)) [17], Pytkowicz etal (175.2°(5)) [39] and Paas et al (173.5°(2)) [57]. All other bond lengths and bond angles are consistent with the reported values [17,39, 56, 57]. Some selected bond length and bond angles are presented in table 3.2 below.

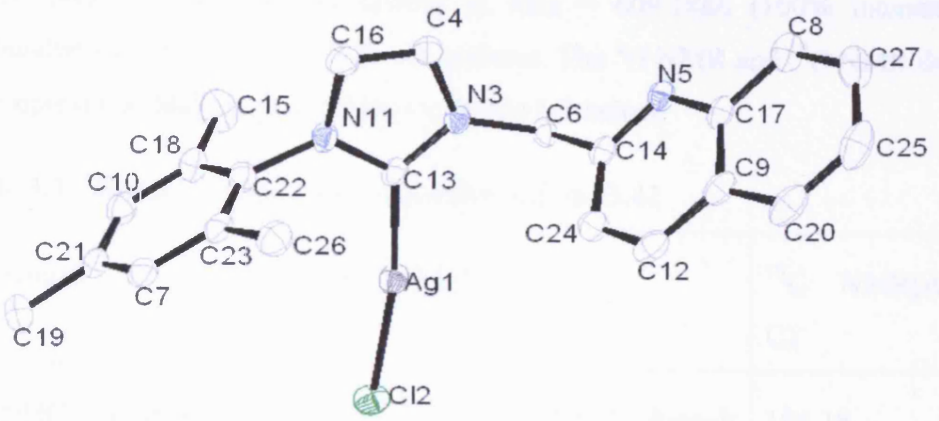


Figure 3.14: ORTEP projection of complex **3.37** excluding hydrogen atoms for clarity showing atom labelling scheme.

Table 3.2: Selected bond lengths (Å) and bond angles (°) of **3.37**

Ag1-Cl2 2.350(9)	N5-C14 1.320(5)	Ag1-C13-N11 123.7(3)
Ag1-Cl3 2.090(3)	C4-C16 1.344(5)	N3-C13-N11 104.9(3)
N3-C13 1.342(5)	C4-N3 1.384(4)	N3-C6-C14 111.6(3)
N11-C13 1.354(4)	C13-Ag1-Cl2 169.03(10)	C13-N11-C22 122.6(3)
N3-C6 1.474(4)	Ag1-C13-N3 131.4(2)	C6-C14-N5 116.2(3)

The formation of complexes **3.38, 3.39 3.40** and **3.41** were confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy. The ^{1}H NMR revealed complete disappearance of the C_2-H protons while the $C_{carbene}$ of complexes **3.38, 3.39** and **3.41** appeared at 184.10, 183.23 and 180.37 ppm respectively, that of complex **3.40** was not observed. High resolution mass spectroscopy of complex **3.41** indicated only the decomposition of the complexes as only the its corresponding imidazolium salt ions was observed at M/z = 351.16 (100% intensity) equivalent

to $[(NHC)+H]^+$. ^1H NMR and ^{13}C NMR spectra of complex **3.38** are consistent with the bis carbene formulation with the $C_{carbene}$ of the complex appearing at 184.10 ppm. HRMS showed cluster at M/z = 609.1886 (100% intensity) attributable to $[Ag(NHC)_2]^+$ of the bis carbene. The ^1H NMR and ^{13}C NMR data of complexes **3. 36-3.41** is presented in Table 3.3 below.

Table 3.3: ^1H and ^{13} NMR data of complexes 3.36- 3.41

Compound	^1H NMR at 298K	^{13}C NMR(Ag-C)
$[Ag(NHC)_2]^+[AgCl_2]^-$ **3.36**	H, 3.55; N, 11.46; Cl, 9.67%. Found: C, 45.71; H, 3.45; N, 11.33; Cl, 9.60%. ^1H NMR ($CDCl_3$. 400MHz, 298K): 8.10 (d, 2H, J = 8.5 Hz, Quin-H), 8.00 (d,2H, J = 8.4 Hz, Quin-H), 7.80 (d, 2H, J = 8.1 Hz, CHHC), 7.5 (d, 2H, J = 8.4 Hz, Quin-H), 7.35 (d, 2H, J = 1.7 Hz, Quin-H) 7.15 (d, 2H, J = 1.8 Hz, Quin-H), 6.95 (s,1H, Quin-H), 5.50 (s, 4H CH_2), 3,85 (s, 6H, CH_3).	181.18
[Ag(NHC)Cl] **3.37**	^1H NMR ($CDCl_3$. 400MHZ, 298K) : 8.10 (d, 1H, J = 8.4 Hz, Quin-H), 8.00 (d, 1H, J = 8.5 Hz, Quin-H), 7.80 (d, 2H, J = 8.1 Hz, CHHC), 7.70 (t, 1H, J = 1.4 Hz, Quin-H), 7.50 (t, 1H, J = 7.0 Hz, Quin-H), 7.35 (t, 2H, J = 8.7 Hz, Quin-H), 6.90 (s, 3H, Aromatic-H), 5.60 (s, 2H, CH_2), 2.25 (s, 3H, m-CH_3), 1.95 (s, 6H, o-CH_3).	N.A.
[Ag(NHC)Cl] **3.38**	^1H NMR ($CDCl_3$. 400MHz, 298K):	184.10

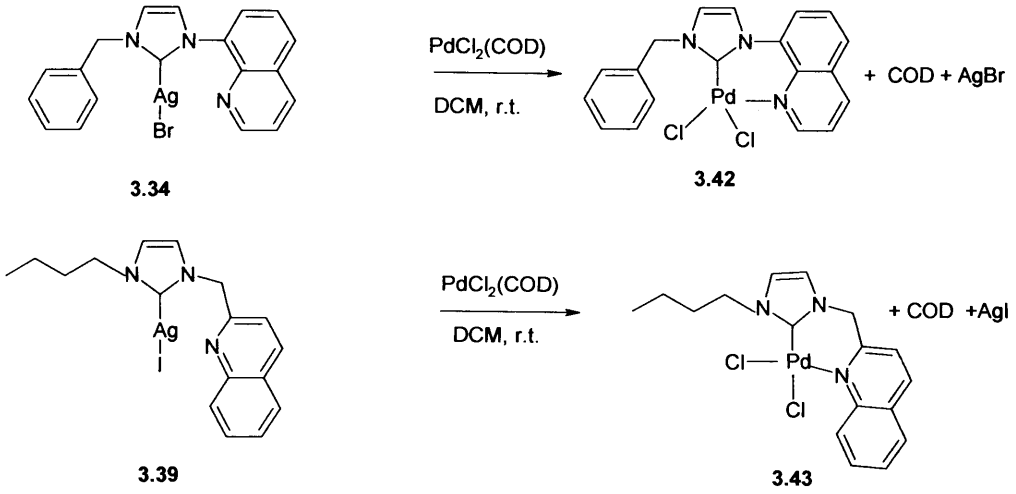
	8.05(d, 2H, J = 8.5 H_Z, quin-H), 7.65(t, 2H, J = 7.0 H_Z, quin-H), 7.50(d, 2H, J =5.2 H_Z, quin-H), 7.10(s, 1H, CHHC), 6.90(s, 1H, CHHC), 5.60(s, 2H, NCH_2C), 4.85(m, 1H, NCHC), 1.35(d, 6H, J = 6.8 H_Z, CH_3).	
[Ag(NHC)Cl] **3.39**	^1H NMR ($CDCl_3$. 400MH_Z, 298K): 8.00(d, 1H, J = 8.5 H_Z, quin-H), 7.90(d, 1H, J = 8.5 H_Z, quin-H), 7.60(m, 2H, J = 8.1 H_Z, quin-H), 7.55(d, 1H, J = 8.5 H_Z, quin-H), 7.40(t, 1H, J = 7.2 H_Z, quin-H), 7.00(s, 1H, CHHC), 6.80(s, 1H, CHHC), 5.60(s, 2H, methylene linker-H), 4.10(t, 2H, NCH_2), 1.70(m, 2H, J = 7.5 H_Z, CH_2), 1.20(m, 2H, J = 7.0 H_Z, CH_2), 0.80(t, 3H, J = 7.3 H_Z, CH_3).	183.23
[Ag(NHC)Cl] **3.40**	^1H NMR ($CDCl_3$. 400MH_Z, 298K): 8.00(d, 2H, J = 10.7 H_Z, quin-H), 7.75(d, 1H, J = 7.1 H_Z, quin-H), 7.60(d,1H, J = 7.5 H_Z, arom-H), 7.50(t, 1H, J = 7.3 H_Z, arom-H), 7.35(s,2H, arom-H), 7.25(s, 2H, CHHC), 7.20(d, IH, J = 6.8 H_Z, quin-H), 7.10(t, 2H, J = 8.4 H_Z, quin-H), 6.90(d, 1H, J = 11.8 H_Z, arom-H), 5.50(s,2H,NCH_2qiun), 2.00(s, 6H, CH_3).	N.A.
[Ag(NHC)Cl] **3.41**	^1H NMR ($CDCl_3$. 400MH_Z, 298K): 8.10(d, 2H, J = 8.4 H_Z, quin-H), 8.00(d, 2H, J = 8.5 H_Z, quin-H), 7.75(d,2H, J =	180.37

	8.1 H_Z, quin-H), 7.65(t, 2H, J = 5.6 H_Z, quin-H), 7.5(t, 2H, J = 7.1 H_Z, quin-H), 7.35(d, 2H, J = 8.5 H_Z, quin-H), 7.15(s, 2H, HHC), 5.5(s, 4H, NCH_2C).	

A look at the data presented in Table 3.3 indicate that there is no significant difference between complexes 3.36 -3.41 in terms of the chemical shift of quinoline protons and that of the methylene linkers and the C- Ag carbene resonances were observed between 180.37 -184.10 which are within the range reported in the literature (180-243 ppm) [13]. Elemental analysis of complex **3.38** returned a satisfactory results consistent with the proposed structure as suitable crystal for X-ray crystallography could not be obtained. Complex **3.39** revealed a cluster at M/z = 637.2189 Da (100% intensity) attributable to the cation of biscarbene $[Ag(NHC)_2]^+$. The ^1H NMR and ^{13}C NMR spectra as well as the elemental analysis of complex **3.40** are consistent with the proposed silver carbene complex. MS analysis revealed a cluster at M/z = 356.1642 Da (100% intensity) and 817.2445 Da (36%) attributable to the cation of the corresponding salt $[(NHC)+H]^+$ and biscarbene ion $[Ag(NHC)_2]^+$ respectively. The observation of the peak attributable to the bis carbene ion may not necessarily indicate that the complex is indeed a biscarbene. Danopoulos and colleagues reported that silver NHCs with solid-state motifs of C-Ag-X and C-Ag-X_2 formed biscarbenes (C_2-Ag) in the gas phase [17].

3.3.2 Pd(II) Quinoline functionalised (NHC) carbene complexes

Two quinoline based Pd(II) (NHC) complexes were prepared according to steps in Scheme 3.8 by the reaction of quinoline functionalised Ag(I)(NHC) complex with one equivalent of $PdCl_2(COD)$ in DCM, over night, the $PdCl_2(COD)$ being synthesised by standard procedures.



3.34 3.42

3.39 3.43

Scheme 3.8: Synthesis of quinoline functionalised Pd(II)(NHC) complexes

Complex **3.42** was characterised by ^{1}H and ^{13}C NMR. Relative to the silver (I) (NHC) complex from which the Pd complex was prepared, the protons where observed to have moved considerably down field indicating that chelation has indeed taken place. Crystal suitable for X-ray crystallography was not obtained but elemental analysis gave satisfactory results in conformity with the proposed structure. Complex 3.43 was characterised by ^{1}H NMR and elemental analysis. The solubility of the complex in $CDCl_3$ was not good enough to get a satisfactory ^{13}C NMR spectrum. Elemental analysis returned unsatisfactory results.

3.4 Conclusions

Ag^{I}(NHC) complexes have been valuable intermediates in the preparation of functionalised Pd^{II}(NHC) complexes that are difficult to be accessed via other methodologies. Thus a range of imidazolium salts synthesised in chapter two was reacted with Ag_2O to form the corresponding silver (I) carbene complexes. The syntheses of the silver complexes were confirmed by the absence of C_2-H in the ^{1}H NMR spectrum, and other analytical techniques.

Compounds **3.36** and **3.37** are the first examples of quinoline functionalised AgI(NHC) complexes and were structurally characterised by X-ray

crystallography and formulated as $[Ag(NHC)_2]^+[AgCl_2]^-$ and [Ag(NHC)Cl] respectively. Results of MS data indicated that complexes **3.38**, **3.39** and **3.40** may have a similar formulation to that of **3.36** because of the presence of cluster attributable to $[Ag(NHC)_2]$. However the MS is not enough to formulate the formula of Ag^{I}(NHC) complexes as Danopoulos and colleagues reported that silver NHCs with solid-state motifs of C-Ag-X and C-Ag-X_2 formed biscarbenes (C_2-Ag) in the gas phase [17]. All the Ag^{I}(NHC) complexes showed stability to air and moisture and were not exposed to light.

In order the extend the synthetic applicability of Ag^{I}(NHC) complexes as transmetallation agents complexes **3.34** and **3.39** were reacted with $PdCl_2COD$ in DCM to obtain quinoline functionalised Pd(II)(NHC) complexes (3.42 and 3.43) respectively. The formation of the Pd(II)(NHC) complexes was confirmed by ^{1}H NMR spectrum as relative to the corresponding Ag^{I}(NHC) complexes , the protons signals of the quinoline moiety of the Pd complexes were observed to have moved down field indication the chelation between the nitrogen of the quinoline moiety and Pd metal. Attempts were made to synthesise the Pd complexes of by reacting the other described quinoline functionalised Ag^{I}(NHC) complexes in this work with $PdCl_2COD$ but a lot of difficulties were encountered in separating the complexes formed from the silver halides .

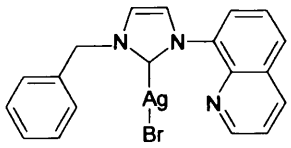
3.5 Experimental

3.5.1 General comments

All reactions were performed under the atmosphere of dry dinitrogen or argon using standard Schlenk techniques, and solvents were purified and dried by usual means [58], unless otherwise indicated. Imidazolium salts were prepared as detailed in Chapter 2, and all other reagents were used as received. All NMR data are quoted δ/ppm. ^{1}H and ^{13}C (proton decoupled) spectra NMR were recorded on a Bruker DPX Advance 400 (^{1}H at 400MHz, ^{13}C at 100.61 MHz) at ambient temperature, unless otherwise stated, and referenced to $SiMe_4$. Electrospray mass spectrometry (ESMS) was performed on a VG Fisons Platform II instrument by the department of Chemistry, Cardiff University. Micro analysis was performed by Warwick Analytical Service. All reactions involving silver compounds were performed with the exclusion of light.

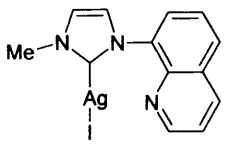
3.5.2 The silver (I) complexes of rigid quinoline functionalised mono –NHC ligands

[Ag(1-benzyl-3- quinolineimidazolin-2-ylidene)Br] 3.34:



A mixture of 1.benzyl-3-quinolineimidazolium bromide (0.7g, 2mmols) and silver (I) oxide (0.222g, 1mmol in 10ml of DCM was stirred over night at 40Oc. The resulting solution was filtered through celite and the solvent removed under reduced pressure to leave a brown coloured solid. The solid was recrystallised from DCM / Hexane to give the desired Ag complex. 0.55g (60.84%). Anal. Calcd. for $C_{19}H_{115}N_3AgBr$: C, 48.23; H, 3.17; N, 8.88%. Found: C, 49.45; H, 3.22; N, 8.96%. ^1H NMR ($CDCl_3$. 400MHZ, 298K): 8.85 (d, 1H, J = 1.7 H_Z, quin-H), 8.25 (d, 1H, J = 6.7 H_Z, quin-H), 7.90(d, 2H, J = 7.7 H_Z, quin-H,) 7.55 (t, 1H, J = 7.8 H_Z, quin-H),7.45 (m, 2H, J = 3.0 H_Z, CHHC), 7.25-7.35 (m, 5H, J = 5.4 H_Z, Ar-H), 7.10 (s, 1H, quin-H), 5.35 (s, 2H, CH_2-Ph). ^{13}C NMR ($CDCL_3$, 100 MH_Z, 298K): 151.75, 142.86, 136.99, 135.60, 130.04, 129.68, 129.60, 129.19, 128.59, 127.54, 126.72, 125.74, 122.77, 120.64, 56.49(CH_2).

[Ag(1-methyl-3-quinolineimidazolin-2-ylidene)I] 3.35:

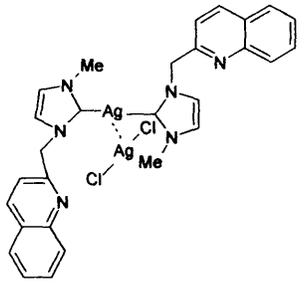


A mixture of 1-methyl-3-quinolineimidazolium iodide (0.44g, 1.31mmol) and silver (I) oxide (0.15g, 0.66mmol) in 10ml of CH_3CN was stirred over night at 40°C. The resulting solution was filtered to remove silver halide through celite and the solvent removed under reduced pressure to leave a tan coloured solid. The solid was then recrystallised from DCM/Hexane to give the desired Ag

complex (0.26g. 63%). ^{1}H NMR ($CDCl_3$. 400MH_Z, 298K): 8.85 (d, 1H, J = 2.7 H_Z, Quin-H), 8.25(d, 1H, J = 7.3 H_Z, quin-H), 7.95 (d, 1H, J = 8.2 H_Z, quin-H), 7.80(d, 1H, J = 7.4 H_Z, quin-H), 7.5 (t, 1H, J = 7.6 H_Z, quin-H), 7.4 (d, 1H, J = 4.2 H_Z, quin-H), 7.35 (s, 2H, CHHC). 3.90 (s, 3H, CH_3). ^{13}C NMR (d_2-DCM, 100 MH_Z, 298K): 163.00, 151.3, 147.6, 145.2, 139.4, 138.5, 136.9, 134.7, 133.2, 131.8, 44 .0(CH_3).

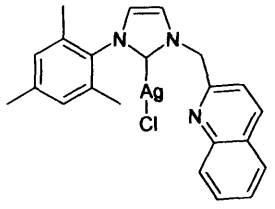
3.5.3: Silver (I) complexes of methylene bridged quinoline functionalised NHC ligands

[Ag (1-methy-3-(-2-methylquinoline) imidazolin-2-ylidine) $_2$][$AgCl_2$] 3.36



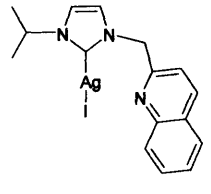
A mixture of 1-methyl-3-(2-methylquinoline) imidazolium chloride (0.30g, 1.16mmol) and Ag_2O (0.14g, 0.59mmol) in dichloromethane was stirred for 12 hours. The solution was filtered through celite and the filtrate concentrated. Diethyl ether was added to precipitate the carbene complex which was repeatedly washed with diethyl ether and dried under vacuum to give the desired silver carbene complex. Crystals suitable for X- ray structure were grown by layering diethyl ether on dichloromethane. Anal. Calcd. for $C_{14}H_{13}N_3AgCl$: C, 45.86; H, 3.55; N, 11.46; Cl, 9.67%. Found: C, 45.71; H, 3.45; N, 11.33; Cl, 9.60%. ^{1}H NMR ($CDCl_3$. 400MH_Z, 298K): 8.10 (d, 2H, J = 8.5 H_Z, Quin-H), 8.00 (d,2H, J = 8.4 H_Z, Quin-H), 7.80 (d, 2H, J = 8.1 H_Z, CHHC), 7.5 (d, 2H, J = 8.4 H_Z, Quin-H), 7.35 (d, 2H, J = 1.7 H_Z, Quin-H) 7.15 (d, 2H, J = 1.8 H_Z, Quin-H), 6.95 (s,1H, Quin-H), 5.50 (s, 4H CH_2), 3,85 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 100MH_Z, 298K): 181.18 (C-Ag), 155. 45, 148.09, 138. 12, 130.55, 129.62, 128.11, 127.92, 127.50, 123.01, 122.31, 120.20, 58.14, 39.27. MS (HRMS, Da): M/z (224.09) $[(NHC)+H]^+$ (100%).

Synthesis of [Ag (1-mesityl-3-(-2-methylquinoline) imidazolin-2-ylidine) Cl] 3.37



A mixture of 1-mesityl 3-(2-methylquinoline) imidazolium chloride 4 (0.50g, 1.38mmol) and Ag_2O in dichloromethane was stirred at room temperature for 12 hours. The solution was filtered through celite and the filtrate concentrated. Diethyl ether was added to precipitate the carbene complex which was repeatedly washed with diethyl ether and dried under vacuum to give the desired silver carbene complex. Crystals suitable for X- ray structure were grown by layering diethyl ether on dichloromethane. Anal. Calcd. for $C_{22}H_{21}N_3AgCl$: C, 56.13; H, 4.46; N, 8.93; Cl, 7.55%. Found: C, 56.23; H, 4.53; N, 8.77; Cl, 7.55%. ^1H NMR ($CDCl_3$. 400MHZ, 298K) : 8.10 (d, 1H, J = 8.4 H_Z, Quin-H), 8.00 (d, 1H, J = 8.5 H_Z, Quin-H), 7.80 (d, 2H, J = 8.1 H_Z, CHHC), 7.70 (t, 1H, J = 1.4 H_Z, Quin-H), 7.50 (t, 1H, J = 7.0 H_Z, Quin-H), 7.35 (t, 2H, J = 8.7 H_Z, Quin-H), 6.90 (s, 3H, Aromatic-H), 5.60 (s, 2H, CH_2), 2.25 (s, 3H, m-CH_3), 1.95 (s, 6H, o-CH_3). ^{13}C NMR ($CDCL_3$, 100 MHZ, R.T.): 155.40, 148.0, 139.20, 138.18, 135.08, 130.59, 129.84, 129.64, 128.16, 127.95, 127.50, 123.57, 122.29, 119.74, 58.16, 21.47, 18.11. MS(HRMS, Da): M/z (328.15) $[(NHC)+H]^+$ (100%).

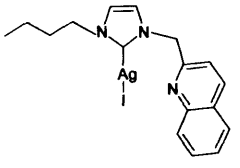
[Ag (1-isopropyl- 3-(2-methylquinolin) imidazolin-2-ylidine) I] 3.38



Following the method for the synthesis of **3.37**, compound **3.38** was synthesized from 1-isopropyl-3-(2-methylquinoline) imidazolium iodide (0.10g, 0.26mmol) and Ag_2O(32mg, 0.14mmol) in dichloromethane.(Yield =0.12g, 73.00%). Anal. Calcd. for $C_{16}H_{17}N_3AgI$: C, 39.52; H, 3.50; N, 8.65; I, 7.55%. Found: C, 39.70; H, 3.42; N, 8.57; I, 25.92%. ^1H NMR ($CDCl_3$. 400MH_Z, 298K): 8.05(d,

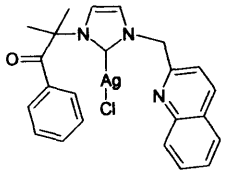
2H, J = 8.5 H_Z, quin-H), 7.65(t, 2H, J = 7.0 H_Z, quin-H), 7.50(d, 2H, J =5.2 H_Z, quin-H), 7.10(s, 1H, CHHC), 6.90(s, 1H, CHHC), 5.60(s, 2H, NCH_2C), 4.85(m, 1H, NCHC), 1.35(d, 6H, J = 6.8 H_Z, CH_3). ^{13}C NMR ($CDCL_3$, 100 MH_Z, R.T.): 184.10(C-Ag), 156.55, 137.91, 130.18, 129.47, 128.12, 127.91, 121.71, 121. MS (HRMS, Da): M/z = 609.1886 $[Ag(NHC)_2]^+$ (100%).

[Ag(1-n-butyl-3-(-2-methylquinolin)imidazolin-2-ylidine)I] 3.39



Following the method for the synthesis of **3.38**, compound **3.39** was synthesized from 1-nbutyl-3-(2-methylquinoline)imidazoliumiodide (0.50g, 1.27mmol) and Ag_2O(0.15g, 0.64mmol) in dichloromethane.(Yield = 0.40g, 62.50%). Required for $C_{17}H_{19}N_3AgI$: C, 40.82; H, 3.80; N, 8.40%. Found: C, 39.90; H, 3.67; N, 7.79%.^1H NMR ($CDCl_3$. 400MH_Z, 298K): 8.00(d, 1H, J = 8.5 H_Z, quin-H), 7.90(d, 1H, J = 8.5 H_Z, quin-H), 7.60(m, 2H, J = 8.1 H_Z, quin-H), 7.55(d, 1H, J = 8.5 H_Z, quin-H), 7.40(t, 1H, J = 7.2 H_Z, quin-H), 7.00(s, 1H, CHHC), 6.80(s, 1H, CHHC), 5.60(s, 2H, methylene linker-H), 4.10(t, 2H, NCH_2), 1.70(m, 2H, J = 7.5 H_Z, CH_2), 1.20(m, 2H, J = 7.0 H_Z, CH_2), 0.80(t, 3H, J = 7.3 H_Z, CH_3). ^{13}C NMR ($CDCL_3$, 100 MH_Z, R.T.): 183.23(C-Ag), 155.02, 146.52, 136.50, 128.80, 128.07, 126.70, 126.50, 126.14, 125.76, 120.30, 119.96, 64.84, 56.56, 50.68, 32.50, 18.75. MS(HRMS, Da): M/z (637.2189) $[Ag(NHC)_2]^+$ (100%)

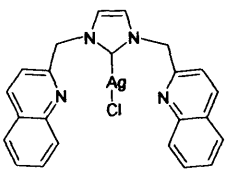
[Ag (1-(-2-methylpropiophenone)-3-(-2-methylquinolin) imidazolin-2-ylidine) Cl] 3.40.



Following the method for the synthesis of **3.39**, compound **3.40** was synthesized from 1-(2-methylpropiophenone)-3-(-2-methylquinolin) imidazolium chloride (0.30g, 0.77mmol) and Ag_2O (90mg, 0.39mmol) in dichloromethane. (Yield = 0.32g, 90.00%). Anal. Calcd. for $C_{23}H_{21}N_3OAgCl$: C, 55.38; H, 4.14; N, 8.43%. Found: C, 55.78; H, 4.18; N, 8.22%. ^1H NMR ($CDCl_3$. 400MH_Z, 298K): 8.00(d,

2H, J = 10.7 H_Z, quin-H), 7.75(d, 1H, J = 7.1 H_Z, quin-H), 7.60(d,1H, J = 7.5 H_Z, arom-H), 7.50(t, 1H, J = 7.3 H_Z, arom-H), 7.35(s,2H, arom-H), 7.25(s, 2H, CHHC), 7.20(d, IH, J = 6.8 H_Z, quin-H), 7.10(t, 2H, J = 8.4 H_Z, quin-H), 6.90(d, 1H, J = 11.8 H_Z, arom-H), 5.50(s,2H,NCH_2qiun), 2.00(s, 6H, CH_3). ^{13}C NMR ($CDCL_3$, 100MH_Z, 298K):196.71(PhCOC), 153.72, 146.53, 136.77, 136.59, 131.72, 129.18, 129.12, 128.17, 127.94, 127.60, 126.72, 126.66, 126.46, 126.12, 120.91, 118.72, 118.43, 118.38, 66.99, 57.61, 27.56. MS(HRMS, Da): M/z (356.1642) $[(NHC)+H]^+$ (100%), 817.2445 $[Ag(NHC)_2]+$ (36%).

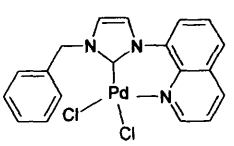
[Ag (bis-1, 3(2-methylquinolin) imidazolin-2-ylidine) Cl] 3.41



Following the method for the synthesis of **3.40**, compound **3.41** was synthesized from bis-1, 3-(2-methylquinoline) imidazolium chloride (0.30g, .78mmol) and Ag_2O (93mg, 0.40mmol) in 20 ml of dichloromethane. (Yield =.0.12g, 40%). Anal. Calcd. for $C_{23}H_{18}N_4AgCl$: C, 55.94; H, 3.65; N, 11.35%. Found: C, 56.39; H, 3.61; N, 11.21%. ^1H NMR ($CDCl_3$. 400MH_Z, 298K): 8.10(d, 2H, J = 8.4 H_Z, quin-H), 8.00(d, 2H, J = 8.5 H_Z, quin-H), 7.75(d,2H, J = 8.1 H_Z, quin-H), 7.65(t, 2H, J = 5.6 H_Z, quin-H), 7.5(t, 2H, J = 7.1 H_Z, quin-H), 7.35(d, 2H, J = 8.5 H_Z, quin-H), 7.15(s, 2H, HHC), 5.5(s, 4H, NCH_2C). ^{13}C NMR ($CDCL_3$, 100 MHZ, 298K): 180.37(C-Ag), 154.09, 146.58, 136.71, 129.08, 128.09, 126.70, 126.47, 126.01, 121.31, 118.75, 56.74. MS (HRMS, Da): M/z (351.16) $[(NHC)+H]^+$ (100%).

