Chelating Carbene Ligands And Their Metal Complexes

By

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The work described in this thesis was carried out in the Department of Chemistry at The University of Wales Cardiff under the supervision of Prof. Kingsley J. Cavell and Dr Ian A. Fallis

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Abstract

This thesis describes the synthesis of a number of functionalised imidazolium salts as precursors to N- heterocyclic carbenes and their subsequent coordination to Ag and Pd. Further a number of the Pd complexes were tested in the Heck reaction and their activities compared to complexes with similar structural features currently within the literature.

A range of imidazolium salts have been synthesised which include quinoline and octahydroacridine moieties and have been characterised by a number of methods including X-ray crystallography. A bis imidazolium salt has also been prepared as a DIOP analogue. The imidazolium salts were successfully reacted with Ag_2O to form the NHCAg(I) complexes. The quinoline and octahydroacridine based NHCs were transmetallated to Pd as chelating ligands, the quinoline based systems appearing as planar, strained complexes in the X-ray structure.

The activities of the quinoline and octahydroacridine based NHCPd(II) complexes in the Heck coupling of 4-bromoacetophenone and 4-chlorobenzaldehyde with n-butyl acrylate were assessed and found to be comparable to similar systems with low to satisfactory conversions.

Chapter One - Introduction

Chapter Two-Ligand Design: Chelating Imidazolium Salts And Their Synthesis

Chapter Three

Silver (I) Complexes Of Functionalized And Bis- N-Heterocyclic Carbene Ligands

Chapter Four

Palladium Carbene Complexes

Chapter Five

Pd catalysed C-C Coupling reactions : The Heck Reaction

APPENDIX

Glossary

Ad	Adamantyl
Ar	Aryl
BA	Butyl acrylate
BAP	4-Bromoacetophenone
BArF	$B[3,5\text{-}(CF_3)_2C_6H_3]_4$-
COD	1, 5-cyclooctadiene
dba	Dibenzylidineacetone
DCM	Dichloromethane
DIPP	2,6-bis(diisopropyl)phenyl
DMAc	N,N-Dimethylacetamide
DMF	N,N-dimethylformamide
DMSO	Dimethylsulfoxide
Et_2O	Diethyl ether
GC	Gas chromatography
L	Neutral, 2 electron donor ligand, e.g. phosphine or carbene
LDA	Lithium Diisopropylamine
M	Metal
Me	Methyl
Mes	Mesityl or 2,4,6-trimethylphenyl
NHC	N-heterocyclic carbene
OAc	Acetate anion
Ph	Phenyl
r.t.	Room temperature
THF	Tetrahydrofuran
X	Anionic Ligand e.g. Halogen

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I must also thank my Mum and Dad and Thuy for supporting me throughout my Ph.D as well as 'ensuring' that I wrote up whilst working!

Chapter One

1.1 Classification Of Carbenes

A carbene is a neutral compound featuring a divalent carbon atom with only six electrons in its valence shell[1]. Because carbenes do not posses an octet of electrons they are generally highly reactive species. For the majority of carbenes the carbon atom's orbitals are bent to some degree away from linearity, which has an effect of breaking the degeneracy of the nonbonding orbitals and causing the carbon to become sp_2 hybridized. The p_y orbital remains almost unchanged and is termed pπ whilst the p_x orbital is stabilized due to the acquisition of some *s* character and is called σ (Figure 1.1(a)). This break from degeneracy leads to different electronic configurations which divide carbenes into two types – singlets and triplets. To form the triplet state the two nonbonding electrons must occupy two different orbitals with parallel spins, while in the singlet state they pair to occupy either the σ or p_π orbital. 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-p_π separation and according to Hoffmann, a value of at least 2 eV is needed to impose this. Anything below 1.5 eV leads to the triplet state[3]. The factors that cause the electrons to adopt one of these configurations will now be considered.

The substituents on the carbene can determine whether a singlet or triplet state is formed through a combination of inductive, mesomeric and steric effects. σ- electron withdrawing groups increase the σ-p_π gap by inductively stabilising the σ nonbonding orbital by increasing its *s* character and thus favouring the singlet state. Conversely, a σ electron donating substituent will induce only a small σ-p_π gap and favour the triplet state. Mesomeric effects influence the ground state multiplicity to a much greater extent and are the dominating feature. The mesomeric effect consists of the interaction of the carbon p_π orbitals with the appropriate *p* or π orbital of the carbene substituents. For illustrative purposes substituents that are π electron donating can be termed X, while π electron withdrawing groups can be termed Y (Figure 1.1(b)). XX carbenes are bents singlets, while most of the YY carbenes are predicted to be linear singlet

carbenes (though truly linear carbenes are extreme cases, bulky substituents can stabilise triplet carbenes by increasing the carbene bond angle and thus bringing the carbene frontier orbitals closer to degeneracy).

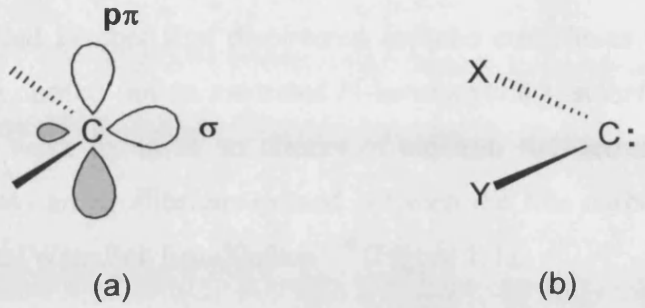


Figure 1.1: Diagram illustrating the loss in degeneracy of the non-bonding orbitals of a free NHC

N-Heterocyclic carbenes (NHCs) (Figure 1.2, (a)) are the subject of this work and are firmly placed within the singlet state. The nitrogen atoms (an X substituent) adjacent to the carbon are responsible for the stability of the NHC by a push pull effect (Figure 1.2 (b)). The nitrogen atoms posses a lone pair of electrons which can π donate to the formally vacant p_π carbon orbital thereby stabilising it. Being more electronegative than the carbon, the nitrogens can inductively remove electron density from the carbene centre which serves to stabilise the carbene lone pair. NHCs are therefore neutral two electron donor nucleophiles. Other heterocyclic carbenes containing a sulphur or oxygen atom are able to stabilise the carbene in a similar manner.

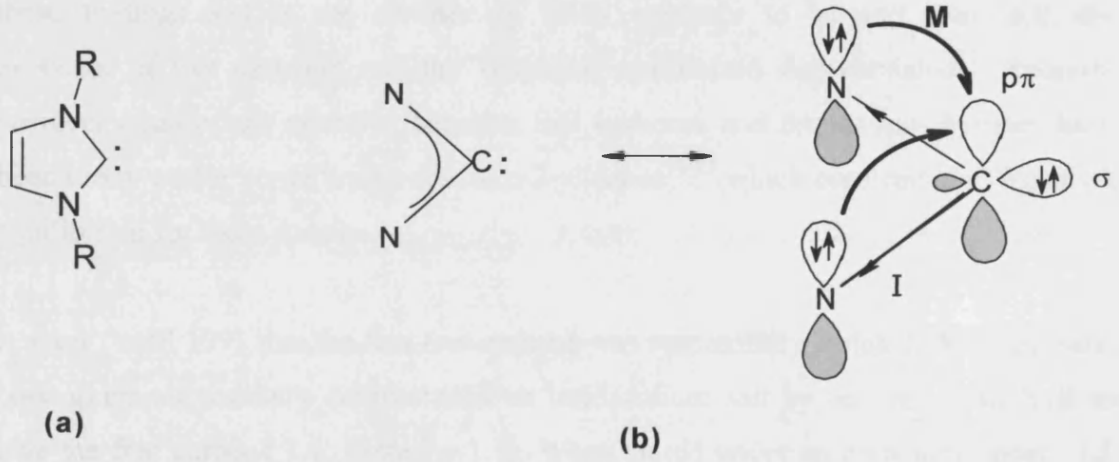


Figure 1.2: (a): A typical NHC, (b): The 'Push-Pull' effect of the adjacent nitrogen atoms which stabilise NHCs. M represents mesomeric effects whilst I is inductive.

1.2 A Brief History of Carbenes

Around the time that Fischer first discovered carbene complexes (1964)[4], extensive studies were being carried out on saturated N-heterocyclic systems by Wanzlick and co-workers. Their work focussed on dimers of electron rich tetraaminoethylenes to which they proposed an equilibrium existed between the free carbene and the dimer and was termed the 'Wanzlick Equilibrium'[5-8] (Figure 1.3).

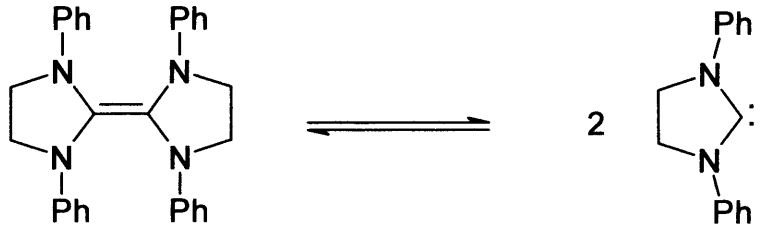
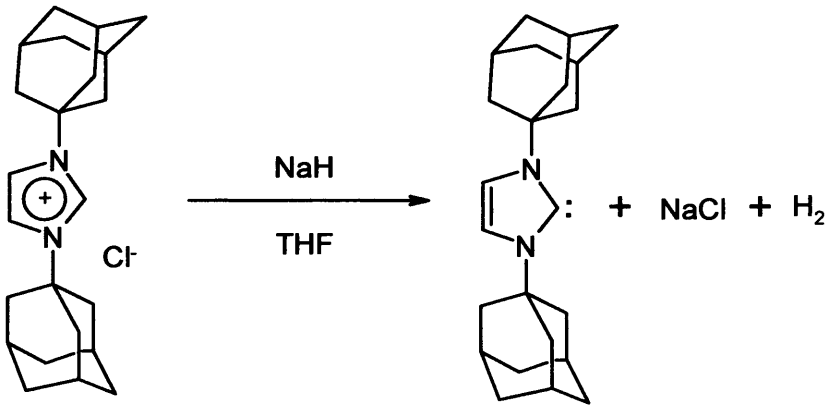


Figure 1.3: The 'Wanzlick equilibrium'. Wanzlick proposed that the dimer dissociated readily into two diaminocarbene 'halves'[13].

Contrary to this hypothesis, Winberg's[9] investigations into the metathesis reaction between cyclic and acyclic enetetramines showed that the corresponding cross products did not occur. Lemal[10] and co-workers also showed that mixed olefins from different enetetramines only occurred in the presence of electrophiles. On the basis of these findings and in the absence of NMR evidence to support Wanzlick, the existence of free carbenes and the Wanzlick equilibrium was excluded[11]. Recently however equilibrium mixtures between free carbenes and tetraaminoethylenes have been observed for some benzimidazolin-2-ylidenes[11-13] which confirms the Wanzlick equilibrium for these species.

It wasn't until 1991 that the first free carbene was successfully isolated. Arduengo and co-workers successfully deprotonated an imidazolium salt by reaction with NaH to give the free carbene **1.1**, (Scheme 1.1). When stored under an inert atmosphere **1.1** was found to be an indefinitively stable colourless crystalline solid and bore an unexpectedly high thermal stability; (melts at 240 °C without decomposition)[14].

Initially the stability of Arduengo's free carbene was thought to be due to the steric bulk of the adamantyl groups preventing nucleophilic attack[14]. However isolation of free carbenes with less sterically demanding groups such as 1,3,4,5 tetramethylimidazolin-2-ylidene[15] and 1,3-dimethylimidazolin-2-ylidene[15] (Figure 1.4, (**1.2**) & (**1.3**)) confirm that the stability arises from the mesomeric effects of the carbene carbons adjacent nitrogens.



1.1

Scheme 1.1: Arduengo's synthesis of the stable NHC 1,3-bis(1-adamantyl)imidazolin-2-ylidene (**1.1**).

1.2 **1.3**

Figure 1.4: 1,3,4,5 tetramethylimidazolin-2-ylidene (**1.2**) and 1,3-dimethylimidazolin-2-ylidene (**1.3**)

Prior to Arduengo's discovery, little research was being carried out in the field of carbenes due to the limitations of creating interesting novel metal complexes. The

method and isolation of **1.1** sparked a huge revival of interest in carbene chemistry which is continuously growing.

Since the isolation of **1.1**, many other stable cyclic (**1.4**[16],**1.6**[17],**1.9**[18], **1.11**[19] and **1.12**[20]) and acyclic (**1.5**[19,21], **1.7**[22],**1.8**[22] and **1.10**[23]) carbenes have been synthesised which include a mixture of heteroatoms, (Figure 1.5)[24]. Compound **1.11** is of interest as it is the first example of a carbene to be stabilised by the donation of lonepairs from two phosphines. (Note the presence of S and O in carbenes **1.6**, **1.7** and **1.8** as being sufficient substitutes for N). The isolation of **1.10** and **1.12** by Bertrand proved that the presence of one nitrogen is sufficient to stabilise carbenes in certain cases. **1.10** was isolated as an indefinitely stable free carbene at room temperature and demonstrated that providing a tertiary alkyl group is bound to the carbene carbon, acyclic (alkyl)(amino) carbenes are isolable and importantly, behave as strong σ donors towards transition metal centres[23]. **1.12**, termed a 'CAAC' (Cyclic alkyl (amino) carbene) was recently reported by the same group and is the first example of a cyclic carbene where one of the electronegative amino substituents of an NHC is replaced by a strong σ donor alkyl group. This makes the ligand more electronegative than diamino NHC's. The quaternary carbon α to the carbene carbon atom also offers a steric environment which is dramatically different from diamino carbenes and phosphines. Further to the isolation of a number of CAAC's, Bertrand successfully prepared [PdCl(alkyl)(CAAC)] complexes as air stable crystals (stable enough to be purified by column chromatography on silica gel) in high yields by the addition of $[\{Pd(alkyl)(Cl)\}_2]$ to the corresponding carbenes. These were subsequently tested as active catalysts in the Pd catalysed α arylation of ketones [25-27]. The same group[28] recently reacted CAAC's with CO to afford amino ketenes (Scheme 1.2 (a)) which are indefinitely stable at room temperature. The formation of such species with diamino NHC's has been shown not to proceed by Arduengo (Scheme 1.2 (b)). The unique steric and electronic properties of these CAAC's coupled with Bertrand's versatile synthetic procedure, indicates that a wealth of CAAC ligands will no doubt follow with potentially important applications.

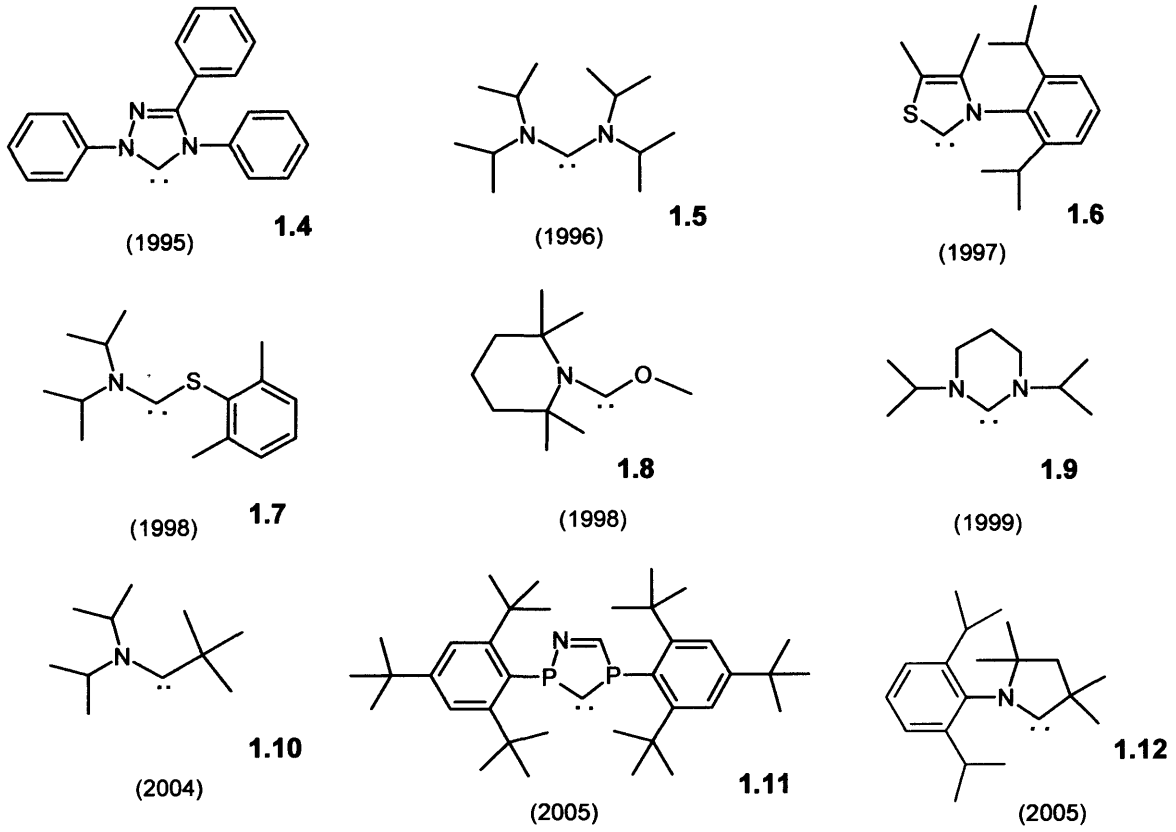
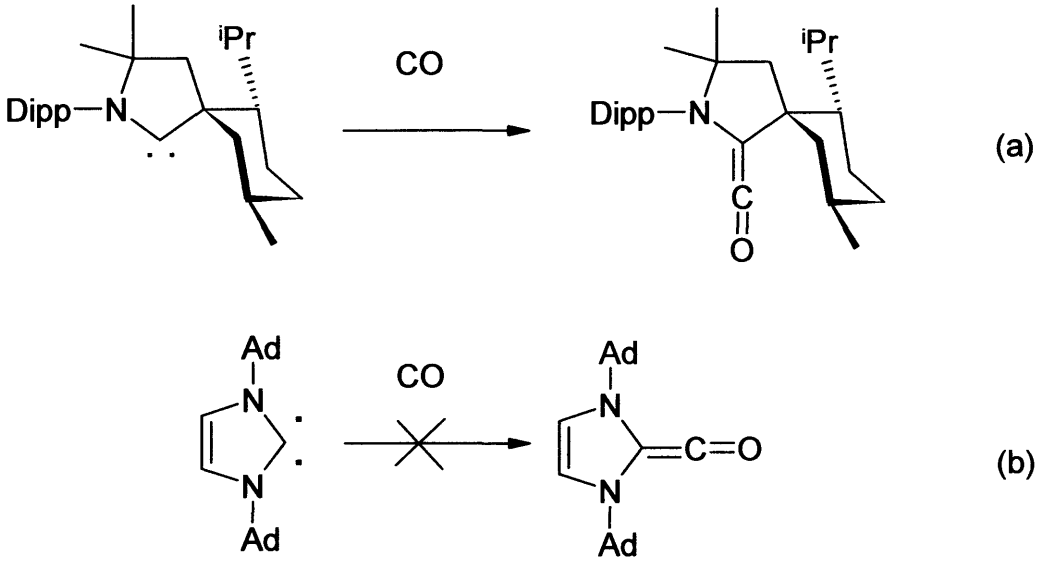


Figure 1.5: Examples of Isolated free carbenes with publication year.



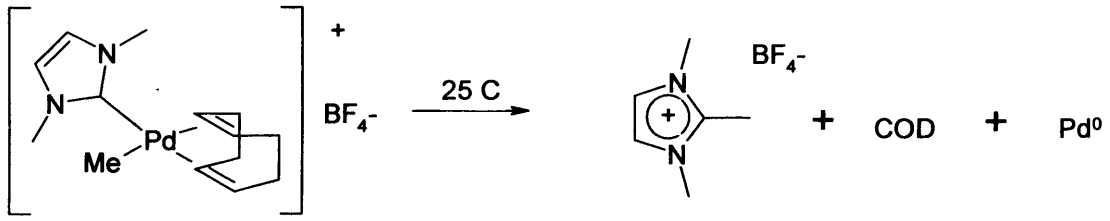
Scheme 1.2: The reaction of CAAC's and traditional NHC's with CO

1.3 N-Heterocyclic Carbenes As Ligands

Carbenes have been[24] and still are compared to phosphines as ligands and it is easy to understand why. Both ligands are neutral, strong two electron σ donors, and have the capacity to have their steric bulk manipulated. It has been shown however that an NHC can form a much stronger bond with a metal than a phosphine[31-33] and that π back bonding is negligible. Studies have shown that even in the case of electron rich late transition metals such as the linear $Pd^0(NHC)_2$ or $Pt^0(NHC)_2$ complexes, bond formation is via donation of σ electron density from the NHCs lone pairs into the hybrid metal bonding orbital ($d_z^2 + s$)[34]. Backbonding from the filled metal d_{xz} and d_{yx} orbitals into the carbene pπ orbital is negligible, due to the occupancy of electron density from the adjacent nitrogens[32]. This absence of a requirement for backbonding has meant that NHC's have the advantage of being able 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[1,35,36], Be[37,38] and hexavalent U[39,40] have been shown to form stable metal complexes with NHCs. X-ray diffraction data also confirms that bond lengths in NHC-M complexes are typical for M-C single bonds[1,33,65,112]. The greater strength of the carbene bond means that in a mixed complex of NHC and phosphine, the phosphine would dissociate in preference to the carbene[42]. Using an NHC should therefore eliminate the need for the large excesses of phosphine ligand in some catalytic reactions, where they are needed to compensate for phosphine degradation by P-C bond cleavage.