3.5.4: Pd(II) quinoline functionalised NHC complexes

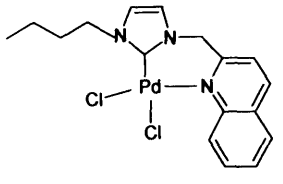
[Pd(1-benzyl-3-quinoline-imidazolin-2-ylidene)Cl_2] 3.42



A solution of $PdCl_2$(COD) (0.092g, 0.32 mmol) in 10ml DCM was added to solution [Ag(1-benzyl-3- quinolineimidazolin-2-ylidene)Br] (0.30g, 0.32mmol) in 10mL DCM and stirred at room temperature for 2 hours. The solution was

then filtered through celite to remove the silver bromide formed and the solvent was concentrated to 5ml. Hexane was added to precipitate the Pd carbene complex which was repeatedly washed with hexane to any 1,5-cyclooctadiene. Anal. Calcd. for $C_{19}H_{15}N_3PdCl_2$: C, 49.31; H, 3.24; N, 9.08%. Found: C, 46.08; H, 3.30; N, 7.78%. ^1H NMR ($CDCl_3$. 400MH_Z, 298K): 9.70(d, 1H, quin-H), 8.40(d, 1H, J = 1,4 H_Z, quin-H), 8.00(d, 1H, J = 6.7 H_Z, quin-H), 7.90 (d, 1H, J = 7.2 H_Z, quin-H), 7.70 (t, 1H, J = 7.9.5 H_Z, quin-H), 7.50(t, 1H, J = 6.3 H_Z, quin-H), 7.40(d, 2H, J = 6.1 H_Z, Ar-H), 7.35(s, 1H, CHHC), 7.30 (m, 3H, J = 7.7 H_Z, Ar-H), 6.95(s,1H, CHHC), 5.25(s, 2H, Ph-CH_2)

[Pd(1-nbutyl-3- (2-methylquinoline)imidazolin-2-ylidene)Cl_2] 3.43



1-nbutyl-3-(2-methylquinoline)imidazolium (0.15g, 0.38mmol) and Ag_2O (44mg, 0.2mmol) in 15mL of DCM were stirred over night and the reaction mixture was filtered via cannula to a solution $PdCl_2COD$ (0.11g, 0.38mmol) in 15mL DCM and the reaction mixture stirred overnight. The reaction mixture was filtered through celite and the filtrate was concentrated over vacuum.

Hexane was added to precipitate the desired Pd complex which repeated recrystallised from hot CH_3CN and diethyl ether. Anal. Calcd. for $C_{17}H_{19}N_3PdCl_2$: C, 46.21; H, 4.30; N, 9.51%. Found: C, 43.92; H, 4.05; N, 6.72%. ^1H NMR (DMSO. 400MH_Z, R.T): 9.20(d, 1H, J = 8.8 H_Z quin-H), 8.70(d, 1H, J = 8.2 H_Z quin-H), 8.10(d, 1H, J = 8.0 H_Z , quin-H), 7.90(t, 2H, J = 5.2 H_Z, Quin-H), 7.70(t, 1H, J = 7.5 H_Z quin-H), 7.60(s, 1H, CHHC), 6.35(s, 1H, CHHC), 6.10(d,1H, J = 15.6 H_Z methylene linker-H), 5.80(d, methylene J = 15.7 H_Z linker-H),4.60(m, 1H, J = 6.6 H_Z NCH2), 4.10(m, 1H, J = 6.6 H_Z NCH_2), 2.90(m, 2H, J = 7.0 H_Z CH_2), 1.15(m, 2H, J = 8.5 H_Z , CH_2), 0.80(t, 3H, J = 7.3 H_Z, CH_3).

3.5.4 X-Ray crystallography

Standard conditions as outlined in section 2.4.7.

Table 3.4: Crystal data and structure refinement for 3.36

Empirical formula	$C_{14}H_{13}AgN_3Cl$	
Formula weight	366.59	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 15.9530(14) Å	α = 90.00°
	b = 6.5010(8) Å	β = 111.937(8)°
	c = 13.8760(13) Å	γ = 90.00°
Volume	1334.90(2) $Å^3$	
Z	4	
Density (calculated)	1.8424Mg/m^3	
Absorption coefficient	1.698mm-1	
F000	728	
Crystal size	0.30 x 0.15 x 0.01 mm^3	
Theta range for data collection	2.61 to 27.40 °	
Index ranges	-19<=h<=20, -8<=k<=7, -17<=l<=16	
Reflections collected	2473	
Independent reflection	2473[R_{int} = 0.0714]	
Completeness of theta = 27.4°	93.20%	
Absorption correction	Semi-empirical from equivalents	
Max and min. transmission	0.6299 and 0.9832	
Refinement method	Full matrix least square on F^2	
Data/restraints/parameters	2473/144/133	
Goodness of fit on F^2	1.094	
Final R indices [I>2 sigma(I)]	R1 = 0.1141, wR2 = 0.2350	
R indices (all data)	R1 = 0.1015, wR2 = 0.2261	
Largest diff. peak hole	1.763 and-1.552e $Å^{-3}$	

Table 3.5: Crystal data and structure refinement for 3.37

Empirical formula	$C_{22}H_{21}AgN_3Cl$
Formula weight	470.75
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 8.9956(3) Å α = 79.2749(17)°
	b = 9.3915(3) Å β = 81.9409(16)°
	c = 12.4646(4) Å γ = 74.7489(16)°
Volume	993.57(6) $Å^3$
Z	2
Density (calculated)	1.573Mg/m^3
Absorption coefficient	1.160mm-1
F000	476
Crystal size	0.20 x 0.20 x 0.20 mm^3
Theta range for data collection	1 to 27 °
Index ranges	-10<=h<=11, -12<=k<=12, -16<=l<=16
Reflections collected	24373
Independent reflection	4440 [R_{int} = 0.145]
Completeness of theta = 25.18°	99.30%
Absorption correction	Semi-empirical from equivalents
Max and min. transmission	0.7900 and 0.7900
Refinement method	Full matrix least square on F^2
Data/restraints/parameters	3644/0/244
Goodness of fit on F^2	1.0042
Final R indices [I>2 sigma(I)]	R1 = 0.0418, wR2 = 0.11129
R indices (all data)	R1 = 0.0505, wR2 = 0.1206
Largest diff. peak hole	0.69 and-1.07e $Å^{-3}$

3.6 References

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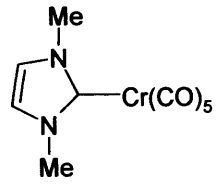
CHAPTER FOUR

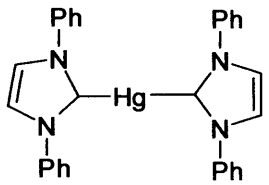
Rhodium(I) and Iridium(I) complexes of quinoline functionalised Heterocyclic Carbene ligands

4.1 Introduction

Prior to the isolation of the first stable crystalline NHC **4.5** in 1991 by Arduengo et al [1], metal complexes of N-heterocyclic carbenes (NHCs) were reported concurrently in1968 by Ofele **4.1** [2] and by Wanzlick and Shonherr **4.2** [3] both being prepared directly from imidazolium salts. In his contribution Lappert prepared a wide range of transition metal- NHC compounds including **4.3** and **4.4** from electron rich olefins in 1970 [4] and complex **4.3** was found to be an active catalyst for hydrosilylation.



4.1



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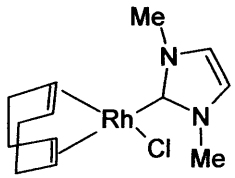
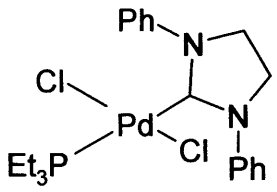
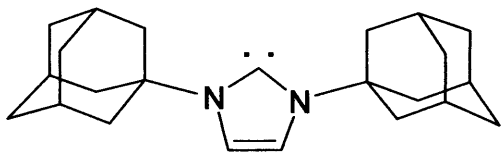


4.3



4.4



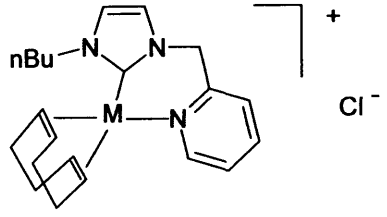
4.5

Figure 5.1: Early metal complexes of NHCs **4.1- 4.4** and first crystalline free Carbene **4.5**

Encouraged by the promise of these early applications utilising Rh(I) complexes of simple monodentate NHC ligands, there was a natural evolution to expand the catalytic applications of Rh and Ir NHC complexes systems

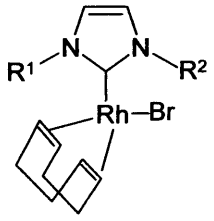
through modification of the NHC ligands. The desired qualities of modified NHC ligands include the incorporation of functional groups leading to easily recoverable catalyst, water or methanol soluble catalyst, and catalyst containing flexible steric bulk as well as chiral and bidentate and pincer ligands [5] and combination of the strongly bound NHC moiety with more weakly nucleophilic functional groups to furnish ligands with hemilabile donor groups as these can increase catalytic activities by stabilising the low valent centres formed during catalysis. These functional groups may be incorporated at one or both of the ring nitrogens to give access to bidentate or tridentate NHC ligands.

Examples of Rh(I) and Ir(I) complexes of functionalised NHC ligands are limited but have increased considerably in the past few years. Functionalised Rh(I) and Ir(I) (NHC) complexes have appeared in the literature with picolyl (**4.5** and **4.6**) [6], **4.17** and **4.18**[11], ether, ester, amide and ketone(**4.7, 4.8, 4.9** and **4.10**) [7], amino (**4.11** , **4.12**) [8], **pyridyl** (**4.13, 4.14, 4.15, 4.16** [9], imino **4.19** [10] Figure 4.2. As this thesis was nearing completion a publication by Webster et al reported quinoline functionalised NHC complexes of rhodium and iridium.



4.5: M = Rh

4.6: M = Ir

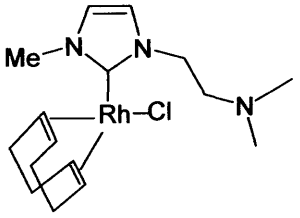


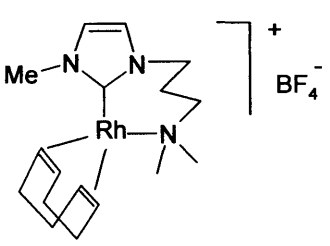
4.7: R^1, R^2 = ether

4.8: R^1, R^2 = ester

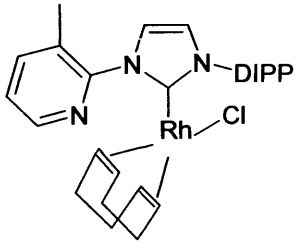
4.9: R^1, R^2 = amide

4.10: R^1, R^2 = ketone



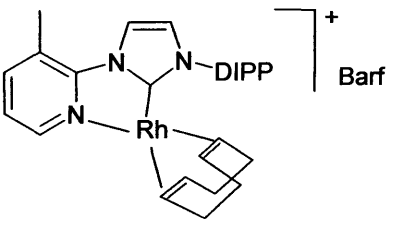


4.12



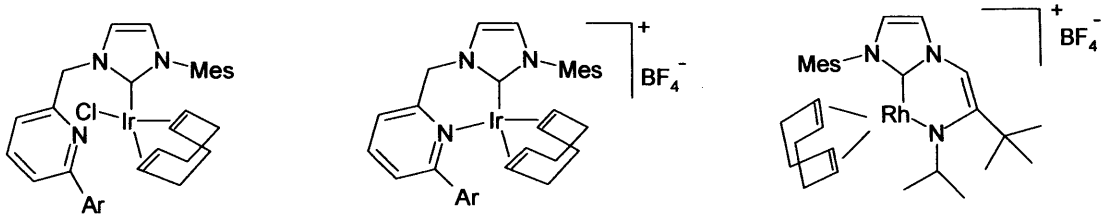
4.13: M = Rh

4.14: M = Ir



4.15: M = Rh

4.16: M = Ir



4.17 **4.18** **4.19**

Figure 5.2: Some of the published Rh(I) and Ir(I) NHC complexes

Other Rh(I) and Ir(I) NHC complexes have also been reported: Crabtree et al [12] reported the effect of linker length and counterion on the formation of chelated complexes of rhodium(I) NHC complexes where they observed that short linker length and non coordinating counter ion favoured chelated rhodium(I) NHC complexes while long linker length and coordinating counterion disfavoured the formation of chelated complexes.

Different approaches are normally employed to prepare Rh and Ir NHC complexes. Of the many coordination strategies available, three are more prominent: oxidative addition of the imidazolium ring, deprotonation of the imidazolium salts with suitable base and transmetallation of the previously obtained silver carbene.

One of the potentially very mild ways to make transition metal NHC complexes is by oxidative addition of the azolium C-H bond to an appropriate low-valent metal centre.Thoertical and experimental work by Cavell et al [13] has shown that this is a viable synthetic route. However, this method will not the desired rhodium(I) and iridium(I) NHC complexes as it always rhodium(III) or iridium (III) NHC complexes that are formed.

The best synthetic method of obtaining Rh(I) and Ir(I) NHC complexes is via deprotonation of the imidazolium precursor with suitable base. However, a strong base such as potassium tert-butoxide or potassium hydride is usually employed to prepare the free carbene. This sometimes causes problems because the acidic protons or electrophilic sites may be attacked by the base.

Gratifyingly, the important work of Wang and Lin [14] demonstrated that silver complexes of NHCs could be synthesized directly from imidazolium salts and Ag_2O or Ag_2CO_3 and silver(I) NHC complexes are capable of transferring the

carbene ligands to other metals such Pd [14, 15], Au [16] including Rh and Ir [6, 7, 8, 9, 10, 11, 16]. Realising the simple way of obtaining our desired Rh(I) and Ir(I) through transmetallation of silver carbene, all the Rh(I) and Ir(I) presented herein were prepared using the silver carbene protocol. However it is worth noting that the reaction yield via silver carbene is depended on the imidazolium salt/ metal ratio and the starting metal complex used. Mas-Marza et al [6] reported that Rh(III) and Ir(III) NHC can also be prepared by the transmetallation, as the silver carbene can play dual role (i) in NHC transfer and (i) as oxidizing agent.

In summary, this chapter presents work pertaining to Rh(I) and Ir(I) NHC complexes of quinoline functionalised imidazolin-2-ylidene ligands and includes a review of literature pertaining to this work.

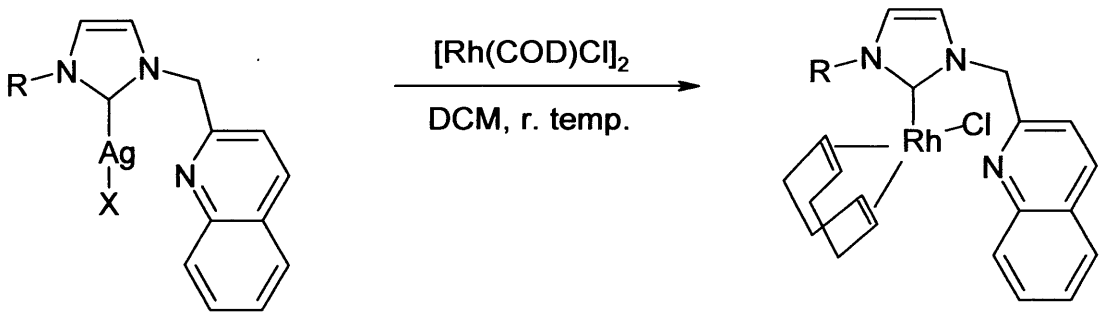
The synthesis and characterisation of a series of [Rh(COD)Cl] NHC and [Ir(COD)Cl] NHC complexes of quinoline functionalised via Ag^{I}(NHC) is outlined. The ligands have range of steric bulk at their 1, 3 positions. Also described are chelated complexes of the corresponding [Rh(COD)Cl] NHC and [Ir(COD)Cl]NHC complexes obtained by treatment of the neutral complexes with $AgBF_4$, although only one such of complexes is presented because of solubility problems encountered in the characterisation of other complexes. All the Rh (I) and Ir NHC complexes obtained are found to be stable to moisture and air.

4.2 Results and Discussions

4.2.1: Synthesis and characterisation of quinoline functionalised Rh(I) NHC complexes.

The use of free carbene route by deprotonation of the imidazolium salts with strong base, which was expected to produce the corresponding free carbene, was not successful presumably because of interference from deprotonation of benzylic methylene protons [17]. Therefore,Å all the Rh(I) NHC complexes presented in this work were prepared from the Ag^{I}(NHC) complexes presented in chapter 3. Treatment of $[Rh(COD)Cl]_2$ with the methylene bridged quinoline functionalised Ag^{I}(NHC) complexes in dichloromethane at ambient temperature

gave the desired rhodium carbene complexes as yellow solids in good yield after work up as shown in Scheme 4.1 below. All the prepared rhodium complexes were characterised by ^{1}H NMR, ^{13}C NMR and mass spectroscopy, elemental analysis and X- ray crystallography. The ^{13}C NMR data for the coordinating carbene carbons for complexes **4.20**, **4.22**, **4.23** and **4.24** appear at δ values of 181.60, 180.38, 178.66 and 183.45ppm respectively, suggesting the formation of the Rh-C bond which are in the usual range for other Rh(I)-NHC complexes [18, 19, 20-22]. The carbenic carbon in complex **4.21** was not observed in the ^{13}C NMR spectrum. The ^{1}H NMR shifts corresponding to the protons of the quinoline ring are essentially similar to those of the silver complexes from which they were made, indicating that the quinoline nitrogen donor remains uncoordinated. Furthermore, ^{1}H NMR spectra show diasterotopic protons for the CH_2 linker (δ = 6.5 and 5.6 for complex **4.20**, 6.5 and 6.1 for complex **4.21**, 6.5 and 5.75 for complex **4.22**, 6.5 and 5.6 for complex **4.23** and 6.5 and 5.8 for complex **4.24**) which suggests that this group is out of the coordination plane of the molecule thus reducing its symmetry.



3.36: R = Me, X = Cl

3.37: R = Mes, X = Cl

3.38: R = iPr, X = I

3.39: R = n-Bu, X = I

3.41: R =$QuinCH_2$, X = Cl

4.20: R = Me

4.21: R = Mes

4.22: R = iPr

4.23: R = n-Bu

4.24: R = $QuinCH_2$

Scheme 4.1: Synthesis of quinoline functionalised Rh(I) NHC complexes.

Elemental analysis results for complex **4.20** were satisfactory but no reasonable data could be obtained from the mass spectrum. Suitable crystals for X-ray single crystal diffraction were obtained from a DCM/ n-pentane solution at ambient temperature. The detailed solid state coordination sphere around the rhodium centre of complex **4.20** is confirmed by the X- ray crystal structural analysis. The complete molecular structure of complex **4.20** is depicted in Figure 4. 3 below. Selected bond distances and bond angles are listed in table 4.1

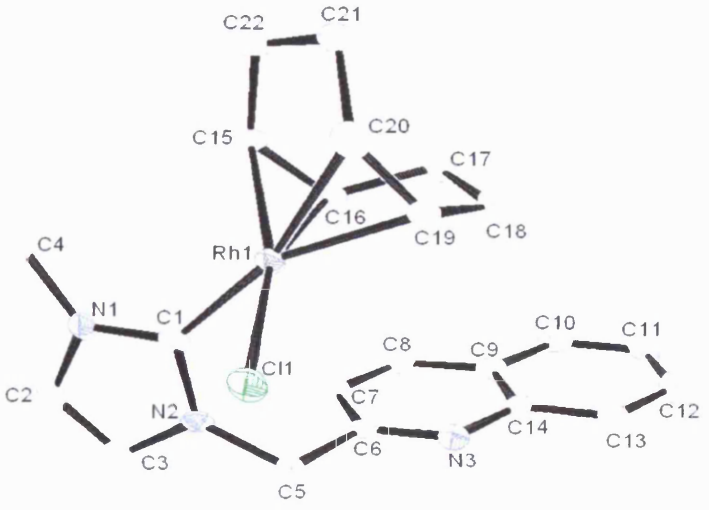


Figure 4.3: ORTEP projection of complex **4.20** excluding hydrogen atoms for clarity,showing atom labelling scheme.

Table 4.1: Selected bond lengths (Å) and bond angles (°) of **4.20**

C1 - N1 1.356(6)	C16 - Rh1 2.126(5)	N1- C1- Rh1 131.4 (4)
C1- Rh1 2.028(5)	C19 - Rh1 2.206(5)	C1- Rh1-Cl1 87.99(14)
C1 - N2 1.362(7)	Rh1- Cl1 2.386(13)	N2- C5- C6 113.90(4)
N2 - C3 1.394(9)	C20- Rh1 2.233(6)	C1-Rh1-C15 92.00(2)
C15 -Rh1 2.123(5)	N1- C1- N2 103.8(4)	C1-N2- C3 111.00(4)

The structural arrangement of complex **4.20** shows that the molecular geometry around the rhodium ion is a square planar arrangement with two coordination

sites occupied by carbene and chloride in a cis fashion. The distances of Rh-C(COD) *trans* to the carbene donor appear to be longer than those in the *cis* arrangement, suggesting that the σ-donor nature of the diaminocarbene is stronger than that of the chloride. No major deviations were observed in the bond lengths and bond angles of complex **4.20** compared with those reported in the literature [23-25].

The ^{1}H NMR shifts for complex **4.21** corresponding to the protons of the quinoline ring are essentially similar to those of the silver complexes from which they were made, indicating that the quinoline nitrogen donor remains uncoordinated with the carbenic carbon not observed in the ^{13}C NMR spectrum. The high resolution MS measurement were consistent with the proposed formulation with $[M- Cl]^{+}$ observed at M/z = 538.18 Da (100% intensity). Crystals suitable for X-ray crystallography were obtained for complex **4.21** by diffusion of n- pentane into the DCM solution of the compound enabling elucidation of the solid state structure as depicted in Figure 4.4. Selected bond distances and bond angles are listed in table 4.2

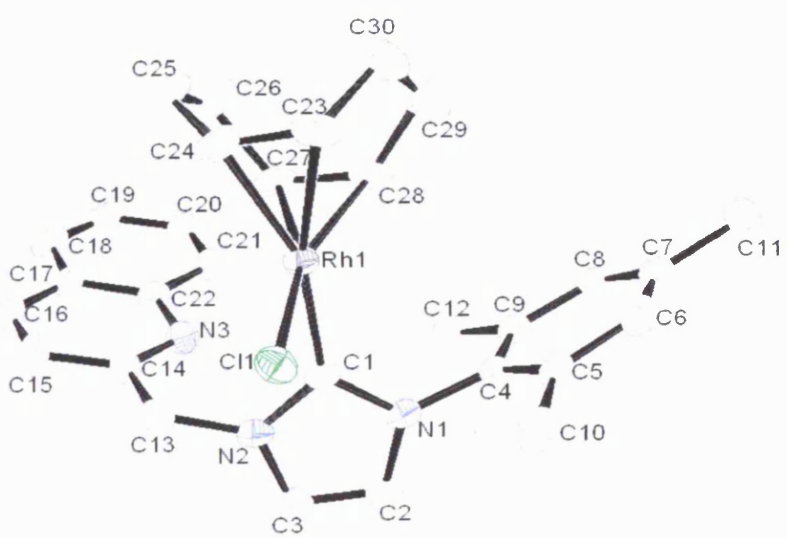


Figure 4.4: ORTEP projection of complex **4.21** excluding hydrogen atoms for clarity showing atom labelling scheme.

Table 4.2: Selected bond lengths (Å) and bond angles (°) of **4.21.**

C1 - N1 1.355(5)	C24 - Rh1 2.179(4)	N1-C1-Rh1 130.8 (4)
C1 - Rh1 2.045(5)	C27- Rh1 2.123(4)	C1-Rh1- Cl1 87.67(11)
C1- N2 1.355(5)	Rh1- Cl1 2.3865(9)	C1- N1- C4 124.3(3)
N2 - C3 1.379(9)	C28 - Rh1 2.112(4)	C1- Rh1-C28 94.63(2)
C23 -Rh1 2.202(4)	N1- C1-N2 103.7(3)	C24-Rh1-Cl1 90.55(14)

Elemental analysis of complex **4.21** returned satisfactory results. There are no significant deviations in terms of the bond lengths and bond angles of complex **4.21** with complex **4.20** and all are within the range reported in the literature [20-22, 23,].

Complex **4.22** was characterised by spectroscopic analysis, elemental analysis and X- ray crystallography. The ^{1}H NMR spectrum for complex **4.22** displays similar pattern with that of complexes **4.20** and **4.21**. The synthesis of complex was confirmed by ^{13}C NMR, which reveals Rh-C resonance at a σ value of 180.38 ppm. The high resolution MS measurement was consistent with the proposed formulation with $[M- Cl]^{+}$ observed at M/z = 462.14 Da (100% intensity) and elemental analysis results were in agreement with the proposed formulation. Crystals suitable for X-ray structural determination were obtained by diffusion of n-pentane into the saturated DCM solution of the compound and Ortep crystal structure is as depicted in Figure 4.5. Selected bond distances and bond angles are listed in table 4.3.

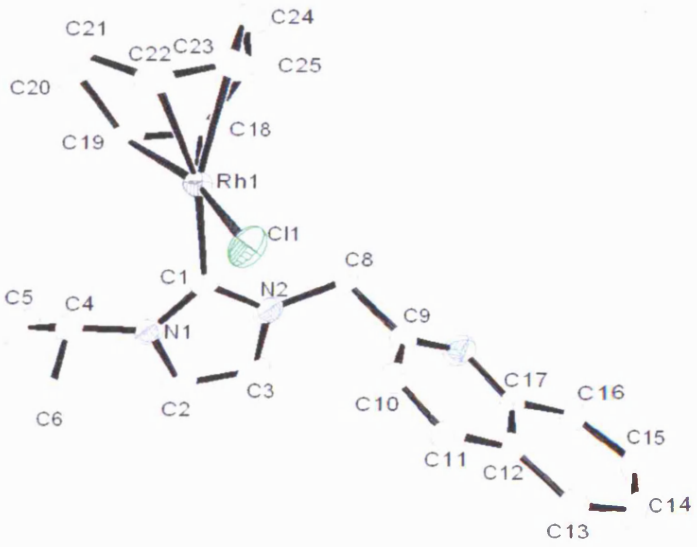


Figure 4.5: ORTEP projection of complex **4.22** excluding hydrogen atoms for clarity showing atom labelling scheme.

The geometry of rhodium in complex **4.22** is square planar and the parameters in terms of bond distances and internal angles in the complex are consistent the reported values [23].

Table 4.3: Selected bond lengths (Å) and bond angles (°) of **4.22.**

C1 - N1 1.343(6)	C19 -Rh1 2.127(5)	N1-C1-Rh1 129.7 (4)
C1- Rh1 2.037(5)	C22- Rh1 2.213(5)	C1-Rh1-Cl1 89.2467(13)
C1- N2 1.345(6)	Rh1-Cl1 2.3755(13)	C1-N1-C4 125.0(4)
N2- C3 1.369(7)	C3- Rh1 2.226(5)	C1-Rh1-C19 93.10(2)
C18- Rh1 2.113(5)	N1-C1-N2 104.7(4)	C23-Rh1-Cl1 94.52(17)

High resolution MS of complex **4.23** displays a cluster of peak M/z = 476.16 Da (100% intensity) assignable to the $[M\text{-}Cl]^+$ and the elemental analysis gave results consistent with the formulation of the complex.

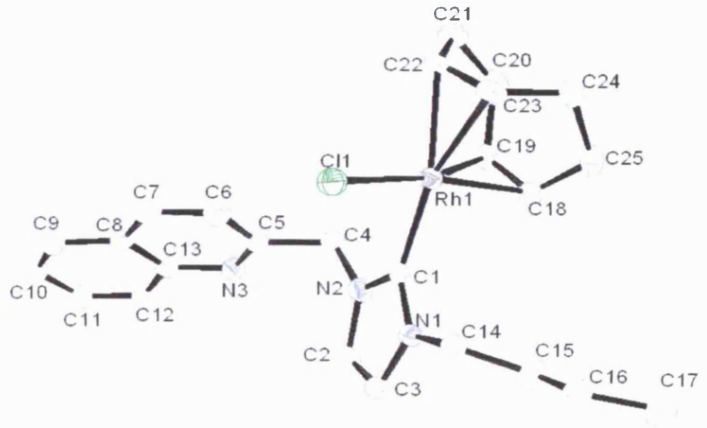


Figure 4.6: ORTEP projection of complex **4.23** excluding hydrogen atoms for clarity, showing atom labelling scheme.

Table 4.4: Selected bond lengths (Å) and bond angles (°) of **4.23.**

C1- N1 1.355(5)	C19 -Rh1 2.114(4)	N1 -C1 -Rh1 126.4 (3)
C1-Rh1 2.032(4)	C22 -Rh1 2.197(4)	C1-Rh1-Cl1 88.03(11)
C1-N2 1.368(5)	Rh1-Cl1 2.3786(10)	C3-N1-C14 123.7(3)
N1-C3 1.387(5)	C23 -Rh1 2.208(4)	C1-Rh1-C18 90.62(15)
C18-Rh1 2.097(4)	N1- C1-N2 103.8(3)	C1-Rh1-C22 163.07(15)

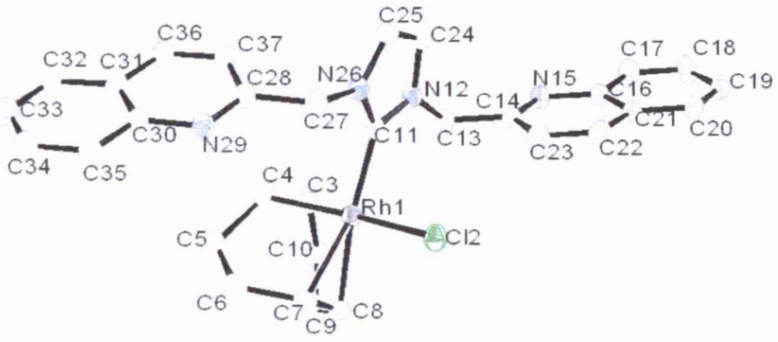


Figure 4.7: ORTEP projection of complex **4.24** excluding hydrogen atoms for clarity, showing atom labelling scheme.