The planarity of the heterocyclic ring, coupled with the space requirements of any N-substituents means that NHC's can be more sterically demanding than phosphines. The majority of NHC complexes have also shown remarkable stability towards air and moisture, as well as high temperatures. These advantages coupled with the strength of the C-M bond and the ability to vary the N substituents, has given carbenes an attraction for catalytic implications. When bound to metals, NHC's are significantly less reactive than the two major classes of carbene ligands, Schrock and Fischer carbenes[42], and have generally been viewed as spectator ligands, though recent work has shown that they are not always such. It has been shown that NHC's can reductively eliminate to give 2-hydrocarbylimidazolium salts from hydrocarbyl-

M-carbene complexes[43-48]. Cavell first reported this decomposition pathway in 1998 during the examination of the synthesis and behaviour of complex **1.13** (Scheme 1.3). Complexes with a Pd-Methyl bond in place of a halide (such as **1.13**) are valuable as pre-catalysts as they have been shown to display increased catalytic activity.



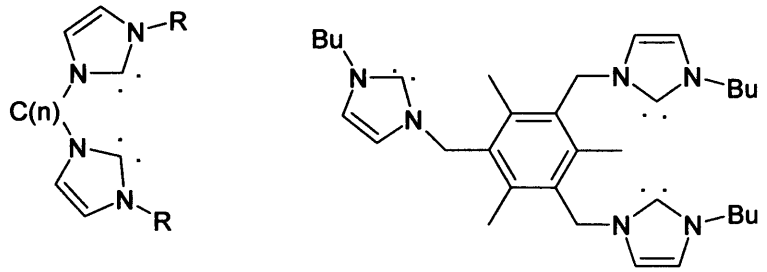
1.13

Scheme 1.3: The reductive elimination of an imidazolium salt from a Pd hydrocarbyl complex.

Complex **1.13** was found to undergo immediate reductive elimination at room temperature generating the 1,2,3-trimethyl-imidazolium tetrafluoroborate salt as well as free cyclooctadiene (COD) and Pd black[49]. Subsequent investigations have found that bulky ligands accelerate this elimination reaction whilst electron rich ligands decrease it. Bidentate ligands have also been shown to decrease the rate by restricting the bite angle[42]. Consequentially this decomposition route via reductive elimination has implications in catalytic reactions, particularly if intermediate complexes with hydrocarbyl ligands are formed during the reaction.

1.4 Chelating And Mixed Donor Ligands

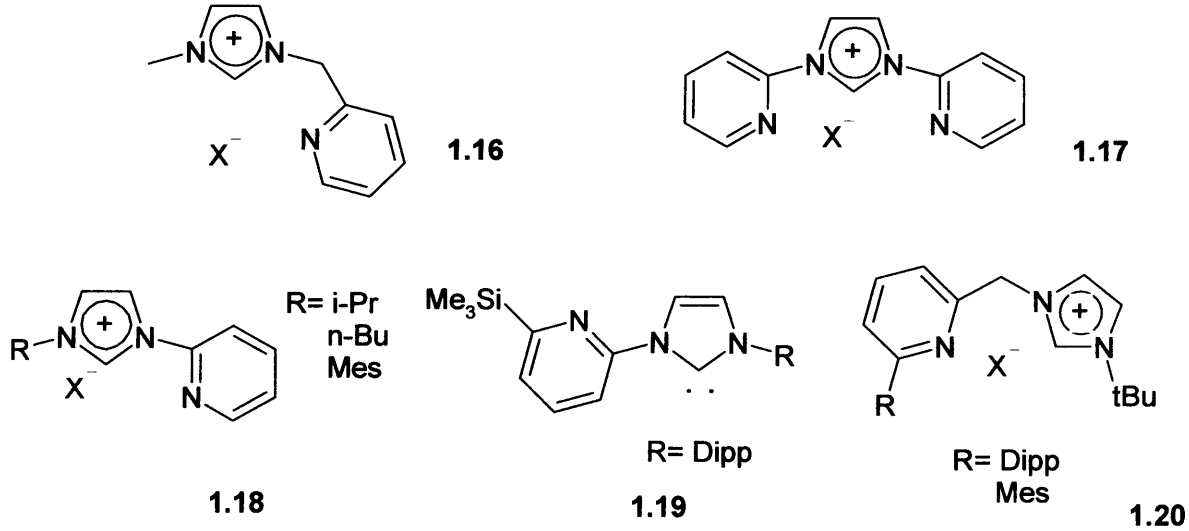
The major role played by bidentate phosphine and phosphite ligands in homogeneous catalysis has naturally led to the development of chelating carbenes in an effort to further exploit these strong σ donor ligands. A wide range of ligands containing two or more NHC groups are now known, a large number of these being modifications of the general bis-carbene **1.14** (Figure 1.6). **1.15** is an example of a tri-NHC ligand isolated by Dias and Jin in 1994[50]. Further examples of bis carbenes are shown in the section covering chiral NHC's.



1.14 1.15

Figure 1.6: Examples of chelating carbenes.

Ligands containing both phosphorus and nitrogen donor atoms have been shown to form strong metal phosphorus bonds and weak metal nitrogen bonds[41] and are important in many catalytic reactions[51-55]. Because 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 bring to a catalytic reaction. In general the hemilabile functionality means that whilst the carbene is bound strongly to the metal centre, the hemilabile arm can offer both stability to the metal via coordination, or allow vacant coordination sites by dissociation. This could prove valuable in extending catalyst life in homogenous reactions. 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[41,56,57]. A number of examples are given in Figure 1.7.



1.16 1.17 1.18 1.19 1.20

Figure 1.7: Examples of pyridyl- functionalised NHC's.

1.16 was used to successfully form the PdMeCl(NHC) complex via transmetallation from the Ag(I)NHC. Subsequent testing in the Heck reaction showed the catalyst to

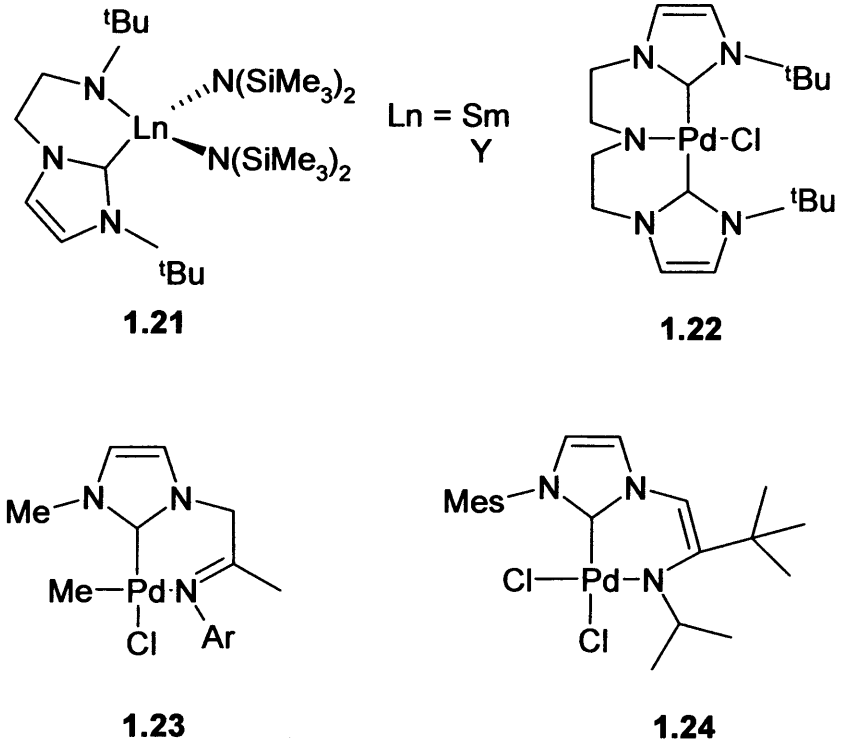
have good stability and gave satisfactory conversions in the coupling of 4-bromoacetophenone/4-chlorobenzaldehyde with n- butyl acrylate. High TONs were also obtained in the Suzuki coupling of 4-bromoacetophenone with $C_6H_5B(OH)_2$ though at the expense of conversions[56]. **1.16** was also used by Jin[58] to form a cationic chelating NHC Ni complex via the reaction of the Ag(I)NHC with $Ni(PPh_3)_2Cl_2$. Preliminary studies showed the complex to be active in the polymerization of norbornene and the polymerization of ethylene. Danopoulos also formed PdMeCl(NHC) complexes from salts analogous to **1.16** where the second N substituent is a ^{t}Butyl or mesityl group. Both showed good activities for the Heck and amination reactions[71]. The potentially terdentate NHC precursor **1.17** was formed by Chen and Lin[41] and used to form Pd complexes in a monodentate and bidentate five membered chelate fashion via the reaction of the salt with $Pd(OAc)_2$. Initial catalytic testing of the copolymerisation of CO and norbornylene showed moderate to good yields. **1.18** was used by Crabtree[131] to form a Pd(0) complex via the oxidative addition of an imidazolium C-H bond to the metal forming bis carbene complexes via double oxidative addition. **1.19** is an example of a free heteroatom functionalised NHC isolated by Danopoulos in 2002[103]. The corresponding imidazolium salt was deprotonated using $KN(SiMe_3)_2$ in THF between -10 and 0°C and crystallisation from petroleum ether afforded the free NHC as air sensitive but stable at room temperature crystals. The same group described **1.20** with a number of other functionalised NHCs regarding their synthesis and structural studies[103].

Danopoulos states four reasons why a pyridine ring tethered to an NHC adds versatility to the ligand design and they are, **(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 hemilability with possible implications on the catalytic activity. **(iii)**. The electronic asymmetry of the chelating N-functionalised NHC ligand renders the corresponding trans sites electronically inequivalent, due to the large difference in the trans effect of the chelating ends. **(iv)**. The donor and steric characteristics of the pyridine and NHC functional groups are easily tuneable by a variety of substituents[103].

Arnold reported the first amido functionalised NHC ligand and the synthesis of its trivalent samarium(III) and yttrium(III) (**1.21,** Figure 1.8) adducts via the

transamination of the corresponding Li carbene-amine[35]. Other amido functionalised NHC's have been prepared by the group and used to form complexes with Uranium[59] and Cerium[60], while the group of Douthwaite[61] prepared the first example of a transition metal NHC-amide (**1.22**).

Imino functionalised carbenes have also been synthesised by various groups and include **1.23**[62] and **1.24**[63] (Figure 1.8). Both were formed from transmetallation from the Ag(I) carbenes. In **1.24** and its Rh(I) analogue the enamine tautomer forms upon complexation with the Pd and Rh centres.

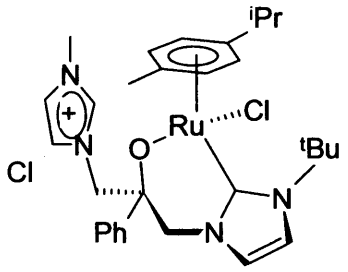


1.21 **1.22**

1.23 **1.24**

Figure 1.8: Amido and Imino functionalised NHC complexes.

Alkoxide and phenoxide groups have also been used to functionalise NHC's. Arnold formed Li[64], Cu[64,65] and Ru[66] (**1.25,** Figure 1.9) complexes of the former, while Hoveyda[67] and Grubbs[68] formed Ru (**1.26**) and Pd (**1.27**) complexes of the latter respectively.



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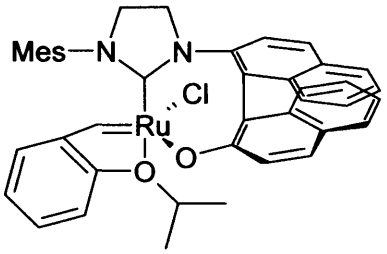

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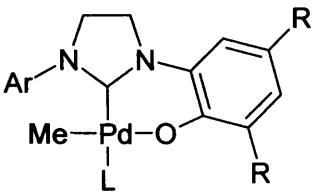

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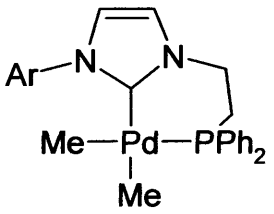
Figure 1.9: Alkoxide and Phenoxide functionalised NHC's.

Because NHC's and phosphines are both strong trans effect/influence ligands they are both able to activate/labilise groups coordinated trans to themselves. In mixed NHC-phosphine chelating square planar complexes the remaining groups attached to the metal centre can evidently not avoid a position with a strong trans influence. This is particularly important if the trans group is a migrating hydrocarbyl species in for example the hydroformylation reaction where the migration process will be promoted. A number of examples of this class of ligand now exist[69,70,88,90]. Nolan was first to show the high efficiency of a phosphine-imidazolium salt in the *in-situ* Heck coupling of an aryl bromide with n-butyl acrylate[69]. Danopoulos published similar ligands in complexes with Pd(II)[70] as well as the free carbene[103]. The crystal structures of Danopoulos's complexes **1.28** and **1.29** showed interesting results. The two Pd-CH_3 bond lengths of **1.28** were approximately equal while the Pd-Br bond in **1.29** trans to the phosphine was actually longer than that trans to the NHC[70]. This is in contrast to what would be expected due to the NHC's stronger σ donor strength and hence greater trans influence.



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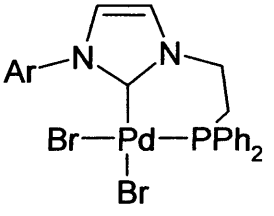

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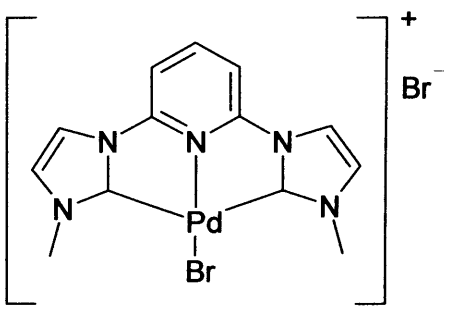
Figure 1.20: Danopoulos's NHC-phosphine complexes.

As previously stated chelating carbenes are also significantly less prone to reductive elimination pathways than monodentate ones. This is possibly due to the NHC being

unable to adopt the correct conformation for reductive elimination due to the conformational rigidity imposed by the chelate[72]. This is significant when dealing with catalytically interesting Pd hydrocarbyl species and will be discussed later. It should be noted that because of the rigid geometry of the five membered planer rings of the NHC, the optimum number of atoms to form an appropriate chelate does not match that for diphosphanes or diamines. Methylene bridged 2,3-dihydro-1H-imidazol-2-ylidenes and 1,2,4-1H-triazol-5-ylidenes form six membered rings upon metal complexation. However the natural bite angle of 78-79° found in transition metal complexes (W, Pd) of these ligands is exactly that of 1,1'-bis(diphenylphosphino)methane (four membered ring)[73].

Tridentate ligands have also appeared in the literature as so called 'pincer' carbenes, both with 2:1 and 1:2 carbene to mixed donor ratios. The pincer framework serves to stabilise M-L bonds. Amongst those in the literature, Crabtree reported the first Pd Pincer NHC complex (**1.30**)[74] (Figure 1.21) as an essentially flat and rigid molecule and as an active catalyst in the Heck reaction. Its low solubility in most non-polar solvents however has reduced its application in other Pd catalysed reactions[75] and as a remedial step Crabtree replaced the methyl wingtip groups for n-butyl to give complex **1.31** which showed both improved solubility and catalytic activities. This increase in solubility is thought to arise from the n-butyl groups causing a deviation from planarity which has an effect of decreasing intermolecular stacking in the solid state. The same group also later reported the Ru pincer complexes **1.32** and **1.33**. **1.32** was reported to be active for hydrogen transfer as well as the oxidation of olefins while **1.33** was shown to be completely inefficient at both reactions[76].



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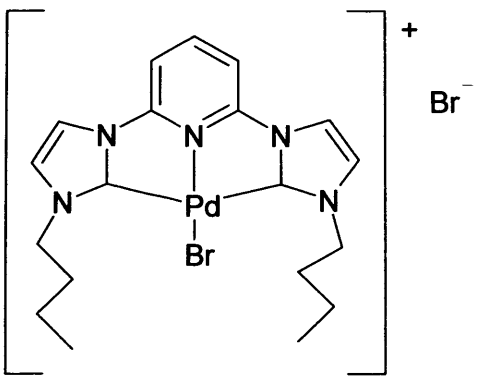

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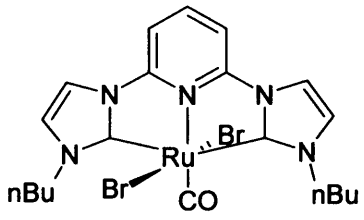
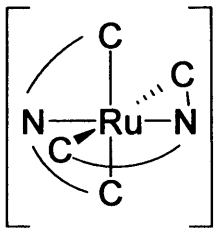
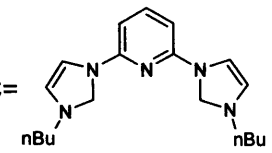




$(PF_6)_2$

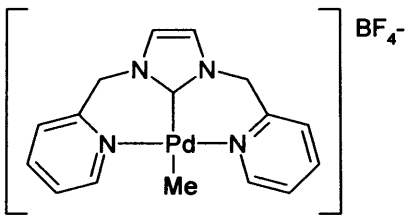
CNC=

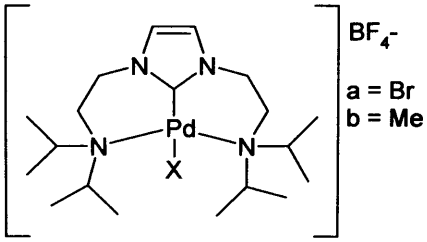


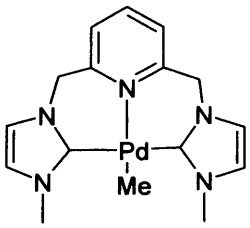
1.32 **1.33**

Figure 1.21: Examples of 'Pincer' Pd complexes reported by Crabtree.

Cavell synthesised the first Pd- hydrocarbyl pincer complex **1.34**[173] (Figure 1.21), which showed good stability with respect to reductive elimination up to 100°C in DMSO and also proved to be an efficient catalyst in the Heck reaction. The analogous complexes **1.35a** and **1.35b** containing the comparatively weaker amino donors were also prepared. **1.35b** was shown to give the reductive elimination product after only a short period in solution while **1.35a** was afforded as a stable solid. Cavell also reported the Pd- hydrocarbyl complex **1.36**[77] which was shown to have high stability and good activity in the Heck reaction with activated aryl bromides.





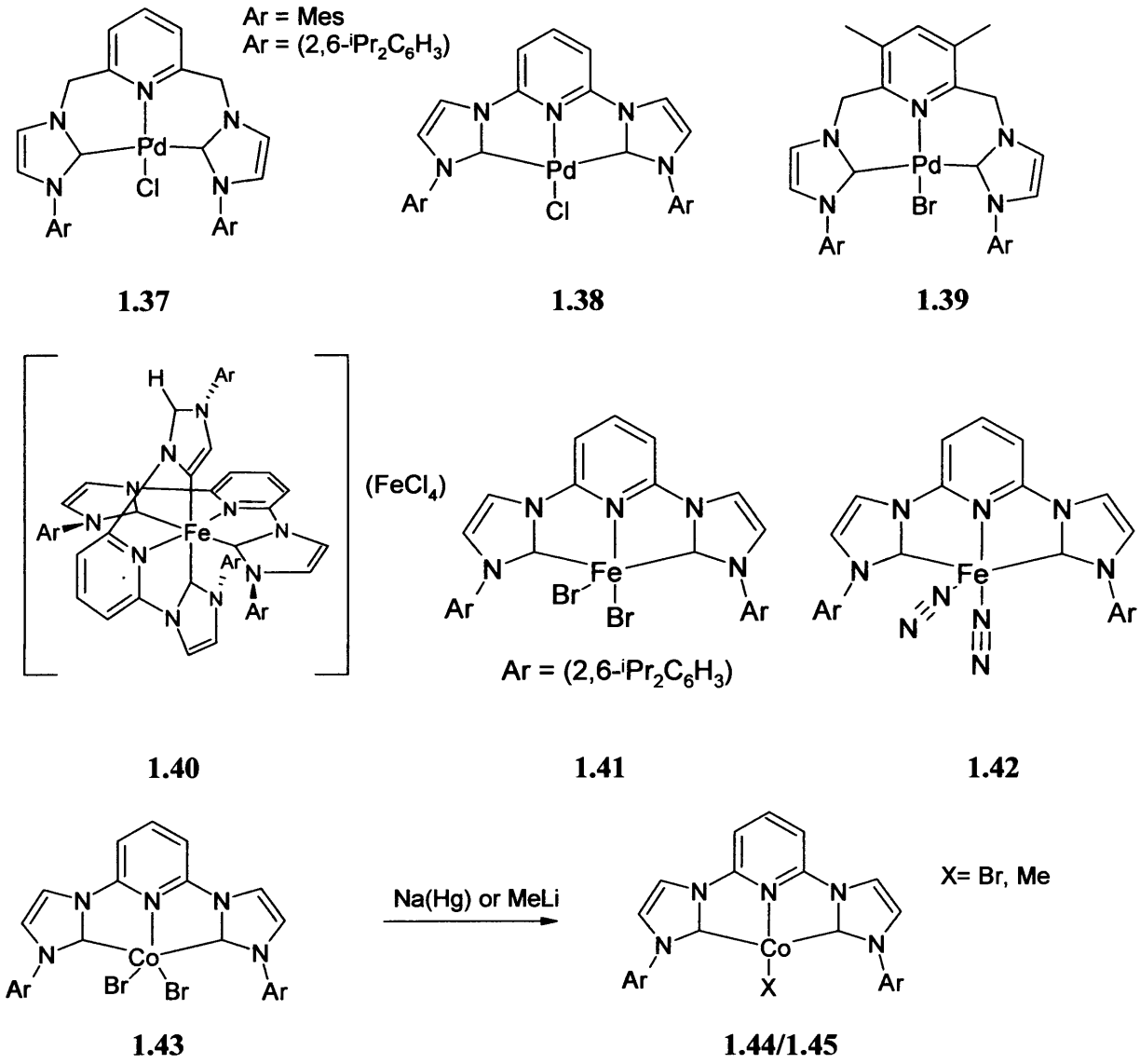


1.34 **1.35** **1.36**

Figure 1.21: Reported examples of Pincer complexes by Cavell.