Table 4.5: Selected bond lengths (Å) and bond angles (°) of **4.24.**

C11- N12 1.358(3)	Rh1-C3 2.105(3)	C11-Rh1- Cl2 87.46 (7)
C11-Rh1 2.016(3)	Rh1-C4 2.121(3)	C11- Rh1- C8 167.02(10)
Rh1-Cl2 2.3794(7)	Cl1-N26 1.358(3)	C11- Rh1 -C3 92.99(10)
Rh1-C8 2.230(3)		C11-N12 -C13 125.20(2)
Rh1-C7 2.196(2)	N12-C11-N26 103.7(2)	C3-Rh1-Cl2 157.31(8)

Due to variations in the steric bulk around the carbene carbon there was the need to compare the structure of all the rhodium(I) carbene complexes **4.20-4.24**. In doing so two planes were chosen to calculate the inter planer angles. The planes chosen are the NHC consisting of the five atoms in the heterocycle carbene ring and the rhodium coordination plane consisting of C1-Rh1-Cl2. The inter planer angles and other important angles are listed in Table 4.6 below.

Table 4.6: Bond angles (°) for compounds **4.20- 4.24** of rhodium complexes of general formula [Rh(Cod)Cl(NHC)]

Compound	Θ(interplaner angle)	N1-C1-N2	C1-Rh1-Cl1	C11-Rh1-(C18-C19)
4.20	76.87	103.80(4)	87.99(14)	165.30(2)
4.21	76.77	103.70(3)	87.67(11)	165.92(11)
4.22	80.31	104.70(4)	89.25(3)	159.6(2)
4.23	76.49	103.80(3)	88.03(11)	163.07(15)
4.24	82.69	103.70(2)	87.46(7)	167.02(10)

From the table presented above, the main structural features of these compounds are:

- A distorted square planar geometry with Cl-Rh-L angles within the range of 87.46-89.25°, the highest being observed in compound **4.22.**
- An average value of 76.71° inter planar angles for compounds **4.20**, **4.21** and **4.23**, 80.31° for **4.22** and 82.69° for **4.24** , thus orientation of the NHC with respect to the coordination approaches perpendicular probably to reduce steric interactions.
- The N1-C1-N2 angle of 103.70° observed around the carbene carbon in all complexes. Only **4.22** slightly differ with a value of 104.70°.
- C1-Rh1-(Cod) angles for the complexes ranges from 159.6(2)-167.02(10)°, with the highest being observed in **4.24**, a significant variation from the normal square planar(180°).

Some important bond distances are listed in Table 4.7 in order to see the variations in the complexes.

Table 4.7: Other bond distances (Å) for complexes of general formula [Rh(Cod)Cl(NHC)]

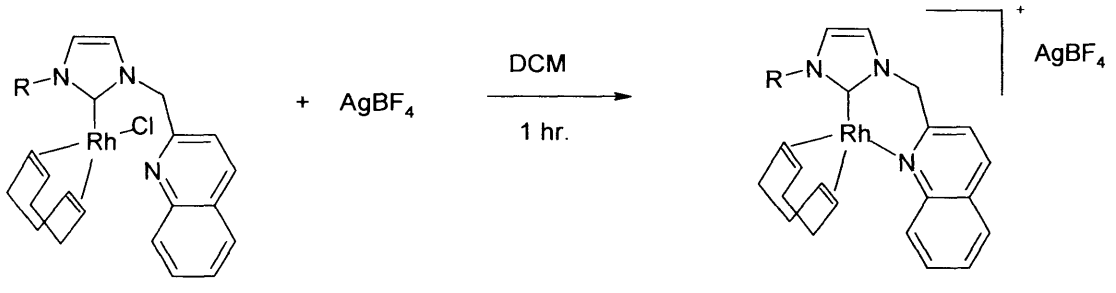
Compound	Rh-C	Rh-Cl	N1-C1	Rh-(C15-C16)	Rh-(C19-C20)
4.20	2.028(5)	2.386(13)	1.336(6)	2,123(5)	2.206(5)
4.21	2.045(5)	2.387(9)	1.355(5)	2.112(4)	2.202(4)
4.22	2.037(5)	2.377(13)	1.343(6)	2.113(5)	2.213(5)
4.23	2.032(4)	2.379(10)	1.355(5)	2.114(4)	2.197(4)
4.24	2.0163(3)	2.379(7)	1.358(3)	2.121(3)	2.105(3)

-The distances between Rh and the NHC ligands are shorter than distances between Rh and the Cod, owing to the strong electron donating ability of NHCs.

- There is no significant difference in the C-N bond distance of NHCs, with an average value of 1.35 Å (Table 4.7), this indicates a degree of C-N double character. This parameter may vary depending on the degree of back donation from Rh to the NHC (more back donation decreases the push mesomeric effect in the NHC and increases the C-N distance), based on these observations, it can be deduced that all the complexes display the same level of back donation. Similarly, from Table 4.6 the N1-Ccarbene-N2 angles (103.95° on average) are very close.

The chelation of **quinN^C-R** toward the rhodium centre was achieved by the treatment of **4.20** and **4.24** with an equimolar amount $AgBF_4$, leading to chloride abstraction and ligand substitution of chloride by the quinoline nitrogen. All of the ^1H NMR signals of the quinoline hydrogen atoms in **4.25** are shifted downfield relative to those in the non chelated rhodium complex **4.20** indicating chelation of the **qiunN^C-R** ligand. The ^1H NMR data for the non chelated complex **4.20** and that of the corresponding chelated complex **4.25** are δ= 8.10 (d, 1H, quin-H), 8.00 (d, 1H, quin-H), 7.75 (d, 1H, quin-H), 7.70 (t, 2H, quin-H), 7.45 (t, 1H, quin-H), 6.80 (s, 2H, CHHC), 6.50 (d, 1H, CH_2l_{inker}), 5.60 (d, 1H, $CH_{2linker}$), 5.00 (m, 2H, COD), 4.10 (s, 3H, CH_3), 3.40 (m, 1H, COD), 3.20 (m, 1H, COD), 2.30 (m, 4H, COD), 1.90 (m, 4H, COD) and δ 8.75 (d, 1H, quin-

H), 8.25 (d, 1H, quin-H), 8.10 (d, 1H, quin-H), 7.85 (t, 2H, quin-H), 7.60 (d, 2H, CHHC, quin-H), 6.65 (s, 1H, CHHC), 6.25 (d, 1H, $CH_{2linker}$), 6.05 (d, 1H, $CH_{2linker}$), 5.50 (m, 1H, COD), 4.70 (m, 1H, COD), 4.40 (m, 2H, COD),4.10 (m, 1H, COD), 3.65 (s, 3H, CH3), 2.80 (m, 1H, COD), 2.40 (m, 4H, COD), 2.10 (m, 2H, COD) respectively. High resolution MS of complex **4.25** displays a cluster of peak M/z = 434.1117 Da (100% intensity) assignable to the $[M- BF_4]^+$. Elemental analysis gave unacceptable results probably because of contamination from silver halides which were difficult to remove.^{13}C NMR spectrum for complex **4.25** could not be obtained because the complex is not soluble in most solvents. Suitable crystals for X-ray crystallography were not obtained for complex **4.25**. Complex **4.26** was not characterised because it is insoluble in most solvents such as DCM, acetonitrile and methylene chloride. The use of DMSO did help solve the problem of solubility but the ^1H NMR spectra of both chelated and non chelated rhodium complexes are essentially similar possibly due to competitive coordination of DMSO. Elemental analysis returned a slightly low percentage of carbon presumably due contamination from silver halide.



4.20: R = Me
4.24: R = $QiunCH_2$

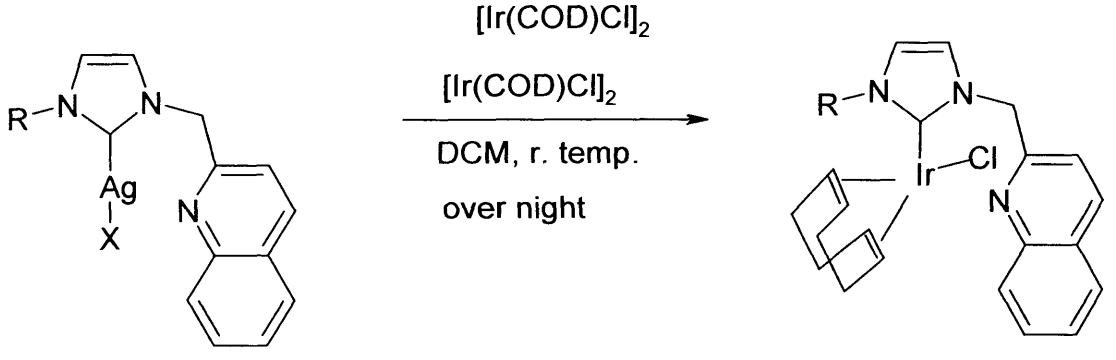
4.25: R = Me
4.26: R = $QiunCH_2$

Scheme 4.2: Synthesis of chelated quinoline functionalised Rh(I) NHC complexes.

4.2.2: Synthesis and characterisation of quinoline functionalised Ir(I) NHC complexes.

The method for the synthesis of quinoline functionalised Ir(I) NHC complexes is similar to that of Rh(I) NHC. Complexes were prepared from the silver carbene complexes prepared in chapter 3. Stirring of silver carbene complexes with 0.5 equivalent of $[Ir(COD)Cl]_2$ in DCM at ambient temperature gave the corresponding Ir(I)NHC complexes in good yield after work up as shown in Scheme 4.3 below.

Characterization of the iridium complexes, **4.27, 4.28, 4.29, 4.30** and **4.31** was performed by NMR spectroscopy, elemental analysis and in most cases by X-ray crystallography. The ^{13}C NMR data for the coordinating carbene carbons appear at δ 180.02 ppm for **4.27**, 178.66 for **4.29**, 179.56 for **4.30** and 180.57 for **4.31**, indicating the formation of the Ir-C bond. All these signals are within the typical range for Ir-C(carbene) observed for analogous complexes [11,23, 24]. There is no evidence of coordination between the nitrogen of the quinoline with the iridium ion as the ^1H NMR shifts corresponding to the proton of the quinoline ring are essentially the same to those of the silver complexes. In all the iridium complexes prepared, the ^1H NMR spectra show diasteropic protons for the CH_2 linker (δ = 6.35 and 5.50 for **4.27**, δ = 6.25 and 5.95 for **4.28**, δ = 6.35 and 5.60 for **4.29**, δ = 6.35 and 5.55 for **4.30** and δ = 6.25 and 5.65 for **4.31** indicating that this group is out of coordination plane of the molecule thus reducing its symmetry [11].



3.36: R = Me, X = Cl

4.27: R = Me

3.37: R = Mes, X = Cl
3.38: R = iPr, X = I
3.39: R = n-Bu, X = I
3.41: R = $QuinCH_2$, X = Cl

4.28: R = Mes
4.29: R = iPr
4.30: R = n-Bu
4.31: R = $QuinCH_2$

Scheme 4.3: Synthesis quinoline functionalised Ir(I) NHC complexes.

Crystals suitable for X-ray chromatography were not obtained but elemental analysis of complex **4.27** gave satisfactory results consistent with the formulation of the compound. Elemental analysis of complex **4.28** gave a satisfactory result and crystals suitable for X- ray crystallography were obtained by diffusion of pentane into the saturated DCM solution of the complex. The crystal structure of complex **4.28** and the selected bond distances and bond angles are presented in Figure 4.8 and Table 4.8 respectively. The Ir coordination is square planar with Ir-C11(carbene) distance of 2.051(11) which is typical for Ir- C single bond [25]. The different trans influences of the carbene and chloride ligands lead to different distances between the coordinated COD carbons atoms and the Ir. The other parameters obtained from the crystal structure in term of bond distances and bond angles are consistent with the reported values in the literatures [25, 26].

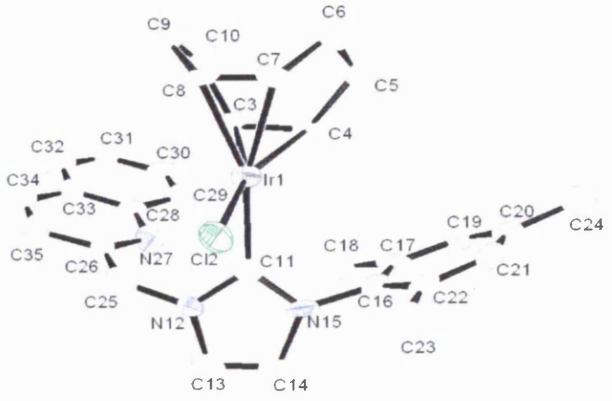


Figure 4.8: ORTEP projection of complex **4.28** excluding hydrogen atoms for clarity showing atom labelling scheme.

Table 4.8: Selected bond lengths (Å) and bond angles (°) of **4.28.**

C11- Ir1 2.051(11)	Ir1 -C8 2.177(11)	C11-Ir1-C4 95.13(4)
C11- N12 1.367(15)	Ir1- C7 2.159(11)	C11-Ir1-Cl2 87.70 (9)
Ir1- Cl2 2.372(2)	C25-N12 1.433(14)	C11-Ir1-C8 157.9(5)
Ir1- C3 2.125(13)	C11- N15 C16 124.7(9)	C4 -Ir1-Cl2 158.2(4)
Ir1-C4 2.096(11)	N12-C11-N15 105.6(9)	C11-N12-C25 125.30(9)

The elemental analysis of complex **4.29** gave results consistent with the formulation of the compound and crystals suitable for X –ray crystallography were obtained by diffusion of n-pentane into a saturated DCM solution of the compound. The molecular structure of the complex was unequivocally confirmed by means of single X-ray crystallography. Figure 4.9 shows the molecular structure of **4.29** which is virtually identical to that of **4.28**. The Ir centre is in square planar geometry and the Ir-C of 2.045(6) Å is in the usual range for Ir^{I}-NHC complexes [25, 26]. Selected bond distances and bond angles are presented in table 4.9.

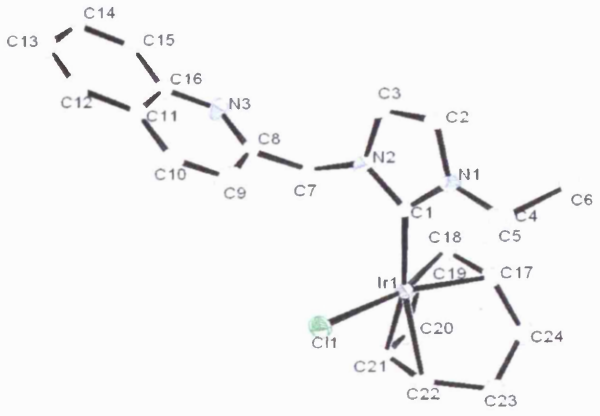


Figure 4.9: ORTEP projection of complex **4.29** excluding hydrogen atoms for clarity showing atom labelling scheme.

Table 4.9: Selected bond lengths (Å) and bond angles (°) of **4.29.**

C1- Ir1	2.045(6)	Ir1-C21	2.196(7)	C1-Ir1- C17	93.10(3)
C1- N1	1.357(8)	Ir1-C22	2.195(6)	C1- Ir1-Cl1	90.04 (19)
Ir1- Cl1	2.3719(16)	C1-N2	1.367(8)	C1-Ir1-C18	88.5(3)
Ir1-C17	2.112(6)	C11-N15-C16	124.7(9)	C1- Ir1- C21	160.0(3)
Ir1-C18	2.104(7)	N1-C1-N2	103.7(5)	C1-N1-C4	124.60(5)

Crystals suitable for X-ray crystallography were not obtained for complex **4.30** but elemental analysis returned satisfactory results in agreement with the proposed structure.

Elemental analysis of complex **4.31** gave results that are in agreement with the formulation of the complex and crystals suitable for X-ray crystallography were obtained by diffusion of n- pentane into saturated DCM solution of the complex. The crystal structure and selected bond distances and angles are shown in Figure 4.10 and Table 4.8 respectively. The iridium exhibits a square planar geometry and the Ir-C11(carbene) bond is typical for an Ir-C single bond [25, 26]. Other parameters in terms of bond lengths and bond angles are similar to that of **4.28** and **4.29**.

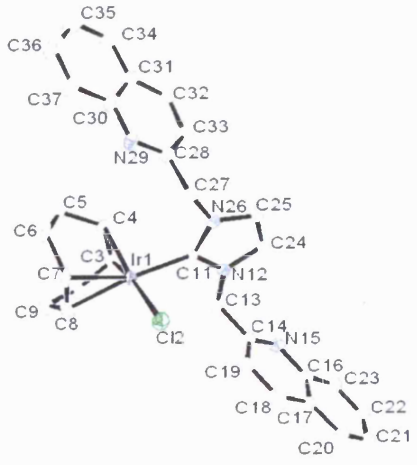


Figure 4.10: ORTEP projection of complex **4.31** excluding hydrogen atoms for clarity showing atom labelling scheme.

Table 4.10: Selected bond lengths (Å) and bond angles (°) of **4.31.**

C11-Ir1 2.022(4)	Ir1-C8 2.196(5)	C11-Ir1-C4 91.42(11)
C11-N12 1.354(5)	Ir1- C7 2.160(4)	C11-Ir1-Cl2 87.54 (12)
Ir1-Cl2 2.3653(11)	C11-N26 1.361(5)	C11-Ir1-C8 168.44(18)
Ir1-C3 2.082(4)	C11-N12- C13 123.7(3)	C8-Ir1-Cl2 82.45(19)
Ir1-C4 2.121(4)	N12-C11-N26 104.0(3)	C11-Ir1-C7 154.57(19)

To compare the structure of the three Ir(I) complexes the interplanar angles between the planes of the carbene ring and Ir coordination plane were calculated as Θ and tabulated in Table 4.11.

Table 4.11: Bond angles (°) for compounds **4.28, 4.29** and **4.31** of iridium complexes of general formula [Ir(Cod)Cl(NHC)].

Compound	Θ(interplaner angle)	N1-C1-N2	C1-Ir1-Cl1	C11-Ir1-(C18-C19)
4.28	76.43	105.6(9)	87.70(14)	158.20(4)
4.29	77.79	103.70(5)	90.04(19)	160.00(3)
4.31	86.76	104.03(3)	87.54(3)	168.44(2)

In general, neutral complexes display slight variation in their geometries and the main structural features of these compounds are:

- Distorted square planar geometry with Cl-Ir-L of around 87.62° on the average for compounds **4.28** and **4.31**, and 90.04° for **4.29** (Table 4.11).
- A value of 77.11°(on average) with respect to the plane of carbene ring and the Ir coordination plane (Cl-Ir-C11) for complexes **4.28** and **4.29** and 86.76° for complex 4.29 which is almost perpendicular, probably to reduce steric interactions.
- C1-Rh1-(Cod) angles for the complexes ranges from 158.20(4)-168.44(2)°, with the highest being observed in **4.31**, a significant variation from the normal square planar(180°).

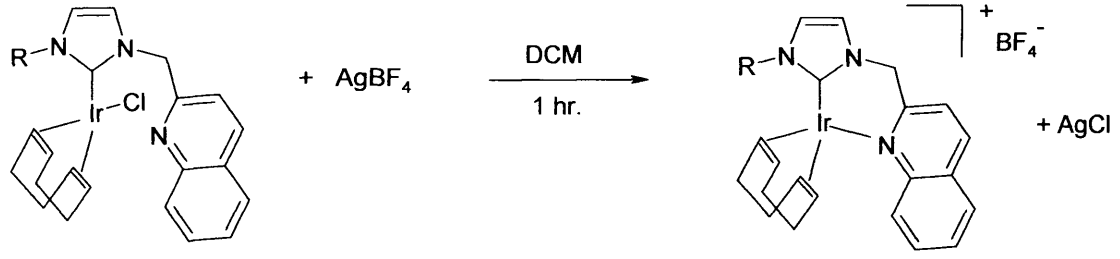
Some important bond distances are listed in Table 4.12 in order to see the variations in the complexes.

Table 4.12: Other bond distances (A) for complexes of general formula [Ir(Cod)Cl(NHC)]

Compound	Ir-C	Ir-Cl	N1-C1	Ir-(C15-C16)	Ir-(C19-C20)
4.28	2.051(11)	2.372(2)	1.367(15)	2.096(11)	2.177(11)
4.29	2.045(6)	2.372(9)	1.357(8)	2.104(7)	2.196(7)
4.31	2.022(5)	2.365(11)	1.354(5)	2.082(4)	2.196(5)

-The distances between Rh and the NHC ligands are shorter than distances between Rh and the Cod, owing to the strong electron donating ability of NHCs.

- There is no significant variation in the C-N bond distance of NHCs, with an average value of 1.36 Å indicating double bond character (Table 4.12). This parameter may vary depending on the degree of back donation from Ir to the NHC (more back donation decreases the push mesomeric effect in the NHC and increases the C-N distance), based on these observations, it can be deduced that all the complexes display the same level of back donation. Similarly, from Table 4.11 the N1-Ccarbene-N2 angles (104.44° on average) are very close.



4.27: R = Me

4.31: R = CH_2Quin

4.32: R = Me

4.33: R = CH_2Quin

Scheme 4.3: Synthesis of chelated quinoline functionalised Ir(I) NHC complexes

The chelation of **quinN^C-R** with the iridium centre was achieved by the treatment of **4.27** and **4.31** with an equimolar amount $AgBF_4$, leading to the ligand substitution of chloride by the quinoline nitrogen as shown in Scheme 4.3 above. All of the ^1H NMR signals of the quinoline hydrogen atoms in **4.32** are shifted downfield relative to those in the silver complex **4.20** indicating chelation of the **qiunN^C-R** ligand. The methylene linker protons shifted from 6.35 and 5.50 ppm for complex **4.20** to 6.80 and 5.90 ppm for complex **4.32** and the protons from the imidazole moiety shifted from 6.80, 6.70 ppm to 7.55 and 6.80 ppm respectively.

Complex **4.33** was not characterized by NMR spectroscopy due to lack of suitable solvent for analysis because it is insoluble in most common solvents. In high polar solvent such as DMSO, the spectrum of chelated and the non chelated complexes are virtually similar possibly due to competitive coordination of DMSO. Elemental analysis of complexes **4.32** and **4.33** returned unacceptable results with low percentage of carbon, nitrogen and hydrogen probably as a result of contamination from silver halides.

4.2.3 Attempted synthesis of Rh(I) and Ir(I) complexes of ligands without methylene separating the quinoline

Attempts were made to prepare the Rh(I) and Ir(I) (NHC) complexes of ligands **2** (1,3-diquinolin-4,5-dihydroimidazolium tetrafluoroborate) and **4** (1,3-diquinoline-3,4,5,6-tetrahydropyrimidinium hexaflouro phosphate) by the treatment the ligands with the following reagents:

i) Ag_2O in dichloromethane, acetonitrile and DMSO

ii) $K[N(SiMe_3)_2]$ and $[Rh(COD)Cl]_2$ in THF

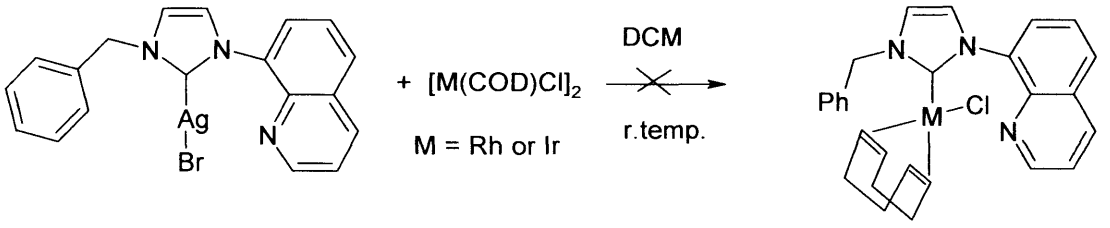
iii) $K[N(SiMe_3)_2]$ and $[Ir(COD)Cl]_2$ in THF

The reaction of the ligands with Ag_2O did not yield the expected carbene complexes as NMR spectra revealed only the starting salts. Performing the reaction at elevated temperature and for longer times did not give the desired carbene complexes. However treatment of the ligands with $K[N(SiMe_3)_2$ in THF showed that the C_2-H has been removed but could not coordinate as addition of $[Rh(COD)Cl]_2$ or $[Ir(COD)Cl]_2$ did not give the desired carbene metal complexes.

Solubility was thought to be responsible for the negative results obtained in the preparation of the silver(I) carbene complexes. With this in mind, it was decided to change the tetrafluoroborate and hexafluorophophate counter ions to sodium tetrakis [(3, 5-trifluoromethyl) phenyl] borate ($NaBArF_{24}$). The replacement of the counter ion solved the problem of solubility but upon reaction with silver oxide followed by $[Rh(COD)Cl]_2$ or $[Ir(COD)Cl]_2$ the desired carbene complexes were not formed. After several problems preparing the complexes with ligands **2** and **4** we decided to diversify and were successful in the synthesis of a variety of compounds by slightly varying the structure of the ligands.

A variation on this type of structure has been to add a methylene linker between the carbene and the quinoline moiety. This will provide extra flexibility and reduce steric strain.

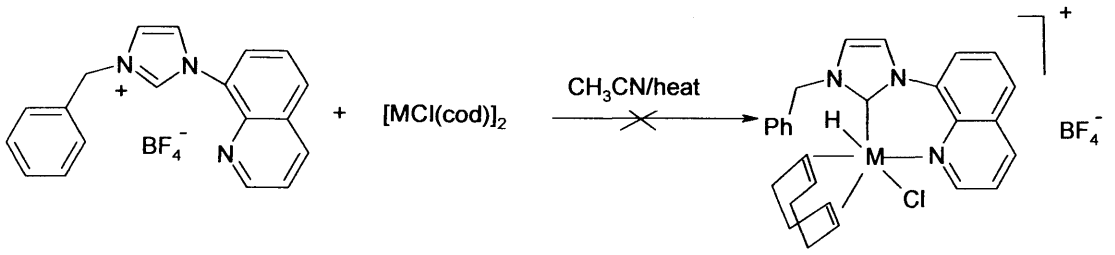
Attempt was also made to synthesise the Rh(I) and Ir(I) (NHC) complexes by the reaction of silver(I) (NHC) complex **3.34** prepared in chapter 3 with [Rh (COD) $Cl]_2$ and [Ir (COD) $Cl]_2$ in DCM as shown in Scheme 4.4 below.



Scheme 4.4: Attempted of rigid quinoline functionalised Rh(I) and Ir(I) (NHC) carbene complexes.

The reaction did not give the desired product, the NMR looked messy and therefore could not be interpreted.

C-H oxidative addition was thought to be another feasible way to obtain the rhodium and iridium complexes, though, this would lead to the synthesis of Rh(III) and Ir(III) (NHC) carbene complexes. Therefore, following the methods reported in the literature [8], 1-benzyl-3-quinolinimidazoliumtetraflouroborate **(6b)** was reacted with $[Rh(COD)Cl]_2$ and $[Ir(COD)Cl]_2$ in refluxing acetonitrile for 24 hours. However the reaction gave the original mixture, even when the reaction was carried out for a longer time (one week). Modification of the reaction conditions (refluxing toluene and DMSO) did not produce any of the expected products.



Scheme 4.5: Attempted of Rh and Ir carbene complex via oxidative addition

4.3 Ir(I) NHC catalysed hydrogen transfer reactions

4.3.1 Catalysis

A catalyst may be defined as a substance that increases the rate at which a chemical reaction approaches equilibrium; thus a catalyst affects the kinetics of a reaction rather than the overall thermodynamics [27]. Different catalysts will also accelerate one reaction with respect to another, and are thus especially valued for their ability to influence product selectivity [28]. In a catalytic cycle, the catalyst remained unchanged, aside from degradation or poisoning by side reactions.

The importance of the catalyst can not be over emphasised due to the fact that many chemical reactions will not proceed to appreciable extent unless in the presence of a suitable catalyst. Apart from the importance of catalysts to the world economy, it is also crucial to the existence of all living organisms through the actions of naturally occurring enzymes. It is worth noting that 75% of all chemicals are produced with the application of some sort of catalyst; and it is up to 90% when only those more modern processes are considered [28].

Catalytic reactions are mainly divided into heterogeneous and homogeneous systems dependent on the phase relationship of the catalyst to the substrate. Enzymatic catalysis as seen in biological reactions constitutes an additional and separate group [27] and these systems are sometimes classified as immobilised catalyst [28].

The current work involves homogeneous systems utilising iridium complexes as precatalysts, i.e. precursors to the actual catalytic species. The essential

characteristics of homogeneous systems have been broadly defined by Cornils and Herrmann [29]:

i) the catalyst is moderately dispersed in the same phase as the reactants;

ii) the catalyst is able to be unequivocally characterised chemically and spectroscopically, and thus able to be synthesised in a reproducible manner;

iii) new catalysts are able to be rationally designed for specific purposes according to known chemical principles;

iv) unequivocally reaction kinetics may be related to each metal atom of the catalyst.

Although the catalytic reactions take place at the metal atom, the supporting ligands bound to the metal are important for promoting and modifying catalytic activity through the prevention of metal aggregation, stabilisation of intermediates, provision of vacant coordination sites at the metal via dissociation equilibria, and modification of the steric and electronic environment about the metal ion [29].

While the market share of homogeneous catalysis is only 10- 15%, recent developments in the application of transition metal complexes as catalysts has led to the prospect of a wide variety of new, high value organic molecules being accessed using relatively simple and affordable substrates and procedure [30]. Progress in these areas of homogeneous catalysis will ultimately lead to the synthesis of highly active, selective, and robust catalyst that use cheap substrates to produce important compounds in an efficient manner.

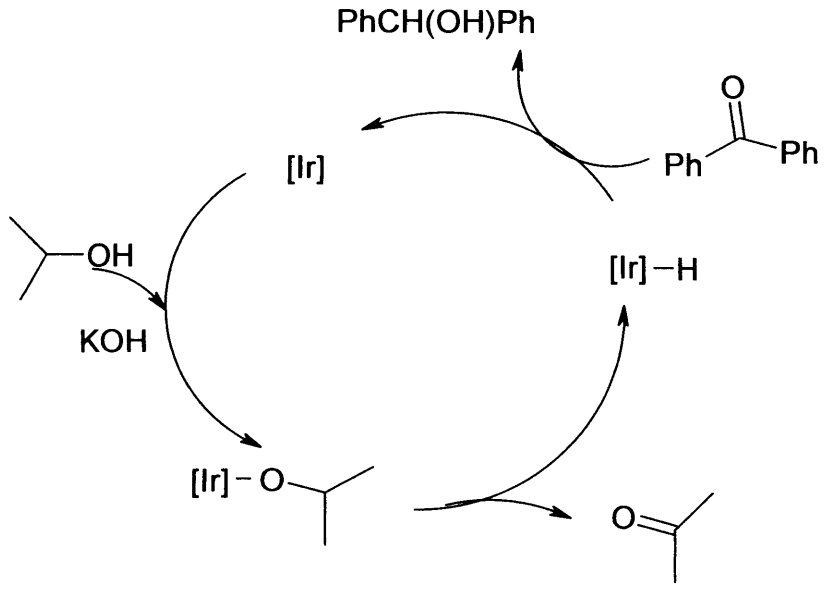
Due to time constraints, catalyst testing of the complexes synthesised in this chapter was confined to the hydrogen transfer reduction.

4.5.2 Hydrogen-transfer reduction

The conventional methods for the hydrogenation of unsaturated bonds have involve the use of molecular hydrogen which has its draw backs due to the difficult handling procedures involved with working at high pressures. Efforts have since been devoted to developing safer, more cost effective methods and transfer hydrogenation represents an ideal alternative.

Transfer hydrogenation hydrogenates a double bond (e.g. C=C in olefins [31], N=O [11] in nitro groups and C=O in carbonyls [33]) by abstracting hydrogen from a proton donor source such as isopropanol, usually present in excess as the reaction solvent. The reaction is carried out in the presence of the catalyst in addition to the base used to assist deprotonation.

The hydrogen transfer reduction of a carbonyl function catalysed by transition metal complexes is well documented [34] and an accepted mechanism for the catalytic transfer hydrogenation on the reduction of benzophenone is given in Scheme 5 below.



Scheme 4.6: mechanism of transfer hydrogenation of benzophenone

The attractiveness of this method lies in its inexpensive starting materials and simple experimental procedure, which has been exploited in the extensive level of development in this area. It is generally agreed that this research area was spearheaded by Noyori et al in 1995 [35]. They discovered that chiral Ru(II) complexes were capable of asymmetric transfer hydrogenation at reflux temperature and had sufficient catalytic activity on aryl ketones at ambient temperatures. The Noyori catalyst is a $Ru(II)Cl_2$ centre complexed with chiral (1S, 2S)-N-(p-toluenesulfonyl)-1, 2-diphenylethylenediamine [(S,S)-TsDPEN]. Buriak et al explored the efficiency of N-heterocyclic carbene ligands in combination with phosphines

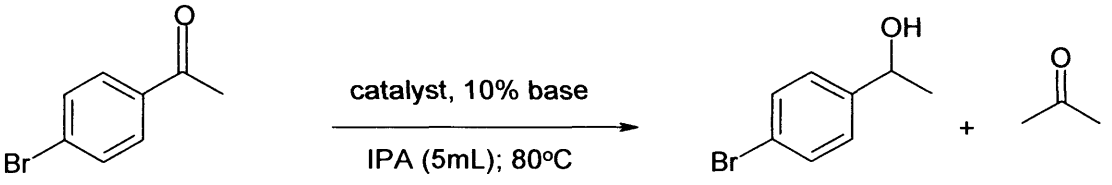
in hydrogenation of olefins [36]. Pyridinyl N-Heterocyclic carbene complexes have also been used in the reduction of nitroarenes and carbonyls [11].

Rh and Ir are known to be effective catalysts for the transfer hydrogenation of unsaturated substrate by hydrogen donors (e.g. cyclohexene or 2-propanol) [32]. Significantly, transfer hydrogenation of carbonyl compounds in iPrOH is the most widely used reaction to test the catalytic properties of Rh and Ir because of its simplicity. It has been established that iridium carbene complexes are more active than their rhodium analogues in transfer hydrogenation [33].

The catalysis presented in this work involves the use quinoline functionalised iridium carbene complexes in transfer hydrogenation.

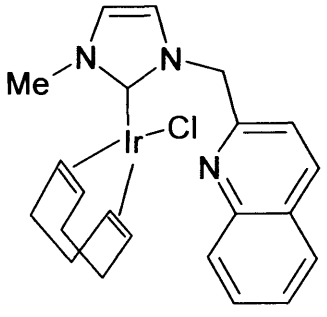
4.5.3 Results and discussions

The catalytic transfer hydrogenation was examined using 2-propanol as the hydrogen source with a KO^{t}Bu base promoter.

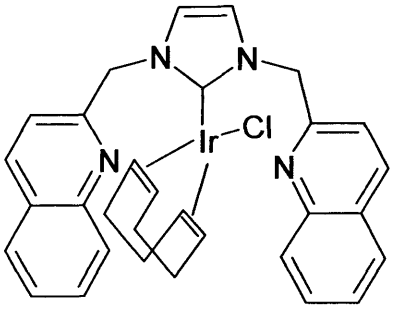


Scheme 4.7: Catalytic hydrogen transfer of 4-bromoacetophenone

Two quinoline based iridium carbene complexes were used in catalytic hydrogen transfer of 4-bromoacetophenone:



4.27



4.31

The activity of iridium complexes **4.27** and **4.31** was tested at different concentrations which enable a direct comparison between the effects of the alkyl and the quinoline on the N-substituents. The results of the catalytic tests are presented in table 4.13 below.

Table 4.13: Catalysis with **4.27** and **4.31** in hydrogen transfer reaction

Entry	Catalyst	Concentration (mole %)	Conversion (%)	TON
1	**4.27**	1	99	99
2	**4.27**	0.1	99	990
3	**4.27**	0.01	65	6500
4	**4.31**	1	99	99
5	**4.31**	0.1	99	990
6	**4.31**	0.01	78	7800

Conditions: substrate: 1.00 mmol; KO^{t}Bu: 1.00 mmol; 80^{o}C; 24hr. Determined by NMR.

As presented in the table above, both of the catalysts showed good catalytic activity towards transfer hydrogenation with no significant change when the catalyst loading was reduced from 1 mole % to 0.1 mole %. When 0.01 mole % of the catalysts was used, the catalysts still showed good activity with virtually no difference

In order to evaluate the differences between catalysts **4.27** and **4.31** carbene complexes, a low catalyst loading (0.01 mol %) at 80 ^{o}C. The yield for the transfer hydrogenation of 4-bromoacetophenone was studied over a period of 3 hours by taking and running the samples after a given time and the results are presented in Figure 4.11 below.

As shown in the diagram below, there is no significant difference between catalysts **4.31** and **4.27** as both catalysts appeared to be highly efficient in the transfer hydrogenation of 4-bromoacetophenone to 1-phenylethanol both giving over 90% conversion after 180 minutes. The performances of the iridium carbene complexes are comparable to the ones reported by Hahn et al [39], though it required longer time to achieve the desired results. It also compares

well with the pyridinyl Ir(I) NHC carbene complexes reported by Peris et al [38].

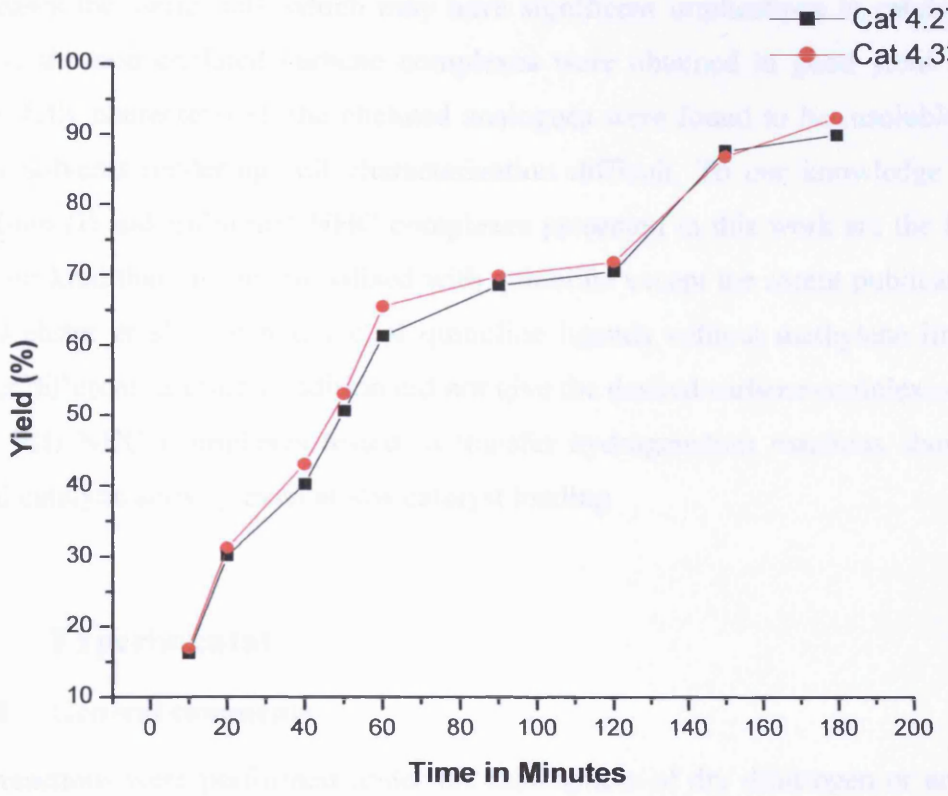


Figure 4.11: Time dependence of the catalytic transfer hydrogenation of 4-bromoacetophenone; 0.01 mol % of cat. (**4.27** and **4.37**), KO^{t}Bu (10 mol%), 10 mol% of 4-bromoacetophenone, solvent 2-propanol (5mL), T = 80 ^oC

The steric properties of the carbene may have played important roles in the selectivity and reactivity of the systems. **4.31** is significantly more sterically hindered than the **4.27** analogue because of the presence of the bulky quinoline moiety. However this steric differences does not seem to influence the activity of the catalyst. Another consideration is partial chelation of the ligand during catalysis.

4.4 Conclusions

In this chapter both of the rhodium(I) carbene complexes and iridium(I) carbene complexes were synthesized from the silver(I) carbene described in chapter 3

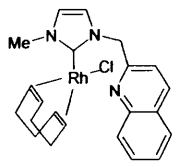
by transmetallation reactions. This procedure was earlier utilised to synthesise the iridium pyridinyl NHC complexes [11] producing both chelated and non chelated complexes. The replacement of the pyridine moiety with quinoline increases the steric bulk which may have significant implications in catalysis. While the non chelated carbene complexes were obtained in good yield and were fully characterized, the chelated analogues were found to be insoluble in most solvents rendering full characterization difficult. To our knowledge the rhodium (I) and iridium(I) NHC complexes presented in this work are the first of their kind that are functionalised with quinoline except the recent publication by Webster et al. The reaction of quinoline ligands without methylene linker under different reaction condition did not give the desired carbene complexes. The Ir(I) NHC Complexes tested in transfer hydrogenation reactions showed good catalytic activity even at low catalyst loading

4.5 Experimental

4.5.1 General comments

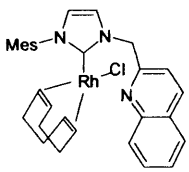
All reactions were performed under the atmosphere of dry dinitrogen or argon using standard Schlenk techniques, and solvents were purified and dried by usual means [40], unless otherwise indicated. Silver(I) NHC complexes were prepared as detailed in Chapter 3, and all other reagents were used as received. All NMR data are quoted δ/ppm. ^{1}H and ^{13}C (proton decoupled) spectra NMR were recorded on a Bruker DPX Advance 400 (^{1}H at 400MHz, ^{13}C at 100.61 MHz) at ambient temperature, unless otherwise stated, and referenced to $SiMe_4$. Electrospray mass spectrometry (ESMS) was performed on a VG Fisons Platform II instrument by the department of Chemistry, Cardiff University. Micro analysis was performed by Warwick Analytical Service. All reactions involving silver compounds were performed with the exclusion of light.

[1-methyl-3-(2-methylquinoline)imidazolin-2-ylidene](1,5-cyclooctadiene)rhodium(I) Chloride 4.20



$[RhCl(cod)]_2$ (99mg, 0.2mmol) in 10ml of DCM was added to 20 ml of DCM solution of [Ag (1-methy-3-(-2-methylquinoline) imidazolin-2-ylidine)$_2$][$AgCl_2$] **3.36** (147mg, 0.40mmol). The reaction mixture was stirred over night and filtered through celite to remove silver chloride and any insoluble residue. The filtrate was concentrated and hexane was added to precipitate out the desired carbene complex as a yellow powder (152mg, 80.42%). Crystals suitable for X-ray crystallography were grown by layering diethyl ether on dichloromethane. Anal. Calcd. for $C_{22}H_{25}N_3RhCl$: C, 56.20; H, 5.33; N, 8.95%. Found: C, 54.80; H, 5.23; N, 8.66%. ^{1}H NMR ($CDCl_3$. 400MH_Z, 298K): δ 8.10(d, 1H, J = 8.5 H_Z, quin-H), 8.00(d, 1H, J = 8.5 H_Z, quin-H), 7.75(d, 1H, J = 8.0 H_Z, quin-H), 7.70(t, 2H, J = 6.7 H_Z quin-H), 7.45(t, 1H, 7.5 H_Z, quin-H), 6.80(s, 2H, CHHC), 6.50(d, 1H, J = 14.8 H_Z $CH_{2linker}$), 5.60(d, 1H, J = 14.8 H_Z $CH_{2linker}$), 5.00(broad, 2H, COD), 4.10(s, 3H, CH_3), 3.40(broad, 1H, COD), 3.20(broad, 1H, COD), 2.30(m, 4H, j= 4.4 H_Z, COD), 1.90(m, 4H, J = 4.2 H_Z COD). ^{13}C NMR ($CDCL_3$, 100MH_Z, 298K): 181.60 (C-Rh), 154.88, 145.53, 135.57, 127.82, 127.05, 125.86, 125.73, 124.78, 120.78, 118.99, 118.87, 96.93(N-CH_3), 66.32, 54.96, 35.83, 31.33, 30.65, 27.20, 26.66.

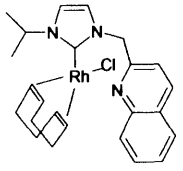
[1-mesityl-3-(2-methylquinoline)imidazolin-2-ylidene](1,5-cyclooctadiene)rhodium(I) Chloride 4.21



Following the procedure for the synthesis of complex **4.20**, **4.21** was obtained from **3.37** (110 mg, 0.23mmmol) and $[RhCl(cod)]_2$ (58 mg, 0.12mmol) . Yield = 95 mg (71.00%). Crystals suitable for X- ray crystallography were grown by

layering diethyl ether on dichloromethane. Anal. Calcd. for $C_{30}H_{33}N_3RhCl$: C, 62.78; H, 5.76; N, 7.32%. Found: C, 61.44; H, 5.48; N, 7.06%. ^1H NMR ($CDCl_3$. 400MHZ, 298K): δ 8.15(m, 1H,J = 8.4 H_Z, quin-H), 8.00(d, 1H,J = 8.1 H_Z, quin-H), 7.80(d, 1H, J = 5.7 H_Z, quin-H), 7.70(s, 1H, Ar-H), 7.50(t, 2H, J = 7.0 H_Z, quin-H), 7.05(t, 2H, quin-H, Ar-H), 6.90(s, 1H, CHHC), 6,70(s, 1H, CHHC), 6.50(d, 1H, J = 15.4 H_Z, $CH_{2linker}$), 6.10(d, 1H, J = 15.4 H_Z $CH_{2linker}$), 4.80(broad, 2H, COD), 3.30(broad, 1H,COD),3.00(broad, 1H, COD), 2.40(broad, 3H, COD), 2.30(s, 3H, p-CH3), 1.80(s, 6H, o-CH3), 1.50(broad, 4H, COD). ^{13}C NMR ($CDCL_3$, 100MHZ, 298K): 155.03, 145.70, 136.61, 135.05, 134.97, 134.01, 132.36, 127.68, 127.52, 126.16, 125.69, 125.48, 124.62, 121.19, 119.73, 118.75, 95.44(NCH_2), 55.14, 31.56, 29.58, 26.93, 25.95(p-CH_3), 19.06(o-CH_3), 17.06, 15.75. HR-MS for $[M - Cl]^+$ = 538.18(100%): calculated, 538.1730($C_{30}H_{33}N_3Rh$), found, 538.1751.

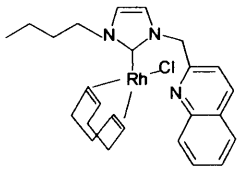
[1-isopropyl-3-(2-methylquinoline)imidazolin-2-ylidene](1,5-cyclooctadiene)rhodium(I) Chloride 4.22



Following the procedure for the synthesis of complex **4.20, 4.22** was obtained from **3.38** (134mg, 0.276mmmol) and $[RhCl(cod)]_2$ (68 mg, 0.14mmol) . Yield = 110 mg (80.29%). Crystals suitable for X- ray crystallography were grown by layering hexane on dichloromethane. Anal. Calcd. for $C_{24}H_{29}N_3RhCl$: C, 57.90; H, 5.83; N, 8.4%. Found: C, 53.85; H, 5.59; N, 7.47%. ^1H NMR ($CDCl_3$. 400MHZ, 298K): δ 8.10(m, 1H, J = 8.5 H_Z, quin-H), 8.00(d, 1H, J = 8.4 H_Z quin-H), 7.70(d, 1H, J = 8.1 H_Z quin-H), 7.65(t, 2H, J = 4.1 H_Z, quin-H), 7.45(t, 1H, J = 7.0 H_Z, quin-H), 6.80(s, 2H, CHHC), 6.50(d, 1H, J = 14.8 H_Z, $CH_{2linker}$), 5.75(m, 1H, J = 6.8 H_Z, iPr-H), 5.60(d, 1H, J = 14.8 H_Z $CH_{2linker}$), 5.00(m, 1H, J = 7.6 H_Z, COD), 4.90(m, 1H, J = 5.2 H_Z ,COD), 3.35(m, 1H, J = 2.6 H_Z, COD), 2.1-2.40(m, 4H, J = 4.5 H_Z COD), 1.7-2.00(m, 4H, J = 6.6 H_Z, COD), 1,5(d, 6H, J = 4.2 H_Z CH_3). ^{13}C NMR ($CDCL_3$, 100MHZ, 298K): 180.38(C-Rh), 155.00,

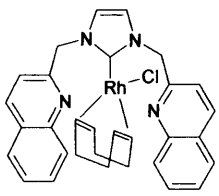
145.53, 135.60, 127.80, 127.04, 126.74, 125.87, 125.73, 124.76, 119.22, 115.25, 97.17,66.24, 55.19, 50.17, 31.50, 30.46, 27,38, 26.45, 22.19, 21.36, 20.72. HR-MS for $[M - Cl]^+$ = 462.1415(100%): calculated, 462.1417($C_{24}H_{29}N_3Rh$), found, 462.1415.

[1-n-butyl-3-(2-methylquinoline)imidazolin-2-ylidene](1,5-cyclooctadiene)rhodium(I) Chloride 4.23



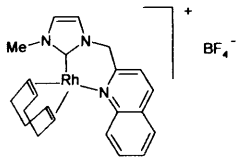
Following the procedure for the synthesis of complex **4.20, 4.23** was obtained from **3.39** (150mg, 0.300mmmol) and $[RhCl(cod)]_2$ (74 mg, 0.15mmol) . Yield = 121 mg (79.08%). Crystals suitable for X- ray crystallography were grown by layering hexane on dichloromethane. Anal. Calcd. for $C_{25}H_{31}N_3RhCl$: C, 58.66; H, 6.06; N, 8.21%. Found: C, 58.44; H, 6.48; N, 7.37%. ^1H NMR ($CDCl_3$. 400MH_Z, 298K): δ 8.10(m, 1H, J = 9.5 H_Z, quin-H), 8.00(d, 1H, J = 8.4 H_Z, quin-H), 7.75(d, 1H, J = 7.9 H_Z, quin-H), 7.65(t, 2H, J = 4.8 H_Z quin-H), 7.45(t, 1H, quin-H), 6.75(s, 2H, CHHC), 6.50(d, 1H, J = 14.8 H_Z, $CH_{2linker}$), 5.60(d, 1H, J = 14.8 H_Z ,$CH_{2linker}$), 5.00(broad, 2H, COD), 4.50(m, 2H, J = 6.1 H_Z, CH_2), 3.30(m, 2H, J = 2.3 H_Z, COD), 2.40(m, 2H, J = 3.3 H_Z CH_2),1.8(m, 4H, J = 2.4 H_Z ,COD) 1.40(m 2H, J = 7.4, CH_2), 1.0(t, 3H, J = 7.4 H_Z, CH_3). ^{13}C NMR ($CDCL_3$, 100MH_Z, 298K): 178.66(C-Rh), 155.72, 146.45, 136.45, 128.73, 127.97, 126.76, 126.62, 125.67, 119.86, 119.73, 115.80, 84.35, 83.04, 55.73, 52.42, 50.97, 33.20, 31.87, 29.14, 28.03, 22.97, 22.08. HR-MS for $[M–Cl]^+$= 476.1578(100%): calculated, 476.1573($C_{24}H_{29}N_3Rh$), found, 476.1578.

[bis-1,3-(2-methylquinoline)imidazolin-2-ylidene](1,5-cyclooctadiene)rhodium(I) Chloride 4.24



Following the procedure for the synthesis of complex **4.20, 4.24** was obtained from **3.41** (300mg, 0.600mmmol) and $[RhCl(cod)]_2$ (150 mg, 0.30mmol) . Yield = 250 mg (68.87%). Crystals suitable for X- ray crystallography were grown by layering hexane on dichloromethane. Anal. Calcd. for $C_{31}H_{30}N_4RhCl$: C, 62.37; H, 5.03; N, 9.39%. Found: C, 61.59; H, 5.13; N, 8.967%. ^1H NMR ($CDCl_3$. 400MH_Z, 298K): δ 8.10(m, 2H, J = 8.5 H_Z, quin-H), 8.00(d, 2H, J = 8.4 H_Z, quin-H), 7.75(d, 2H, J = 8.1 H_Z, quin-H), 7.65(m, 4H, J = 4.8 H_Z, quin-H), 7.50(t, 2H, J = 7.0 H_Z, quin-H), 6.85(s, 2H, CHHC), 6.50(d, 1H, J = 14.9 H_Z $CH_{2linker}$), 5.80(d, 1H, J = 14.8 H_Z $CH_{2linker}$), 5.00(broad, 2H, COD), 4.50(broad, 2H,CH_2), 3.30(m, 2H, J = 2.7 H_Z, COD), 2.30(m, 4H, J = 4.0 H_Z, COD),1.90(m, 4H, J = 8.5 H_Z, COD). ^{13}C NMR ($CDCL_3$, 100MH_Z, R.T): 183.45(C-Rh), 155.64, 146.52, 136.52, 128.78, 128.03, 126.75, 126.61, 125.74, 120.58, 119.78, 98.38(CH_2) 67.93, 55.92, 32.84, 30.56, 27.81, 26.98, 21.63. HR-MS for $[M–Cl]^+$= 561.1548(100%): calculated, 561.1526($C_{31}H_{30}N_4Rh$), found, 561.1548.

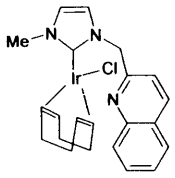
[1-methyl-3-(2-methylquinoline)imidazolin-2-ylidene](1,5-cyclooctadiene)rhodium(I) tetraflouroborate 4.25



AgBF4 (26 mg, 0.132mmol) was added to a stirred solution of complex **4.20** (62 mg, 0.132mmol) in 10 ml of DCM. The reaction mixture was stirred for 1 hour and reaction filtered through celite to remove silver chloride and any insoluble residue. The filtrates was then added drop by drop to a stirring solution of hexane to precipitate the compound which was then dried in vacuum to afford the desired compound as a deep yellow powder(42 mg, 60.87%). Anal. Calcd. for $C_{22}H_{25}N_3RhBF_4$: C, 50.70; H, 4.80; N, 8.07%. Found: C, 42.18; H, 4.26; N, 6.20%. ^1H NMR ($CDCl_3$. 400MHZ, 298K): δ 8.75(d, 1H, J = 8.5 H_Z, quin-H), 8.25(d, 1H, J = 8.3 H_Z, quin-H), 8.10(d, 1H, J = 8.3 H_Z, quin-H), 7.85(t, 2H, J = 8.2 H_Z,quin-H), 7.60(d, 2H, CHHC, J = 5.3 H_Z, quin-H), 6.65(s, 1H, CHHC), 6.25(d, 1H, J = 15.4 H_Z, $CH_{2linker}$), 6.05(d, 1H, J = 15.4 H_Z, $CH_{2linker}$), 5.50(broad, 1H, COD), 4.70 (broad, 1H, COD), 4.40(broad, 2H, COD),4.10(broad, 1H, COD), 3.65(s, 3H, CH3), 2.80(broad, 1H, COD),

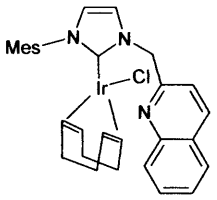
2.40(broad, 4H, COD), 2.10(broad, 2H, COD). HRMS for $[M–BF_4]^+$: calculated for $C_{22}H_{25}N_3Rh$ (M^+)434.1104, found, 434.1117.

[1-methyl-3-(2-methylquinoline)imidazolin-2-ylidene](1,5-cyclooctadiene)iridium(I) Chloride 4.27



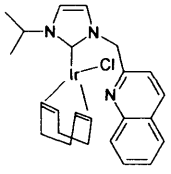
$[IrCl(cod)]_2$ (180mg, 0.27mmol) in 10ml of DCM was added to 20 mL of DCM solution of [Ag (1-methy-3-(-2-methylquinoline) imidazolin-2-ylidine) $_2$][$AgCl_2$] **3.36** (196mg, 0.54mmol). The reaction mixture was stirred over night and filtered through celite to remove silver chloride and any insoluble residue. The filtrate was concentrated and hexane was added to precipitate the desired carbene complex as a yellow powder (210mg, 70.23%). Crystals suitable for X-ray crystallography were grown by layering hexane on dichloromethane. Anal. Calcd. for $C_{22}H_{25}N_3IrCl$: C, 47.25; H, 4.48; N, 7.52%. Found: C, 46.83; H, 4.51; N, 6.14%. ^1H NMR ($CDCl_3$. 400MH_Z, 298K): δ 8.10(d, 1H, J = 8.5 H_Z, quin-H), 8.00(d, 1H, J = 8.4 H_Z, quin-H), 7.75(d, 1H, J = 8.1 H_Z, quin-H), 7.65(t, 1H, J =5.6 H_Z, quin-H), 7.60(t, 1H, J = 8.5 H_Z, quin-H), 7.45(d, 1H, J = 5.6 H_Z, quin-H), 6.80(s, 1H, CHHC), 6.70(s, 1H, CHHC), 6.35(d, 1H, J = 14.7 H_Z, CH_2l_{inker}), 5.50(d, 1H, J = 14.7 H_Z, $CH_{2linker}$), 4.60(m, 2H, J = 4.6 H_Z, COD), 3.90(s, 3H, CH_3), 3.00(m, 1H, J = 4.4 H_Z, COD), 2.80(m, 1H, J = 4.10 H_Z, COD), 2.20(m, 4H, J = 3.2 H_Z, COD), 1.70(m, 4H, J = 3.3 H_Z, COD). ^{13}C NMR ($CDCL_3$, 100MH_Z, R.T): 180.02 (C-Rh), 155.56, 146.43, 136.42, 128.75, 127.96, 126.75, 126.60, 125.70, 121.38, 119.68, 119.43, 83.40(N-CH_3), 55.48, 51.00(, 36.44), 32.91, 32.12, 30.56, 28.18, 21.63.

1-mesityl-3-(2-methylquinoline)imidazolin-2-ylidene](1,5-cyclooctadiene)iridium(I) Chloride 4.28



Following the procedure for the synthesis of complex was obtained from 3.37 (200 mg, 0.425mmmol) and $[IrCl(cod)]_2$ (140 mg, 0.21mmol) . Yield: 151 mg (53.55%). Crystals suitable for X- ray crystallography were grown by layering hexane on dichloromethane. Anal. Calcd. for $C_{30}H_{33}N_3IrCl$: C, 54.32; H, 4.98; N, 6.34; Cl, 5.37%. Found: C, 53.59; H, 5.08; N, 6.07; Cl, 5.25%. ^1H NMR ($CDCl_3$. 400MHZ, 298K): δ 8.15(m, J = 8.4 H_Z, 1H, quin-H), 7.90(d, 1H, J = 8.0 H_Z, quin-H), 7.80(d, 1H, J = 8.1 H_Z, quin-H), 7.70(d, 2H, J = 7.0 H_Z, Ar-H), 7.50(t, 1H, J = 7.7 H_Z, quin-H), 7.40(t, 1H, J = 10.3 H_Z, quin-H), 7.30(t, 1H, J = 7.8 H_Z, quin-H,), 7.1(s, 1H, CHHC), 6,70(s, 1H, CHHC), 6.25(d, 1H, J = 15.2 H_Z, $CH_{2linker}$), 5.95(d, 1H, J = 15.3 H_Z, $CH_{2linker}$), 4.40(broad, 2H, COD), 2.90(m, 1H,COD),2.70(m, 1H, J = 4.8 H_Z, COD), 2.30(broad, 4H, COD), 2.2(s, 3H, p-CH3), 1.80(s, 6H, o-CH3), 1.50(m, 4H, J = 5.9 H_Z, COD). ^{13}C NMR ($CDCL_3$, 100MH_Z, 298K):

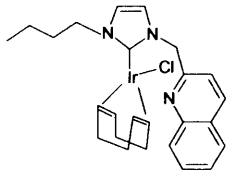
[1-isopropyl-3-(2-methylquinoline)imidazolin-2-ylidene](1,5-cyclooctadiene)iridium(I) Chloride 4.29



Following the procedure for the synthesis of complex was obtained from **3.38** (120mg, 0.250mmmol) and $[IrCl(cod)]_2$ (83 mg, 0.13mmol) . Yield 121 mg (73.78%). Crystals suitable for X- ray crystallography were grown by layering hexane on dichloromethane. Anal. Calcd. for $C_{24}H_{29}N_3IrCl$: C, 49.09; H, 4.94; N, 7.16%. Found: C, 47.98; H, 5.44; N, 6.98%. ^1H NMR ($CDCl_3$. 400MH_Z, 298K): δ 8.10(m, 1H, J = 8.5 H_Z, quin-H), 8.00(d, 1H, J = 8.4 H_Z, quin-H), 7.70(d, 1H, J = 8.2 H_Z, quin-H), 7.65(t, 1H, J = 5.8 H_Z, quin-H), 7.60(d, 1H, J =

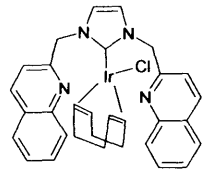
8.5 H_Z, quin-H), 7.45(d, 1H, J = 7.0 H_Z, quin-H), 6.80(s, 2H, CHHC), 6.35(d, 1H, J = 14.8 H_Z, $CH_{2linker}$), 5.60(m, 1H, J = 6.8 H_Z, iPr-H), 5.50(d, 1H, J = 14.8 H_Z, $CH_{2linker}$), 4.60(m, 1H, J = 3.5 H_Z, COD), 4.50(m, 1H, J = 4.2 H_Z, COD), 3.0(m, 1H, J =5.2 H_Z, COD), 2.80(m, 1H, J = 4.0 H_Z, COD), 2.20(m, 4H, J = 6.9 H_Z, COD), 1.6(m, 4H, J = 6.6 H_Z, COD), 1,3(d, 6H, J = 8.0 H_Z, CH_3). ^{13}C NMR ($CDCL_3$, 100MH_Z, R.T): 178.66(C-Ir), 155.72, 146.45, 136.45, 128.73, 127.97, 126.76, 126.62, 125.67, 124.76, 119.86, 115.80, 84.35, 83.04, 55.73, 52.42, 51.23, 33.20, 31.87, 29.14, 28.03, 22.97, 22.08. LRMS-ES for $[M - Cl]^+$ = 552.23(100%).