Around the same time that Cavell published **1.36**, Danopoulos synthesised the analogous complexes **1.37** and **1.38**[180] and also demonstrated their stability and activity in the Heck reaction. The same group also went on to synthesis **1.39**[78] as well as reporting Co and Fe pincer complexes. The Fe complex **1.40** is the first to feature C2 and C5 metallation modes coexisting on the same metal centre[79]. The same paper also demonstrated the synthesis of the paramagnetic complex **1.41** by direct metallation of the imidazolium salt with $[Fe(N(SiMe_3)_2]$, the structure of which was determined by X-ray crystallography. **1.41** was later used to synthesis the first dinitrogen complex stabilised by NHC's (**1.42**)[80]. This 'aminolysis' method of

carbene complex synthesis was further extended by the same group via reaction of $Co[N(SiMe_3)_2]_2$ with a bis imidazolium salt to give **1.43**. **1.43** was subsequently used to form a number of complexes including **1.44** and **1.45** by reaction of Na(Hg) and MeLi respectively[81].



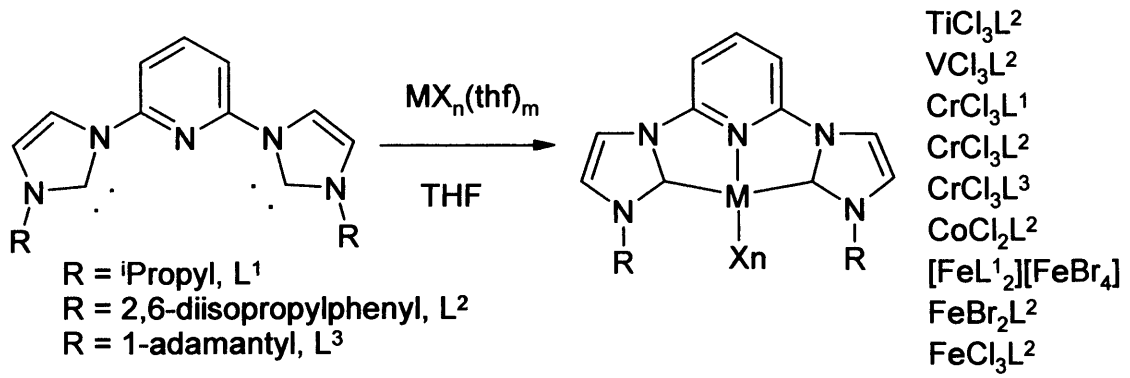
1.37 **1.38** **1.39**

1.40 **1.41** **1.42**

1.43 **1.44/1.45**

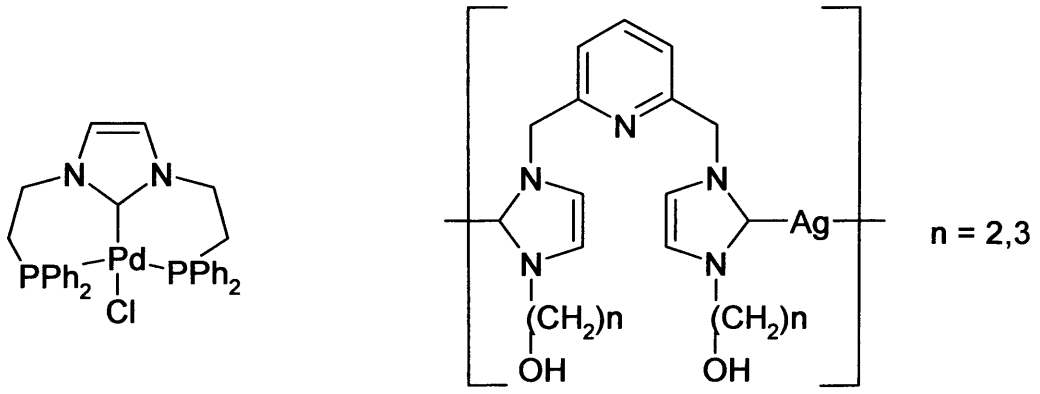
Figure 1.22: Examples of Danopoulos' pincer carbene complexes.

Gibson has reported a host of complexes according to Scheme 1.4[82] and tested these in the oligomerisation and polymerisation of ethylene. Whilst the Fe complexes showed evidence of alkyl carbene coupling, the V, Cr and Ti complexes were shown to be less prone to this chemistry, with the Cr system showing particularly high activities in the catalytic runs. These observations hint towards the usefulness of early transition metal complexes of NHC's in olefin oligomerization and polymerization[48,82].



Scheme 1.4: Gibson's pincer carbene complexes[82]

The Pd PCP pincer complex **1.46** was prepared by Lee in 2004 and is an example of a pincer containing three strong σ-donors. This was shown to be effective in the Heck and Suzuki reaction, although longer reaction times were needed with unactivated substrates[83]. As an indication of the potential versatility of NHC complexes, the Ag NHC pincer motif **1.47** was functionalised with hydroxyl groups to give a water soluble complex and was shown to be a useful antimicrobial agent[84].



1.46 **1.47**

Figure 1.23: Further examples of the pincer carbene motif.

1.5 Chirality in Carbenes

The addition of chiral centres to NHC's is a logical development due to the obvious use of chiral ligands in enantioselective catalysis. The number of chiral NHC's appearing in the literature has increased over the years with two reviews covering these up to 2004[85,86]. Many of the early examples reflect familiar themes in asymmetric synthesis: the use of pinene- and camphor- derived chiral auxiliaries,

oxazolines from optically active amino acids, atropisomerisms in binaphthyl systems and the planar chirality of ferrocene[85]. The understanding of the key structural elements which induce high stereoselectivity is still under development due to the distinctly different stereochemical 'topography' of NHCs from diarylphosphines. NHCs will not create an 'edge to face' arrangement of their aryl substituents – a structural feature common to many chiral diphosphines such as derivatives of DIOP and Binap etc.[86,87] In their review[86] Gade *et al* define six classes of ligand characterised by the position of the chiral structural motif in relation to the donor unit.

1. NHC's with N-substituents containing centres of chirality.

The ability to vary the N-substituents of NHCs means that the introduction of any substituent containing a chiral centre is limited only within the constraints of the synthetic methods of NHCs discussed in Chapter two. Herrmann[88] and Enders[89] first formed chiral NHCs of this type in 1996 (**1.48, 1.49,** Figure 1.24).

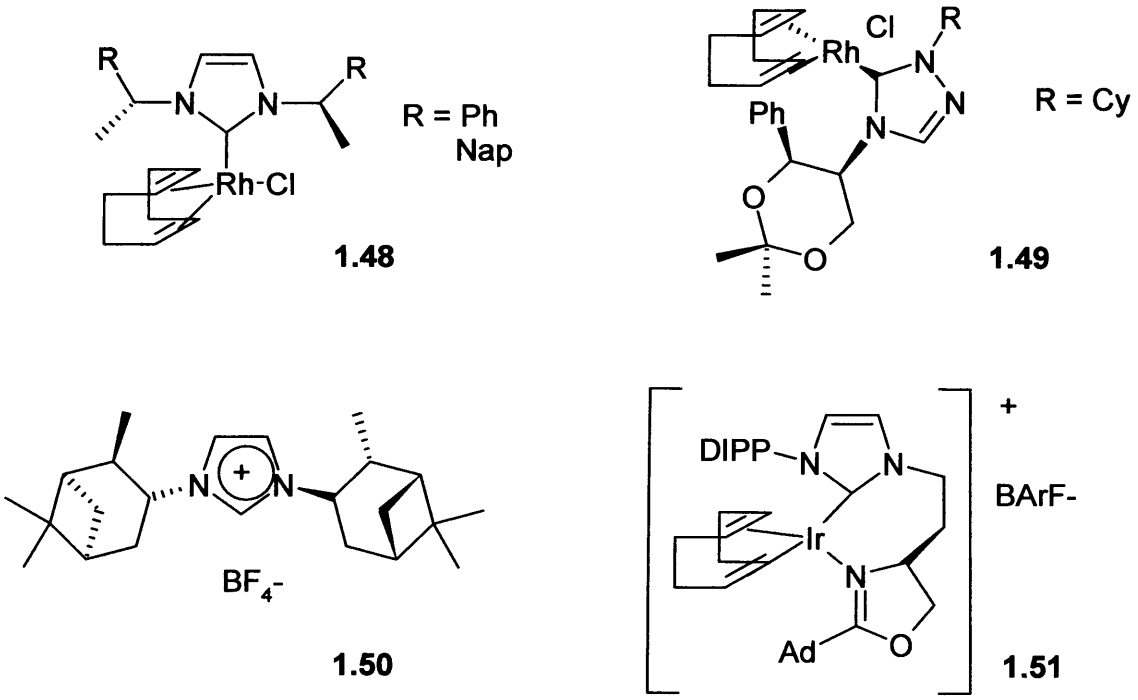


Figure 1.24: Examples of NHC's possessing chiral N-substituents.

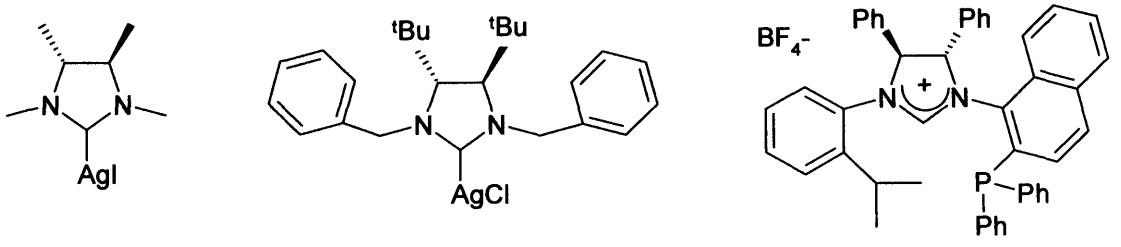
1.48 showed good activity but low stereoselectivity for the hydrosilylation of acetophenone (32% ee). **1.49** was generated as a mixture of diastereoisomers as a consequence of the non symmetrical carbene ligand. The mixture was tested in the

hydrosilylation of methyl ketones giving low to moderate enantioselectivites (ee's up to 44%). Hartwig's[90] ligand **1.50**, was tested as a stereodirecting ligand in the Pd catalysed asymmetric oxindole reaction and gave superior results to those of established chiral phosphines. Burgess[91] successfully applied **1.51** in the hydrogenation of unfunctionalised alkenes with an enantiomeric excess of >90% which is comparable to the best phosphine or phosphate-oxazoline iridium complexes[92-94]. Gade concludes that NHCs containing chiral N- substituents may be efficient as stereo directing ligands if the N substituents are either very sterically demanding or locked in fixed conformations, and that chiral induction is greater the closer the chiral centre is located with respect to the N- substituents. This type of chiral NHC generally gives moderate results in asymmetric catalysis.

2. NHC ligands with chiral elements within the ring.

The 4 and 5 positions of NHCs may be rendered chiral centres by an appropriate substitution and the chiral information transmitted to the metal centres active site via the N substituents. Systematic studies by the groups of Mangeney and Alexakis[95,96] employed chiral imidazolinylidenes of this type in the alkylation of α enones. In their studies the Cu NHC catalyst, generated by Ag(I) transmetallation, was used for the asymmetric addition of diethyl zinc to cyclohexanone. One of the observations from these studies showed that the two methyl N- substituents of **1.52** (Figure 1.25) were inefficient in transmitting the chiral information from the C4 and C5 positions (ee 23%) whereas the steric repulsion between the t-butyl groups and the benzyl groups of **1.53** leads to a C2 symmetry arrangement with respect to the carbene donor function thus transmitting the chirality to the reaction centre. **1.52** produced an ee of 58%.

Grubbs[97,98] also synthesised chiral NHCs with N- aryl substituents of this type and employed them in the stereoselective ring closing metathesis of olefins. Helmchen[79] formed two Rh(I) diastereomeric atropisomers (from **1.54**) of a chelating NHC-phosphine ligand via transmetallation of the Ag(I) complex. These were subsequently tested in the catalytic hydrogenation of dimethylitaconate and Z-acetamidoacrylate with relatively high yields and excellent enantioselectivities (98-99%).



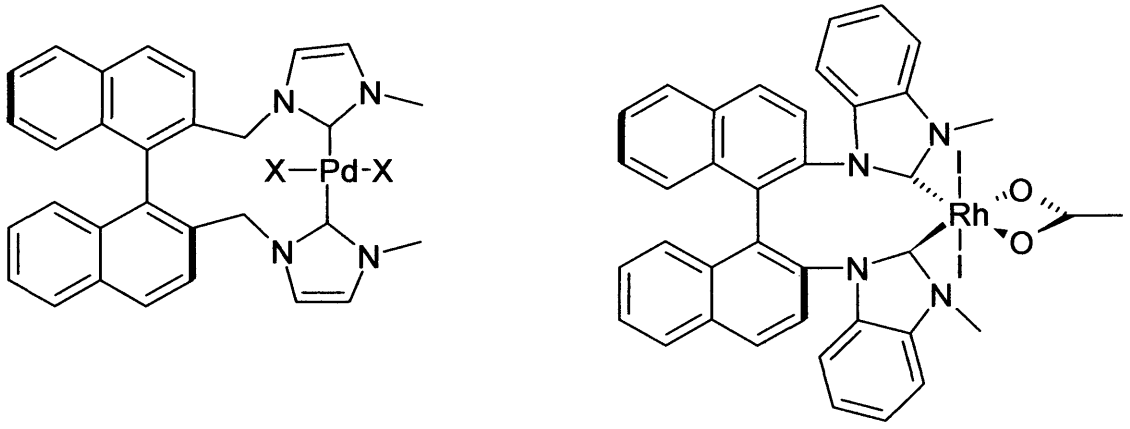
1.52 **1.53** **1.54**

Figure 1.25: Examples of chiral NHC's with a chiral ring.

It is evident from these and other examples that chiral information from the NHC backbone may be transmitted to the metal centre in varying degrees depending on the nature of the N- substituents involved. The combination of chiral N substituents with a chiral NHC ring is an area yet to be fully explored.

3. NHC ligands containing an element of axial chirality.

Rajanbabu[100] published the first chiral bidentate bis carbene complex of Pd (**1.55,** Figure 1.26) based around the 1,1'-binaphthyl unit as the chiral element. The chirality arises from the blocked rotation around the C-C axis linking the two naphthyl units giving configurationally stable atropoisomers. On complexation with Pd the ligand forms cis-trans mixtures as a result of the flexibility of the ligand and as such, no stereoselective catalysis has been employed with this ligand. A related bis carbene was reported by Min Shi[101] and has the NHC's directly linked to the binaphthyl backbone. The Rh(III) complex **1.56** was synthesised and employed in the asymmetric hydrosilylation of ketones, giving good activity and excellent enantioselectivity for aryl alkyl ketones.



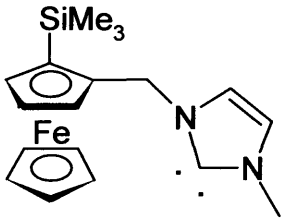
1.55 **1.56**

Figure 1.26: Examples of NHC complexes with axial chirality.

Hoveyda's complex[67] (**1.26**, Figure 1.9) and complexes of the groups subsequently modified ligands, were also used in asymmetric olefin metathesis and showed excellent enantioselectivities for asymmetric ring opening cross metathesis.

4. NHC's containing an element of planar chirality.

1.57 (Figure 1.27) was the first reported planar chiral NHC by the group of Bolm in 2002, though its application in the Rh catalysed hydrosilylation of ketones yielded only a racemic mixture of secondary alcohols[102]. A number of other NHC ferrocence derivatives have also appeared in the literature including those with mixed second donors and have shown a variety of activities in enantioselective catalysis.

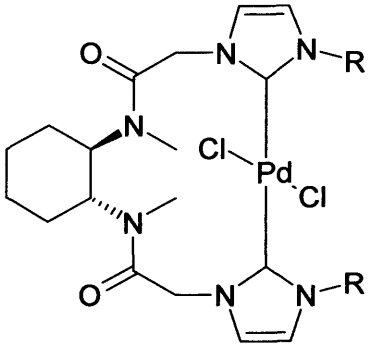


1.57

Figure 1.27: An example of an NHC with planar chirality.

5. NHC's joined by a chiral trans cyclohexadiamine ligand backbone.

Trans- cyclohexadiamine has been used as a chiral backbone by both Burgess[103] (**1.58** Figure 1.28) and Douthwaite[104] (**1.59**) (**1.60**). **1.59** was tested in Pd catalysed allylic alkylations and led to high enantioselectivities, while **1.60** showed poor selectivity in the enantioselective α- arylation of amides.



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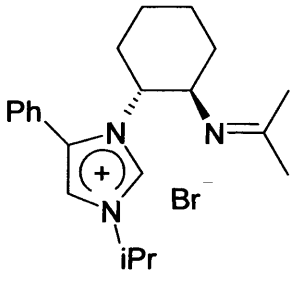

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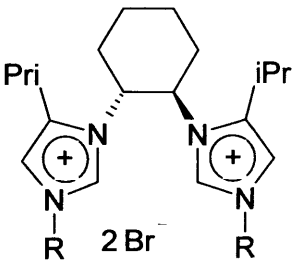
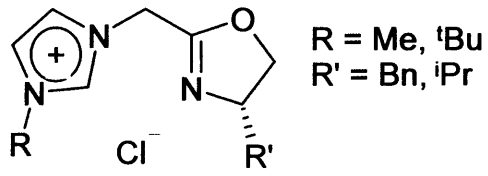


1.60

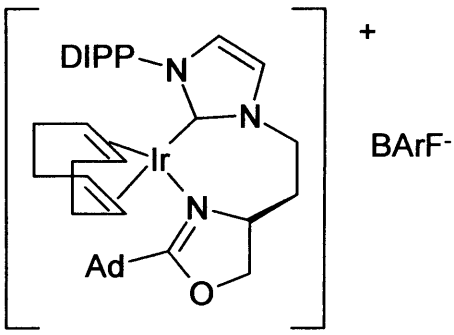
Figure 1.28: Examples of NHCs on a chiral backbone.

6. NHCs incorporating oxazoline units.

Herrmann reported the first bidentate chiral carbene containing an oxazoline ring (**1.61** Figure 1.29)[105]. The oxazoline unit has been established for a number of years in asymmetric catalysis with its key features being its rigidity and quasi planarity. Burgess's catalyst[106] (**1.62**) showed excellent activity and enantioselectivity for the asymmetric hydrogenation of E-1,2-diphenylpropene, the author attributing the high selectivity to the bulky 2,6-(^{i}Pr)$_2$C$_6$H$_3$ group blocking one of the quadrants of the active catalyst space, allowing control of the geometry of the coordination reaction sphere.



R = Me, ^{t}Bu
R' = Bn, ^{i}Pr



1.61 **1.62**

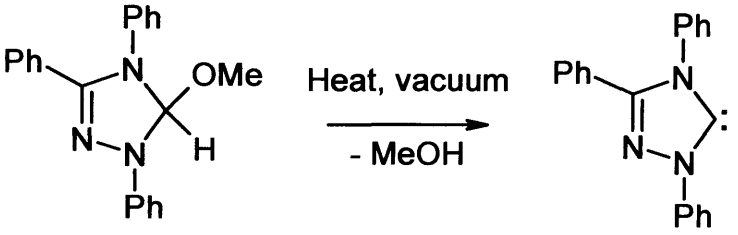
Figure 1.29: NHCs incorporating oxazoline units.

1.6 Routes To Forming Carbene Complexes

There exist a number of different routes to forming NHC(M) complexes. The most appropriate route however, depends on the nature of the carbene precursor itself, as well as the desired substituents on the metal centre.

The most obvious route is via the free carbene and is probably the best route for forming Pd(0) NHCs and simple Pd(II)MeX(NHC)s. This is usually achieved by deprotonation at the C2 position of imidazolium salts with a suitable base. KO^{t}Bu used in a stoichiometric amount or NaH/KH in the presence of a catalytic amount of KO^{t}Bu has been used in THF at room temperature[14,73,107,108]. In base sensitive functionalised salts where the C2 proton may not be exclusively removed due to acidic protons on linkers etc, an amide may be used and include Li(N^{i}Pr$_2$), (LDA) or

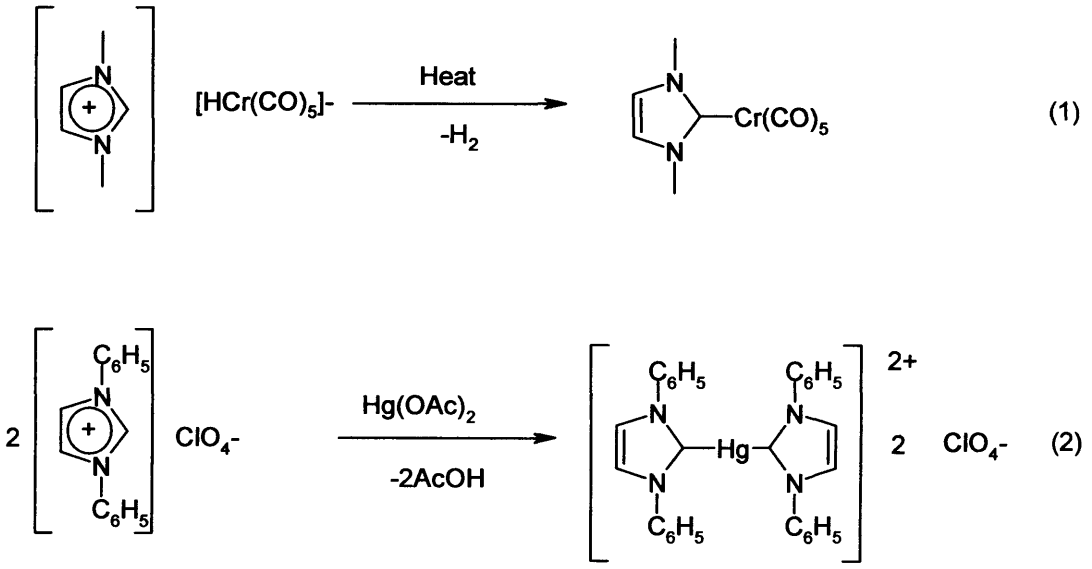
$K[N(SiMe_3)_2]$[108-112]. If the free carbenes prove to be too unstable to be made at room temperature, a liquid ammonia route may also be used where the azolium salt is dissolved or suspended in a mixture of liquid ammonia and a polar aprotic solvent and deprotonated at very low temperatures by NaH[113,114] or BuLi[115,119]. Khun demonstrated that free carbenes could also be generated by reacting imidazole-2-thiones with potassium in refluxing THF. This was achieved with 1,3,4,5-tetramethyl-2-(methylthio)imidazolium iodide to give the product in good yield[116]. The free carbene may also be formed via the thermal elimination of small molecules such as MeOH from imidazolidines[5,124-126], benzimidazolines[127] and 1,2,4-triazolines[16] (Scheme 1.5) to yield the corresponding NHC. This method however is limited to thermally stable NHCs. Once formed stoichiometric amounts of free NHC can displace other donor ligands quantitatively from the coordination sphere of suitable Pd(0)[34,117-120] and Pd(II)[49,72,108,110-123] precursors. Displacing 1-5 cyclooctadiene (COD) from Pd(II)XY(COD) precursors is particularly valuable when X is a methyl and Y a halide[68,70,71]. The free carbene route suffers where the high air and moisture sensitivity of the free carbene is concerned meaning generation and manipulation of these species may be problematic.