[1-n-butyl-3-(2-methylquinoline)imidazolin-2-ylidene](1,5-cyclooctadiene) iridium(I) Chloride 4.30



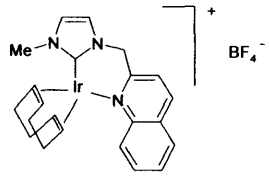
Following the procedure for the synthesis of complex was obtained from **3.39** (150mg, 0.30mmol) and $[IrCl(cod)]_2$ (74 mg, 0.15mmol) . Yield:125 mg (69.44%). Anal. Calcd. for $C_{25}H_{31}N_3IrCl$: C, 49.94; H, 5.16; N, 6.99%. Found: C, 49.42; H, 5.43; N, 4.86%. ^1H NMR ($CDCl_3$. 400MH_Z, 298K): δ 8.1(m, 1H, J = 8.5 H_Z quin-H), 8.0(d, 1H, J = 8.5 H_Z, quin-H), 7.75(d, 1H, J = 8.0 H_Z, quin-H), 7.65(t, 1H, J = 7.1 H_Z quin-H), 7.55(d, 1H, J = 8.5 H_Z, quin-H), 7.45(d, 1H, J = 7.1 H_Z quin-H), 6.80(s, 2H, CHHC), 6.35(d, 1H, J = 14.8 H_Z, $CH_{2linker}$), 5.55(d, 1H, J = 14.8 H_Z, $CH_{2linker}$), 4.60(broad, 2H, COD), 4.40(m, 2H, J = 6.0 H_Z, CH_2), 2.90(m, 2H, J = 7.3 H_Z COD), 2.20(m, 2H, J = 5.5 H_Z CH_2), 1.60(m, 4H, J = 8.3 H_Z, COD) 1.4(m 2H, J = 7.3 H_Z, CH_2), 1.00(t, 3H, J = 7.3 H_Z, CH_3). ^{13}C NMR ($CDCL_3$, 100MH_Z, R.T): 179.56(C-Ir), 155.67, 146.44, 136.43, 128.73, 127.97, 126.75, 126.61, 125.68, 119.73, 119.57, 119.47, 83.93, 83.64, 55.65, 51.07, 50.79, 49.27, 32.58, 31.91, 30.56, 29.94, , 28.55, 21.63, 19.04, 13.12.

[bis-1,3-(2-methylquinoline)imidazolin-2-ylidene](1, 5-cyclooctadiene)iridium(I) Chloride 4.31



Following the procedure for the synthesis of complex was obtained from **3.41** (300mg, 0.600mmmol) and $[IrCl(cod)]_2$ (200 mg, 0.30mmol) . Yield: 261 mg (62.14%). Crystals suitable for X- ray crystallography were grown by layering hexane on dichloromethane. Anal. Calcd. for $C_{31}H_{30}N_4IrCl$: C, 54.23; H, 4.37; N, 8.16%. Found: C, 53.73; H, 4.30; N, 7.71%. ^1H NMR ($CDCl_3$. 400MH_Z, 298K): δ 8.1(m, 2H, J = 8.5 H_Z, quin-H), 8.00(d, 2H, J = 8.5 H_Z, quin-H), 7.75(d, 2H, J = 8.2 H_Z, quin-H), 7.65(m, 4H, J = 4.6 H_Z, quin-H), 7.50(t, 2H, J = 7.0 H_Z, quin-H), 6.85(s, 2H, CHHC), 6.25(d, 1H, J = 14.9 H_Z, $CH_{2linker}$), 5.65(d, 1H, J = 14.9 H_Z, $CH_{2linker}$), 4.60(m, 2H, J = 2.8 H_Z, COD), 2.90(m, 2H, J = 3.0 H_Z, COD), 2.10(m, 4H, J = 3.4 H_Z, COD), 1.70(m, 4H, J = 11.6 H_Z, COD). ^{13}C NMR ($CDCL_3$, 100MH_Z, 298K): 180.57(C-Ir), 155.43, 146.52, 136.48, 128.81, 128.03, 126.74, 126.60, 125.75, 120.25, 119.60, 84.73(CH_2) 64.85, 55.53, 51.48, 32.47, 28.48, 14.26.

1-methyl-3-(2-methylquinoline)imidazolin-2-ylidene](1,5-cyclooctadiene)iridium(I) tetraflouroborate 4.32



$AgBF_4$ (18 mg, 0.092mmol) was added to a stirred solution of complex **4.27**(50 mg, 0.089mmol) in 10 ml of DCM. The reaction mixture was stirred for 1 hour and reaction filtered through celite to remove silver chloride and any insoluble

residue. The filtrates was then added drop by drop to a stirring solution of hexane to precipitate the compound which was then dried in vacuum to afford the desired compound as a deep yellow powder(42.00 mg, 60.87%). Anal. Calcd. for $C_{22}H_{25}N_3IrBF_4$: C, 43.33; H, 4.09; N, 6.89%. Found: C, 35.11; H, 3.10; N, 5.09%. ^{1}H NMR ($CDCl_3$. 400MHz, 298K): δ 8.80(d, 1H, J = 8.6 Hz, quin-H), 8.25(d, 1H, J = 8.4 Hz, quin-H), 8.10(d, 1H, J = 8.4 Hz, quin-H), 7.90(t, 1H, J = 8.2 Hz, quin-H), 7.85(t, 1H, J = 8.2 Hz, quin-H), 7.60(t, 1H, J = 7.7 Hz, quin-H), 7.55(s, 1H, CHHC), 6.80(s,1H, CHHC),5.90(d, J = 15.4 Hz, 1H, $CH_{2linker}$), 5.70(d, 1H, J = 15.4 Hz, $CH_{2linker}$), 5.50(broad, 1H, COD), 4.70 (m, 1H, J = 5.2 Hz, COD), 4.00(m, 2H, J = 8.4 Hz, COD),3.80(m, 1H, J = 4.2 Hz, COD), 3.70(s, 3H, CH3), 2.75(m, 1H, J = 10.2 Hz, COD), 2.3(m, 4H, J = 7.4 Hz, COD), 2.0(m, 2H, J = 6.7 Hz, COD).

4.5.2: Catalysis

General Comments. All air sensitive experiments were performed under nitrogen atmosphere in an MBraun glove box or under dinitrogen by standard Schlenk techniques. Isopropanol was distilled from calcium hydride under N_2 atmosphere. The iridium complexes were synthesised as described above and ^{1}H NMR spectra were recorded using a Bruker Advance DPX_{400} spectrometer.

4.5.3 Transfer hydrogenation

The iridium catalyst precursor was dissolved in a solution of K^{t}BuO (1 mmol) in 2-propanol and 4-bromoacetophenone (1 mmol) was added in a Schlenk tube. The solution heated to 353K for 24 hours, volatiles were evaporated and the percentage conversion was calculated by ^{1}H NMR.

The progress of the reaction was monitored by GC-MS analysis in order to calculate the time dependence of the transfer hydrogenation of 4-bromoacetophenone. Aliquots of 0.1 mL were taken every 10 minutes for the first 1 hour and every 30 minutes for the next hours. The samples were filtered through a short pad of silica, and the silica was washed with DCM.

4.5.4 X-Ray crystallography

Standard conditions as outlined in section 2.4.7 were used.

Table 4.14: Crystal data and structure refinement for 4.20

Empirical formula	$C_{22}H_{25}RhN_3Cl$	
Formula weight	469.81	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.5160(2) Å	α = 94.2310(10)°
	b = 11.4580(3) Å	β = 99.2930(10)°
	c = 11.6750(4) Å	γ = 99.204(2)°
Volume	974.31(5) $Å^3$	
Z	2	
Density (calculated)	1.602Mg/m^3	
Absorption coefficient	1.025mm-1	
F000	480	
Crystal size	0.13 x 0.07 x 0.01 mm^3	
Theta range for data collection	3.03 to 27.47 °	
Index ranges	-9<=h<=9, -14<=k<=14, -15<=l<=15	
Reflections collected	15668	
Independent reflection	4449[R_{int} = 0.1609]	
Completeness of theta = 27.47°	99.50%	
Absorption correction	Semi-empirical from equivalents	
Max and min. transmission	0.8782 and 0.9898	
Refinement method	Full matrix least square on F^2	
Data/restraints/parameters	4449/0/245	
Goodness of fit on F^2	1.044	
Final R indices [I>2 sigma(I)]	R1 = 0.1609, wR2 = 0.1153	
R indices (all data)	R1 = 0.641, wR2 = 0.1488	
Largest diff. peak hole	1.426 and-2.812e $Å^{-3}$	

Table 4.15: Crystal data and structure refinement for 4.21

Empirical formula	$C_{30}H_{33}RhN_3Cl$	
Formula weight	573.95	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P212121	
Unit cell dimensions	a = 9.9380(2) Å	$\alpha = 90^o$
	b = 14.6240(3) Å	$\beta = 90^o$
	c = 17.8520(4) Å	$\gamma = 90^o$
Volume	2594.49(9) $Å^3$	
Z	4	
Density (calculated)	1.469Mg/m^3	
Absorption coefficient	0.785mm-1	
F000	1184	
Crystal size	0.10 x 0.05 x 0.05 mm^3	
Theta range for data collection	3.03 to 27.51 °	
Index ranges	-10<=h <12, -18<=k<=18, -23<=l<=23	
Reflections collected	43795	
Independent reflection	5932[R_{int} = 0.0689]	
Completeness of theta = 27.51°	99.60%	
Absorption correction	Semi-empirical from equivalents	
Max and min. transmission	0.9618 and 0.9256	
Refinement method	Full matrix least square on F^2	
Data/restraints/parameters	5932/0/319	
Goodness of fit on F^2	1.053	
Final R indices [I>2 sigma(I)]	R1 = 0.0537, wR2 = 0..0882	
R indices (all data)	R1 = 0..0423, wR2 = 0.0836	
Largest diff. peak hole	0.560 and-0.722e $Å^{-3}$	

Table 4.16: Crystal data and structure refinement for 4.22

Empirical formula	$C_{24}H_{30}RhN_3Cl$	
Formula weight	540.33	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P212121	
Unit cell dimensions	a = 13.1930(10) Å	$\alpha = 90^o$
	b = 20.8640(2) Å	$\beta = 90^o$
	c = 8.5280(4) Å	$\gamma = 90^o$
Volume	2347.41(11) $Å^3$	
Z	4	
Density (calculated)	1.529Mg/m^3	
Absorption coefficient	0.972mm-1	
F000	1108	
Crystal size	0.25 x 0.22 x 0.10 mm^3	
Theta range for data collection	3.01 to 27.61 °	
Index ranges	-17<=h< 17, -26<=k<=27, -10<=l<=11	
Reflections collected	38012	
Independent reflection	5371[R_{int} = 0.0669]	
Completeness of theta = 27.61°	98.70%	
Absorption correction	Semi-empirical from equivalents	
Max and min. transmission	0.9090 and 0.7931	
Refinement method	Full matrix least square on F^2	
Data/restraints/parameters	5371/3/292	
Goodness of fit on F^2	1.057	
Final R indices [I>2 sigma(I)]	R1 = 0.0669, wR2 = 0.1103	
R indices (all data)	R1 = 0..0457, wR2 = 0.0996	
Largest diff. peak hole	0.840 and-0.902e $Å^{-3}$	

Table 4.17: Crystal data and structure refinement for 4.23

Empirical formula	$C_{25}H_{31}RhN_3Cl$
Formula weight	511.89

Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.0680(3) Å	$\alpha = 95.0950(10)^{o}$
	b = 10.6960(3) Å	$\beta = 91.6400(10)^{o}$
	c = 10.8350(4) Å	$\gamma = 98.0910(10)^{o}$
Volume	1149.61(6) $Å^3$	
Z	2	
Density (calculated)	1.479Mg/m^3	
Absorption coefficient	0.876mm-1	
F000	528	
Crystal size	0.50 x 0.50 x 0.05 mm^3	
Theta range for data collection	3.01 to 27.53 °	
Index ranges	-12<=h< 13, -13<=k<=13, -14<=l<=14	
Reflections collected	19594	
Independent reflection	5209[R_{int} = 0.0956]	
Completeness of theta = 27.53°	98.50%	
Absorption correction	Semi-empirical from equivalents	
Max and min. transmission	0.9575 and 0.6686	
Refinement method	Full matrix least square on F^2	
Data/restraints/parameters	5371/3/292	
Goodness of fit on F^2	1.060	
Final R indices [I>2 sigma(I)]	R1 = 0.0851, wR2 = 0.1124	
R indices (all data)	R1 = 0..0504, wR2 = 0.0978	
Largest diff. peak hole	0.747 and-1.059e $Å^{-3}$	

Table 4.18: Crystal data and structure refinement for 4.24

Empirical formula	$C_{31}H_{30}RhN_4Cl$
Formula weight	600.90
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic

Space group	P-1	
Unit cell dimensions	a = 11.8769(2) Å	α = 89.9829(10)°
	b = 11.9874(2) Å	β = 118.0475(10)°
	c = 12.3176(2) Å	γ = 106.1171(9)°
Volume	1469.26(4) $Å^3$	
Z	2	
Density (calculated)	1.541Mg/m^3	
Absorption coefficient	0.883mm-1	
F000	696	
Crystal size	0.25 x 0.25 x 0.38 mm^3	
Theta range for data collection	3.114 to 27.643 °	
Index ranges	-15<=h< 15, -15<=k<=15, -15<=l<=16	
Reflections collected	24833	
Independent reflection	11368[R_{int} = 0.052]	
Completeness of theta = 27.643°	97.20%	
Absorption correction	Semi-empirical from equivalents	
Max and min. transmission	0.800 and 0.800	
Refinement method	Full matrix least square on F^2	
Data/restraints/parameters	11368/0/362	
Goodness of fit on F^2	0.9877	
Final R indices [I>2 sigma(I)]	R1 = 0.0526, wR2 = 0.1120	
R indices (all data)	R1 = 0.0461, wR2 = 0.1073	
Largest diff. peak hole	1.63 and-1.88e $Å^{-3}$	

Table 4.19: Crystal data and structure refinement for 4.28

Empirical formula	$C_{30}H_{33}IrN_3Cl$	
Formula weight	663.28	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P212121	
Unit cell dimensions	a = 9.9463(2) Å	α = 90°
	b = 14.5997(3) Å	β = 90°

	c = 17.8669(5) Å	γ = 90°
Volume	2594.51(10) $Å^3$	
Z	4	
Density (calculated)	1.698Mg/m^3	
Absorption coefficient	5.273mm-1	
F000	1312	
Crystal size	0.04 x 0.17 x 0.38 mm^3	
Theta range for data collection	3.014 to 27.394 °	
Index ranges	-12<=h< 10, -18<=k<=18, -23<=l<=23	
Reflections collected	42001	
Independent reflection	5841[R_{int} = 0.199]	
Completeness of theta = 27.394°	99.30%	
Absorption correction	Semi-empirical from equivalents	
Max and min. transmission	0.8100 and 0.4100	
Refinement method	Full matrix least square on F^2	
Data/restraints/parameters	5841/0/317	
Goodness of fit on F^2	0.5948	
Final R indices [I>2 sigma(I)]	R1 = 0.0740, wR2 = 0.1219	
R indices (all data)	R1 = 0.0422, wR2 = 0.997	
Largest diff. peak hole	2.85 and-3.59e $Å^{-3}$	

Table 4.20: Crystal data and structure refinement for 4.29

Empirical formula	$C_{24}H_{30}IrN_3Cl$	
Formula weight	629.61.28	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P212121	
Unit cell dimensions	a = 8.562(2) Å	α = 90°
	b = 13.267(3) Å	β = 90°
	c = 21.012(5) Å	γ = 90°
Volume	2386.80(10) $Å^3$	
Z	4	

Density (calculated)	1.752Mg/m^3
Absorption coefficient	5.835mm-1
F000	1236
Crystal size	0.20 x 0.20 x 0.10 mm^3
Theta range for data collection	2.57 to 33.73 °
Index ranges	-13<=h< 13, -20<=k<=20, -32<=l<=32
Reflections collected	9511
Independent reflection	9511[R_{int} = 0.0589]
Completeness of theta = 33.73°	99.80%
Absorption correction	Semi-empirical from equivalents
Max and min. transmission	0.5930 and 0.3882
Refinement method	Full matrix least square on F^2
Data/restraints/parameters	9511/9/291
Goodness of fit on F^2	1.036
Final R indices [I>2 sigma(I)]	R1 = 0.065, wR2 = 0.1242
R indices (all data)	R1 = 0.0500, wR2 = 0.1144
Largest diff. peak hole	3.528 and-2.850e $Å^{-3}$

Table 4.21: Crystal data and structure refinement for 4.31

Empirical formula	$C_{31}H_{30}IrN_4Cl$	
Formula weight	686.28	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P - 1	
Unit cell dimensions	a = 6.59420(10) Å	α = 104.4358(8)°
	b = 12.1294(2) Å	β = 100.9896(8)°
	c = 17.2628(3) Å	γ = 97.8041(10)°
Volume	1298.61(4) $Å^3$	
Z	4	
Density (calculated)	1.755Mg/m^3	
Absorption coefficient	5.272mm-1	
F000	676	

Crystal size	0.15 x 0.20 x 0.38 mm^3
Theta range for data collection	3.158 to 27.503 °
Index ranges	-8<=h< 7, -15<=k<=15, -21<=l<=22
Reflections collected	22471
Independent reflection	21713[R_{int} = 0.073]
Completeness of theta = 23.503°	99.50%
Absorption correction	Semi-empirical from equivalents
Max and min. transmission	0.45 and 0.35
Refinement method	Full matrix least square on F^2
Data/restraints/parameters	10018/0/335
Goodness of fit on F^2	0.9719
Final R indices [I>2 sigma(I)]	R1 = 0.0469, wR2 = 0.1073
R indices (all data)	R1 = 0.0417, wR2 = 0.1029
Largest diff. peak hole	2.13 and-1.79e $Å^{-3}$

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CHAPTER FIVE

5.1 Conclusions

Ligands containing both phosphorus and nitrogen donor have been shown to form strong metal phosphorus bonds and weak nitrogen bonds [1] and are important in many catalytic reactions [2, 3]. In realisation of this many groups have made the natural progression from unidentate mono carbenes towards mixed donor chelating carbenes. The interest stems from the potential advantages a hemilabile ligand may offer to a catalytic reaction. A number of research groups have successfully incorporated a second donor to the carbene ligand, with early progress being made with pyridine functions as the N-substituents [1, 4, and 5]. In furtherance of the use of a hemilabile group on N-substituents quinoline based imidazolium salts were thought to be ideal candidates. Towards this end, a series of quinoline based imidazolidinium salts have been synthesised and characterised as precursors to the corresponding NHC ligands. A range of N-substituents imparts variable steric bulk to the imidazolium rings.

Crystallographically characterised examples include the saturated 1, 3-diquinolin-4, 5-dihydroimidazoluim tetraflouroborate **2b,** the unsaturated imidazolium salts **6a-6c**, and the analogous methylene bridged quinoline-functionalised imidazolium salts **9a- 9f**.

An additional example reported includes the acridine based imidazolium salt **16** which can offer a secondary donor group for chelation as well as sp3 hybridized carbons. The sp3 hybridized carbon can make the ligand chiral and increase the steric bulk if required.

Quinoline based pyrimidinium salt **4** was also prepared following the same procedure for 2b was crystallographically characterised. All the quinoline based salts are new compound as there is no reported synthesis of any of them

Ag^{I}(NHC) complexes have reported to be a versatile transmetallation reagents for the preparation of transition metal- NHC complexes. Accordingly, a range of Ag^{I} complexes of methylene bridge quinoline functionalised NHC ligands were prepared by reaction of the corresponding imidazolium salts with Ag_2O in

DCM. Of these Ag^{I}(NHC) complexes **3.36-3.41**, two (**3.36** and **3.37**) were Crystallographically characterised with the silver geometry in both cases being a quasi linear. Additional Ag^{I} complexes of quinoline functionalised NHC ligands were synthesised in a similar manner and utilised as transmetallation agent in the synthesis of Pd^{II}(NHC) complexes **3.42** and **3.43**. Efforts to prepare other Pd^{II}(NHC) complexes were not successful due to high insolubility of the complexes in most solvents. Indeed difficulty was encountered in separating the desired complexes from the silver halides.

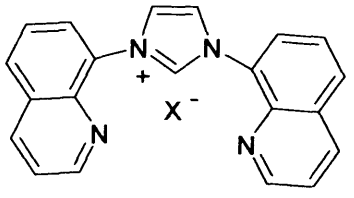
The synthesis of a series of Rh(I) (NHC) of the methylene bridged quinoline functionalised NHC ligands via transmetallation from Ag(I) complexes is reported. All the rhodium complexes were fully characterised and the crystallographic data show consistent pattern. The reaction of the $[Rh(cod)Cl]_2$ with Ag_2O gave the neutral rhodium complexes **4.20-4.24** and there was no evidence of chelation between the nitrogen of the quinoline ring and the rhodium metal as evidenced by the ^{1}H NMR data being essentially similar to that of the corresponding Ag(I) complexes from which they were made. Chelation was achieved by the reaction of Rh(I) (NHC) complexes with one equivalent of $AgBF_4$ in DCM. However the chelated Rh(I) (NHC) complexes could not be fully characterised due to high insolubility of the compounds in most solvent. Attempts to improve the solubility by replacing the tetraflouroborate counter ion with Barf solve the problem of solubility but difficulty was encountered in separation.

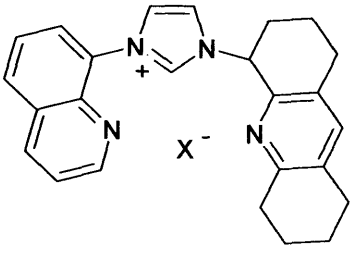
In a similar fashion Ir (I) (NHC) complexes **4.27-4.32** were synthesised via transmetallation of the corresponding Ag(I) complexes with $[Ir(cod)Cl)_2$ in DCM. The trend observed for the rhodium complexes are essentially similar to that of the iridium complexes. Thus both chelated and non chelated Ir(I) (NHC) complexes were prepared.

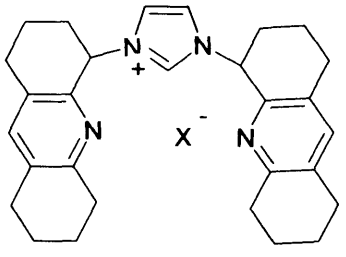
Finally two of the neutral Ir (I) (NHC) complexes prepared **4.27** and **4.31** were catalytically tested towards transfer hydrogenation of 4-bromoacetophenone. The two iridium complexes have shown good activity upon hydrogen transfer reduction of carbonyl in 4-bromoacetophenone at different catalyst concentrations.

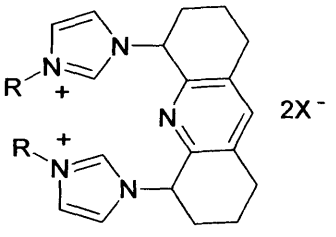
5.2 Future work

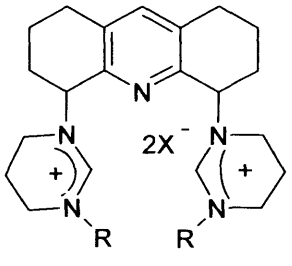
Attempts to prepare the unsymmetrical quinoline based unsaturated imidazolium and pyrimidinium salts following the established procedures [5] were not successful. However it will be interesting if the following quinoline and acridine based ligands will be prepared and investigated.

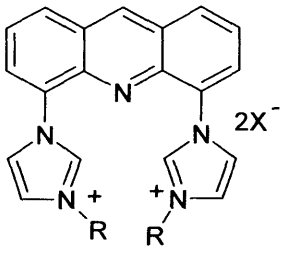


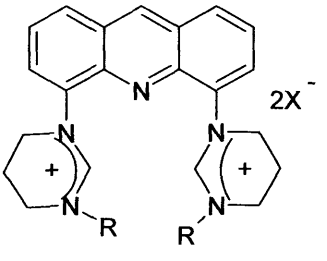












It will be interesting to compare these potential pincer ligands with the pincer ligands reported by Gibson, Cavell, Danopoulos and Crabtree.

Also to be investigated are the metal complexes **2b** and **4** which we were unable to prepare in this work.

It is recommended that the quinoline based palladium complexes prepared in this work be tested in some important catalytic reactions such as Heck coupling reactions.

The Rh(I) and Ir(I) (NHC) complexes should be tested in different catalytic reaction such as reduction of alkenes via direct hydrogenation and transfer hydrogenation. Efforts should be to isolate pure soluble chelated versions of the

Rh(I) and Ir(I) (NHC) complexes , their catalytic activities compared with that of the unchelated complexes and the results obtained compared with that of the iridium pyridinyl N-heterocyclic carbene complexes reported by Wang et al [6]. Other interesting future work will be to look into the metal complexes of the ligands reported in chapter two such as Pt, Ni, Co, and Fe.