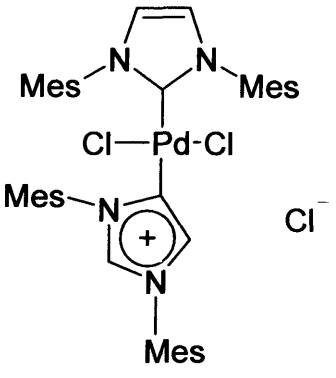
Scheme 1.5: The thermal elimination of MeOH.

Another route to the formation of metal complexes is by reaction of an imidazolium salt with a metal containing precursor of sufficient basicity to deprotonate the organic substrate[73]. The formation of a strong metal-carbene bond is presumably an important factor in driving the reaction. This was the method used by Ofele[128] (equation 1, Scheme 1.6) and Wanzlick[129] (equation 2) who made chromium and mercury carbene complexes respectively and this approach has been widely employed in the preparation of many other NHC complexes. The application of $Pd(OAc)_2$ in this manner has led to a number of mono and bidentate imidazol-2-ylidene and triazol-5-ylidene Pd(II) complexes being prepared[113,130,131]. Each of the basic ligands of the M

precursor deprotonates one imidazolium salt resulting in the new metal complex and acetic acid[73]. The general formula of this $Pd(OAc)_2$ route is $Pd(NHC)_2X_2$. The use of ramped temperatures and DMSO has also been developed which has shown an improvement in yield for certain chelating Pd(II) dicarbene complexes[132-135]. The $Pd(OAc)_2$ route led to the first example of an NHC bound through the C5 carbon. Reported by Nolan the reaction of N, N' Bis(2,4,6-trimethylphenyl)imidazolium chloride with $Pd(OAc)_2$ in dioxane at 80°C led to the formation of **1.63** (Figure 1.30), though reactions giving abnormal C-4 and C-5 metallation are very sensitive to conditions as well as counter ions[166]. Surprisingly **1.63** also proved to be a better cross coupling catalyst than certain complexes with conventionally bound carbenes[136].



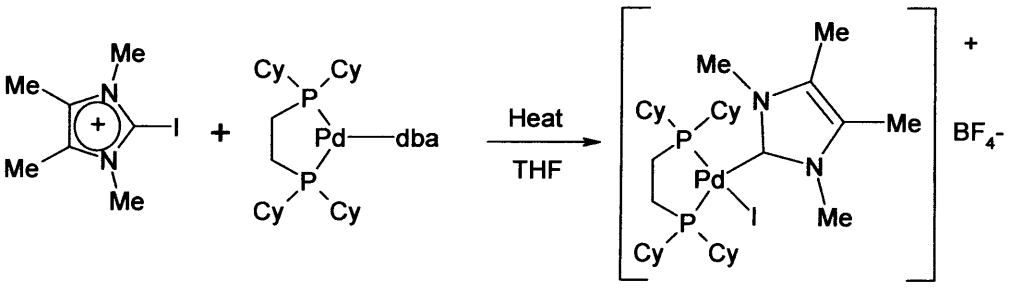
Scheme 1.6: Reaction of imidazolium salts with basic metal precursors.



1.63

Figure 1.30: The first example of an NHC bound through the C5 carbon.

Oxidative addition of imidazolium or amidinium species to low valent metal centres also yield M(NHC) species. In 2001 Cavell demonstrated the facile formation of NHC complexes via the oxidative addition of 2-haloimidazolium salts to Pd^0 substrates[137] (Scheme 1.7, Equation 3). Furstner[138] and co-workers also utilized the oxidative addition of C2-X in their synthesis of metal carbene products, and the groups of Nolan[139] and Crabtree[140] (Scheme 1.7, equation 4) provided evidence for the oxidative addition of imidazolium salts to Pd[141], although no Pd-hydride complex was isolated. Oxidative addition to a C-H bond is a most desirable means for carbene complex formation as no base is used, atom economy is maintained and the product can be the potentially catalytically active species. After publishing density functional calculations on the oxidative addition of 2-H imidazolium salts to zero valent group 10 metal precursors[134] to form M(II)(Hydrido)(NHC) complexes and the initial synthesis of Pt Hydrido(NHC) complexes, Cavell further supported this oxidative addition route by forming Pt bis-(NHC) complexes via C-H activation at room temperature as well as the synthesis of (NHC) M-Hydride complexes of Ni and Pd [138] (Scheme 1.7, Equation 5). Both the Ni and Pd complexes were shown to be surprisingly stable both in solution and in the solid state.



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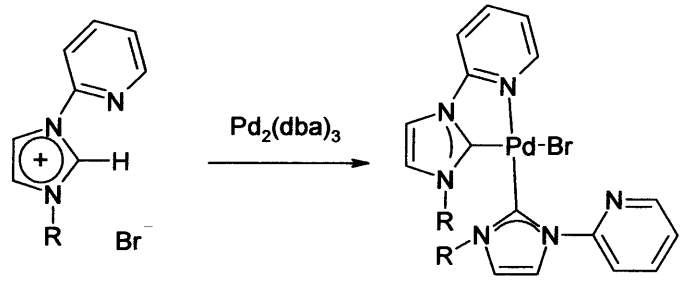
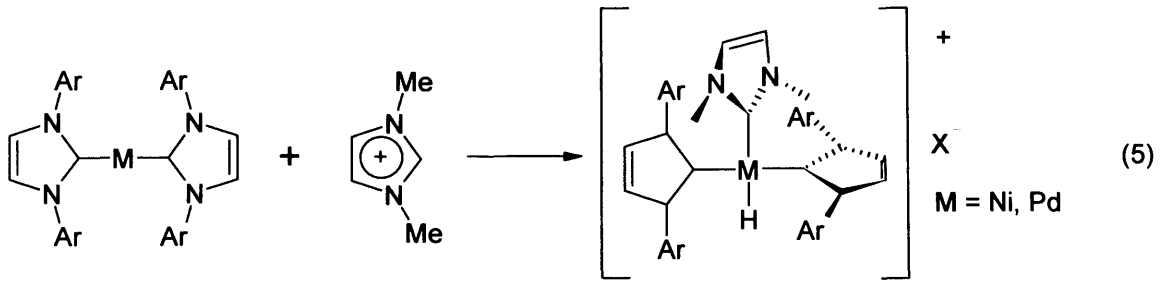


(4)

(R = i-Pr, n-Bu)



(5)

Scheme 1.7: Oxidative addition for NHC complex formation.

In cases where the functionalised NHC precursor contains acidic protons about its linker chain or those in which the free carbene is not easily accessible, an NHC transfer reaction can be valuable. The use of Ag(I) NHC complexes has become particularly useful as a transmetallation agent. The Ag(I) complex can be prepared via the reaction of imidazolium salts with the weakly basic Ag_2O, which is then reacted with an appropriate metal precursor such as $PdX_2(COD)$ to give the $PdX_2(NHC)$ complex. The silver transfer route is described in more detail in Chapter 3. The use of other transition metal complexes have also been reported to transfer NHCs to Pd. $(NHC)M(CO)_5$, where M is W, Mo or Cr has been used in the transfer of saturated NHC ligands onto a range of metals in good yield[142,143].

The co-condensation of Ni, Pd and Pt vapour with 1,3-di-N-tert-butylimidazol-2-ylidene has been shown to produce stable, two coordinate homoleptic metal carbene complexes of each respective metal. This method proved to not only be a straight forward novel synthetic method, but also produced a complex which was previously inaccessible by solution techniques[144].

Complexes bearing saturated NHCs can be prepared by the thermal cleavage of certain electron rich tetraaminoethylenes in the presence of appropriate metal precursors. This method was used by Lappert and co-workers in the 1970s to form a range of NHC-M complexes.[193]

1.7 Catalysis and NHCs

A catalyst is a substance that brings about or accelerates a specific reaction or reaction type, which proceeds in parallel with any other existing thermal or catalytic reaction within the particular system[145], but does not affect the position of the equilibrium. Thus a catalyst affects the kinetics of a reaction and not the thermodynamics, and although a catalyst participates in chemical reactions it is regenerated back to its original state after it has completed its catalytic cycle (excluding catalyst poisoning or degradation).

Specificity is a key factor in homogeneous catalysts. The market share of homogeneous catalysis (1999) is low, around 10-15%[148] and is a reflection of some of the economic disadvantages of classical homogeneous catalysts. However the current developments of transition metal complexes as catalysts has opened up the possibilities of utilising these complexes in new C-C and C-N coupling processes using simple substrates and reaction conditions which were not possible using traditional synthetic methods.

1.7.1 C-C and C-N coupling reactions.

Carbon-carbon and carbon-nitrogen bond forming reactions are key steps in the synthesis of many organic chemicals, with many of these cross coupling reactions mediated by palladium and nickel catalysts. Catalysed cross coupling reactions such as Kumada[149-151], Negishi[149,152], Stille[149,153] and Suzuki[149,154-156] also make use of transmetallating agents including organoboron, organomagnesium and organozinc reagents. A summary of some of these Pd catalysed coupling reactions are given in Figure 1.31. The widespread uptake of these Pd catalysed cross coupling reactions have previously been impeded by the high cost of the aryl iodides and bromides traditionally used in such reactions. Industry, and indeed academia, has looked towards using aryl chlorides to replace these, due to their low cost and high stability. This high stability however also prevents the aryl chlorides from readily undergoing oxidative addition to 14 e- Pd(0) phosphine complexes[157,158] and is the reason why it has been hard to find general coupling protocols that are economically sound.

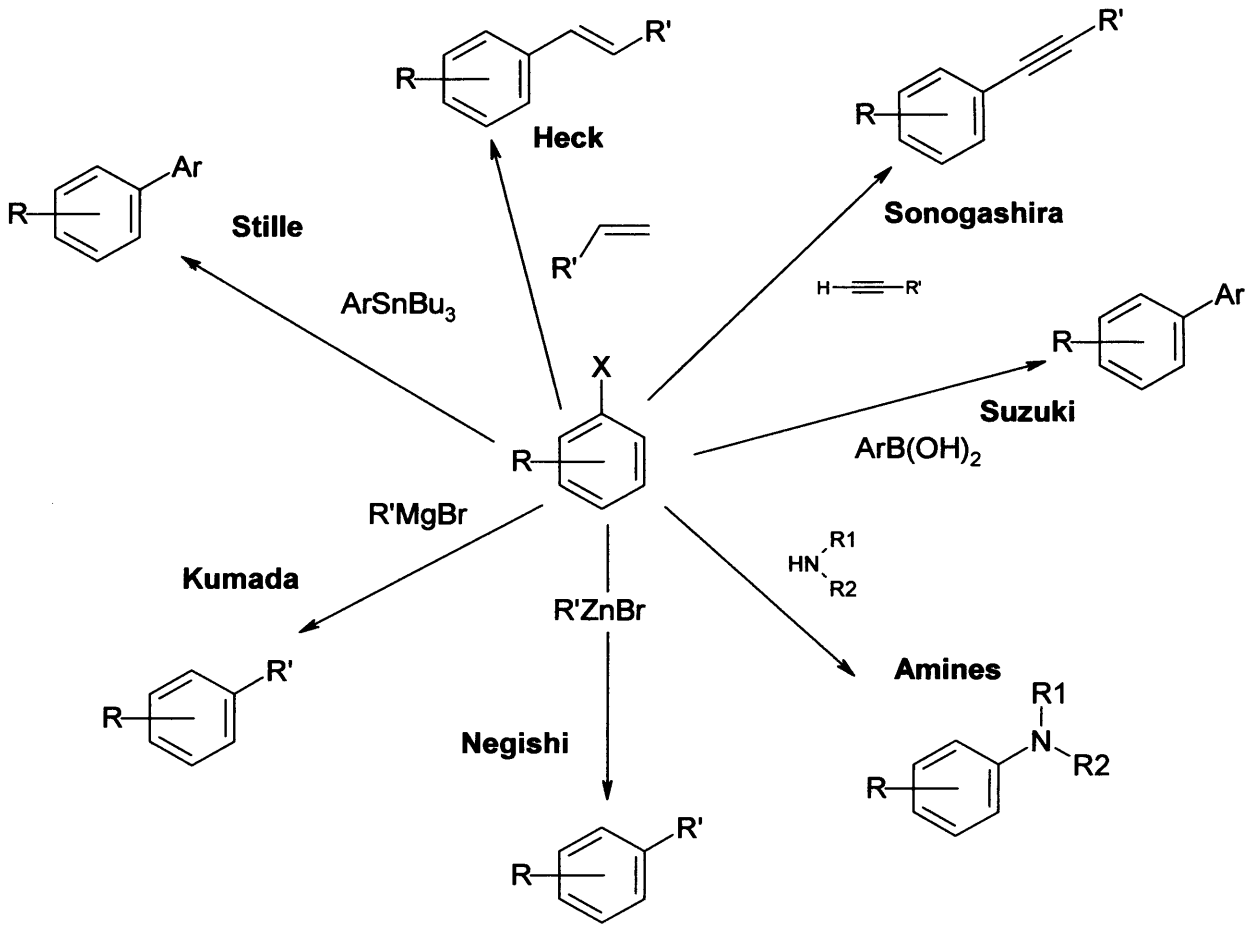


Figure 1.31: A selection of C-C and C-N catalytic reactions mediated by Pd. A number of papers and reviews cover these reactions in more detail[149,154,155,159-166].

In recent years research has shown that electron deficient substrates have efficiently undergone the Heck reaction at room temperature[167] and deactivated aryl chlorides can also be coupled in Heck, Suzuki and aryl amination protocols through the application of appropriate catalyst systems[168,169]. This has been largely brought about by careful selection and modification of the electronic and steric properties of the catalysts ligands. Coupling reactions are therefore suitable areas of application for NHC complexes due to the relative ease of varying the ligands properties and the current fertility in the area. A number of examples of carbene complexes utilised as catalysts have already been given in other sections of this chapter. Due to the

relevance of the Heck reaction in this work the rest of this section will focus on this well studied reaction.

1.7.2 Mechanistic Aspects Of The Palladium Catalysed Heck Reaction

The generally accepted mechanism for the Heck reaction is given in Figure 1.32. The reaction involves the cycling of a Pd centre between its 0 and 2+ oxidation states[88,117,130,170-172]and it has been suggested that in particular systems when the Pd complex contains a phosphinito PCP pincer ligand, the Pd centre cycles between the 2+ and 4+ oxidation states[117,173-175]. Herrmann discussed the possible mechanisms involved for palladacycles with Pd(0)-Pd(II) Verses Pd(II) – Pd(IV)[176], but later ruled out the Pd(IV) intermediate for phosphapalladacycles[177].

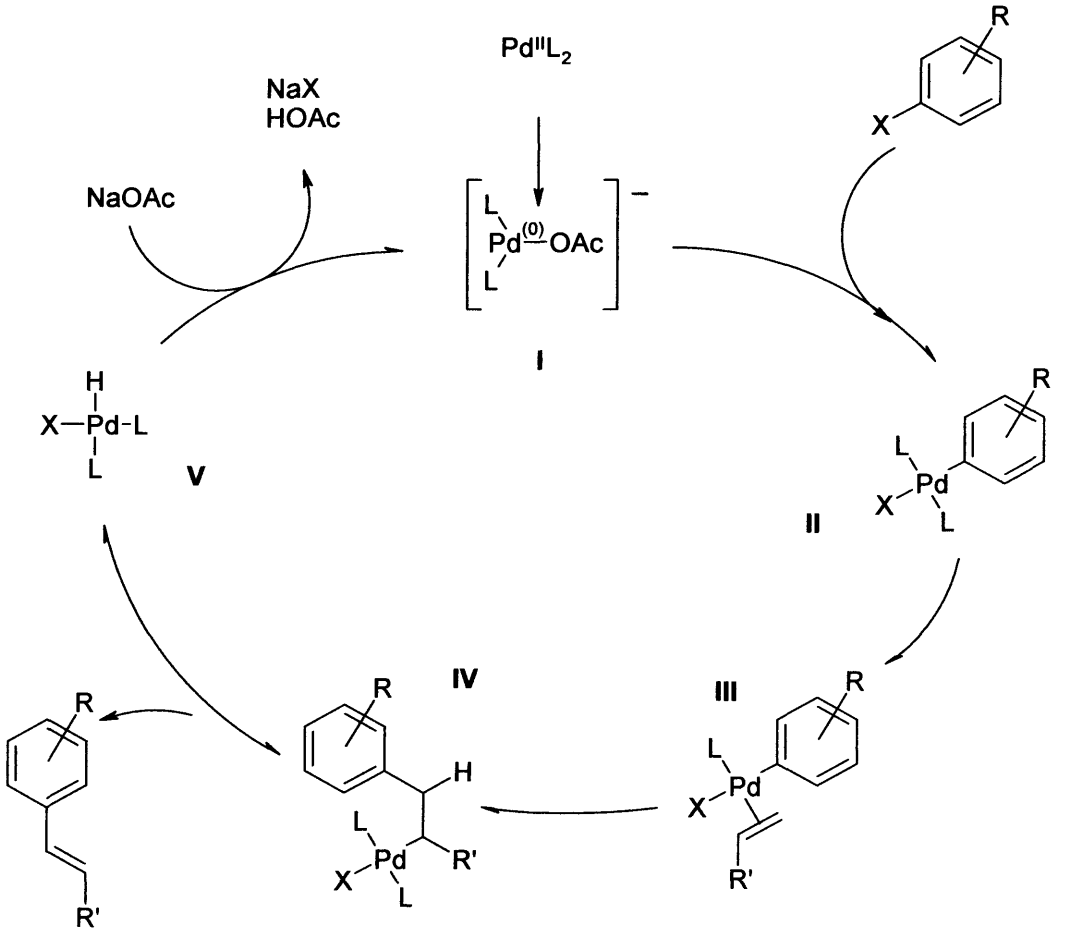


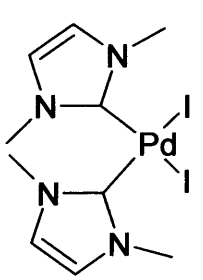
Figure 1.32: The generally accepted Heck reaction pathway.

On examining the mechanism for the Heck reaction it can be seen that it is composed of several fundamental steps, preactivation of the catalyst, oxidative addition, migratory insertion, β-hydride elimination and reductive elimination. In order to form (**I**), Pd(II) complexes must first be reduced to Pd(0) by employment of suitable reducing agents such as hydrazine or sodium formate, failure of this leads to an inductive phase[130]. The actual catalytic species (**I**), assumed to be a coordinatively unsaturated 14e- Pd(0) species[168,169,178], is generated by the coordination of acetate anions. This was demonstrated by Armatore and Jutand for Pd/PAr_3 systems who showed that acetate anions, present from the NaOAc employed as base, under catalytic conditions coordinate to the Pd centre to give an anionic Pd(0) species[170,178]. This also provides a good explanation for the hydride removal from the Palladium. Pd(0) complexes may also be used as the catalyst eliminating the reduction step, though ligand dissociation from the pre-catalyst may be required to form the coordinatively unsaturated active catalyst. Oxidative addition of an aryl halide then takes place with (**I**) to give (**II**) as a concerted process where the C-X bond breaks and corresponds with the formation of M-C and M-X bonds. The reactivity of the aryl halide decreases drastically in the order of I > Br > Cl[179]. The strength of these bonds in C_{aryl}-X compounds (kJ mol^{-1}) are PhCl (402), PhBr (339) and PhI (272)[180]. The cis isomer is also formed in this process, though only the thermodynamically more stable trans-isomer is shown in the catalytic cycle. Dissociation of a ligand or halide then provides a vacant coordination site for which the olefin can attach to give (**III**), followed by olefin insertion into the Pd-aryl bond to give (**IV**). A β-hydride elimination process then occurs to give the coupled product thereby leaving the Pd species to undergo reductive elimination in the presence of base to regenerate the initial Pd(0) species (**I**).

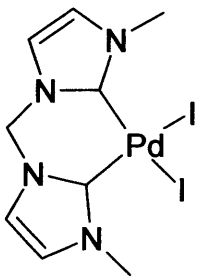
1.7.3 NHCs As Efficient Ligands For The Heck Reaction

Herrmann first demonstrated the advantages of NHC's over their traditional phosphine counterparts for the Heck reaction in 1995. Generally in traditional systems using triarylphosphines an excess of the phosphine ligand is needed to control the equilibrium in the activation and propagation steps of the catalytic cycle[130] due to

phosphane degradation by P-C bond cleavage[181]. This excess contributes to higher running costs in technical plants. Other disadvantages of phosphines are their sensitivity towards air and moisture. The inherent stability of the M-NHC bond gives rise to NHC catalysts that are active for long periods at elevated temperatures, often without the need for specially purified solvents or inert atmospheres. Herrmann's Pd(II) complexes (**1.64**, **1.65**) were shown to be extraordinarily stable to heat, oxygen and water[130], and under catalytic conditions **1.64** was shown to give high TON's as a result of its pronounced thermal stability in solution. Herrmann concluded that the catalytic advantages of complex **1.64**, was that it could form stable active species for long periods of time and at high temperatures which are essential properties for the activation of chloroarenes[130]. In the same paper Herrmann prepared a [Pd(0)(carbene)$_2$] complex by the addition of two equivalents of free 1,3-dimethyldihydroimidazole-2-ylidene with [Pd(dba)$_2$] and demonstrated that if the initial Pd complex is a Pd(0) one, then an induction period does not occur. This lack of induction period coupled with the high activity due to the carbene ligand resulted in high TON's (in comparison to non NHC Pd(0) complexes). These findings led to a number of groups synthesising and testing mono PdNHC complexes[49,117,182-184] in the Heck (and related) reaction(s). Further work carried out in this area with chelating, functionalised carbenes has extended the range of substrates used as well as demonstrated how ligand design can affect overall activities[32,56,74,109,185-190]. A number of pyridine functionalised carbene complexes of Pd have been shown to be active catalysts for the Heck reaction (with some examples given in previous section of this chapter) and are relevant to the complexes synthesised within this work[56,74,75,109,182,189]



1.64



1.65

Figure 1.33: Herrmann's first NHC Pd complexes.

1.8 Aims Of This Thesis

The main aim of this work is the synthesis of novel chelating carbene complexes of the catalytically interesting Pd metal. The investigation of the catalytic abilities of the complexes is also of priority. The ligands formed herein were designed with the aim to contain a combination of features that could lend an advantage in catalytic systems. These were chosen to be chelation, rigidity, hemilability and chirality.

Chapter 2 describes the synthesis and characterisation of a number of novel imidazolium salts encompassing bis-imidazolium salts and functionalised imidazolium salts.

Chapter 3 gives the synthesis and characterisation of Ag(I)NHC complexes of the imidazolium salts described in chapter 2, which were synthesised for the purpose of being intermediate transmetallation agents for the synthesis of the desired Pd(II) complexes of chapter 4.

The successful transfer from Ag(I) to Pd(II) of a number of the Ag complexes of chapter 3 are discussed in chapter 4. Both the di-chloro and the catalytically important hydrocarbyl complexes are synthesised for a number of ligands, and are characterised and supported by crystallographic evidence.

Chapter 5 presents catalytic results for a selection of the Pd complexes of chapter 4 in the Heck reaction of 4-bromoacetophenone and n-butyl acrylate, as well as 4-chlorobenzaldehyde with n-butyl acrylate. The results are compared to complexes with similar structural features previously synthesised by McGuinness[56], and are shown to be comparable with respect to the coupling of 4-bromoacetophenone and inferior with respect to 4-chlorobenzaldehyde.

1.9 References

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Chapter Two

Ligand Design: Chelating Imidazolium Salts And Their Synthesis

2.1 Introduction.

Imidazolium salts are not the only route to forming carbenes[1-4], though they are used throughout this work to form the NHC's and associated metal complexes. Herrmann's description of an imidazolium salt is a 5 membered heterocycle with nitrogens at the 1 and 3 positions and a substituent (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.[5] A typical imidazolium salt is shown in (**I**) (Figure 2.1).

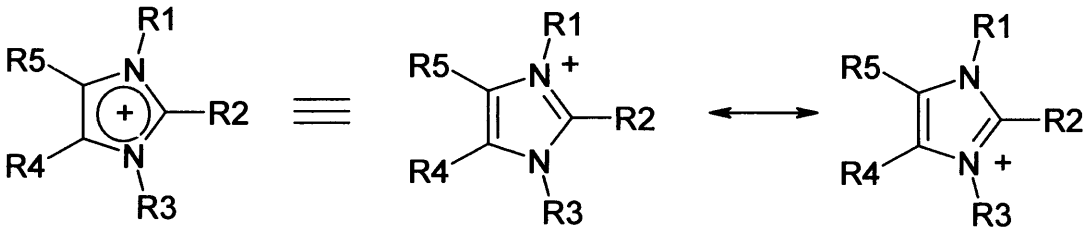


Figure 2.1: N-Heterocyclic free carbenes and their corresponding salts

The numbering shown in (**I**) will be used throughout this work and unless otherwise stated, $R_2 = R_4 = R_5 = H$. Free carbenes (**II**) and (**IV**) are derived from (**I**) and (**III**) respectively and are named according to the degree of saturation on the C_4-C_5

backbone. i.e. (**II**) is an imidazolin-2-ylidene and (**IV**) an imidazolidin-2-ylidene. The work contained within this thesis will consist of types (**I**) and (**II**).

Chapter one noted that a chelate forming ligand can be especially beneficial in terms of offering stability to hydrocarbyl-M-carbene complexes with respect to reductive elimination[6]. The general theme of this chapter is thus based upon the design and synthesis of imidazolium salts as chelating carbene precursors with the majority of the imidazolium salts synthesised being functionalized mono-imidazolium salts with one example of a bis imidazolium salt. Two of the synthesised imidazolium salts also contain chiral centres.

A new chelating, rigid mixed donor ligand was desired that could be comparative to previous ligands and complexes synthesised by Cavell (**2.1** and **2.2**, Scheme 2.1)[7] and others that were effectively employed in the Heck reaction. Chelating ligands, and in particular those having both strong and weak donors (hemilabile ligands), are particularly interesting in terms of catalysis. The weak hemilabile part of the ligand is capable of reversible dissociation from the metal centre, thereby creating vacant coordination sites during catalytic cycles and stabilising the metal centre by re-coordination when it is catalytically non active, or coordinatively unsaturated.

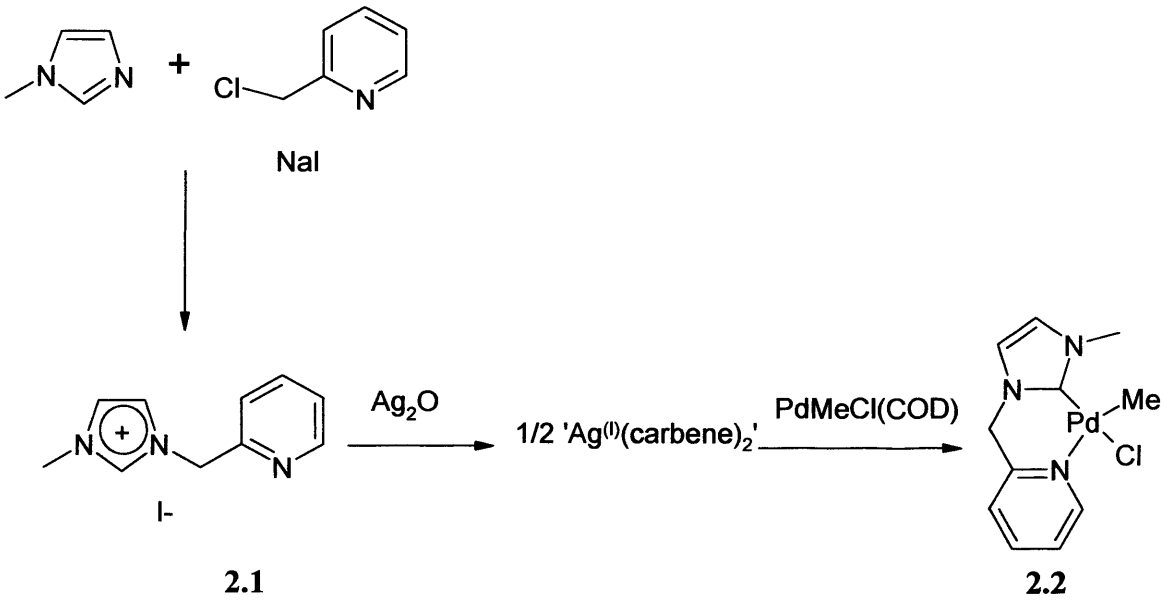


Figure 2.1: Reaction scheme showing the synthesis of Cavell's mixed donor ligand precursor and its corresponding Pd complex.

The majority of functionalised chelating carbenes have utilized $(CH_2)_n$ chains as linkers to bridge the NHC and secondary donors together which are highly convenient from a synthetic viewpoint. A selection of these are given in Figure 2.2. However it has become apparent that there are drawbacks in that the CH_2 protons can be too acidic and may be abstracted by the strong bases traditionally used in the deprotonation step for free carbene formation[7]. Using an aromatic ring system to bridge the donors will overcome this, and so an imidazolium salt with a quinoline structure as one of the N-substituents (Figure 2.3) was thought to be an ideal candidate. The imidazolium salt also has the added feature that it is a highly delocalized system extending over three rings. In order to assess the effect of sterics in the ligands associated complexes, a secondary objective in forming these salts is the manipulation of steric bulk of the R- group (Figure 2.3) as well as the addition of a group on the 2 position of the quinoline moiety (Figure 2.3) which may lead to increased hemilability.

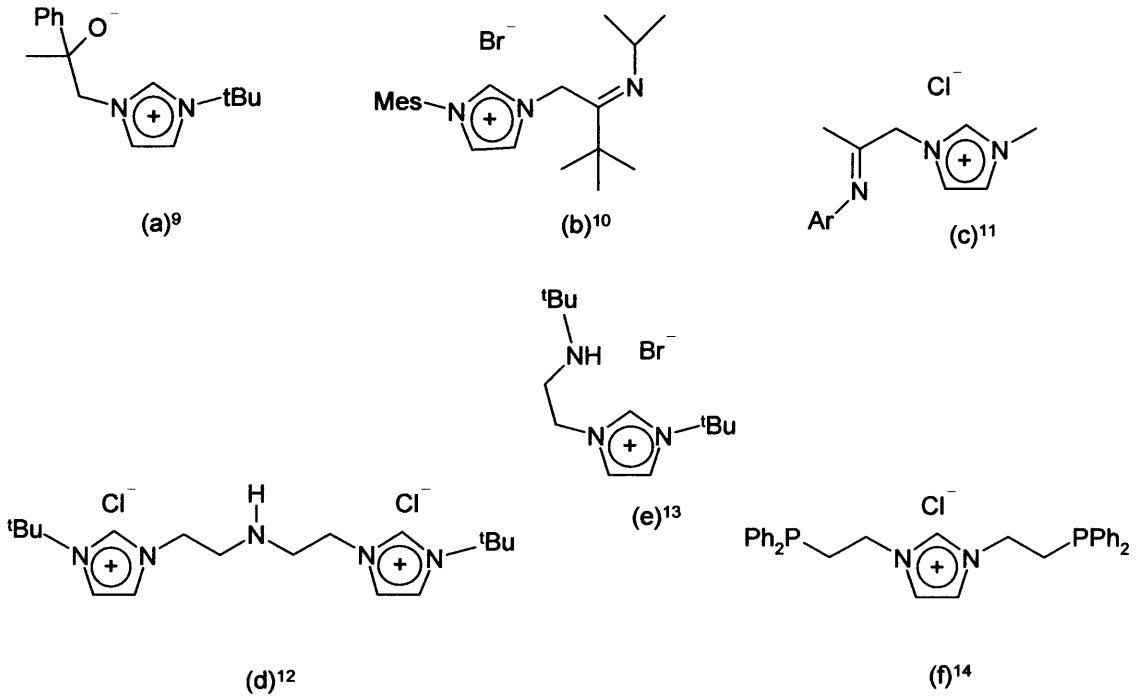


Figure 2.2: A selection of functionalised NHC precursors with their donors bridged by $CH_{2(n)}$ linkers[9-14].

2.2 Results and discussion

2.2.1 Preparation of functionalized imidazolium salts.

2.2.1.1 Quinoline based imidazolium salts.

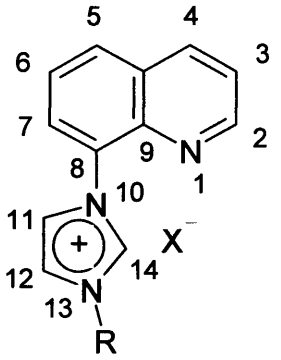
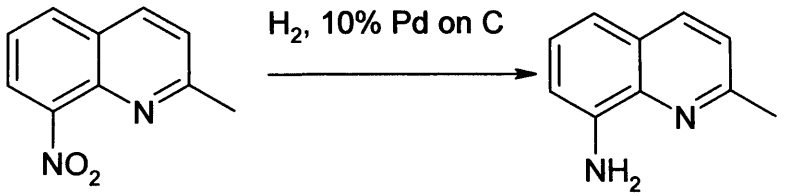


Figure 2.3: Target quinoline based salt including the numbering scheme for the quinoline moiety.

The commercial availability of 8-aminoquinoline and 2-methyl-8-nitroquinoline removes the need for a synthetic method for which to construct a quinoline based compound suitable for the salt synthetic routes outlined in Chapter one, thereby reducing the total number of synthetic steps for imidazolium salt synthesis.

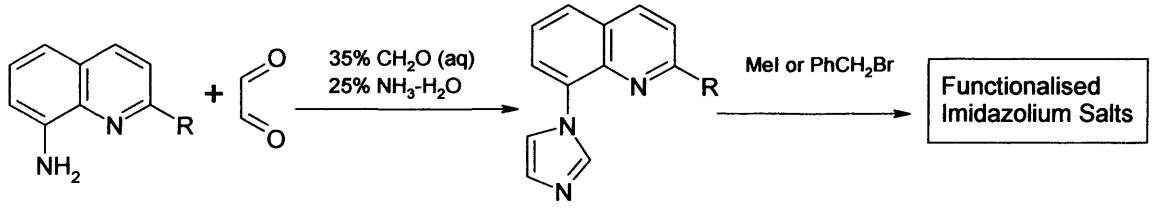
2-Methyl-8-aminoquinoline (**2.3,** Scheme 2.2) was synthesised by vigorously stirring a solution of 2-methyl-8-nitroquinoline (less than 0.5g in ca. 20ml THF) with catalytic amounts of 10% Pd on carbon under an atmosphere of H_2 overnight. The reaction mixture was then filtered through celite and the solvent removed under reduced pressure. ^{1}H NMR indicated that the reaction had gone to completion, observed by a broad peak at around 4.5-5ppm corresponding to the NH_2. 2-methyl-8-aminoquinoline was used for the imidazole synthesis without further purification. As this reaction was successful, this method was preferred over other reduction methods, such as zinc/hydrazinium monoformate, despite the long periods of time required to convert significant amounts of the starting material.



2.3

Scheme 2.2: Reduction of 2-methyl-8-nitroquinoline.

The synthetic strategy for the imidazole ring synthesis of **2.5** was adopted from Zhang's modified procedure for the synthesis of 1-arylimidazoles[15] such as **2.4**. The imidazolium salts were formed by standard N-alkylation using methyl iodide or benzyl bromide (Scheme 2.3).



2.4 (R= H)
2.5 (R= CH_3)

Scheme 2.3: Stepwise imidazolium salt synthesis.

The formation of the 1-aromatic substituted imidazoles (**2.4** and **2.5**) proceeded according to the literature preparative method[15] (Scheme 2.3), although these reactions both suffered from low yields (~30%) which is a recognised problem in the literature with most 1-aromatic substituted imidazoles[16,17]. The generation of large amounts of an unknown material as well as inorganic salts during neutralization proved to be problematic and may have contributed to the low yields. Vigorous agitation and copious volumes of Et_2O during the extraction of the amine marginally improved product yield. Smaller scale reactions were more efficient in terms of yields, although overall yields were highly variable.

The second R group was limited to methyl and benzyl due to the readily availability and reactivity of the respective alkyl halides as N-alkylation of the imidazole ring follows typical S_N2 reactivity, i.e. quarternization is difficult to achieve with any

nucleophile less reactive than a secondary alkyl bromide (though not impossible). The functionalized imidazoles were reacted with either methyl iodide or benzyl bromide in THF overnight to give the required imidazolium salts as light brown solids which show good stability towards air and moisture. The following imidazolium salts have been prepared (Figure 2.4), and were characterised by ^{1}H, ^{13}C NMR and Mass Spectrometry (MS). The characteristic peak in the ^{1}H NMR is the imidazolium proton (Position 14, Figure 2.3) as a singlet at 10.15-10.75ppm.

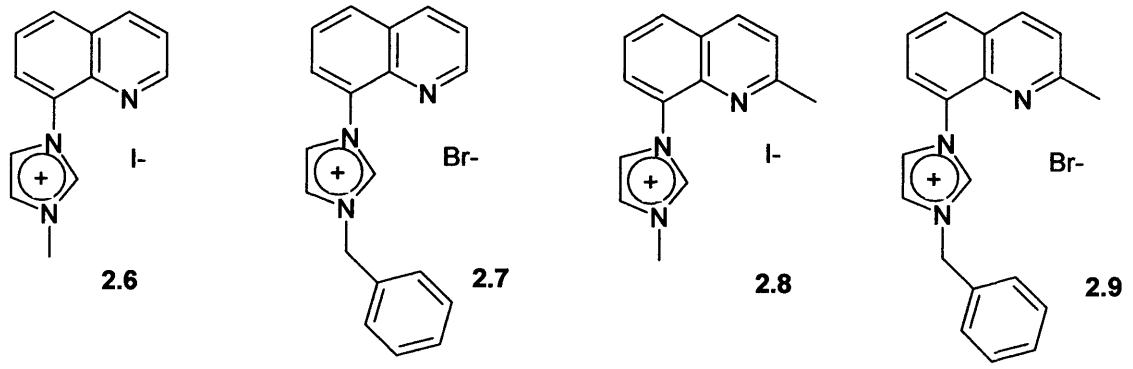


Figure 2.4: The range of quinoline functionalised imidazolium salts synthesised within this work.

The inclusion of a methyl group at the 2 position of the quinoline moiety (salts **2.8** and **2.9**) offers additional steric bulk which satisfies one of the objectives of this section and may have an effect of increasing the lability of the donor group by sterically crowding the coordination sphere. This would be advantageous in some catalytic cycles where hemilability contributes both to catalyst stabilization and the creation of vacant coordination sites.

Crystals of 1-methyl-3-(2-methyl-quinoline)-imidazolium iodide (**2.8**) suitable for X-ray crystallography were grown by layering hexane onto a DCM solution of the salt. The structure and labelling scheme of the cation of **2.8** is shown in Figure 2.5 along with a packing diagram for the salt (Figure 2.6). Selected bond lengths and angles are given in Table 2.1.

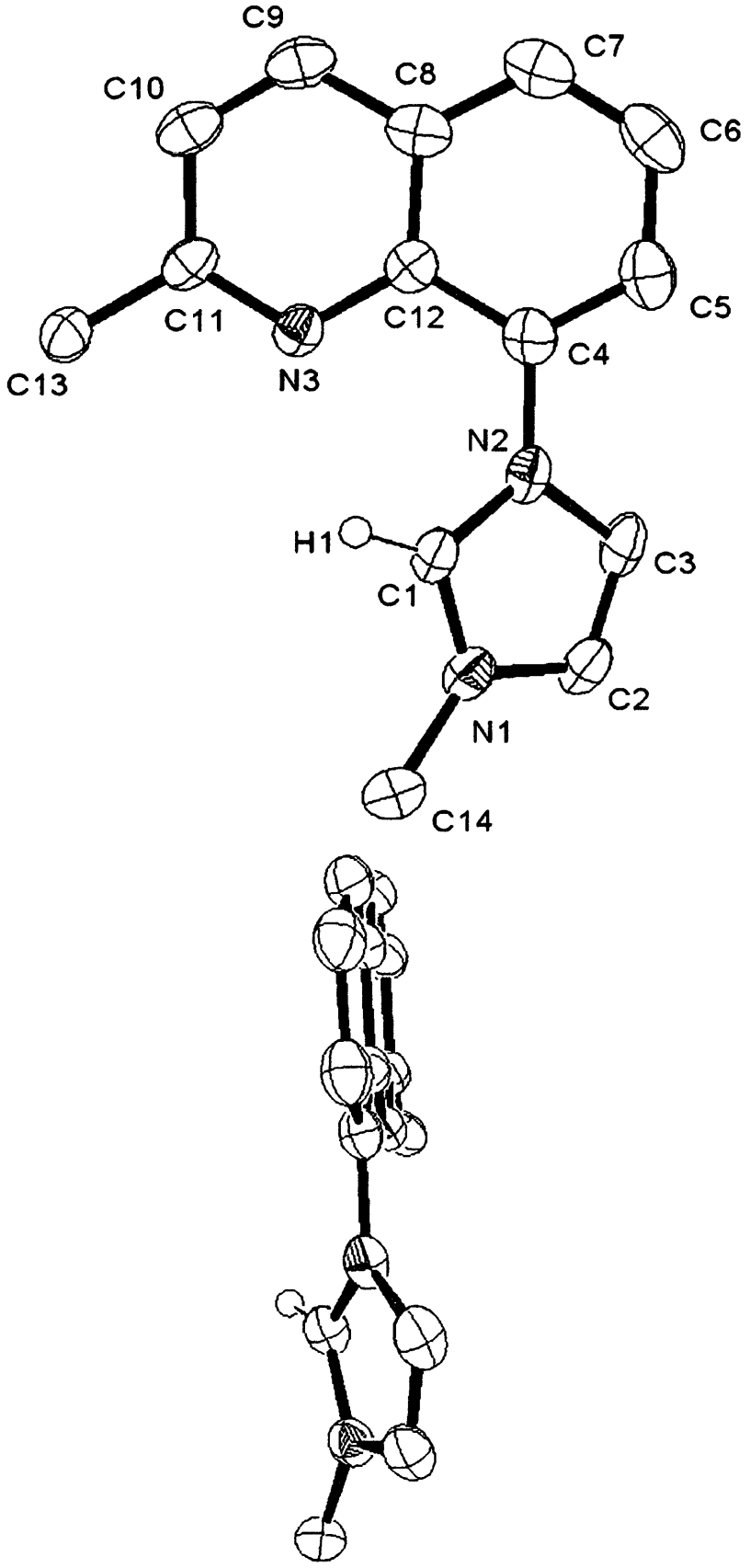


Figure 2.5: ORTEP representations of 1-methyl-3-(2-methyl-quinoline)-imidazolium iodide (**2.8**) (50% probability of thermal ellipsoids). Hydrogen and iodide atoms are omitted for clarity.