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APPENDIX

Tables of bond distances and angles

Table A1.1: Bond lengths for 1, 3-diquinoline-3, 4, 5, 6-tetrahydropyrimidinium hexaflouro phosphate (**4**):

Bond lengths (Å)		Bond lengths (Å)		Bond lengths (Å)	
C1- N2	1.317(3)	C9- C13	1.419(3)	C21- N4	1.323(3)
C1- N1	1.317(3)	C10 -C11	1.351(3)	C21- H21	0.9500
C1- H1	0.9500	C10- H10	0.9500	C22- N4	1.372(3)
C2- N1	1.479(3)	C11- C12	1.413(3)	F1-P1	1.6054(16)
C2- C3	1.513(3)	C11- H11	0.9500	F2-P1	1.5933(18)
C2- H2A	0.9900	C12- N3	1.322(3)	F3-P1	1.5912(16)
C2 -H2B	0.9900	C12- H12	0.9500	F4-P1	1.5876(18)
C3- C4	1.507(3)	C13 -N3	1.370(3)	F5-P1	1.5784(18)
C3- H3A	0.9900	C14-C15	1.371(3)	F6-P1	1.5853(17)
C3- H3B	0.9900	C14- C22	1.425(3)		
C4 -N2	1.485(3)	C14 -N2	1.429(3)		
C4- H4A	0.9900	C15- C16	1.405(3)		
C4- H4B	0.9900	C15- H15	0.9500		
C5 -C6	1.365(3)	C16- C17	1.365(3)		
C5- C13	1.422(3)	C16 -H16	0.9500		
C5- N1	1.439(3)	C17- C18	1.415(3)		
C6- C7	1.417(3)	C17 -H17	0.9500		
C6- H6	0.9500	C18- C22	1.415(3)		
C7 -C8	1.356(4)	C18- C19	1.422(3)		
C7- H7	0.9500	C19- C20	1.353(4)		
C8- C9	1.417(3)	C19 -H19	0.9500		
C8- H8	0.9500	C20- C21	1.403(4)		
C9- C10	1.418(3)	C20- H20	0.9500		
Bond angles (°)		Bond angles (°)		Bond angles (°)	
N2- C1- N1	124.2(2)	C7- C8- H8	119.6	C20-C19-C18	119.4(2)
N2- C1- H1	117.9	C9- C8- H8	119.6	C20- C19- H19	120.3

N1- C1- H1	117.9	C8-C9-C10	122.8(2)	C18- C19- H19	120.3
N1-C2-C3	109.03(18)	C8-C9-C13	119.3(2)	C19-C20-C21	119.2(2)
N1- C2- H2A	109.9	C10-C9-C13	117.9(2)	C19-C20-H20	120.4
C3- C2- H2A	109.9	C11-C10-C9	119.5(2)	C21-C20-H20	120.4
N1- C2- H2B	109.9	C11-C10-H10	120.3	N4-C21-C20	124.6(2)
C3- C2- H2B	109.9	C9- C10- H10	120.3	N4-C21-H21	117.7
H2A- C2- H2B	108.3	C10-C1-C12	118.7(2)	C20-C21-H21	117.7
C4-C3-C2	109.48(19)	C10-C11-H11	120.7	N4-C22-C18	123.2(2)
C4- C3- H3A	109.8	C12-C11-H11	120.7	N4-C22-C14	118.6(2)
C2- C3- H3A	109.8	N3-C12-C11	124.6(2)	C18-C22-C14	118.2(2)
C4- C3- H3B	109.8	N3-C12-H12	117.7	C1-N1-C5	120.71(18)
C2- C3- H3B	109.8	C11-C12-H12	117.7	C1-N1-C2	120.41(18)
H3A- C3 -H3B	108.	N3-C13-C9	122.2(2)	C5-N1-C2	118.73(18)
N2-C4-C3	108.91(17)	N3-C13-C5	119.63(19)	C1-N2-C14	120.32(18)
N2- C4- H4A	109.9	C9-C13-C5	118.18(19)	C1-N2-C4	120.78(19)
C3- C4- H4A	109.9	C15-C14-C22	120.7(2)	C14-N2-C4	118.88(17)
N2- C4- H4B	109.9	C15-C14-N2	120.38(19)	C12-N3-C13	117.06(19)
C3- C4 -H4B	109.9	C22-C14-N2	118.9(2)	C21-N4-C22	116.5(2)
H4A- C4- H4B	108.3	C14-C15-C16	120.3(2)	F5-P1-F6	91.17(11)
C6- C5 -C13	121.4(2)	C14-C15-H15	119.8	F5-P1-F4	90.55(12)
C6- C5- N1	120.3(2)	C16-C15-H15	119.8	F6-P1-F4	90.78(11)
C13-C5-N1	118.33(19)	C17-C16-C15	120.6(2)	F5-P1-F3	89.22(10)
C5- C6- C7	119.7(2)	C17-C16-H16	119.7	F6-P1-F3	179.52(11)
C5- C6- H6	120.2	C15-C16-H16	119.7	F4-P1-F3	89.49(10)
C7 -C6 -H6	120.2	C16-C17-C18	120.3(2)	F5-P1-F2	179.18(11)
C8- C7- C6	120.6(2)	C16-C17-H17	119.8	F6-P1-F2	89.24(11)
C8- C7 -H7	119.7	C18-C17-H17	119.8	F3-P1-F2	90.36(10)
C6- C7- H7	119.7	C22-C18-C17	119.8(2)	F5-P1-F1	90.66(10)
C7- C8 -C9	120.9(2)	C22-C18-C19	117.1(2)	F6-P1-F1	90.50(10)
		C17-C18-C19	123.1(2)	F4-P1-F1	178.22(11)
				F3-P1-F1	89.22(9)
				F2-P1-F1	88.64(9)

Table A1.2: Bond Lengths and angles for 1-benzyl-3-quinolinimidazolium tetraflouroborate (**6a**):

Bond lengths (Å)		Bond lengths (Å)	
F1-B2	1.386(2)	C15-H151	0.994
B2-F3	1.386(2)	C16-C17	1.404(3)
B2-F4	1.387(2)	C16-H161	0.942
B2-F5	1.387(2)	C17-H171	0.944
N6-C7	1.391(2)	C18-C19	1.419(2)
N6-C10	1.3405(19)	C18-C27	1.369(2)
N6-C18	1.4411(19)	C19-N20	1.367(2)
C7-C8	1.349(2)	C19-C24	1.424(2)
C7-H71	0.961	N20-C21	1.315(2)
C8-N9	1.381(2)	C21-C22	1.416(2)
C8-H81	0.963	C21-H211	0.942
N9-C10	1.324(2)	C22-C23	1.361(2)
N9-C11	1.4846(19)	C22-H221	0.946
C10-H101	0.961	C23-C24	1.411(2)
C11-C12	1.498(2)	C23-H231	0.964
C11-H111	1.005	C24-C25	1.417(2)
C11-H112	0.922	C25-C26	1.365(2)
C12-C13	1.389(3)	C25-H251	0.972
C12-C17	1.376(3)	C26-C27	1.410(2)
C13-C14	1.381(3)	C26-H261	1.000
C13-H131	0.922	C27-H271	0.956
C14-C15	1.360(4)		
C14-H141	0.955		
C15-C16	1.373(4)		

Bond angles (°)		Bond angles (°)	
F1-B2-F3	108.2815)	C15-C16-H161	122.2
F1-B2-F4	109.03(16)	C17-C16-H161	117.7
F3-B2-F4	110.49(16)	C16-C17-C12	119.8(2)
F1-B2-F5	110.07(15)	C16-C17-H171	123.0

F3-B2-F5	109.55(16)	C12-C17-H171	117.1
F4-B2-F5	109.40(15)	C14-C15-H151	118.7
C7-N6-C10	108.30(13)	C16-C15-H151	120.9
C7-N6-C18	124.30(13)	C15-C-16-C17	120.0(2)
C10-N6-C18	127.40(13)	N6-C18-C19	119.76(14)
N6-C7-C8	106.97(14)	N6-C18-C27	118.31(14)
N6-C7-H71	124.4	C19-C18-C27	121.88(14)
C8-C7-H71	128.6	C18-C19-N20	119.85(14)
C7-C8-N9	107.09(15)	C18-C19-C24	117.31(14)
C7-C8-H81	131.2	N20-C19-C24	122.83(15)
N9-C8-H81	121.7	C19-N20-C21	117.12(14)
C8-N9-C10	109.25(13)	N20-C21-C22	124.60(15)
C8-N9-C11	125.68(14)	N20-C21-H211	116.6
C10-N9-C11	124.91(14)	C22-C21-H211	118.8
N6-C10-N9	108.38(14)	C21-C22-C23	118.32(16)
N6-C10-H101	124.8	C21-C22-H221	123.0
N9-C10-H101	126.8	C23-C22-H221	118.7
N9-C11-C12	111.31(14)	C22-C23-C24	119.98(15)
N9-C11-H111	110.0	C22-C23-H231	119.9
C12-C11-H111	110.2	C24-C23-H231	120.1
N9-C11-H112	100.3	C19-C24-C23	117.13(15)
C12-C11-H112	111.1	C19-C24-C25	119.96(15)
H11-C11-H112	113.6	C23-C24-C25	122.91(14)
C11-C12-C13	119.83(18)	C24-C25-C26	120.57(15)
C11-C12-C17	121.41(18)	C24-C25-H251	117.2
C13-C12-C17	118.75(19)	C26-C25-H251	122.3
C12-C13-C14	121.2(2)	C25-C26-C27	120.31(15)
C12-C13-H131	118.5	C25-C26-H261	121.8
C14-C13-H131	120.3	C27-C26-H261	117.8
C13-C14-C15	119.8	C26-C27-C18	119.95(15)
C13-C14-H14	117.5	C26-C27-H27	118.2
C15-C14-H141	122.5	C18-C27-H271	121.8
C14-C15-C16	120.4(2)		

Table A1.3: Bond length for 1-methyl-3-qiunolinimidazolium iodide (**6c**)

Bond lengths (Å)		Bond lengths (Å)	
C1-C2	1.367(4)	C8-N1	1.325(4)
C-C9	1.428(4)	C8-H8	0.9500
C1-N2	1.439(4)	C9-N1	1.365(4)
C2-C3	1.411(4)	C10-N3	1.319(4)
C2-H2	0.9500	C10-N2	1.340(4)
C3-C4	1.364(4)	C10-H10	0.9500
C3-H3	0.9500	C11-C12	1.347(4)
C4-C5	1.409(4)	C11-N2	1.386(4)
C4-H4	0.9500	C11-H11	0.9500
C5-C6	1.420(4)	C12-N3	1.382(4)
C5-C9	1.423(4)	C12-H12	0.9500
C-C7	1.356(4)	C13-N3	1.461(4)
C6-H6	0.9500	C13-H13A	0.9800
C7-C8	1.399(4)	C13-H13B	0.9800
C7-H7	0.9500	C13-H13C	0.9800

Table A1.4: Bond angles for 1-methyl-3-qiunolinimidazolium iodide (**6c**)

Bond angles (°)		Bond angles (°)	
C2-C1-C9	121.3(3)	N1-C9-C1	119.5(2)
C2-C1-N2	118.7(2)	C5-C9-C1	117.2(2)
C9-C1-N2	119.8(2)	N3-C10-N2	108.9(2)
C1-C2-C3	120.5(3)	N3-C10-H10	125.5
C1-C2-H2	119.8	N2-C10-H10	125.5
C3-C2-H2	119.8	C12-C11-N2	106.9
C4-C3-C2	120.0(3)	C12-C11-H11	126.6
C4-C3-H3	120.0	N2-C11-H11	126.6
C2-C3-H3	120.0	C11-C12-N3	107.5(3)
C3-C4-C5	120.7(3)	C11-C12-H12	126.3
C3-C4-H4	119.7	N3-C12-H12	126.3

C5-C4-H4	119.7	N3-C13-H13A	109.5
C4-C5-C6	123.0(3)	N3-C13-H13B	109.5
C4-C5-C9	120.3(2)	H13-A13-13B	109.5
C6-C5-C9	116.7(3)	N3-C13-H13C	109.5
C7-C6-C5	119.5(3)	H13-C13-H13	109.5
C7-C6-H6	120.2	H13-C13-H13C	109.5
C5-C6-H6	120.2	C8-N1-C9	116.8(2)
C6-C7-C8	119.4(3)	C10-N2-C11	108.1(2)
C6-C7-H7	120.3	C10-N2-C1	127.4(2)
C8-C7-H7	120.3	C11-N2-C1	124.4(2)
N1-C8-C7	124.3(3)	C10-N3-C12	108.6(2)
N1-C8-H8	117.9	C10-N3-C13	125.3(3)
C7-C8-H8	117.9	C12-N3-C13	125.9(3)
N1-C9-C5	123.2(2)		

Table A1.5: Bond lengths for 1-mesityl 3-(-2-methylquinoline)imidazolium chloride **9b:**

Bond lengths (Å)		Bond lengths (Å)		Bond lengths (Å)	
C1-N2	1.323(3)	C7-C8	1.389(4)	C19-H19	0.9500
C1-N1	1.340(3)	C7-C11	1.515(4)	C20-C21	1.373(4)
C1-H1	0.9500	C8-C9	1.390(4)	C20-H20	0.9500
C2-C3	1.356(3)	C8-H8	0.9500	C21-C22	1.409(4)
C2-N1	1.374(3)	C9-C12	1.500	C21-H21	0.9500
C2-H2	0.9500	C10-H10A	0.9800	C22-N3	1.374(3)
C3-N2	1.370(3)	C13-N2	1.463(3)	B1-F2	1.333(4)
C3-H3	0.9500	C13-C14	1.506(3)	B1-F4A	
C4-C5	1.392(3)	C13-H13A	0.9900	1.360(10)	
C4-C9	1.402(3)	C13-H13B	0.9900	B1-F3	1.383(3)
C4-N1	1.446(3)	C14-N3	1.306(3)	B1-F1	1.393(4)
C5-C6	1.377(3)	C14-C15	1.406(3)	B1-F4	1.402(3)
C5-C10	1.507(4)	C15-C16	1.354(3)	B1-F2A	1.414(9)

C6-C7	1.382(4)	C15-H15	0.9500	B1-F1A	1.425(8)
C6-H6	0.9500	C16-C17	1.410(4)	F1-F4A	1.06(3)
C10-H10B	0.9800	C16-H16	0.9500	F- F1A	1.57(2)
C10-H10C	0.9800	C17-C22	1.414(3)	F1A-F2	1.17(2)
C11-H11A	0.9800	C17-C18	1.418(3)	F2-F2A	1.23(2)
C11-H11B	0.9800	C18-C19	1.350(4)	F2A-F4	1.58(3)
C11-H11C	0.9800	C18-H18	0.9500	F4-F4A	1.37(3)
C12-H12A	0.9800	C19-C20	1.402(4)		
C12-H12B	0.9800				
C12-H12C	0.9800				

Table A1.6: Bond angles for 1-mesityl 3-(-2-methylquinoline)imidazolium chloride **9b:**

Bond angles (°)		Bond angles (°)	
N2-C1-N1	108.2(2)	C19-C18-H18	119.7
N2-C1-H1	126.5	C17-C18-H18	119.7
N1-C1-H1	125.9	C18-C19-C20	120.5(2)
C-C2-N1	107.0(2)	C18-C19-H19	119.7
C3-C2-H2	126.5	C20-C19-H19	119.7
N1-C2-H2	126.5	C21-C20-C19	120.5(3)
C2-C3-N2	107.0(2)	C21-C20-H20	119.8
C2-C3-H3	126.5	C19-C20-H20	119.8
N2-C3-H3	126.5	C20-C21-C22	120.5(2)
C5-C4-C9	123.0(2)	C20 C21 H21	119.8
C5-C4-N1	119.3(2)	C22-C21-H21	119.8
C9-C4-N1	117.6(2)	N3-C22-C21	119.0(2)
C6-C5-C4	117.5(2)	N3-C22-C17	122.4(2)
C6-C5-C10	120.8(2)	C21-C22-C17	118.7(2)
C4-C5-C10	121.7(2)	C1-N1-C2	108.5(2)
C5-C6-C7	122.5(2)	C1-N1-C4	126.2(2)
C5-C6-H6	118.8	C2-N1-C4	109.3(2)
C7-C6-H6	118.8	C1-N2-C13	125.3(2)
C6-C7-C8	118.0(2)	C3-N2-C13	125.0(2)
C6-C7 -C11	121.1(3)	C14-N3-C22	117.13(19)

C8-C7-C11	120.9(3)	F2-B1-F4A	120.3(10)
C7-C8-C9	122.8(3)	F2-B1-F3	111.9(3)
C7-C8-H8	118.6	F4A-B1-F3	126.9(11)
C9-C8-H8	118.6	F2-B1-F1	111.1(3)
C8-C9-C4	116.1(2)	F4A-B1-F1	45.1(12)
C8-C9-C12	122.2(2)	F3-B1-F1	107.8(3)
C4-C9-C12	121.6(2)	F2-B1-F4	111.4(3)
C5-C10H-10A	109.5	F4A-B1-F4	59.4(12)
C5-C10-0H10B	109.5	F3-B1-F4	110.2(2)
H10A-C10-H10B	109.5	F1-B1-F4	104.1(3)
C5-C10-H10C	109.5	F2-B1-F2A	52.9(11)
H10A-C10-H10C	109.5	F4A-B1-F2A	118.1(16)
H10B-C10-H10C	109.5	F3-B1-F2	100.0(7)
C7-C11-H11A	109.5	F1-B1-F2A	152.0(7)
C7-C11-H11B	109.5	F4-B1-F2A	68.5(12)
H11A-C11-H11B	109.5	F2-B1-F1A	50.2(10)
C7-C11-H11C	109.5	F4A-B1-F1A	102.8(13)
H11A-C11-H11C	109.5	F3-B1-F1A	102.8(6)
H11B-C11-H11C	109.5	F1-B1-F1A	67.7(10)
C9-C12-H12A	109.5	F4-B1-F1A	146.8(7)
C9-C12-H12B	109.5	F2A-B1-F1A	103.0(15)
H12A-C12-H12B	109.5	F4A-F1-B1	65.8(7)
C9-C12-H12C	109.5	F4A-F- F1A	110.5(12)
H12A-C12-H12C	109.5	B1-F1-F1A	57.1(6)
H12B-C12-H12C	109.5	F2-F1A-B1	60.8(5)
N2-C13-C14	112.9(2)	F2-F1A-F1	109.2(8)
N2-C13-H13A	109.0	B1-F1A-F1	55.2(6)
C14-C13-H13A	109.0	F1A-F2-F2A	135.6(10)
N2-C13-H13B	109.0	F1A-F2-B1	68.9(7)
C14-C13-H13B	109.0	F2A-F2-B1	66.9(7)
H13A-C13-H13B	107.8	F2-F2A-B1	60.1(6)
N3-C1-C15	124.4(2)	F2-F2A-F4	106.3(8)
N3-C14-C13	119.7(19)	B1-F2A-F4	55.4(7)
C15-C14-C13	116.5	F4A-F4-B1	58.8(6)

C16-C15-C14	119.2(2)	F4A-F4-F2A	107.1(10)
C16-C15-H15	120.4	B1-F4-F2A	56.1(7)
C14-C15-H15	120.4	F1-F4A-B1	69.0(8)
C15-C16-C17	119.2(2)	F1-F4A-F4	130.1(10)
C15-C16-H16	120.4	B1-F4A-F4	61.8(8)
C17-C16-H16	120.4		
C16-C17-C22	117.7(2)		
C22-C17-C18	119.3(2)		
C19-C18-C17	120.6(2)		

Table A1.7 : Bond lengths for 1-isopropyl -3-(2-methylquinoline) imidazolium iodide (**9c**)

Bond lengths (Å)		Bond lengths (Å)		Bond lengths (Å)	
N1-C1	1.30(2)	C4-C5	1.53(2)	C20-C21	1.52(2)
N1-C2	1.42(2)	C7-C8	1.4888	C20-C22	1.57(2)
N1-C4	1.50(2)	N3-C12	1.3899	C23-C24	1.4359
N2-C3	1.34(2)	N3-C8	1.3899	N6-C28	1.3899
N2-C1	1.369(19)	C8-C9	1.3888	N6-C24	1.3899
N2-C7	1.515(15)	C9-C10	1.3898	C24-C25	1.3888
N4-C18	1.31(2)	C10-C11	1.3899	C25-C26	1.3898
N4-C17	1.37(2)	C11-C12	1.3888	C26-C27	1.3899
N4-C20	1.475(19)	C11-C16	1.3899	C27-C28	1.3888
N5-C17	1.30(2)	C12-C13	1.3899	C27-C32	1.3899
N5-C19	1.41(2)	C13-C14	1.3898	C28-C29	1.3899
N5-C23	1.421(16)	C14-C15	1.3888	C29-C30	1.3898
C2-C3	1.35(3)	C15-C16	1.3899	C30-C31	1.3888
C4-C6	1.46(2)	C18-C19	1.34(3)	C31-C32	1.3888

Table A1.8 : Bond angles for 1-isopropyl -3-(2-methylquinoline) imidazolium iodide (**9c**)

Bond angles (°)		Bond angles (°)	
C1-N1-C2	111.4(11)	C11-C12-C13	120.0
C1-N1-C4	124.4(11)	N3-C12-C13	120.0
C2-N1-C4	124.2(12)	C14-C13-C12	120.0
C3-N2-C1	109.8(15)	C15-C14-C13	120.0
C3-N2-C7	120.7(13)	C14-C15-C16	120.0
C1-N2-C7	129.5(13)	C11-C16-C15	120.1
C18-N4-C17	104.7(15)	N5-C17-N4	111.2(14)
C18-N4-C20	128.7(15)	N4-C18-C19	112.5(16)
C17-N4-C20	126.5(14)	C18-C19-N5	104.8(15)
C17-N5-C19	106.8(15)	N4-C20-C21	109.9(13)
C17-N5-C23	124.5(11)	N4-C20-C22	107.6(14)
C19-N5-C23	128.5(13)	C21-C20-C22	114.3(15)
N1-C1-N2	105.9(12)	N5-C23-C24	120.1(5)
C3-C2-N1	103.6(13)	C28-N6-C24	120.1
N2-C3-C2	109.3(16)	C25-C24-N6	120.0
C6-C4-N1	110.5(14)	C25-C24-C23	125.0
C6-C4-C5	109.7(14)	N6-C24-C23	114.8
N1-C4-C5	109.7(13)	C24-C25-C26	120.0
C8-C7-N2	111.2(5)	C25-C26-C27	120.0
C12-N3-C8	120.1	C28-C27-C32	120.0
C9-C8-N3	120.0	C28-C27-C26	120.0
C9-C8-C7	120.7	C32-C27-C26	120.1
N3-C8-C7	119.2	C27-C28-N6	120.0
C8-C9-C10	120.0	C27-C28-C29	120.0
C9-C10-C11	120.1	N6-C28-C29	120.0
C12-C11-C16	120.0	C30-C29-C28	120.0
C12-C11-C10	120.0	C31-C30-C29	120.0
C16-C11-C10	120.1	C30-C31-C32	120.0
C11-C12-N3	120.0	C27-C32-C31	120.1

Table A1.9: Bond lengths for Bis-1, 3- (2-methylquinolin) imidazolium chloride (**9f**)

Bond lengths (Å)		Bond lengths (Å)		Bond lengths (Å)	
N2-C3	1.474(3)	C10-C17	1.415(3)	C19-C24	1.40(3)
N2-C6	1.335(3)	C11-C12	1.413(3)	N20-C21	1.410(4)
N2-C18	1.467(3)	C11-C14	1.420(4)	C21-C28	1.415(3)
C3-C4	1.350(3)	C12-C13	1.362(4)	C22-C23	1.414(3)
C3-H31	0.943	C12-H121	0.942	C22-C25	1.416(4)
C4-N5	1.383(3)	C13-H131	0.940	C23-C24	1.360(3)
C4-H41	0.959	C14-C15	1.370(3)	C23-H231	0.938
N5-C6	1.327(3)	C14-H141	0.933	C24-H241	0.962
N5-C7	1.461(3)	C15-C16	1.400(3)	C25-C26	1.366(4)
C6-H61	0.940	C15-H151	0.956	C25-H251	0.963
C7-C8	1.511(3)	C16-C17	1.360(4)	C26-C27	1.394(4)
C7-H72	0.991	C16H161	0.966	C26-H261	0.916
C7-H71	0.962	C17-H171	0.938	C27-C28	1.365(4)
C8-N9	1.316(3)	C18-C19	1.514(3)	C27-H271	0.945
C8-C13	1.407(3)	C18-H181	0.975	C28-H281	0.971
N9-C10	1.371(3)	C19-N20	1.323(3)		
C10-C11	1.41(3)				

Table A1.10: Bond angles for Bis-1, 3- (2-methylquinolin) imidazolium chloride (**9f**)

Bond angles (°)		Bond angles (°)		Bond angles (°)	
C3-N2-C6	108.7(2)	C13-C12-H121	118.9	C19-C18-H181	108.1
C3-N2-C18	126.6(2)	C8-C13-C12	119.2(2)	N2-C18-H182	108.3
C6-N2-C18	124.7(2)	C8-C13-H131	119.5	C19-C18-H182	107.7
N2-C3-C4	107.4(2)	C12-C13-H131	121.3	H181-C18 H182	111.4
N2-C3-H31	124.9	C11-C14-C15	120.1(2)	C18-C19-N20	113.7(2)
C4-C3-H31	127.7	C11-C14-H141	118.3	C18-C19-C24	122.4(2)
C3-C4-N5	106.6(2)	C15-C14-H141	121.6	N20-C19-C24	123.9(2)
C3-C4-H41	127.3	C14-C15-C16	120.4(2)	C19-N20-C21	117.2(2)
N5-C4-H41	126.0	C11-C10-C17	118.7(2)	N20-C21-C22	123.1(2)
C4-N5-C6	109.0(2)	C10-C11-C12	117.7(2)	N20-C21-C28	118.4(3)
C4-N5-C7	125.6(2)	C10-C11-C14	119.2(2)	C22-C21-C28	118.5(2)
C6-N5-C7	125.0(2)	C12-C11-C14	123.1(2)	C21-C22-C23	117.2(2
N2-C6-N5	108.3(2)	C11-C12-C13	119.2(2)	C21-C22-C25	119.7(2)
N2-C6-H61	124.7	C11-C12-H121	121.9	C23-C22-C25	123.2(3)
N5-C6-H61	127.0	C13-C12-H121	118.9	C22-C23-C24	119.8(3)
N5-C7-C8	112.07(19)	C8-C13-C12	119.2(2)	C22-C23-H231	118.8
N5-C7-H72	109.8	C8-C13-H131	119.5	C24-C23-H231	121.3
C8-C7-H72	109.0	C12-C13-H131	121.3	C19-C24-C23	118.8(2)
N5-C7-H71	107.4	C11-C14-C15	120.1(2)	C19-C24-H241	121.5
C8-C7-H71	108.5	C11-C14-H141	118.3	C23-C24-H241	119.7
H72-C7-H71	110.0	C15-C14-H141	121.6	C22-C25-C26	120.3(3)
C7-C8-N9	117.6(2)	C14-C15-C16	120.4(2)	C22-C25-H251	117.4
C7-C8-C13	118.4(2)	C14-C15-H151	117.9	C26-C25-H251	122.2
N9-C8-C13	124.0(2)	C16-C15-H151	121.	C25-C26-C27	119.8(3)
C8-N9-C10	117.5(2)	C15-C16-C17	120.7(2)	C25-C26-H261	119.3
N9-C10-C11	122.5(2)	C15-C16-H161	119.2	C27-C26-H261	120.9
N9-C10-C17	118.8(2)	C17-C16-H161	120.2	C26-C27-C28	121.5(3)
C11-C10-C17	118.7(2)	C10-C17-C16	120.8(2)	C26-C27-H271	118.2
C10-C11-C12	117.7(2)	C10C17H171	120.3	C28-C27-H271	120.3
C10-C11-C14	119.2(2)	C16-C17-H171	118.9	C21-C28-C27	120.2(3)

C12-C11-C14	123.1(2)	N2-C18-C19	113.0(2)	C21-C28-H281	120.3
C11-C12-C13	119.2(2)	N2-C18-H181	108.4	C27-C28-H281	119.5
C11-C12-H121	121.9				

Table A1.11: Bond lengths and angles for [Ag (1-methy-3-(-2-methylquinoline) imidazolin-2-ylidine) $_2$][$AgCl_2$] (**3.36**)

Bond lengths (Å)		Bond angles (°)		Bond angles (°)	
C1-N2	1.351(14)	N2-C1-N1	104.0(10)	C12-C13-C14	120.0
C1-N1	1.353(16)	N2-C1-Ag1	130.6(8)	C9-C14-C13	120.0
C1-Ag1	2.106(12)	N1-C1-Ag	125.2(9)	C1-Ag1-C1	170.8(8)
C2-C3	1.32(2)	C3-C2-N1	107.8(11)	C1-Ag1-Ag2	94.6(4)
C2-N1	1.378(16)	C2-C3-N2	105.8(12)	C1-Ag1-Ag2	94.6(4)
C3-N2	1.392(19)	N2-C5-C6	112.7(13)	C1-Ag1-Ag2	85.4(4)
C4-N1	1.480(19)	C1-N1-C2	110.1(11)	C1-Ag1-Ag2	85.4(4)
C5-N2	1.446(18)	C1-N1-C4	125.4(12)	Ag2-Ag1-Ag2	180.0(3)
C5-C6	1.48(2)	C2-N1-C4	122.4(12)	Cl1-Ag2-Cl1	176.6(11)
N3 -C6	1.3900	C1-N2-C3	109.9(9)	Cl1-Ag2-Ag1	88.3(5)
N3-C10	1.3900	C1-N2-C5	119.3(10)	Cl1-Ag2-Ag1	88.3(5)
C6-C7	1.3900	C3-N2-C5	130.2(10)	Cl1-Ag2-Ag1	91.7(5)
C7-C8	1.3900	C6-N3-C10	120.0	Cl1-Ag2-Ag1	91.7(5)
C8-C9	1.3900	N3-C6-C7	120.0	Ag1-Ag2-Ag1	180.0
C9-C14	1.3900	N3-C6-C5	116.5(11)		
C9-C10	1.3900	C7-C6-C5	123.5(10)		
C10-C11	1.3900	C6-C7-C8	120.0		
C11-C12	1.3900	C9-C8-C7	120.0		
C12-C13	1.3900	C14-C9-C10	120.0		
C13-C14	1.3900	C14-C9-C8	120.0		
Cl1-Ag2	2.290(5)	C10-C9-C8	120.0		
Ag1-C1	2.106(12)	C9-C10-C11	120.0		
Ag1-Ag2	3.201(4)	C9-C10-N3	120.0		
Ag1-Ag2	3.300(4)	C11-C10-N3	120.0		
Ag2-Cl1	2.290(5)	C12-C11-C10	120.0		

Ag2-Ag1	3.201(4)	C11-C12-C13	120

Table A1.12: Bond lengths and angles for [Ag (1-mesityl-3-(-2-methylquinoline) imidazolin-2-ylidine) Cl] **3.37**

Bond lengths (Å)		Bond angles (°)		Bond angles (°)	
Ag1-Ag1	3.8010(5)	Ag1-Ag1-Cl2	37.997(17)	C4-C16-H161	128.2
Ag1-Cl2	3.2126(10)	Ag1-Ag1-Cl2	57.31(2)	C8-C17-C9	119.1(3)
Ag1-Cl2	2.3501(9)	Cl2-Ag1-Cl2	95.30(3)	C8-C17-N5	118.0(3)
Ag1-C13	2.090(3)	Ag1-Ag1-C13	133.23(10)	C9-C17-N5	123.0(3)
N3-C4	1.384(4)	Cl2-Ag1-C13	95.29(10)	C15-C18-C10	120.5(4)
N3-C6	1.474(4)	Cl2-Ag1-C13	169.03(10)	C15-C18-C22	122.0(4)
N3-C13	1.342(5)	Ag1-Cl2-Ag1	84.70(3)	C10-C18-C22	117.5(4)
C4-C16	1.344(5)	C4-N3-C6	123.9(3)	C21-C19-H193	112.7
C4-H41	0.950	C4-N3-C13	111.1(3)	C21-C19-H191	108.8
N5-C14	1.320(5)	C6-N3-C13	125.0(3)	H193-C19-H191	107.4
N5-C17	1.373(5)	N3-C4-C16	106.9(3)	C21-C19-H192	110.3
C6-C14	1.516(5)	N3-C4-H41	124.8	H193-C19-H192	108.2
C6-H62	0.974	C16-C4-H41	128.2	H191-C19-H192	109.4
C6-H61	0.967	C14-N5-C17	117.2(3)	C9-C20-C25	120.0(4)
C7-C21	1.396(5)	N3-C6-C14	111.6(3)	C9-C20-H201	119.4
C7-C23	1.390(5)	N3-C6-H62	108.1	C25-C20-H201	120.6
C7-H71	0.957	C14-C6-H62	107.4	C19-C21-C7	120.6(4)
C8-C17	1.422(5)	N3-C6-H61	109.2	C19-C21-C10	120.3(4)
C8 C27	1.366(6)	C14-C6-H61	109.7	C7-C21-C10	119.1(3)
C8 H81	0.932	H62-C6-H61	110.9	N11-C22-C18	118.9(3)
C9 C12	1.421(6)	C21-C7-C23	121.6(3)	N11-C22-C23	118.0(3)
C9 C17	1.410(6)	C21-C7-H71	119.2	C18-C22-C23	123.1(3)
C9 C20	1.417(5)	C23-C7-H71	119.2	C22-C23-C7	117.3(3)
C10C18	1.399(5)	C17-C8-C27	120.1(4)	C22-C23-C26	121.5(3)
C10 C21	1.384(6)	C17-C8-H81	120.2	C7-C23-C26	121.2(3)
C10-H101	0.948	C27-C8-H81	119.8	C14-C24-C12	119.2(4)
N11-C13	1.353(4)	C12-C9-C17	117.6(3)	C14-C24-H241	120.4

N11-C16	1.389(5)	C12-C9-C20	122.8(4)	C12-C24-H241	120.3
N11-C22	1.445(4)	C17-C9-C20	119.6(4)	C20-C25-C27	120.7(4)
C12-C24	1.371(6)	C18-C10-C21	121.3(4)	C20-C25-H251	119.6
C12-H121	0.934	C18-C10-H101	119.0	C27-C25-H251	119.7
C14-C24	1.407(5)	C21-C10-H101	119.7	C23-C26-H262	109.5
C15-C18	1.510(6)	C13-N11-C16	110.9(3)	C23-C26-H263	111.4
C15-H152	0.945	C13-N11-C22	122.6(3)	H262-C26-H263	108.2
C15-H153	0.960	C16-N11-C22	126.5(3)	C23-C26-H261	111.2
C15-H151	0.961	C9-C12-C24	118.9(4)	H262-C26-H261	106.3
C16-H161	0.945	C9-C12-H121	119.3	H263-C26-H261	110.1
C18-C22	1.389(5)	C24-C12-H121	121.8	C25-C27-C8	120.6(4)
C19-C21	1.509(5)	N11-C13-N3	104.9(3)	C25-C27-H271	119.4
C19-H193	0.950	N11-C13-Ag1	123.7(3)	C8-C27-H271	120.0
C19-H191	0.942	N3-C13-Ag1	131.4(2)		
C19-H192	0.945	C6-C14-N5	116.2(3)		
C20-C25	1.366(7)	C6-C14-C24	119.7(3)		
C20-H201	0.931	N5-C14-C24	124.1(3)		
C22-C23	1.391(5)	C18-C15-H152	109.5		
C23-C26	1.498(5)	C18-C15-H153	111.6		
C24-H241	0.936	H152-C15-H153	105.3		
C25-C27	1.409(7)	C18-C15-H151	113.5		
C25-H251	0.946	H152-C15-H151	107.4		
C26-H262	0.954	H153-C15-H151	109.1		
C26-H263	0.962	N11-C16-C4	106.2(3)		
C26-H261	0.954	N11-C16-H161	125.6		
C27-H271	0.930				

Table 1.13: Bond lengths and angles for 1-methyl-3-(2-methylquinoline)imidazolin-2-ylidene](1,5-cyclooctadiene)rhodium(I) Chloride **4.20**

Bond lengths (Å)		Bond angles (°)		Bond angles (°)	
C1-N1	1.356(6)	N1-C1-N2	103.8(4)	Rh1-C16-H16	86.6
C1-N2	1.362(7)	N1-C1-Rh1	131.4(4)	C18-C17-C16	112.8(4)
C1-Rh1	2.028(5)	N2-C1-Rh1	124.9(4)	C18 C17 H17A	109.0
C2-C3	1.345(8)	C3-C2-N1	107.1(5)	C16 C17 H17A	109.0
C2-N1	1.371(7)	C3-C2-H2	126.5	C18 C17 H17B	109.0
C2-H2	0.9500	N1-C2-H2	126.5	C16-C17-H17B	109.0
C3-N2	1.394(7)	C2-C3-N2	106.3(5)	H17A-C17-H17B	107.8
C3-H3	0.9500	C2-C3-H3	126.9	C19-C18-C17	113.3(4)
C4-N1	1.466(7)	N2-C3-H3	126.9	C19-C18-H18A	108.9
C4-H4A	0.9800	N1-C4-H4A	109.5	C17-C18-H18A	108.9
C4-H4B	0.9800	N1-C4-H4B	109.5	C19-C18-H18B	108.9
C4-H4C	0.9800	H4A-C4-H4B	109.5	C17-C18-H18B	108.9
C5-N2	1.461(6)	N1-C4-H4C	109.5	H18A-C18-H18B	107.7
C5-C6	1.508(7)	H4A-C4-H4C	109.5	C20-C19-C18	125.8(5)
C5-H5A	0.9900	H4B-C4-H4C	109.5	C20-C19-Rh1	73.0(3)
C5-H5B	0.9900	N2-C5-C6	113.9(4)	C18-C19-Rh1	106.6(4)
C6-N3	1.320(7)	N2-C5-H5A	108.8	C20-C19-H19	117.1
C6-C7	1.420(7)	C6-C5-H5A	108.8	C18-C19-H19	117.1
C7-C8	1.378(8)	N2-C5-H5B	108.8	Rh1-C19-H19	90.5
C7-H7	0.9500	C6-C5-H5B	108.8	C19-C20-C21	125.3(5)
C8-C9	1.412(7)	H5A-C5-H5B	107.7	C19-C20-Rh1	70.9(3)
C8-H8	0.9500	N3-C6-C7	123.5(5)	C21-C20-Rh1	111.6(4)
C9-C10	1.408(7)	N3-C6-C5	114.7(5)	C19-C20-H20	117.3
C9-C14	1.417(7)	C7-C6-C5	121.8(5)	C21-C20-H20	117.3

C10-C11	1.372(8)	C8-C7-C6	118.8(5)	Rh1-C20-H20	87.4
C10-H10	0.9500	C8-C7-H7	120.6	C20-C21-C22	112.5(5)
C11-C12	1.405(8)	C6-C7-H7	120.6	C20-C21-H21A	109.1
C11-H11	0.9500	C7-C8-C9	119.8(5)	C22-C21-H21A	109.1
C12-C13	1.377(8)	C7-C8-H8	120.1	C20-C21-H21B	109.1
C12-H12	0.9500	C9-C8-H8	120.1	C22-C21-H21B	109.1
C13-C14	1.416(7)	C10-C9-C8	123.5(5)	H21A-C21-H21B	107.8
C13-H13	0.9500	C10-C9-C14	119.1(5)	C15-C22-C21	113.5(4)
C14-N3	1.378(7)	C8-C9-C14	117.4(5)	C15-C22-H22A	108.9
C15-C16	1.410(7)	C11-C10-C9	120.8(5)	C21-C22-H22A	108.9
C15-C22	1.499(8)	C11-C10-H10	119.6	C15-C22-H22B	108.9
C15-Rh1	2.123(5)	C9-C10-H10	119.6	C21-C22-H22B	108.9
C15-H15	0.9500	C10-C11-C12	120.1(5)	H22A-C22-H22B	107.7
C16-C17	1.526(7)	C10-C11-H11	120.0	C1-N1-C2	111.9(4)
C16-Rh1	2.126(5)	C12-C11-H11	120.0	C1-N1-C4	124.5(5)
C16-H16	0.9500	C13-C12-C11	120.8(5)	C2-N1-C4	123.5(4)
C17-C18	.526(8)	C13-C12-H12	119.6	C1-N2-C3	111.0(4)
C17-H17A	0.9900	C11-C12-H12	119.6	C1-N2-C5	124.1(4)
C17-H17B	0.9900	C12-C13-C14	119.8(5)	C3-N2-C5	124.7(4)
C18-C19	1.524(8)	C12-C13-H13	120.1	C6-N3-C14	117.9(5)
C18-H18A	0.9900	C14-C13-H13	120.1	C1-Rh1-C15	92.0(2)
C18-H18B	0.9900	N3-C14-C13	117.8(5)	C1-Rh1-C16	93.2(2)
C19-C20	1.375(8)	N3-C14-C9	122.8(5)	C15-Rh1-C16	38.8(2)
C19-Rh1	2.206(5)	C13-C14-C9	119.4(5)	C1-Rh1-C19	158.3(2)
C19-H19	0.9500	C16-C15-C22	125.7(5)	C15-Rh1-C19	97.2(2)
C20-C21	1.506(8)	C16-C15-Rh1	70.7(3)	C16-Rh1-C19	82.0(2)
C20-Rh1	2.233(6)	C22-C15-Rh1	111.4(4)	C1-Rh1-C20	165.5(2)

C20-H20	0.9500	C16-C15-H15	117.2	C15-Rh1-C20	80.7(2)
C21-C22	1.544(8)	C22-C15-H15	117.2	C16-Rh1-C20	88.8(2)
C21-H21A	0.9900	Rh1-C15-H15	87.8	C19-Rh1-C20	36.1(2)
C21-H21B	0.9900	C15-C16-C17	123.8(5)	C1-Rh1-Cl1	87.99(14)
C22-H22A	0.9900	C15-C16-Rh1	70.5(3)	C15-Rh1-Cl1	161.31(15)
C22-H22B	0.9900	C17-C16-Rh1	113.0(4)	C16-Rh1-Cl1	159.89(15)
Rh1-Cl1	2.3862(13)	C15-C16-H16	118.1	C19-Rh1-Cl1	89.44(15)
		C17-C16-H16	118.1	C20-Rh1-Cl1	95.03(15)

Table A1.14: Bond lengths and angles for [1-mesityl-3-(2-methylquinoline)imidazolin-2-ylidene](1,5-cyclooctadiene)rhodium(I) Chloride **4.21**

Bond lengths (Å)		Bond angles (°)		Bond angles (°)	
C1-N1	1.355(5)	N1-C1-N2	103.7(3)	C22-C21-H21	119.8
C1-N2	1.355(5)	N1-C1-Rh1	130.8(3)	N3-C22-C17	122.7(4)
C1-Rh1	2.043(4)	N2-C1-Rh1	125.3(3)	N3-C22C21	118.2(3)
C2-C3	1.336(6)	C3-C2- N1	106.4(4)	C17-C22-C21	119.1(4)
C2-N1	1.397(5)	C3-C2-H2	126.8	C24-C23-C30	123.6(5)
C2-H2	0.9500	N1-C2-H2	126.8	C24-C23-Rh1	70.9(3)
C3-N2	1.379(5)	C2-C3-N2	106.8(4)	C30-C23-Rh1	111.2(3)
C3-H3	0.9500	C2-C3-H3	126.6	C24-C23-H23	118.2
C4-C9	1.394(6)	N2-C3-H3	126.6	C30-C23-H23	118.2
C4-C5	1.396(6)	C9-C4-C5	122.8(3)	Rh1-C23-H23	88.0
C4-N1	1.447(5)	C9-C4-N1	117.3(3)	C23-C24-C25	125.3(5)
C5-C6	1.406(6)	C5-C4-N1	119.8(4)	C23-C24-Rh1	72.7(3)
C5-C10	1.497(6)	C4-C5-C6	116.8(4)	C25-C24-Rh1	109.6(3)

C6-C7	1.385(7)	C4-C5-C10	121.3(4)	C23-C24-H24	117.3
C6-H6	0.9500	C6-C5-C10	121.9(4)	C25-C24-H24	117.3
C7-C8	1.378(6)	C7-C6-C5	122.1(4)	Rh1-C24-H24	87.6
C7-C11	1.512(6)	C7-C6-H6	118.9	C26-C25-C24	115.7(5)
C8-C9	1.410(6)	C5-C6 H6	118.9	C26-C25-H25A	108.4
C8-H8	0.9500	C8-C7-C6	119.1(4)	C24-C25-H25A	108.4
C9-C12	1.505(5)	C8-C7-C11	119.7(4)	C26-C25-H25B	108.4
C10-H10A	0.9800	C6-C7-C11	121.2(4)	C24-C25-H25B	108.4
C10-H10B	0.9800	C7-C8-C9	121.6(4)	H25A-C25-H25B	107.4
C10-H10C	0.9800	C7-C8-H8	119.2	C25-C26-C27	115.3(5)
C11-H11A	0.9800	C9-C8-H8	119.2	C25-C26-H26A	108.5
C11-H11B	0.9800	C4-C9-C8	117.4(4)	C27-C26-H26A	108.5
C11-H11C	0.9800	C4-C9-C12	121.8(3)	C25-C26-H26B	108.5
C12-H12A	0.9800	C8-C9-C12	120.8(4)	C27-C26-H26B	108.5
C12-H12B	0.9800	C5-C10-H10A	109.5	H26A-C26-H26B	107.5
C12-H12C	0.9800	C5-C10-H10B	109.5	C28-C27-C26	122.7(5)
C13-N2	1.451(5)	H10A-C10-H10B	109.5	C28-C27-Rh1	70.4(3)
C13-C14	1.521(6)	C5-C10-H10C	109.5	C26-C27-Rh1	112.9(3)
C13-H13A	0.9900	H10A-C10-H10C	109.5	C28-C27-H27	118.7
C13-H13B	0.9900	H10B-C10-H10C	109.5	C26-C27-H27	118.7
C14-N3	1.320(5)	C7-C11-H11A	109.5	Rh1-C27-H27	86.7
C14-C15	1.419(6)	C7-C11-H11B	109.5	C27-C28-C29	126.8(5)
C15-C16	1.360(6)	H11A-C11-H11B	109.5	C27-C28-Rh1	71.3(3)
C15-H15	0.9500	C7-C11-H11C	109.5	C29-C28-Rh1	110.8(3)
C16-C17	1.403(6)	H11A-C11-H11C	109.5	C27-C28-H28	116.6
C16-H16	0.9500	H11B-C11-H11C	109.5	C29-C28-H28	116.6
C17-C22	1.415(5)	C9-C12H-12A	109.5	Rh1-C28-H28	87.9

C1-C18	.417(6)	C9-C12-H12B	109.5	C30-C29-C28	116.9(6)
C18-C19	1.352(7)	H12A-C12-H12B	109.5	C30-C29-H29A	108.1
C18-H18	0.9500	C9-C12-H12C	109.5	C28-C29-H29A	108.1
C19-C20	1.408(6)	H12A-C12-H12C	109.5	C30-C29-H29B	108.1
C19-H19	0.9500	H12B-C12-H12C	109.5	C28-C29-H29B	108.1
C20-C21	.366(6)	N2-C13-C14	112.6(3)	H29A-C29-H29B	107.3
C20-H20	0.9500	N2-C13-H13A	109.1	C29-C30-C23	113.8(5)
C21-C22	1.421(6)	C14-C13-H13A	109.1	C29-C30-H30A	108.8
C21-H21	0.9500	N2-C13-H13B	109.1	C23-C30-H30A	108.8
C22-N3	1.365(5)	C14-C13-H13B	109.1	C29-C30-H30B	108.8
C23-C24	1.369(6)	H13A-C13-H13B	107.8	C23-C30-H30B	108.8
C23-C30	1.514(7)	N3-C14-C15	122.9(4)	H30A-C30-H30B	107.7
C23-Rh1	2.202(4)	N3-C14-C13	118.6(3)	C1-N1-C2	111.1(3)
C23-H23	0.9500	C15-C14-C13	118.5(4)	C1-N1-C4	124.3(3)
C24-C25	1.509(7)	C16-C15-C14	118.8(4)	C2-N1-C4	123.7(3)
C24-Rh1	2.179(4)	C16-C15-H15	120.6	C1-N2-C3	111.9(3)
C24-H24	0.9500	C14-C15-H15	120.6	C1-N2-C13	124.0(3)
C25-C26	1.480(7)	C15-C1-C17	120.2(4)	C3-N2-C13	123.9(3)
C25-H25A	0.9900	C15-C16-H16	119.9	C14-N3-C22	118.1(3)
C25-H25B	0.9900	C17-C16-H16	119.9	C1-Rh1-C28	94.63(17)
C26-C27	1.515(7)	C16-C17-C22	117.2(4)	C1-Rh1-C27	93.45(15)
C26-H26A	0.9900	C16-C17-C18	124.5(4)	C28-Rh1-C27	38.31(15)
C26-H26B	0.9900	C22-C17-C18	118.3(4)	C1-Rh1-C24	157.59(17)
C27-C28	1.389(6)	C19-C18-C17	121.6(4)	C28-Rh1-C24	94.88(19)
C27-Rh1	2.123(4)	C19-C18-H18	119.2	C27-Rh1-C24	81.68(17)
C27-H27	0.9500	C17-C18-H18	119.2	C1-Rh1-C23	165.92(17)
C28-C29	1.499(7)	C18-C19-C20	120.1(4)	C28-Rh1-C23	81.26(16)

C28-Rh1	2.112(4)	C18-C19-H19	120.0	C27-Rh1-C23	91.58(18)
C28-H28	0.9500	C20-C19-H19	120.0	C24-Rh1-C23	36.42(16)
C29-C30	1.476(7)	C21-C20-C19	120.5(4)	C1-Rh1-Cl1	87.67(11)
C29-H29A	0.9900	C21-C20-H20	119.8	C28-Rh1-Cl1	159.29(13)
C29-H29B	0.9900	C19-C20-H20	119.8	C27-Rh1-Cl1	162.22(13)
C30-H30A	.9900	C20-C21-C22	120.3(4)	C24-Rh1-Cl1	90.55(14)
C30-H30B	0.9900	C20-C21-H21	119.8	C23-Rh1-Cl1	91.55(13)
Rh1-Cl1	2.3865(9)				

Table A1.15: Bond lengths and angles for [1-isopropyl-3-(2-methylquinoline)imidazolin-2-ylidene](1,5-cyclooctadiene)rhodium(I) Chloride **4.22**

Bond lengths (Å)		Bond angles (°)		Bond angles (°)	
C1-N1	1.343(6)	N1-C1-N2	104.7(4)	C20-C19-Rh1	112.9(4)
C1-N2	1.345(6)	N1-C1-Rh1	129.8(3)	C18-C19-H19	117.8
C1-Rh1	2.037(5)	N2-C1-Rh1	125.1(4)	C20-C19-H19	117.8
C2-C3	1.351(8)	C3-C2-N1	105.8(5)	Rh1-C19-H19	87.1
C2-N1	1.389(7)	C3-C2 -H2	127.1	C21-C20-C19	114.5(4)
C2-H2	0.9500	N1-C2-H2	127.1	C21-C20-H20A	108.6
C3-N2	1.369(7)	C2-C3-N2	106.9(5)	C19-C20-H20A	108.6
C3-H3	0.9500	C2-C3-H3	126.5	C21-C20-H20B	108.6
C4-N1	1.477(6)	N2-C3-H3	126.5	C19-C20-H20B	108.6
C4-C6	1.506(8)	N1-C4-C6	109.8(4)	H20A-C20-H20B	107.6
C4-C5	1.521(7)	N1-C4-C5	110.2(5)	C22-C21-C20	114.2(5)
C4-H4	1.0000	C6-C4-C5	112.4(5)	C22-C21-H21A	108.7

C5-H5A	0.9800	N1-C4-H4	108.1	C20-C21-H21A	108.7
C5-H5B	0.9800	C6-C4-H4	108.1	C22-C21-H21B	108.7
C5-H5C	0.9800	C5-C4-H4	108.1	C20-C21-H21B	108.7
C6-H6A	0.9800	C4-C5-H5A	109.5	H21A-C21-H21B	107.6
C6-H6B	0.9800	C4-C5-H5B	109.5	C23-C22-C21	125.4(6)
C6-H6C	0.9800	H5A-C5-H5B	109.5	C23-C22-Rh1	72.6(3)
C8-N2	1.467(7)	C4-C5-H5C	109.5	C21-C22-Rh1	108.8(3)
C8-C9	1.525(7)	H5A-C5-H5C	109.5	C23-C22-H22	117.3
C8-H8A	0.9900	H5B-C5-H5C	109.5	C21-C22-H22	117.3
C8-H8B	0.9900	C4-C6-H6A	109.5	Rh1-C22-H22	88.5
C9-N3	1.311(7)	C4-C6-H6B	109.5	C22-C23-C24	123.0(6)
C9-C10	1.413(7)	H6A-C6-H6B	109.5	C22-C23-Rh1	71.5(3)
C10-C11	1.381(7)	C4-C6-H6C	109.5	C24-C23-Rh1	110.4(4)
C10-H10	0.9500	H6A-C6-H6C	109.5	C22-C23-H23	118.5
C11-C12	1.422(7)	H6B-C6-H6C	109.5	C24-C23-H23	118.5
C11-H11	0.9500	N2-C8-C9	110.7(4)	Rh1-C23-H23	88.1
C12-C17	1.396(7)	N2-C8-H8A	109.5	C23-C24-C25	113.2(5)
C12-C13	1.422(7)	C9-C8-H8A	109.5	C23-C24-H24A	108.9
C13-C14	1.371(8)	N2-C8-H8B	109.5	C25-C24-H24A	108.9
C13-H13	0.9500	C9-C8-H8B	109.5	C23-C24-H24B	108.9
C14-C15	1.405(8)	H8A-C8-H8B	108.1	C25-C24-H24B	108.9
C14-H14	0.9500	N3-C9-C10	24.6(5)	H24A-C24-H24B	107.8
C15-C16	1.364(7)	N3-C9-C8	115.7(5)	C18-C25-C24	113.9(5)
C15-H15	0.9500	C10-C9-C8	119.7(5)	C18-C25-H25A	108.8
C16-C17	1.425(7)	C11-C10-C9	118.5(5)	C24-C25-H25A	108.8
C16-H16	0.9500	C11-C10-H10	120.8	C18-C25-H25B	108.8
C17-N3	1.378(6)	C9-C10-H10	120.8	C24-C25-H25B	108.8

C18-C19	1.410(9)	C10-C11-C12	118.7(5)	H25A-C25-H25B	107.7
C18-C25	1.496(9)	C10-C11-H11	120.6	C1-N1-C2	111.1(4)
C18-Rh1	2.113(5)	C12-C11-H11	120.6	C1-N1-C4	125.0(4)
C18-H18	0.9500	C17-C12-C13	120.0(4)	C2-N1-C4	123.7(4)
C19-C20	1.523(7)	C17-C12-C11	118.0(5)	C1-N2-C3	111.4(5)
C19-Rh1	2.127(5)	C13-C12-C11	122.0(5)	C1-N2-C8	125.7(5)
C19-H19	0.9500	C14-C13-C12	119.1(5)	C3-N2-C8	122.8(5)
C20-C21	1.522(8)	C14-C13-H13	120.5	C9-N3-C17	117.1(5)
C20-H20A	0.9900	C12-C13-H13	120.5	C1-Rh1-C18	88.1(2)
C20-H20B	0.9900	C13-C14-C15	121.0(5)	C1-Rh1-C19	93.1(2)
C21-C22	1.495(7)	C13-C14-H14	119.5	C18-Rh1-C19	38.8(2)
C21-H21A	0.9900	C15-C14-H14	119.5	C1-Rh1-C22	164.3(2)
C21-H21B	0.9900	C16-C15-C14	120.8(5)	C18-Rh1-C22	96.6(2)
C22-C23	1.367(8)	C16-C15-H15	119.6	C19-Rh1-C22	81.5(2)
C22-Rh1	2.213(5)	C14-C15-H15	119.6	C1-Rh1-C23	159.6(2)
C22-H22	0.9500	C15-C16-C17	119.5(5)	C18-Rh1-C23	81.2(2)
C23-C24	1.506(9)	C15-C16-H16	120.2	C19-Rh1-C23	89.4(2)
C23-Rh1	2.226(5)	C17-C16-H16	120.2	C22-Rh1-C23	35.9(2)
C23-H23	0.9500	N3-C17-C12	123.1(5)	C1-Rh1-Cl1	89.24(13)
C24-C25	1.516(10)	N3-C17-C16	117.4(5)	C18-Rh1-Cl1	159.1(2)
C24-H24A	0.9900	C12-C17-C16	119.5(4)	C19-Rh1-Cl1	162.05(18)
C24-H24B	0.9900	C19-C18-C25	125.7(6)	C22-Rh1-Cl1	91.45(14)
C25-H25A	0.9900	C19-C18-Rh1	71.1(3)	C23-Rh1-Cl1	94.52(17)
C25-H25B	0.9900	C25-C18-Rh1	110.5(4)	Cl3-C26-Cl2	106.8(6)
Rh1-Cl1	2.3755(13)	C19-C18-H18	117.1	Cl3-C26-H26A	110.4
Cl3-C26	1.758(9)	C25-C18-H18	117.1	Cl2-C26-H26A	110.4
Cl2-C26	1.788(9)	Rh1-C18-H18 88.3		Cl3-C26-H26B	110.4

C26-H26A	0.9900	C18-C19-C20	124.5(5)	Cl2-C26-H26B	110.4
C26-H26B	0.9900	C18-C19-Rh1	70.0(3)	H26A-C26-H26B	108.6

Table A1.16: Bond lengths and angles for [1-n-butyl-3-(2-methylquinoline)imidazolin-2-ylidene](1,5-cyclooctadiene)rhodium(I) Chloride **4.23**

Bond lengths (Å)		Bond angles (°)		Bond angles (°)	
C1-N1	1.355(5)	N1-C1-N2	103.8(3)	C25-C18-Rh1	111.3(3)
C1-N2	1.368(5)	N1-C1-Rh1	126.4(3)	C19-C18-H18	117.8
C1-Rh1	2.032(4)	N2-C1-Rh1	129.6(3)	C25-C18-H18	117.8
C2-C3	1.340(6)	C3-C2-N2	106.7(4)	Rh1-C18-H18	87.3
C2-N2	1.379(5)	C3-C2-H2	126.6	C18-C19-C20	123.6(4)
C2-H2	0.9500	N2-C2-H2	126.6	C18-C19-Rh1	70.0(2)
C3-N1	1.387(5)	C2-C3-N1	107.0(4)	C20-C19-Rh1	113.4(3)
C3-H3	0.9500	C2-C3-H3	126.5	C18-C19-H19	118.2
C4-N2	1.467(5)	N1-C3-H3	126.5	C20-C19-H19	118.2
C4-C5	1.508(6)	N2-C4-C5	112.4(3)	Rh1-C19-H19	86.6
C4-H4A	0.9900	N2-C4-H4A	109.1	C19-C20-C21	114.2(3)
C4-H4B	0.9900	C5-C4-H4A	109.1	C19-C20-H20A	108.7
C5-N3	1.320(5)	N2-C4-H4B	109.1	C21-C20-H20A	108.7
C5-C6	1.405(6)	C5-C4-H4B	109.1	C19-C20-H20B	108.7
C6-C7	1.361(6)	H4A-C4-H4B	107.9	C21-C20-H20B	108.7
C6-H6	0.9500	N3-C5-C6	124.6(4)	H20A-C20-H20B	107.6
C7-C8	1.416(6)	N3-C5-C4	115.6(4)	C22-C21-C20	113.9(3)
C7-H7	0.9500	C6-C5-C4	119.8(4)	C22-C21-H21A	108.8
C8-C13	1.407(6)	C7-C6-C5	118.9(4)	C20-C21-H21A	108.8

C8-C9	1.415(6)	C7-C6-H6	120.5	C22-C21-H21B	108.8
C9-C10	1.364(6)	C5-C6-H6	120.5	C20-C21-H21B	108.8
C9 -C9	0.9500	C6-C7-C8	119.5(4)	H21A-C21-H21B	107.7
C10-C11	1.403(6)	C6-C7-H7	120.3	C23-C22-C21	123.2(4)
C10-H10	0.9500	C8-C7-H7	120.3	C23-C22-Rh1	72.3(2)
C11-C12	1.360(6)	C13-C8-C9	119.1(4)	C21-C22-Rh1	109.3(3)
C11-H11	0.9500	C13-C8-C7	117.4(4)	C23-C22-H22	118.4
C12-C13	1.416(5)	C9-C8-C7	123.4(4)	C21-C22-H22	118.4
C12-H12	0.9500	C10-C9-C8	120.0(4)	Rh1-C22-H22	88.4
C13-N3	1.380(5)	C10-C9-H9	120.0	C22-C23-C24	123.5(4)
C14-N1	1.464(5)	C8 -9-H9	120.0	C22-C23-Rh1	71.4(2)
C14-C15	1.518(6)	C9-C10-C11	120.9(4)	C24-C23-Rh1	111.5(3)
C14-H14A	0.9900	C9-C10-H10	119.6	C22-C23-H23	118.2
C14-H14B	0.9900	C11-C10-H10	119.6	C24-C23-H23	118.2
C15-C16	1.509(6)	C12-C11-C10	120.3(4)	Rh1-C23-H23	87.1
C15-H15A	0.9900	C12-C11-H11	119.8	C23-C24-C25	112.9(3)
C15-H15B	0.9900	C10-C11-H11	119.8	C23-C24-H24A	109.0
C16-C17	1.522(6)	C11-C12-C13	120.2(4)	C25-C24-H24A	109.0
C16-H16A	0.9900	C11-C12-H12	119.9	C23-C24-H24B	109.0
C16-H16B	0.9900	C13-C12-H12	119.9	C25-C24-H24B	109.0
C17-H17A	0.9800	N3-C13-C8	123.2(4)	H24A-C24-H24B	107.8
C17-H17B	0.9800	N3-C13-C12	117.4(4)	C18-C25-C24	113.4(3)
C17-H17C	0.9800	C8-C13-C12	119.4(4)	C18-C25-H25A	108.9
C18-C19	1.395(5)	N1-C14-C15	113.3(3)	C24-C25-H25A	108.9
C18-C25	1.520(5)	N1-C14-H14A	108.9	C18-C25-H25B	108.9
C18-Rh1	2.097(4)	C15-C14-H14A	108.9	C24-C25-H25B	108.9
C18-H18	0.9500	N1-C14-H14B	108.9	H25A-C25-H25B	107.7