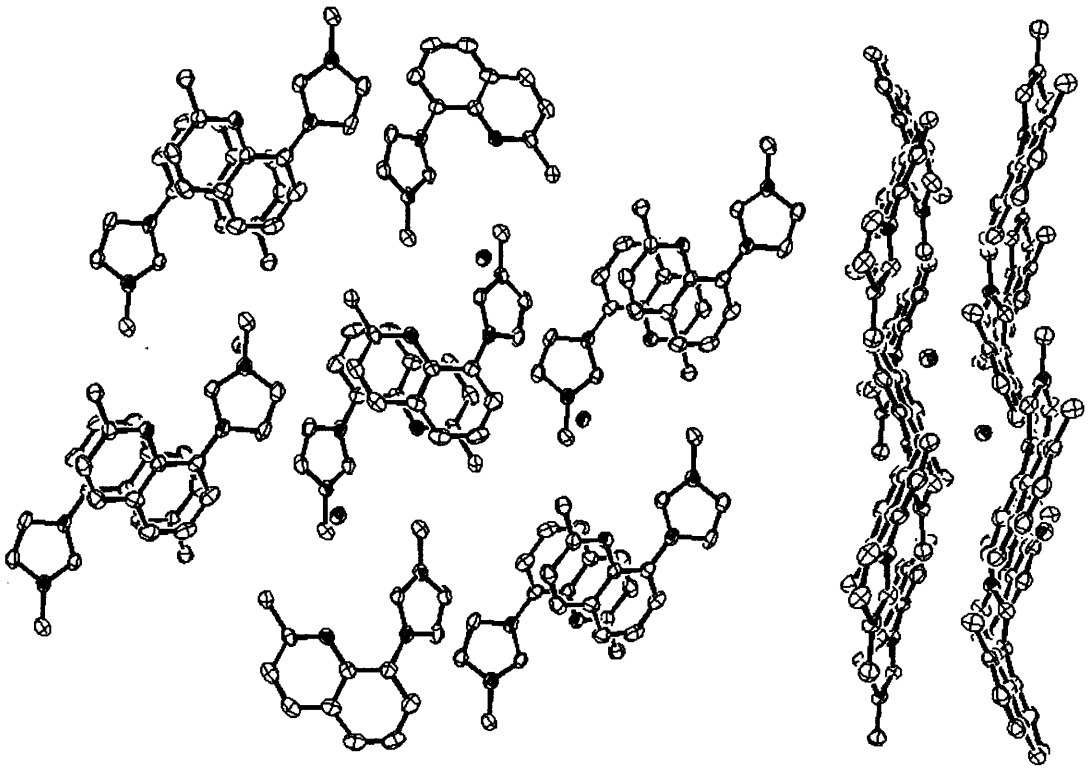


Figure 2.6: ORTEP packing representation of 1-methyl-3-(2-methyl-quinoline)-imidazolium iodide (**2.8**) (Hydrogen atoms omitted for clarity).

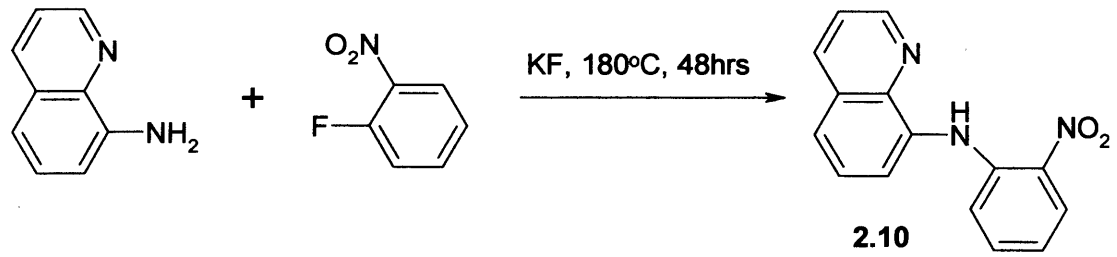
C1	N1	1.326(4)	N1	C14	1.460(5)	N1	C1	N2	108.8(3)
C1	N2	1.336(4)	N2	C4	1.439(4)	C1	N1	C14	126.0(3)
C2	C3	1.340(6)	C4	C12	1.424(4)	C1	N2	C4	127.5(3)
C2	N1	1.376(4)	C12	N3	1.360(4)	N3	C12	C4	119.7(3)
C3	N2	1.397(4)							

Table 2.1: Selected bond lengths (Å) and angles (°) of **2.8**

The planes of the imidazolium and quinoline rings make an angle of approximately 33.1°. The imidazole ring is typical of others with an N1-C1-N2 bond angle of 108.8(3)°, and bond lengths of 1.326(4)Å and 1.336(4)Å respectively[18-19]. The packing diagram shows π-π interactions between layers of stacked quinoline moieties.

It could be envisaged that if the ligand were to form a chelated complex, a biaxial chirality could be present by this deviation from co-planarity. In an attempt to exploit this, it was thought that by increasing the steric bulk on the C3 and C5 positions

(Figure 2.5) it may be possible to increase the torsional angle between the two planes and increase the energy barrier of interconversion. An aromatic carbene backbone was thought to be an ideal candidate, and so a suitable synthetic method was sought. A method was found in the literature[20] and was successfully applied with 8-aminoquinoline to give **2.10** which was obtained in moderately good yield (~45%) (Scheme 2.4) and was characterized by ^{1}H NMR.

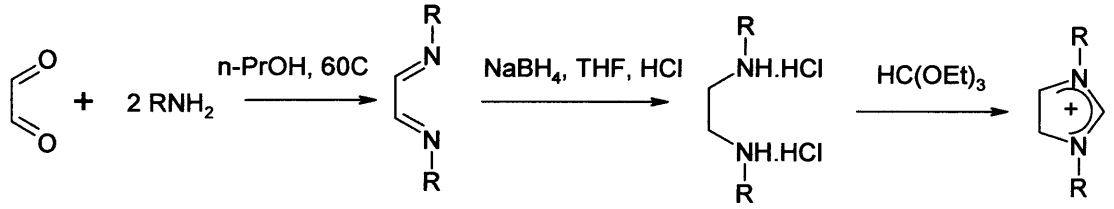


2.10

Scheme 2.4: Reaction between 8-aminoquinoline and 2-fluoronitrobenzene.

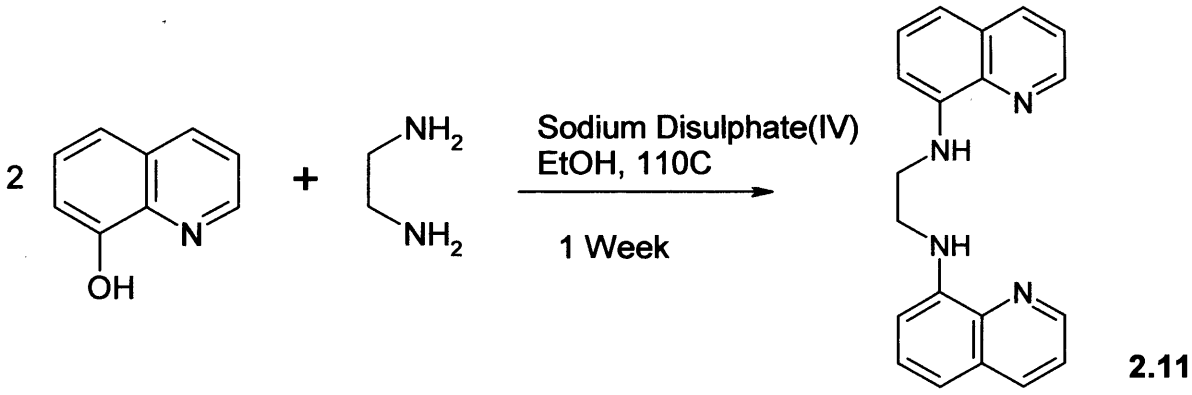
It was expected that reduction of the nitro group to an amine would proceed smoothly and could be followed by ring closure and nitrogen quarternisation to form the imidazolium salt. However, attempts to reduce the nitro group by using the same method as for the reduction of 2-methyl-8-nitroquinoline, gave a complex mixture of products. This coupled with the relative expense of the starting materials, poor yields and time constraints led to this synthesis being abandoned.

The symmetrical quinoline imidazolium salts could not be formed according to the established procedures[21] (Scheme 2.5)[22]. This was possibly due to salt formation via the acid reacting with the quinoline function and thereby influencing solubilities. The resulting product had extremely low solubilities in a large range of solvents including DMSO.



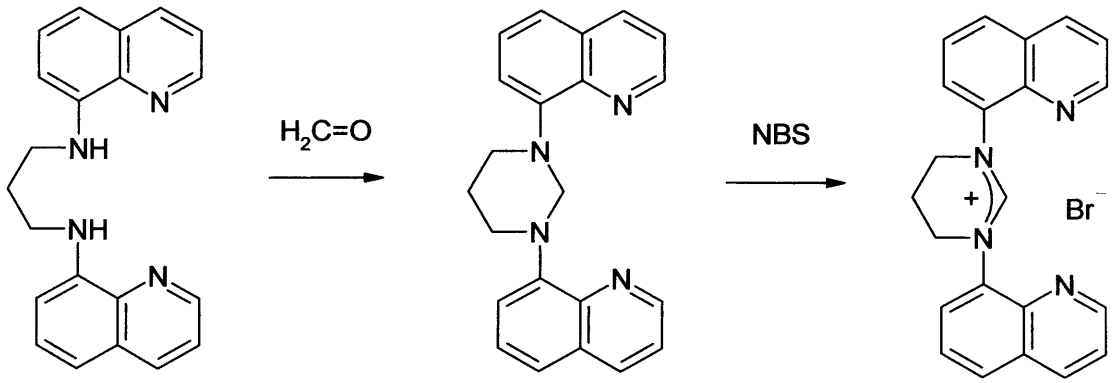
Scheme 2.5: Reaction scheme showing the stepwise formation of a symmetrical imidazolium salt.

It is a matter of interest that the diamine (**2.11**) was also formed from the considerably cheaper hydroxy starting material according to a literature method[23] (Scheme 2.6). This method was also used by T. Okada[24] to make N,N-di-8-quinolyl-1,3-propanediamine (**2.12** Scheme 2.7), which, providing ring closure could be achieved, would be a useful precursor to form the six membered NHC (**2.14**). Ring closure by standard methods also failed to yield the cyclized product of **2.11.**



2.11

Scheme 2.6: Synthesis of **2.11** adapted from the literature method[23] of diamine synthesis.



NBS= N-bromosuccinimide.

2.12 **2.13** **2.14**

Scheme 2.7: Proposed reaction scheme to form the symmetrical 6 membered imidazolium salt.

2.14 could be theoretically synthesised according to the preparative routes of other six membered NHCs[25]. Formation of **2.13** could be achieved by cyclization with aqueous formaldehyde and the imidazolium salt obtained by reaction of **2.13** with N-bromosuccinimide.

2.2.1.2 An Octahydroacridine based imidazolium salt

Further to the quinoline functionalised salts it was of interest to form a ligand that would have increased hemilability as well as a chiral aspect for catalytic applications. The aromaticity and therefore lack of sp^3 hybridized carbons of the quinoline based systems made them unsuitable for the task, thus octahydroacridine (Figure 2.7) was thought to be a suitable candidate. Octahydroacridine can offer a secondary donor function for chelation as well as sp^3 hybridized carbons. These tetrahedral carbons can offer the ability to make the ligand chiral as well as provide a framework for the addition of extra steric bulk if needed.

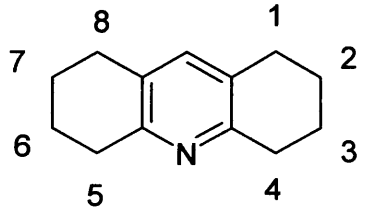
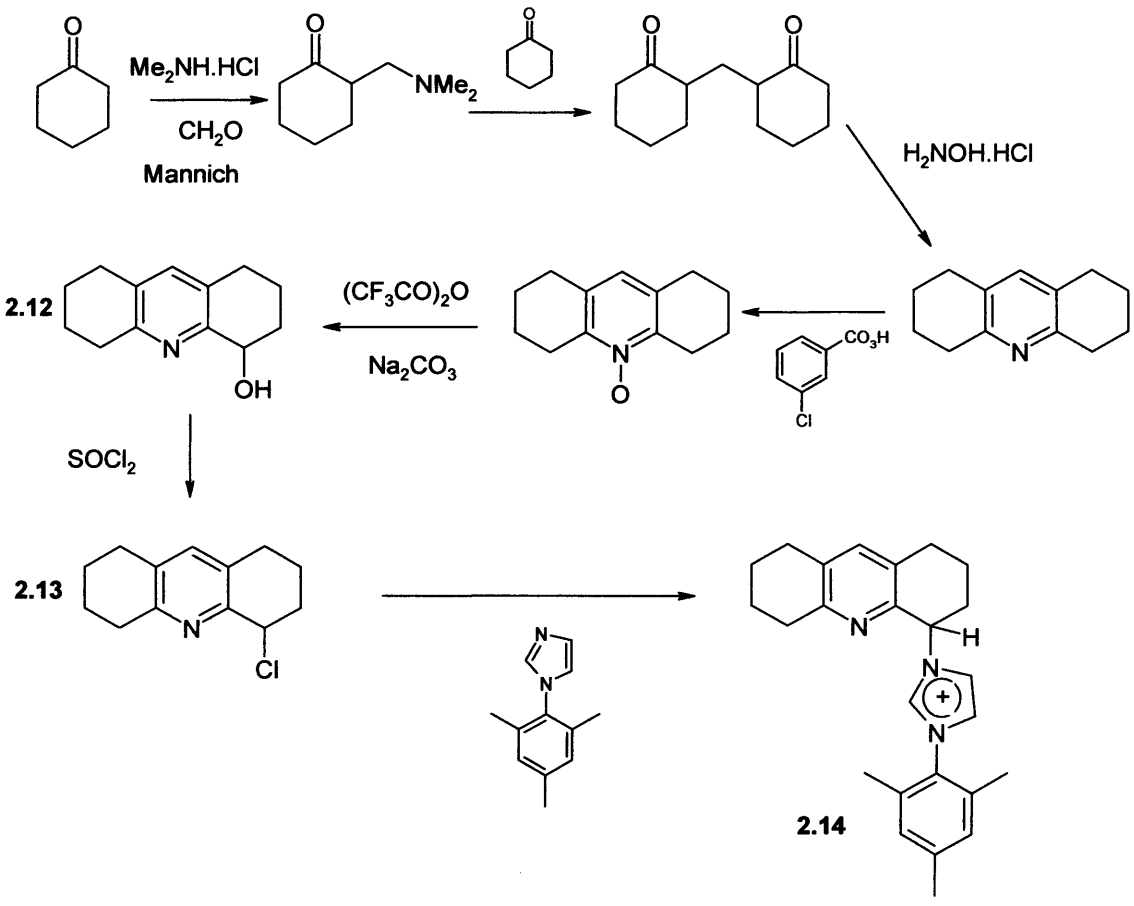


Figure 2.7: 1,2,3,4,5,6,7,8-octahydroacridine with atom labelling.



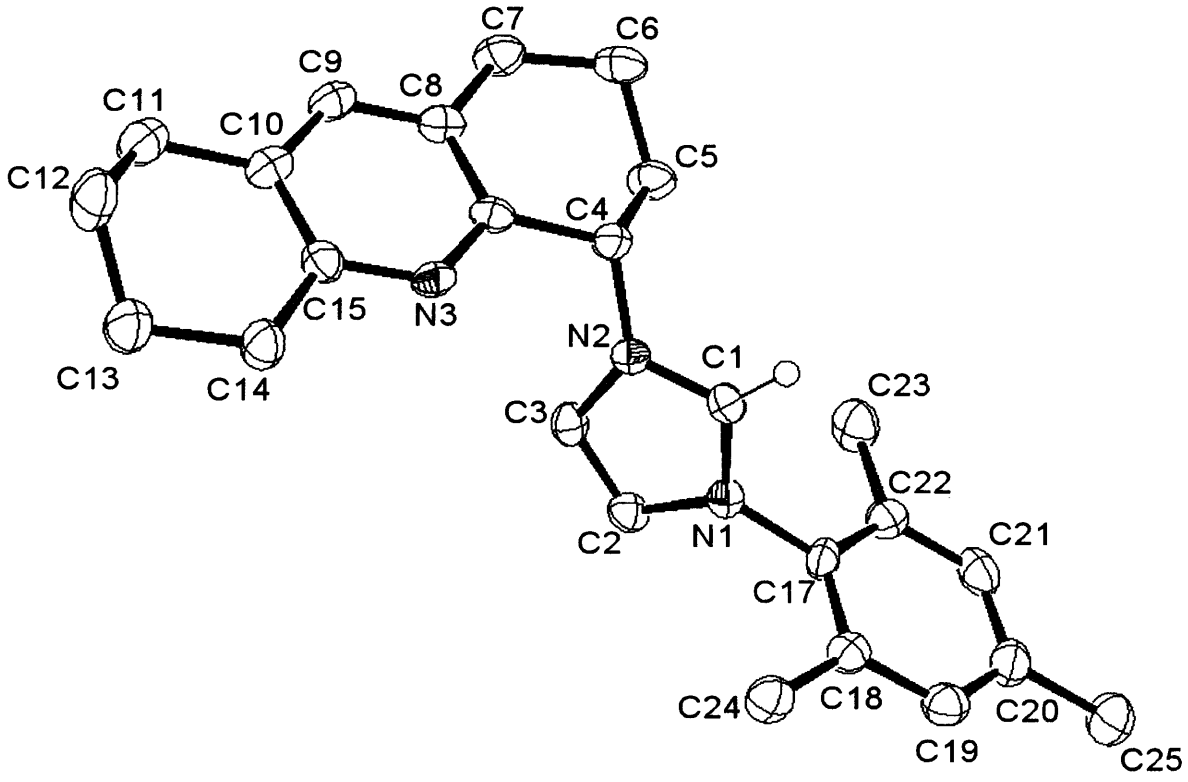
Scheme 2.8: Stepwise synthesis for **2.14**.

Due to the lack of commercial availability of octahydroacridine, the established synthetic procedures of Paine[26] and Bell[27] were considered. Both methods were used, however the former was the preferable. Bell's method proved to have fewer synthetic steps as well as less forceful reaction conditions. However the yield stated within the paper (50% overall) was subject to very specific reaction conditions and deviation from the procedure led to the formation of large amounts of by products. As well as having one extra synthetic step, Paine's method also has the disadvantages of more forceful reaction conditions and the overall synthetic procedure took a longer period of time. However the procedure was found to be more reliable and gave cleaner products. Scheme 2.8 shows Paines synthetic procedure as well as the subsequent steps for imidazolium salt synthesis.

In order to halogenate the octahydroacridine system for subsequent N-alkylation, it was first necessary to functionalise it with a hydroxyl group. Paine's procedure includes a synthetic strategy for the functionalisation with a hydroxyl group in the 4 position of the ring. This involves formation of the N-oxide by reaction with 3-chloroperoxybenzoic acid and following work up, reaction with an excess of boiling acetic anhydride. An alternative method however was used and adapted from the procedure of Fontenas[28], which replaces the large excess of acetic anhydride with trifluoroacetic anhydride with the reaction being carried out at room temperature. This method gave the desired hydroxyl substituted octahydroacridine (**2.12**). Conversion to 4-chlorooctahydroacridine (**2.13**) was achieved by reaction with thionyl chloride which upon work up gave a stable yellow solid. 1-mesitylimidazole was made according to the literature method[29].

The final step of the reaction scheme shows the reaction between 4-chlorooctahydroacridine (**2.13**) and 1-mesitylimidazole. As previously noted N-alkylation follows a typical S_N2 pathway and, as the alkylhalide in question is a secondary alkylchloride, we would expect the reactivity to be low. The 4-chlorooctahydroacridine was reacted with the mesityl imidazole (1:1) under extremely forcing reaction conditions. The mixture was dissolved in THF and held at 90°C in an ACE pressure tube for periods of up to 14 days. This was successful in producing a precipitate of the desired imidazolium salt, though the reaction had to be carried out over long periods to obtain sufficient quantities for analysis and further reactions.

Crystals suitable for X-Ray diffraction were grown by layering a DCM solution of the salt with hexanes. The crystal structure of **2.14** and a numbering scheme are given in Figure 2.8, along with selected bond lengths and angles (Table 2.2). It should be noted that the final imidazolium salt (**2.14**) was obtained as a racemate and no attempt was made during the course of this work to separate the enantiomers.



(a)

Figure 2.8: ORTEP representations of (**2.14**) (50% probability of thermal ellipsoids). Hydrogen and chloride atoms omitted for clarity.

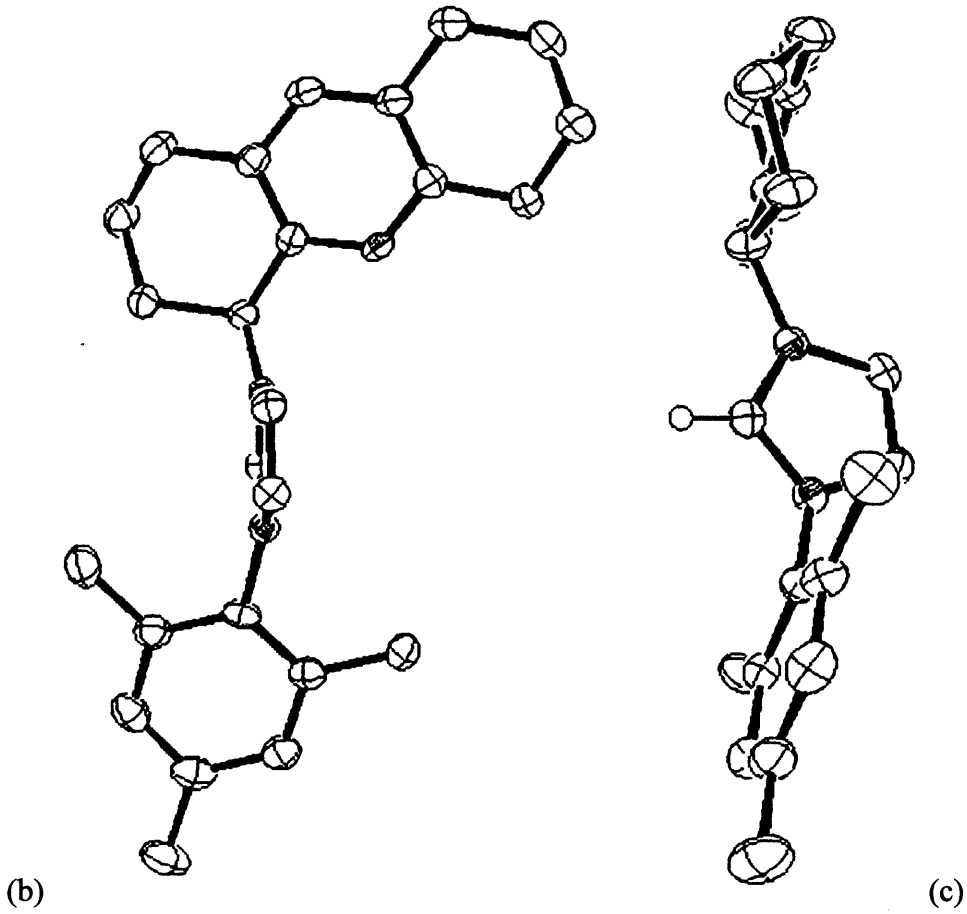


Figure 2.8 *cont.*: ORTEP representations of (**2.14**) (50% probability of thermal ellipsoids). Hydrogen and chloride atoms omitted for clarity.

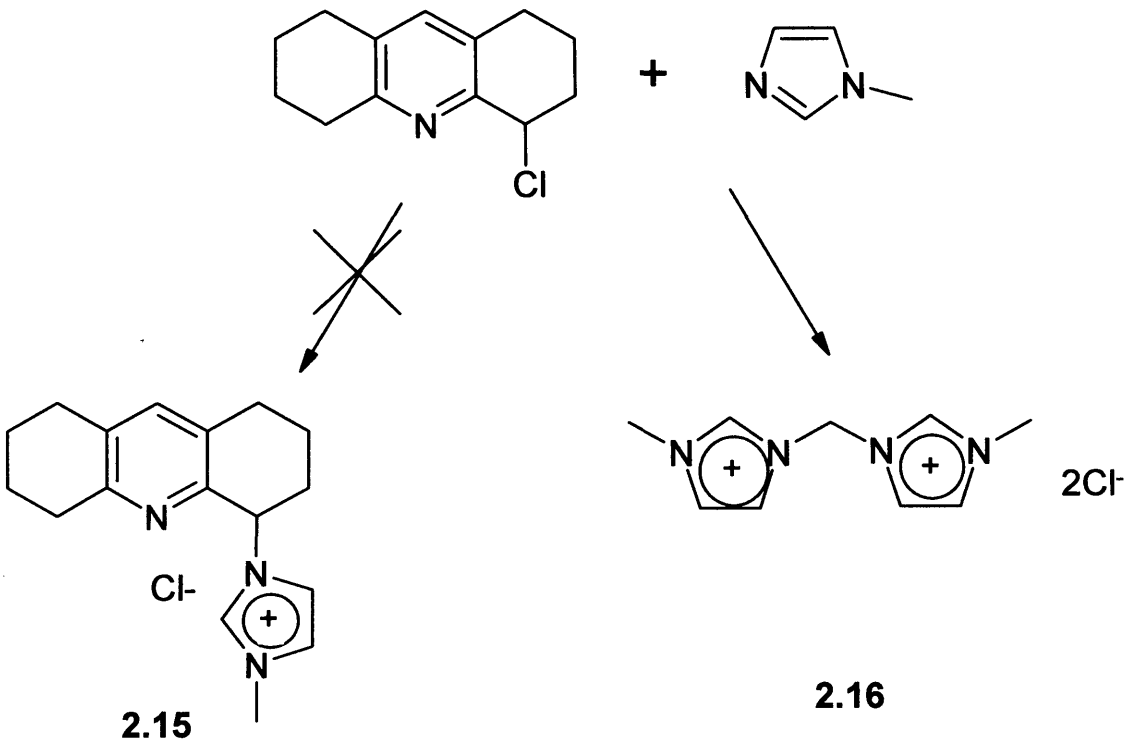
C1	N1	1.328(6)	C4	N2	1.469(6)	N1	C1	N2	108.5(4)
C1	N2	1.334(6)	C4	C16	1.516(7)	C1	N1	C17	122.5(4)
C2	C3	1.361(7)	C16	N3	1.349(6)	C1	N2	C4	121.5(4)
C2	N1	1.382 (6)	C17	N1	1.457(6)	N3	C16	C4	118.4(4)
C3	N2	1.381(6)							

Table 2.2: Bond lengths (Å) and angles (°) for **2.14**

Figure 2.8 shows the C1 proton is pointed towards the opposite side of the molecule to the N3. The planes of the imidazole and the octahydroacridine form an angle of approximately 71.8° and the planes of the imidazole and mesityl form an angle of approximately 91.0°. This divergence from ring coplanarity is most likely due to the

influence of combined steric crowding from the mesityl's C23 and C24 protons and the C5 proton of the octahydroacridine function with the imidazole C2 and C3 protons. The N1-C1-N2 of the NHC make an angle of 108.5(4)° with bond lengths of 1.328(6) and 1.334(6) respectively and are not unusual[18,19].

Due to the severe reaction conditions used in the synthesis of **2.14** an alternative procedure was developed with the aim to form **2.15** (Scheme 2.9) which replaces the mesityl imidazole with 1-methylimidazole. 1-methyl imidazole can act in this case as both solvent and reagent and reduces the hazards of the reaction due to its high boiling point (198°C). The reaction was carried out by the addition of 4-chlorooctahydroacridine to an excess of 1-methylimidazole and stirred at 90°C for one week. The resulting precipitate was analyzed by ^{1}H NMR which indicated that the desired imidzolium salt was not formed. The ^{1}H NMR gave singlets at 9.9ppm (2H), 8.7 (2H), 7.9 (2H), 7.0 (2H) and 4.0 (6H). The peak at 9.9 however is typical of an imidazolium salt and so in an attempt to clarify the structure of the product, crystals suitable for X-ray diffraction were grown. The solid state structure of the undesired product (**2.16**) is shown in Figure 2.9. N-alkylation of this type usually requires the alkyl halide to be an excess, so the desired imidazolium salt may have formed but in extremely small quantities and lost during the work up. Compound **2.16** may have formed by reaction of methyl imidazole with an unknown decomposition product of the chlorooctahydroacridine, or less likely by reaction with DCM introduced to the reaction mixture as a contaminant. Established procedures for the synthesis of **2.16** (diiodide salt) use a mixture of 1-methyl imidazole and diiodomethane (2:1) in THF, in a pressure tube at 130°C for 16 hours[30]. Further attempts to synthesis **2.15** were abandoned due to time constraints.



Scheme 2.9: Reaction scheme showing the desired (**2.15**) and undesired (**2.16**) imidazolium salts.

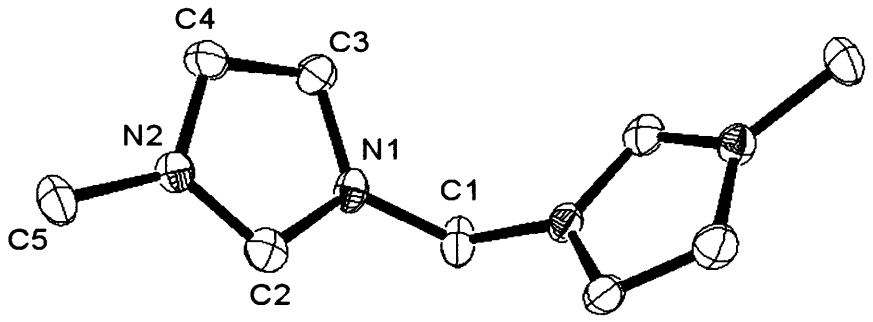
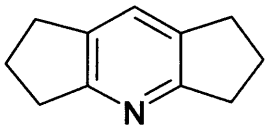


Figure 2.9: ORTEP representation of (**2.16**) (50% probability of thermal ellipsoids). Hydrogen and chloride atoms omitted for clarity.

The crystal structure of **2.16** shows the N1- C2 and C2- N2 bond lengths to be 1.325(5) and 1.329(6) respectively and form an angle of 108.0(4) and are not unusual. Crystal structures of **2.16** as a chelating ligand in complexes of Pd, Pt and Ni have been reported in the literature[30-33].

In order to extend ligand series, dicyclopentylpyridine (**2.17**, Figure 2.10) was formed by substituting cyclohexanone with cyclopentanone in Paines synthetic method for

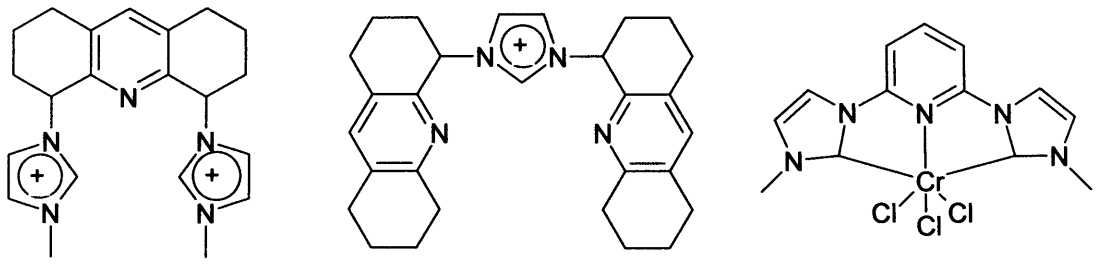
octahydroacridine. **2.17** was successfully functionalized with the hydroxyl group (confirmed by ^{1}H and ^{13}C) by the same procedure as for the octahydroacridine. Continuing the synthetic method, halogenating the hydroxyl compound with thionyl chloride in CH_3Cl caused the solution to darken. Heating the reaction mixture caused the solution to darken further, rapidly transforming the once straw coloured solution to a progressively blacker one. Upon work up, ^{1}H NMR gave complex spectra of unidentified products. Time constraints again prevented further development of this ring system in favour of pursuing the 6 membered ring system.



2.17

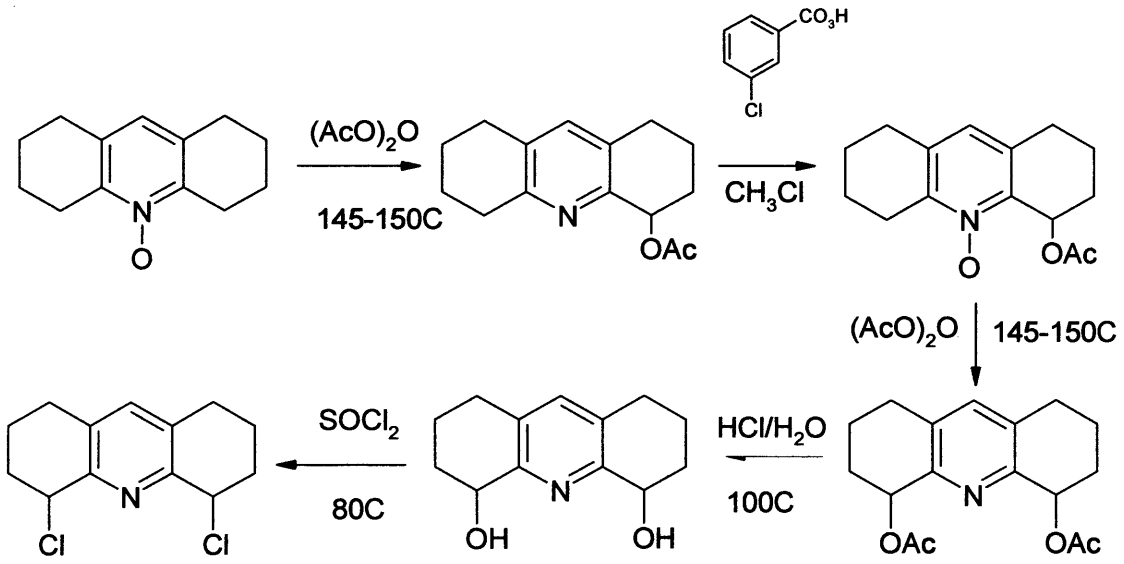
Figure 2.10: Dicyclopentylpyridine.

The octahydroacridine frame can offer the potential of forming a pincer ligand with two carbenes on the 4 and 5 positions of the ring system (**2.18**, Figure 2.11), or a pincer consisting of an NHC function with two octahydroacridines as N substituents (**2.19**). In an attempt to form **2.18**, the dihalo 4,5-dichlorooctahydroacridine was synthesised according to the literature method[26] (Scheme 2.10) and was reacted with 1-mesitylimidazole under the same reaction conditions as for **2.14**. The formation of **2.18** would prove extremely interesting in comparison to Gibson's pincer chromium complex (**2.20**)[34] as an active catalyst for the oligomerization of ethylenes. **2.18** was not formed however as it was found that monosalt formation by reaction of one of the halides rendered the compound sufficiently insoluble in THF thereby preventing further reaction. This coupled with the length of the reaction time meant that only the monosalt was formed. Changing the halide by using thionyl bromide in the synthetic stage and/or improving the solubility with solvent mixes or DMF/HMPA may be ways of overcoming this. These solutions however were not tried in this work, though the addition of sodium iodide to the reaction mixture was tried with no observable effects.



2.18 2.19 2.20

Figure 2.11: Proposed imidazolium salts for 'pincer' ligands (**2.18** & **2.19**) and Gibson's Cr 'pincer' complex (**2.20**)

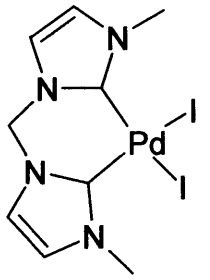


Scheme 2.10: Synthetic method for 4,5-dichlorooctahydroacridine.

2.2.2 Bis imidazolium salts.

Like the monofunctionalised imidazolium salts, bis imidazolium salts have generally been synthesised by simple starting materials and involve two imidazoles separated by a linker group, usually $(CH_2)_n$ with variable steric bulk on the second imidazolium nitrogens. The simplest example of a bis-imidazolium salt would be 3,3-dimethyl-1,1-

methylenediimidazolium iodide which was used to form a palladium(II) complex (**2.21**) by Herrmann *et al* via reaction with palladium acetate.[35]



2.21

Figure 2.12: Herrmann's Pd(II) complex of 3,3-dimethyl-1,1-methylenediimidazolium iodide.

Prior to the start of this work only a few examples of bis carbenes with chiral backbones were reported in the literature, the first example of which was made by RajanBabu *et al*[36] (**2.22**, Figure 2.13). During the course of this work a similar ligand to our own (**2.27**, Figure 2.14) was also described (**2.23**) and complexed with Pd by Harrison *et al*[37] (submitted 18/03/04) Our ligand however was submitted (23/02/04) for publication in a joint paper with M. Beller and others[38] in a study of the Pd catalysed telomerization reaction and was published around the same time. During the course of this work, other notable chiral bis imidazolium salts and their carbene metal complexes were also synthesised by various other groups (**2.24**)[39] and (**2.25**)[40].

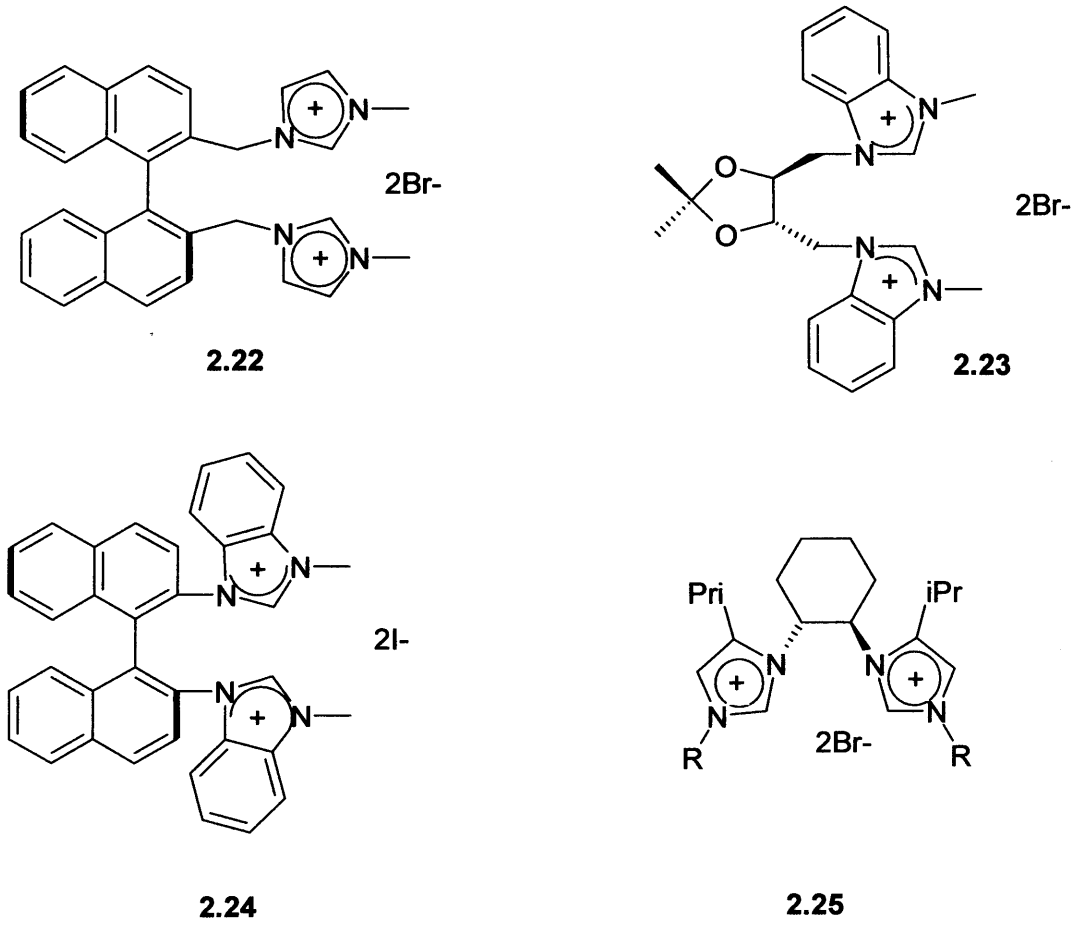
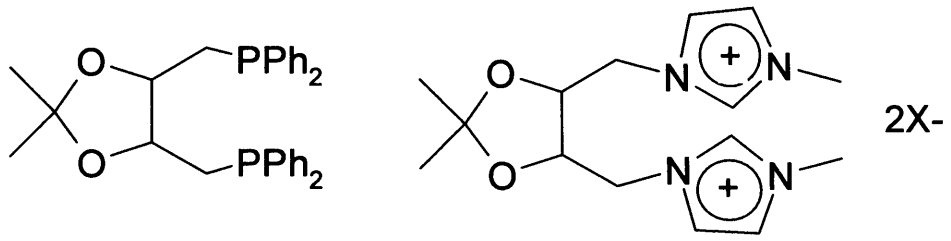


Figure 2.13: Examples of chiral bis imidazolium salts in the literature (at writing)[36,37,39,40].

2.2.2.1 Preparation of an imidazolium salt DIOP analogue.

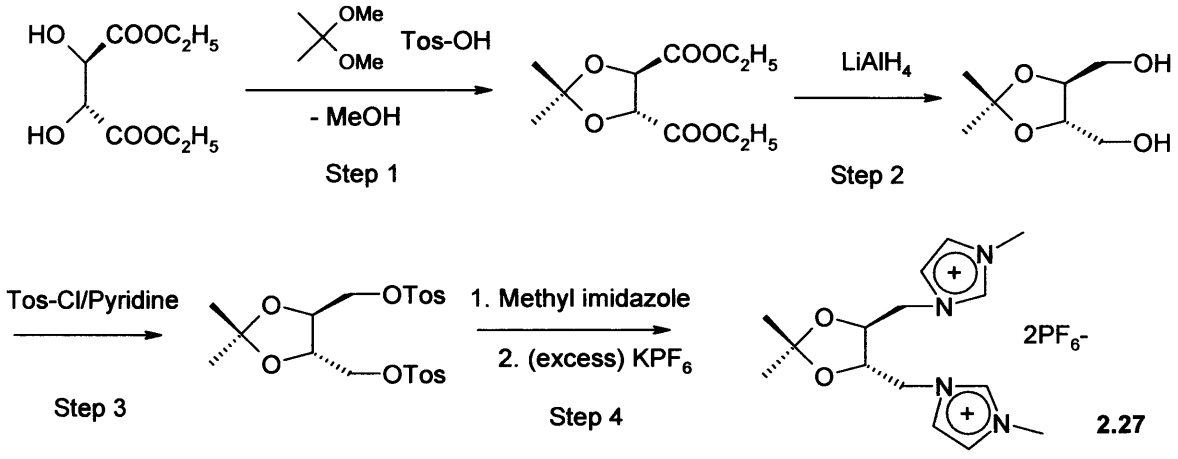
DIOP (**2.26**, Figure 2.14) is one of the earliest and most extensively explored chiral phosphine ligands in asymmetric hydrogenation and has shown synthetic chemists that the chirality does not have to be on the phosphorous centres for a phosphine compound to be a highly selective ligand for asymmetric catalysis, while the chiral backbone can play a significant role in the asymmetric induction[41]. For these reasons a carbene analogue of DIOP (**2.27**) was thought to be useful both as a comparison to a well studied phosphine ligand as well as a welcome addition to the canon of phosphine DIOP analogues[42].



2.26 **2.27**

Figure 2.14: DIOP (**2.26**) and our target imidazolium salt analogue (**2.27**).

It was decided to add the imidazolium functions on to an existing chiral backbone for synthetic simplicity. Just as RajanBabu used a binapthelene template to build upon for **2.22**, we used diethyl tartrate. The synthetic work for the bis-imidazolium salt was based largely on Brown's improved preparation of DIOP[43]. The chiral backbone was built according to Brown's literature method[43] up to step 3 (Scheme 2.11).



Scheme 2.11: Stepwise formation of **2.27**, taken from Browns DIOP synthesis.

2.27 was smoothly transformed from the tosyl dioxolan by a two step process, first by reaction with neat 1-methylimidazole at 90°C overnight, followed by the addition of H_2O and an excess of KPF_6 to precipitate a white solid of **2.27** as the *trans* product. Recrystallisation from a minimum amount of acetone gave crystals suitable for characterisation by X-ray diffraction. **2.27** was also characterized by ^1H and ^{13}C NMR.

The structure and numbering scheme of **2.27** are given in Figure 2.15 along with selected bond lengths and angles in Table 2.3.