C19-C20	1.517(5)	C15-C14-H14B	108.9	C1-N1-C3	111.1(3)
C19-Rh1	2.114(4)	H14A-C14-H14B	07.7	C1-N1-C14	125.2(3)
C19-H19	0.9500	C16-C15-C14	111.4(4)	C3-N1-C14	123.7(3)
C20-C21	1.530(6)	C16-C15-H15A	109.3	C1-N2-C2	111.3(3)
C20-H20A	0.9900	C14-C15-H15A	109.3	C1-N2-C4	124.3(3)
C20-H20B	0.9900	C16-C15-H15B	109.3	C2-N2-C4	124.3(3)
C21-C22	1.502(6)	C14-C15-H15B	109.3	C5-N3-C13	116.4(3)
C21-H21A	0.9900	H15A-C15-H15B	108.0	C1-Rh1-C18	90.62(15)
C21-H21B	0.9900	C15-C16-C17	113.8(4)	C1-Rh1-C19	95.45(15)
C22-C23	1.373(6)	C15-C16-H16A	108.8	C18-Rh1-C19	38.70(15)
C22-Rh1	2.197(4)	C17-C16-H16A	108.8	C1-Rh1-C22	163.07(15)
C22-H22	0.9500	C15-C16-H16B	108.8	C18-Rh1-C22	97.47(16)
C23-C24	1.508(6)	C17-C16-H16B	108.8	C19-Rh1-C22	81.99(15)
C23-Rh1	2.208(4)	H16A-C16-H16B	107.7	C1-Rh1-C23	160.58(15)
C23-H23	0.9500	C16-C17-H17A	109.5	C18-Rh1-C23	81.65(16)
C24-C25	1.530(6)	C16-C17-H17B	109.5	C19-Rh1-C23	89.62(15)
C24-H24A	0.9900	H17A-C17-H17B	109.5	C22-Rh1-C23	36.32(14)
C24-H24B	0.9900	C16-C17-H17C	109.5	C1-Rh1-Cl1	88.03(11)
C25-H25A	0.9900	H17A-C17-H17C	109.5	C18-Rh1-Cl1	159.47(11)
C25-H25B	0.9900	H17B-C17-H17C	109.5	C19-Rh1-Cl1	161.73(11)
2.3786(10)		C19-C18-C25	124.3(4)	C22-Rh1-Cl1	89.46(11)
		C19-C18-Rh1	71.3(2)	C23-Rh1-Cl1	93.01(11)

Table A1.17: Bond lengths and angles for [bis-1,3-(2-methylquinoline)imidazolin-2-ylidene](1, 5-cyclooctadiene)rhodium(I) Chloride **4.24**

Bond lengths (Å)		Bond angles (°)		Bond angles (°)	
Rh1-Cl2	2.3794(7)	Cl2-Rh1-C3	158.31(8)	C14-N15-C16	117.8(2)
Rh1-C3	2.105(3)	Cl2-Rh1-C4	162.93(8)	N15-C16-C17	118.8(2)
Rh1-C4	2.121(3)	C3-Rh1-C4	38.70(10)	N15-C16-C21	122.5(2)
Rh1-C7	2.196(2)	Cl2-Rh1-C7	89.99(8)	C17-C16-C21	118.8(2)
Rh1-C8	2.230(3)	C3-Rh1-C7	97.74(10)	C16-C17-C18	120.3(3)
Rh1-C11	2.016(3)	C4–Rh1-C7	82.16(11)	C16-C17-H171	118.7
C3-C4	1.400(4)	Cl2-Rh1-C8	93.69(8)	C18-C17-H171	120.9
C3-C10	1.514(4)	C3-Rh1-C8	81.19(10)	C17-C18-C19	121.0(3)
C3-H31	0.979	C4-Rh1-C8	88.89(10)	C17-C18-H181	119.9
C4-C5	1.523(4)	C7-Rh1-C8	36.16(10)	C19-C18-H181	119.1
C4-H41	0.989	Cl2-Rh1-C11	87.46(7)	C18-C19-C20	120.0(3)
C5-C6	1.531(4)	C3-Rh1-C11	92.99(10)	C18-C19-H191	119.6
C5-H52	0.972	C4-Rh1-C11	93.80(10)	C20-C19-H191	120.4
C5-H51	0.976	C7-Rh1-C11	156.82(11)	C19-C20-C21	120.6(3)
C6-C7	1.505(4)	C8-Rh1-C11	167.02(10)	C19-C20-H201	119.0
C6-H62	0.970	Rh1-C3-C4	71.26(15)	C21-C20-H201	120.4
C6-H61	0.980	Rh1-C3-C10	110.76(18)	C16-C21-C20	119.3(2)
C7-C8	1.374(4)	C4-C3-C10	126.0(2)	C16-C21-C22	117.2(2)
C7-H71	0.975	Rh1-C3-H31	110.3	C20-C21-C22	123.5(2)
C8-C9	1.514(4)	C4-C3-H31	117.0	C21-C22-C23	120.0(2)
C8-H81	0.977	C10-C3-H31	112.4	C21-C22-H221	120.6
C9-C10	1.528(4)	C3-C4-Rh1	70.04(15)	C23-C22-H221	119.4

C9-H92	0.985	C3-C4-C5	125.5(3)	C14-C23-C22	118.9(2)
C9-H91	0.969	Rh1-C4-C5	112.58(19)	C14-C23-H231	119.8
C10-H102	0.967	C3-C4-H41	115.5	C22-C23-H231	121.3
C10-H101	0.982	Rh1-C4-H41	110.8	N12-C24-C25	106.8(2)
C11-N12	1.358(3)	C5-C4-H41	113.4	N12-C24-H241	124.4
C11-N26	1.358(3)	C4-C5-C6	112.7(2)	C25-C24-H241	128.7
N12-C13	1.466(3)	C4-C5-H52	108.3	C24-C25-N26	106.3(2)
N12-C24	1.388(3)	C6-C5-H52	108.1	C24-C25-H251	129.0
C13-C14	1.512(3)	C4-C5-H51	108.5	N26-C25-H251	124.7
C13-H132	0.986	C6-C5-H51	109.7	C25-N26-C11	111.7(2)
C13-H131	0.982	H52-C5-H51	109.5	C25-N26-C27	124.2(2)
C14-N15	1.313(3)	C5-C6-C7	113.5(2)	C11-N26-C27	124.1(2)
C14-C23	1.426(4)	C5-C6-H62	106.9	N26-C27-C28	114.2(2)
N15-C16	1.372(3)	C7-C6-H62	108.5	N26-C27-H272	107.2
C16-C17	1.413(4)	C5-C6-H61	109.2	C28-C27-H272	108.9
C16-C21	1.421(4)	C7-C6-H61	109.5	N26-C27-H271	107.1
C17-C18	1.367(4)	H62-C6-H61	109.1	C28-C27-H271	109.6
C17-H171	0.944	C6-C7-Rh1	106.55(18)	H272-C27-H271	109.8
C18-C19	1.409(4)	C6-C7-C8	126.7(3)	C27-C28-N29	114.6(2)
C18-H181	0.940	Rh1-C7-C8	73.24(15)	C27-C28-C37	122.0(2)
C19-C20	1.364(4)	C6-C7-H71	113.8	N29-C28-C37	123.3(2)
C19-H191	0.951	Rh1-C7-H71	108.4	C28-N29-C30	117.7(2)
C20-C21	1.416(4)	C8-C7-H71	116.4	N29-C30-C31	123.0(2)
C20-H201	0.954	Rh1-C8-C7	70.60(15)	N29-C30-C35	118.2(3)
C21-C22	1.416(3)	Rh1-C8-C9	110.60(18)	C31-C30-C35	118.8(3)
C22-C23	1.349(4)	C7-C8-C9	124.7(3)	C30-C31-C32	119.7(3)
C22-H221	0.944	Rh1-C8-H81	108.1	C30-C31-C36	117.0(2)

C23 -H231	0.941	C7-C8-H81	116.6	C32-C31-C36	123.3(3)
C24-C25	1.343(4)	C9-C8-H81	114.8	C31-C32-C33	120.1(3)
C24-H241	0.945	C8-C9-C10	112.6(2)	C31-C32-H321	118.9
C25-N26	1.391(3)	C8-C9-H92	108.1	C33-C32-H321	121.0
C25-H251	0.952	C10-C9-H92	107.9	C32-C33-C34	120.4(3)
N26-C27	1.462(3)	C8-C9-H91	109.6	C32-C33-H331	120.0
C27-C28	1.516(4)	C10-C9-H91	109.9	C34-C33-H331	119.6
C27-H272	0.985	H92-C9-H91	108.7	C33-C34-C35	120.8(3)
C27-H271	0.974	C9-C10-C3	112.7(2)	C33-C34-H341	120.4
C28-N29	1.317(3)	C9-C10-H102	108.3	C35-C34-H341	118.7
C28-C37	1.414(4)	C3-C10-H102	108.1	C30-C35-C34	120.2(3)
N29-C30	1.375(3)	C9-C10-H101	110.0	C30-C35-H351	119.9
C30-C31	1.406(4)	C3-C10-H101	109.3	C34-C35-H351	119.9
C30-C35	1.421(4)	H102-C10-H101	108.3	C31-C36-C37	119.9(3)
C31-C32	1.418(4)	Rh1-C11-N1	129.86(18)	C31-C36-H361	120.3
C31-C36	1.415(4)	Rh1-C11-N26	126.25(18)	C37-C36-H361	119.8
C32-C33	1.361(4)	N12-C11-N26	103.7(2)	C28-C37-C36	119.0(3)
C32-H321	0.950	C11-N12-C13	125.2(2)	C28-C37-H371	120.1
C33-C34	1.404(5)	C11-N12-C24	111.5(2)	C36-C37-H371	120.9
C33-H331	0.939	C13-N12-C24	122.9(2)	Cl38-C39-Cl40	117.3(3)
C34-C35	1.364(4)	N12-C13-C14	110.8(2)	Cl38-C39-H392	107.3
C34-H341	0.953	N12-C13-H132	105.9	Cl40-C39-H392	106.7
C35-H351	0.951	C14-C13-H132	108.1	Cl38-C39-H391	108.7
C36-C37	1.364(4)	N12-C13-H131	109.9	Cl40-C39-H391	105.0
C36-H361	0.955	C14-C13-H131	110.5	H392-C39-H391	112.0
C37-H371	0.943	H132-C13-H131	111.5		
Cl38-C39	1.713(4)	C13-C14-N15	116.6(2)		

C39-Cl40	1.676(4)	C13-C14-C23	119.8(2)
C39-H392	0.994	N15-C14-C23	123.6(2)
C39-H391	0.993		

Table A1.18 Bond lengths and angles for 1-mesityl-3-(2-methylquinoline)imidazolin-2-ylidene](1,5-cyclooctadiene)iridium(I) Chloride **4.28**

Bond lengths (Å)		Bond angles (°)		Bond angles (°)	
Ir1-Cl2	2.372(2)	Cl2-Ir1-C3	161.2(4)	C14-N15-C16	125.0(9)
Ir1-C3	2.125(13)	Cl2-Ir1-C4	158.2(4)	C11-N15-C16	124.7(9)
Ir1-C4	2.096(11)	C3-Ir1-C4	40.4(4)	N15-C16-C17	117.0(9)
Ir1-C7	2.159(11)	Cl2-Ir1-C7	91.5(3)	N15-C16-C22	120.4(9)
Ir1-C8	2.177(11)	C3-Ir1-C7	92.5(5)	C17-C16-C22	122.5(10)
Ir1-C11	2.051(11)	C4-Ir1-C7	79.9(4)	C16-C17-C18	121.1(10)
C3-C4	1.456(16)	Cl2-Ir1-C8	89.6(4)	C16-C17-C19	117.5(9)
C3-C10	1.532(18)	C3-Ir1-C8	82.5(5)	C18-C17-C19	121.4(9)
C3-H31	0.991	C4-Ir1-C8	95.3(5)	C17-C18-H181	109.3
C4-C5	1.509(18)	C7-Ir1-C8	37.4(4)	C17-C18-H182	109.9
C4-H41	0.984	Cl2-Ir1-C11	87.7(3)	H181-C18-H182	108.9
C5-C6	1.477(15)	C3-Ir1-C11	93.1(4)	C17-C18-H183	110.7
C5-H51	0.970	C4-Ir1-C11	95.3(4)	H181-C18-H183	109.3
C5-H52	0.970	C7-Ir1-C11	164.6(5)	H182-C18-H183	108.8
C6-C7	1.510(17)	C8-Ir1-C11	157.9(5)	C17-C19-C20	120.9(10)
C6-H61	0.975	Ir1-C3-C4	68.7(8)	C17-C19-H191	119.5
C6-H62	0.969	Ir1-C3-C10	113.8(9)	C20-C19-H191	119.7
C7-C8	1.389(16)	C4-C3-C10	118.7(13)	C19-C20-C21	119.2(10)
C7-H71	0.984	Ir1-C3-H31	115.0	C19-C20-C24	119.0(11)

C8-C9	1.512(18)	C4-C3-H31	116.0	C21-C20-C24	121.7(11)
C8-H81	0.981	C10-C3-H31	116.0	C20-C21-C22	123.1(11)
C9-C10	1.512(16)	C3-C4-Ir1	70.9(7)	C20-C21-H211	117.8
C9-H91	0.968	C3-C4-C5	128.6(13)	C22-C21-H211	119.1
C9-H92	0.976	Ir1-C4-C5	113.7(7)	C16-C22-C21	116.5(11)
C10-H101	0.972	C3-C4-H41	111.7	C16-C22-C23	120.5(11)
C10-H102	0.971	Ir1-C4-H41	112.2	C21-C22-C23	122.9(11)
C11-N12	1.367(15)	C5-C4-H41	112.5	C22-C23-H231	109.5
C11-N15	1.347(14)	C4-C5-C6	113.3(14)	C22-C23-H232	108.8
N12-C13	1.389(14)	C4-C5-H51	108.1	H231-C23-H232	109.5
N12-C25	1.433(14)	C6-C5-H51	108.2	C22-C23-H233	111.7
C13-C14	1.330(16)	C4-C5-H52	108.6	H231-C23-H233	108.3
C13-H131	0.935	C6-C5-H52	108.9	H232-C23-H233	109.1
C14-N15	1.402(13)	H51-C5-H52	109.8	C20-C24-H241	108.2
C14-H141	0.936	C5-C6-C7	113.8(12)	C20-C24-H242	108.8
N15-C16	1.426(13)	C5-C6-H61	108.0	H241-C24-H242	110.1
C16-C17	1.413(14)	C7-C6-H61	108.8	C20-C24-H243	109.9
C16-C22	1.416(14)	C5-C6-H62	107.7	H241-C24-H243	110.5
C17-C18	1.489(14)	C7-C6-H62	108.5	H242-C24-H243	109.3
C17-C19	1.406(15)	H61-C6-H62	110.0	N12-C25-C26	114.3(9)
C18-H181	0.964	Ir1-C7-C6	113.4(7)	N12-C25-H251	107.9
C18-H182	0.960	Ir1-C7-C8	72.0(7)	C26-C25-H251	108.1
C18-H183	0.966	C6-C7-C8	123.6(14)	N12-C25-H252	108.4
C19-C20	1.380(15)	Ir1-C7-H71	112.7	C26-C25-H252	107.8
C19-H191	0.936	C6-C7-H71	114.2	H251-C25-H252	110.3
C20-C21	1.401(18)	C8-C7-H71	113.6	C25-C26-N27	116.9(9)
C20-C24	1.527(16)	Ir1-C8-C7	70.6(7)	C25-C26-C35	119.9(10)

C21-C22	1.372(16)	Ir1-C8-C9	109.2(8)	N27-C26-C35	123.2(10)
C21-H211	0.930	C7-C8-C9	123.5(14)	C26-N27-C28	116.9(9)
C22-C23	1.497(16)	Ir1-C8-H81	113.6	N27-C28-C29	117.3(9)
C23-H231	0.966	C7-C8-H81	115.7	N27-C28-C33	123.3(10)
C23-H232	0.964	C9-C8-H81	115.0	C29-C28-C33	119.4(10)
C23-H233	0.964	C8-C9-C10	117.0(11)	C28-C29-C30	119.8(10)
C24-H241	0.961	C8-C9-H91	107.8	C28-C29-H291	119.6
C24-H242	0.963	C10-C9-H91	109.0	C30-C29-H291	120.6
C24-H243	0.959	C8-C9-H92	106.9	C29-C30-C31	120.3(12)
C25-C26	1.502(15)	C10-C9-H92	107.3	C29-C30-H301	119.4
C25-H251	0.970	H91-C9-H92	108.7	C31-C30-H301	120.3
C25-H252	0.975	C3-C10-C9	113.0(12)	C30-C31-C32	119.9(11)
C26-N27	1.348(13)	C3-C10-H101	108.7	C30-C31-H311	120.4
C26-C35	1.412(15)	C9-C10-H101	108.8	C32-C31-H311	119.7
N27-C28	1.379(13)	C3-C10-H102	108.8	C31-C32-C33	121.4(11)
C28-C29	1.413(14)	C9-C10-H102	107.8	C31-C32-H321	119.9
C28-C33	1.413(15)	H101-C10-H102	109.6	C33-C32-H321	118.7
C29-C30	1.371(14)	Ir1-C11-N12	123.7(8)	C28-C33-C32	119.2(11)
C29-H291	0.936	Ir1-C11-N15	130.6(9)	C28-C33-C34	117.7(11)
C30-C31	1.421(17)	N12-C11-N15	105.6(9)	C32-C33-C34	123.1(11)
C30-H301	0.938	C11-N12-C13	110.2(9)	C33-C34-C35	119.3(12)
C31-C32	1.356(16)	C11-N12-C25	125.3(9)	C33-C34-H341	119.5
C31-H311	0.938	C13-N12-C25	123.9(9)	C35-C34-H341	121.2
C32-C33	1.395(16)	N12-C13-C14	106.8(10)	C26-C35-C34	119.6(11)
C32-H321	0.935	N12-C13-H13	125.6	C26-C35-H351	119.2
		C14-C13-H131	127.6	C34-C35-H351	121.2
		C13-C14-N15	107.9(10)		

C33-C34	1.415(17)	C13-C14-H141	126.7
C34-C35	1.374(17)	N15-C14-H141	125.4
C34-H341	0.934	C14-N15-C11	109.5(10)
C35-H351	0.937		

Table A1.19: Bond lengths and angles for [1-isopropyl-3-(2-methylquinoline)imidazolin-2-ylidene](1,5-cyclooctadiene)iridium(I) Chloride **4.29**

Bond lengths (Å)		Bond angles (°)		Bond angles (°)	
C1-N1	1.357(8)	N1-C1-N2	103.7(5)	C1-N1-C2	111.0(6)
C1-N2	1.367(8)	N1-C1-Ir1	130.1(5)	C1-N1-C4	124.6(5)
C1-Ir1	2.045(6)	N2-C1-Ir1	125.8(5)	C2-N1-C4	124.1(6)
C2-C3	1.340(10)	C3-C2-N1	106.9(6)	C1-N2-C3	111.6(6)
C2-N1	1.390(8)	C2-C3-N2	106.8(6)	C1-N2-C7	124.5(6)
C3-N2	1.374(9)	N1-C4-C5	110.1(6)	C3-N2-C7	123.9(6)
C4-N1	1.471(9)	N1-C4-C6	109.7(6)	C8-N3-C16	118.0(6)
C4-C5	1.518(12)	C5-C4-C6	112.6(7)	C1-Ir1-C18	88.5(3)
C4-C6	1.531(10)	N2-C7-C8	111.2(6)	C1-Ir1-C17	93.1(3)
C7-N2	1.472(9)	N3-C8-C9	123.1(7)	C18-Ir1-C17	39.3(3)
C7-C8	1.499(10)	N3-C8-C7	116.8(7)	C1-Ir1-C22	163.6(3)
C8-N3	1.324(9)	C9-C8-C7	120.1(7)	C18-Ir1-C22	97.1(3)
C8-C9	1.432(10)	C10-C9-C8	119.2(7)	C17-Ir1-C22	81.8(3)
C9-C10	1.358(11)	C9-C10-C11	119.8(7)	C1-Ir1-C21	160.0(3)
C10-C11	1.411(10)	C10-C11-C16	117.8(6)	C18-Ir1-C21	81.0(3)
C11-C16	1.429(9)	C10-C11-C12	123.8(7)	C17-Ir1-C21	89.4(3)
C11-C12	1.439(10)	C16-C11-C12	118.5(6)	C22-Ir1-C21	36.3(3)

C12-C13	1.368(12)	C13-C12-C11	120.4(7)	C1-Ir1-Cl1	90.09(18)
C13-C14	1.432(12)	C12-C13-C14	120.4(7)	C18-Ir1-Cl1	159.1(2)
C14-C15	1.366(10)	C15-C14-C13	120.2(7)	C17-Ir1-Cl1	161.5(2)
C15-C16	1.413(9)	C14-C15-C16	120.9(7)	C22-Ir1-Cl1	90.04(19)
C16-N3	1.379(9)	N3-C16-C15	118.4(6)	C21-Ir1-Cl1	93.8(2)
C17-C18	1.419(11)	N3-C16-C11	122.1(6)	C25-Cl2-C25	41.5(10)
C17-C24	1.531(10)	C15-C16-C11	119.5(6)	Cl3-Cl3-C25	85.6(6)
C17-Ir1	2.112(6)	C18-C17-C24	124.2(7)	Cl3-Cl3-C25	56.5(5)
C18-C19	1.509(11)	C18-C17-Ir1	70.0(4)	C25-Cl3-C25	35.5(9)
C18-Ir1	2.104(7)	C24-C17-Ir1	114.4(5)	Cl2-C25-Cl3	105.2(9)
C19-C20	1.513(12)	C17-C18-C19	124.6(7)		
C20-C21	1.532(11)	C17-C18-Ir1	70.6(4)		
C21-C22	1.367(11)	C19-C18-Ir1	112.2(5)		
C21-Ir1	2.196(7)	C18-C19-C20	113.3(6)		
C22-C23	1.533(10)	C19-C20-C21	112.3(6)		
C22-Ir1	2.195(6)	C22-C21-C20	122.9(7)		
C23-C24	1.547(11)	C22-C21-Ir1	71.8(4)		
Cl1-Ir1	2.3719(16)	C20-C21-Ir1	111.8(5)		
Cl2-C25	1.648(17)	C21-C22-C23	124.3(7)		
Cl2-C25	1.786(18)	C21-C22-Ir1	71.9(4)		
Cl3-Cl3	1.296(13)	C23-C22-Ir1	110.0(4)		
Cl3-C25	1.759(14)	C22-C23-C240	112.6(6)		
Cl3-C25	2.103(16)	C17-C24-C23	113.9(5)		

Table A1.20: Bond lengths and angles for [bis-1,3-(2-methylquinoline)imidazolin-2-ylidene](1, 5-cyclooctadiene)iridium(I) Chloride **4.31**

Bond lengths (Å)		Bond angles (°)		Bond angles (°)	
Ir1-Cl2	2.3653(11)	Cl2-Ir1-C3	158.86(14)	H132-C13-H131	112.3
Ir1-C3	2.082(4)	Cl2-Ir1-C4	161.77(14)	C13-C14-N15	116.5(4)
Ir1-C4	2.121(4)	C3-Ir1-C4	39.36(19)	C13-C14-C19	119.7(4)
Ir1-C7	2.160(4)	Cl2-Ir1-C7	90.72(14)	N15-C14-C19	123.8(4)
Ir1-C8	2.196(5)	C3-Ir1-C7	98.15(19)	C14-N15-C16	117.3(4)
Ir1-C11	2.022(4)	C4-Ir1-C7	82.45(19)	N15-C16-C17	123.4(4)
C3-C4	1.416(7)	Cl2-Ir1-C8	94.70(14)	N15-C16-C23	117.8(4)
C3-C10	1.518(6)	C3-Ir1-C8	81.47(18)	C17-C16-C23	118.7(4)
C3-H31	0.960	C4-Ir1-C8	89.95(18)	C16-C17-C18	116.9(4)
C4-C5	1.515(6)	C7-Ir1-C8	36.9(2)	C16-C17-C20	119.1(4)
C4-H41	0.998	Cl2-Ir1-C11	87.54(12)	C18-C17-C20	124.0(4)
C5-C6	1.543(8)	C3-Ir1-C11	92.36(17)	C17-C18-C19	119.6(4)
C5-H52	0.987	C4-Ir1-C11	91.42(17)	C17-C18-H181	120.5
C5-H51	0.977	C7-Ir1-C11	154.57(19)	C19-C18-H181	119.9
C6-C7	1.531(7)	C8-Ir1-C11	168.44(18)	C14-C19-C18	118.9(4)
C6-H62	0.982	Ir1-C3-C4	71.8(3)	C14-C19-H191	121.6
C6-H61	0.965	Ir1-C3-C10	113.7(3)	C18-C19-H191	119.5
C7-C8	1.379(8)	C4-C3-C10	124.7(4)	C17-C20-C21	120.3(5)
C7-H71	0.990	Ir1-C3-H31	114.7	C17-C20-H201	120.0
C8-C9	1.534(8)	C4-C3-H31	112.8	C21-C20-H201	119.7
C8-H81	0.996	C10-C3-H31	112.9	C20-C21-C22	121.2(5)
C9-C10	1.554(7)	Ir1-C4-C3	68.8(2)	C20-C21-H211	119.4
C9-H92	0.981	Ir1-C4-C5	113.5(3)	C22-C21-H211	119.4

C9-H91	0.984	C3-C4-C5	124.5(4)	C21-C22-C23	119.1(5)
C10-H101	0.968	Ir1-C4-H41	111.6	C21-C22-H221	119.3
C10-H102	0.965	C3-C4-H41	116.5	C23-C22-H221	121.7
C11-N12	1.354(5)	C5-C4-H41	113.1	C16-C23-C22	121.5(5)
C11-N26	1.361(5)	C4-C5-C6	112.8(4)	C16-C23-H231	117.8
N12-C13	1.461(5)	C4-C5-H52	108.6	C22-C23-H231	120.7
N12-C24	1.383(5)	C6-C5-H52	106.7	N12-C24-C25	106.7(4)
C13-C14	1.512(6)	C4-C5-H51	110.6	N12-C24-H241	125.3
C13-H132	0.971	C6-C5-H51	108.1	C25-C24-H241	128.0
C13-H131	0.978	H52-C5-H51	109.9	C24-C25-N26	106.6(4)
C14-N15	1.318(5)	C5-C6-C7	113.0(4)	C24-C25-H251	127.7
C14-C19	1.424(6)	C5-C6-H62	108.2	N26-C25-H251	125.7
N15-C16	1.372(6)	C7-C6-H62	108.8	C25-N26-C11	111.1(3)
C16-C17	1.414(6)	C5-C6-H61	108.4	C25-N26-C27	126.3(4)
C16-C23	1.420(6)	C7-C6-H61	111.6	C11-N26-C27	122.5(3)
C17-C18	1.426(6)	H62-C6-H61	106.6	N26-C27-C28	114.2(3)
C17-C20	1.418(6)	C6-C7-Ir1	108.6(3)	N26-C27-H271	107.6
C18-C19	1.362(7)	C6-C7-C8	25.2(5)	C28-C27-H271	109.0
C18-H181	0.939	Ir1-C7-C8	72.9(3)	N26-C27-H272	108.6
C19-H191	0.955	C6-C7-H71	113.7	C28-C27-H272	110.1
C20-C21	1.365(7)	Ir1-C7-H71	114.9	H271-C27-H272	107.2
C20-H201	0.965	C8-C7-H71	114.1	C27-C28-N29	114.5(4)
C21-C22	1.416(8)	Ir1-C8-C7	70.1(3)	C27-C28-C33	121.4(4)
C21-H211	0.931	Ir1-C8-C9	111.9(3)	N29-C28-C33	123.9(4)
C22-C23	1.364(7)	C7-C8-C9	123.8(5)	C28-N29-C30	117.0(4)
C22-H221	0.954	Ir1-C8-H81	112.1	N29-C30-C31	122.6(4)
C23-H231	0.942	C7-C8-H81	115.0	N29-C30-C37	118.8(4)

C24-C25	1.344(6)	C9-C8-H81	114.8	C31-C30-C37	118.6(4)
C24-H241	0.951	C8-C9-10	112.3(4)	C30-C31-C32	117.8(4)
C25-N26	1.388(5)	C8-C9-H92	107.7	C30-C31-C34	119.2(5)
C25-H251	0.947	C10-C9-H92	110.8	C32-C31-C34	123.0(5)
N26-C27	1.460(5)	C8-C9-H91	111.4	C31-C32-C33	119.3(4)
C27-C28	1.521(6)	C10-C9-H91	109.2	C31-C32-H321	119.9
C27-H271	0.981	H92-C9-H91	105.2	C33-C32-H321	120.8
C27-H272	0.969	C9-C10-C3	111.7(4)	C28-C33-C32	119.2(4)
C28-N29	1.327(6)	C9-C10-H101	111.3	C28-C33-H331	120.2
C28-C33	1.415(6)	C3-C10-H101	111.3	C32-C33-H331	120.6
N29-C30	1.374(6)	C9-C10-H102	106.3	C31-C34-C35	121.0(5)
C30-C31	1.415(7)	C3-C10-H102	106.5	C31-C34-H341	119.1
C30-C37	1.422(7)	H101-C10-H102	109.5	C35-C34-H341	119.9
C31-C32	1.416(7)	Ir1-C11-N12	130.5(3)	C34-C35-C36	120.0(5)
C31-C34	1.415(7)	Ir1-C11-N26	125.4(3)	C34-C35-H351	118.8
C32-C33	1.357(7)	N12-C11-N26	104.0(3)	C36-C35-H351	121.1
C32-H321	0.956	C11-N12-C13	123.7(3)	C35-C36-C37	120.3(5)
C33-H331	0.940	C11-N12-C24	111.5(3)	C35-C36-H361	120.5
C34-C35	1 .366(8)	C13-N12-C24	124.7(3)	C37-C36-H361	119.2
C34-H341	0.944	N12-C13-C14	111.2(4)	C30-C37-C36	120.8(5)
C35-C36	1.412(9)	N12-C13-H132	107.2	C30-C37-H371	119.5
C35-H351	0.933	C14-C13-H132	109.4	C36-C37-H371	119.7
C36-C37	1.367(8)	N12-C13-H131	107.7		
C36-H361	0.946	C14-C13-H131	108.9		
C37-H371	0.935				