The imidazolium moieties of **2.27** are orientated about their pendant bonds so that the C2 and C11 protons are facing towards opposite directions of the molecule, though free rotation about the N2-C5 and N4-C8 bonds should allow for chelation to a metal centre. The imidzolium N-C-N bond lengths and angles are typical of other imidazolium salts.

2.27 clearly represents a precursor to the carbene analogue of DIOP, though the nature of the carbenes means that upon chelation, **2.27** would form a nine membered chelate ring compared to the seven membered ring of a DIOP chelate. The ligand is very rigid and because of this would probably only form the cis product upon metal complexation.

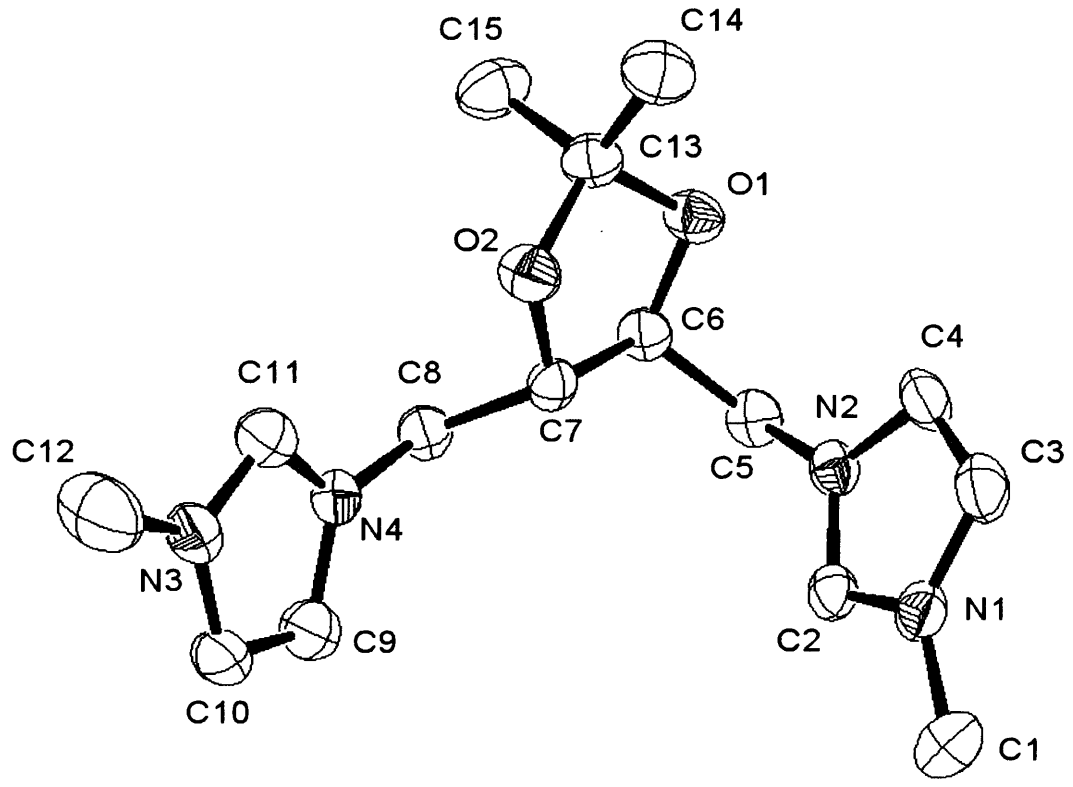


Figure 2.15: ORTEP representation of (**2.27**) (50% probability of thermal ellipsoids). Hydrogen and PF_6 atoms omitted for clarity.

C2	N1	1.331(5)	C11	N3	1.323(5)	N1	C2	N2	108.8(4)
C2	N2	1.328(5)	C11	N4	1.327(5)	C1	N1	C2	124.9(4)
C3	N1	1.375(5)	C12	N3	1.466(3)	C2	N2	C5	124.3(5)
C3	C4	1.351(5)	C9	N4	1.364(3)	N3	C11	N4	108.4(5)
C4	N2	1.386(3)	C10	N3	1.364(3)	C12	N3	C11	125.9(5)
N2	C1	1.470(6)	C9	C10	1.327(5)	C8	N4	C9	125.4(3)
N2	C5	1.468(6)	N4	C8	1.466(5)				

Table 2.3: Selected bond lengths (Å) and angles (°) for (**2.27**)

2.3 Conclusions

A range of imidazolium salts have been synthesised and characterised as precursors to the corresponding NHC ligands. The majority of these have combined a functional group with an imidazolium moiety and display a range of varying degrees of steric bulk. The quinoline based ligands offer a rigid chelate based around a delocalised electron ring system, whilst the octahydroacridine based system offers a more flexible chelate as well as a chiral centre. A chiral bis-imidazolium salt DIOP analogue has also been synthesised offering the potential for comparison in enantioselective catalysis with the well studied DIOP ligand. All the imidazolium salts were characterised by spectroscopic means including ^{1}H, ^{13}C NMR and Mass Spec. A few examples have been crystalographically characterised.

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 a nitrogen glove box. Glassware was 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 degassed by refluxing under dinitrogen and over sodium wire and benzophenone. Dichloromethane (DCM), methanol (MeOH), and acetonitrile (MeCN) were dried over calcium hydride. All

other anhydrous solvents were obtained by distillation from the appropriate drying agents under dinitrogen. Deoxygenation of solvents and reagents was carried out by freeze thaw degassing

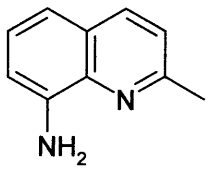
All NMR solvents were purchased from Aldrich and Goss, dried over 3Å molecular sieves and freeze-thaw degassed three times. All reagents were purchased from commercial sources and used without purification, unless otherwise stated.

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

The following compounds were prepared by established literature methods. 8-imidazol-1-yl-quinoline (**2.4**)[15], octahydroacridine N-oxide[26], 4,5-dichlorooctahydroacridine[26], mesityl imidazole, and *trans*-4,5-bis[tosyloxymethyl]-2,2-dimethyl-1,3-dioxolan[43].

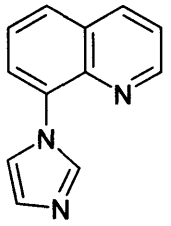
2.4.1.1 Synthesis Of Functionalised Imidazolium salts

Synthesis of 2-methyl-quinolin-8-amine (2.3):



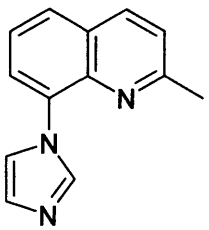
2-methyl-8-nitroquinoline (1.09g) in 30ml THF was placed in a 1lt flask with a catalytic amount of Pd on Carbon (10% mol) and a drop of MeOH. The atmosphere was then replaced with H_2 and the mixture allowed to stir overnight. The solution was then filtered through celite and the solvent removed to give a pale yellow powder. **^{1}H NMR** ($CDCl_3$, 400MHz, δ) 7.9 (m, 1H, Quin H), 7.15 (m, 2H, Quin H), 7.05 (m, 1H, Quin H), 6.85 (m, 1H, Quin H), 4.9 (s, br, 2H, NH_2), 2.60 (s, 3H, CH_3).

Synthesis of 8-Imidazol-1-yl-quinoline (2.4).



8-Imidazol-1-yl-quinoline was made according to a modified literature method[14]. 8-Amino quinoline (5g, 35mmol) in 120ml MeOH was mixed with 40% glyoxal (5.07g, 35mmol) overnight to give a yellow mixture. NH_4Cl (3.7g, 69mmol) and 37% aq. formaldehyde (5.67g, 69mmol) was added to the mixture which was then diluted with MeOH (100ml) and refluxed for one hour. H_3PO_4 (5.5ml, 85%) was then slowly added to the mixture before being refluxed overnight. After removal of the solvent the dark residue was poured onto ice (400g) and neutralized with aq. 40% KOH until pH9. The resulting mixture was then extracted with Et_2O (4x150ml). The ethereal phase was washed with H_2O, brine and dried with Na_2SO_4. The organic solvent was removed to give a brown solid of 8-imidzol-1-yl-quinoline (1.77g, 26%) which was used without further purification. **^{1}H NMR**(MeOD 250MHz, δ): 7.28 (s, 1H, NCHN), 6.78 (m, 1H, Ar-H), 6.61 (m, 1H, Ar-H), 6.36 (m, 1H, Ar-H), 6.19 (m, 1H, Ar-H) 6.06 (m, 1H, Ar-H), 5.99 (s, 1H, Ar-H), 5.96 (m, 1H, Ar-H) 5.59 (s, 1H, Ar-H). **^{13}C NMR** ($CDCl_3$, 100MHz, δ): 151.1, 141.8, 138.9, 136.8, 134.3, 129.7, 128.4, 127.6, 126.4, 127.9, 122.3, 121.7.

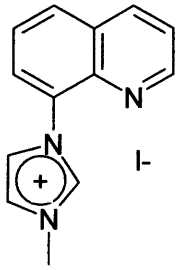
Synthesis of 8-(1H-imidazol-1-yl)-2-methylquinoline (2.5):



8-(1H-imidazol-1-yl)-2-methylquinoline was made using the same procedure as for **2.4**. 2-methyl-quinolin-8-amine (1.40g, 8.8mmol) was mixed with 40% glyoxal (1.27g, 8.8mmol) in 30ml MeOH overnight to give a yellow mixture. NH_4Cl (0.94g, 17.6mmol) and 37% Aq. formaldehyde (1.42g, 17.6mmol) were then added to the mixture which was diluted by the addition MeOH (150ml). The mixture was refluxed for an hour. H_3PO_4 (1.6ml, 85%) was then slowly added to the mixture before being

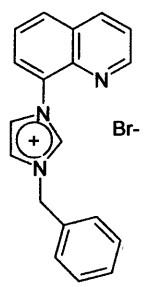
refluxed overnight. After removal of the solvent the dark residue was poured onto ice (100g) and neutralized with aq. 40% KOH until pH9. The resulting mixture was then extracted with Et_2O (4x100ml). The ethereal phase was washed with H_2O, brine and dried with Na_2SO_4. The organic solvent was removed to give the light brown 8-(1H-imidazol-1-yl)-2-methylquinoline. (0.56g, 31%). **^{1}H NMR**($CDCl_3$ 250MHz, δ): 8.15 (s, 1H, NCHN), 8.00 (m, 1H, Quin H4), 7.70 (m, 1H, Quin H), 7.55 (m, 1H, Quin H), 7.45 (m, 2H, Quin H) 7.25 (m, 1H, HCCH), 7.15 (m, 1H, HCCH), 2.60 (s, 3H, CH_3). **^{13}C NMR** ($CDCl_3$, 100MHz, δ): 159.0, 140.5, 138.5, 136.0, 135.5, 128.5, 127.0, 126.8, 125.0, 123.0, 122.5, 120.5, 25.0

Synthesis of 1-methyl-3-quinoline-imidazolium iodide (2.6):



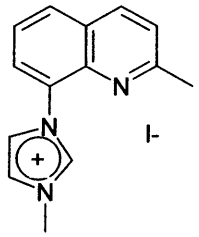
Methyl iodide (2g) was added to a solution of 8-imidazol-1-yl-quinoline (0.521g, 3.3mmol) in 20ml THF. The resulting mixture was allowed to stir overnight at room temperature. The resulting yellow/orange precipitate was filtered using a filter stick and washed with further amounts of fresh THF (3x5ml) to afford a brown powder. This was then recrystalized from DCM/Hexane to give the desired imidazolium salt. (0.86g, 87%) **^{1}H NMR**($CDCl_3$, 400MHz, δ): 10.2 (s, 1H, NCHN), 8.95 (m, 1H, quinH2), 8.30 (m, 2H, HCCH), 8.00 (m, 1H, Quin H4), 7.85 (m, 1H, Quin H6), 7.70 (m, 1H, Quin H8), 7.50-7.6 (m, 2H, Quin H3,7) 4.3 (s, 3H, NCH_3) **MS** (ES) m/z (%): 210.2 (38) [M-I]+, 155.0 (59), 141.0 (88), 139.9 (100).

Synthesis of 1-benzyl-3-quinolinimidazolium bromide (2.7):



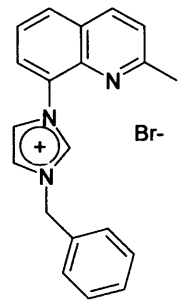
Benzyl bromide (2g) was added to a solution of 8-imidazol-1-yl-quinoline (1.03g, 6.8mmol) in 20ml THF. The resulting mixture was allowed to stir overnight at room temperature. The resulting yellow/brown precipitate was filtered using a filter stick and washed with fresh THF (3x5ml) to afford a brown powder. This was then recrystallized from DCM/Hexane to give the desired imidazolium salt (1.7g, 75%). **^{1}H NMR**(C_6D_6, 250MHz, δ): 10.75 (s, 1H, NCHN), 8.85 (m, 1H, Quin H2), 8.20 (m, 2H, Ar H), 7.95 (m,2H, Ar H, HCCH), 7.60-7.75 (m, 4H, HCCH Ar H), 7.50 (m, 1H, Ar H), 7.35 (m, 3H, Ar H), 5.85(s, 2H, CH_2-Ph). **MS** (ES) m/z (%): 285.3 (73) [M-Br]+, 155.0 (48), 127.9 (59), 114.8 (100). MS (ESI) m/z (%): found: 285.1449 [M-Br]+; expected: 258.3482

Synthesis of 1-methyl-3-(2-methyl-quinoline)-imidazolium iodide (2.8):



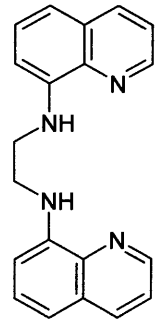
Methyl iodide (2g) was added to a solution of 8-(1H-imidazol-1-yl)-2-methylquinoline (1g 4.67mmol) in 20ml THF. The resulting mixture was allowed to stir overnight at room temperature. The resulting yellow/orange precipitate was filtered using a filter stick and washed with THF (3x5ml) to afford a brown powder. This was then recrystallized from DCM/Hexane to give the desired imidazolium salt (1.4g, 84%). **^{1}H NMR** ($CDCl_3$, 400MHz, δ): 10.15 (s, 1H, NCHN), 8.15 (m, 2H, HCCH), 7.8-7.95 (m, 2H, Quin H4,6), 7.55-7.7 (m, 2H, Quin H7,8), 7.35 (m, 1H, Quin H3), 4.30 (s, 3H, NCH_3), 2.65 (s, 3H, CH_3). **^{13}C NMR** ($CDCl_3$, 100MHz, δ): 161.30, 139.9, 137.4, 136.7, 130.4, 130.3, 127.5, 125.9, 125.3, 124.4, 123.9, 123.3, 37.7, 25.8. **MS** (ES) m/z (%): 224.2 (35) [M-I]+, 181.1 (52), 154 (95), 139.9 (100).

Synthesis of 1-benzyl-3-(2-methyl-quinoline)-imidazolium bromide (2.9):



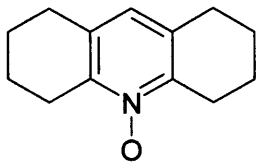
Benzyl bromide (2g) was added to a solution of 8-(1H-imidazol-1-yl)-2-methylquinoline (1.03g 4.93mmol) in 20ml THF. The resulting mixture was allowed to stir overnight at room temperature. The resulting yellow/orange precipitate was filtered using a filter stick and washed with THF (3x5ml) to afford a brown powder. This was then recrystallized from DCM/Hexane to give the desired imidazolium salt (1.2g, 63%). **^{1}H NMR** ($CDCl_3$, 250MHz, δ): 10.7 (s, 1H, NCHN), 8.15 (m, 2H, ArH), 7.85 (m, 2H, ArH), 7.45-7.65 (m, 3H, ArH) 7.35 (m, 5H, ArH), 5.85 (s, 2H, CH_2-Ph), 2.65(s, 3H, Quin CH_3). **MS** (ES) m/z (%): 300.3 (98) [M-Br]+, 286.3 (18), 181.1 (19), 155.0 (25), 114.8 (100).

Synthesis of N, N' – di-8-quinolyl-1,2-ethanediamine (2.11):



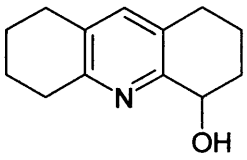
An aqueous mixture of 8-hydroxyquinoline (2.90g, 0.02mol), 1,2-ethanediamine (0.4g, 0.01mol) and sodium disulphate (3.80g, 0.02mol) was refluxed for one week at 110°C. Recrystallization of the subsequent orange solid from ethanol gave light orange plates of **2.11** (0.6g, 18%). **^{1}H NMR** ($CDCl_3$, 400MHz, δ): 8.6 (m, 2H), 7.95 (m, 2H), 7.3 (m, 4H), 7.0 (m, 2H), 6.65 (m, 2H), 6.3 (s, br, 2H, N*H*), 3.65 (s, 4H).

Synthesis of Octahydroacridine N-oxide:



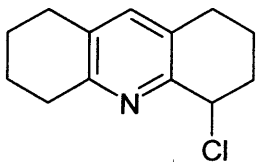
Octahydroacridine N-oxide was made according to the stepwise literature method of Paine[25].

Synthesis of 1,2,3,4,5,6,7,8-octahydroacridin-4-ol (2.12): (Adapted from the literature method[28])



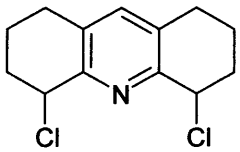
Trifluoroacetic anhydride (10.2ml, 0.072mol, 2.5 equivalents) was slowly added to a stirred solution of octahydroacridine N-oxide (5.85g, 0.0288mol) in dry DCM (50ml) causing a slight increase in temperature of the solution. The solution was allowed to stir for a further hour at room temperature. The volatiles were then removed under reduced pressure to leave a yellow viscous residue, which was then taken up in 50ml 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 extracts were then combined and washed with water and brine and then dried over magnesium sulphate. The solvent was then removed to give octahydroacridin-4-ol (4.98g, 85%). **^{1}H NMR** ($CDCl_3$, 250MHz, δ): 7.05 (s, 1H, ArH), 4.55 (m, 1H, C*H*OH), 4.05 (Br s, 1H, CHO*H*), 2.8 (m, 2H, CH_2), 2.7 (m, 4H, CH_2), 2.2 (m, 1H, CH_2), 1.6-2.0 (m, 7H, CH_2). **^{13}C NMR**($CDCl_3$, 100MHz, 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.

Synthesis of 4-chlorooctahydroacridine (2.13): (Adapted from the literature method)



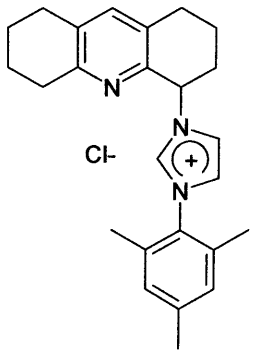
Thionyl chloride (30ml) in $CHCl_3$ (30ml) was added to a solution of octahydroacridin-4-ol (14g, 0.069mol) in 50ml DCM. The mixture was stirred at room temperature for 10 minutes, then refluxed for an hour at 80°C. The excess thionyl chloride and volatile by-products were then removed under reduced pressure and the residue dissolved in DCM (150ml). The solution was then extracted with Na_2CO_3 (15g) in water (250ml) and the aqueous phase (pH= 8.5) was washed with DCM (2x200ml). 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 (9.80g, 64.3%). **^{1}H NMR** ($CDCl_3$, 250 MHz, δ): 7.05 (s, 1H, ArH), 5.20 (m, 1H, C*H*Cl), 2.55-2.95 (m, 6H, CH_2), 2.05-2.35 (m, 3H, CH_2), 1.65-1.85 (m, 5H, CH_2). **^{13}C NMR** ($CDCl_3$, 100MHz, δ): 155.53, 151.22, 137.96, 132.35, 128.97, 59.44, 32.65, 32.24, 28.6, 27.54, 23.15, 22.65, 17.42.

Synthesis of 4,5-dichlorooctahydroacridine:



4,5-dichlorooctahydroacridine was made according to the literature method of Gan[26].

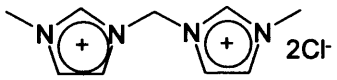
Synthesis of 1-mesityl-3-octahydroacridinimidazolium chloride (2.14):



4-chlorooctahydroacridine (1g, 4.5mmol) and 1- mesityl imidazole (0.84g 4.5mmol) were placed in an ACE pressure tube with 10ml 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 a beige solid of the imidazolium salt (0.2g, 11%). The filtrate was placed back under reflux where it continued to react further over time (13% overall). **^{1}H NMR** ($CDCl_3$, 400MHz, δ) 10.15 (s, 1H, NCHN), 8.18 (s, 1H,

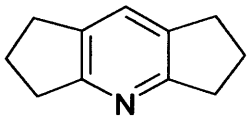
HCCH), 7.65 (s, 1H, HCCH), 7.20 (s, 1H, ArH), 6.95 (m, 2H, ArH), 6.55 (s, 1H, CHN), 1.80-3.40 (m, 23H, CH2, CH3) **MS** (ES) m/z (%): 372.3 (29) [M-Cl]+, 186.2 (70), 170.1 (97), 156.0 (100), 142.0 (97), 114.8 (96). **MS** (ESI) m/z (%): found 372.3424 [M-Cl]+; expected: 372.5333.

Synthesis of 1,1-dimethyl-3,3-methylene-diimidazolium dichloride (2.16):



2.16 was synthesised during the attempted synthesis of **2.15**. **2.13** (1g, 4.5mmol) was dissolved in 1-methylimidazole (5g, 60mmol) and stirred at 90°C for one week. The resulting beige precipitate was filtered and recrystallized from DCM to give **2.16** (0.4g). **^{1}H NMR** ($CDCl_3$, 400MHz, δ): 9.9ppm (s, 2H), 8.7 (s, 2H), 7.9 (s, 2H), 7.0 (s, 2H) and 4.0 (s, 6H).

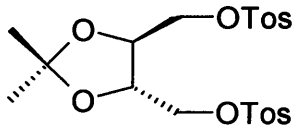
Synthesis of Dicyclopentylpyridine (2.17):



2.17 was made according to the modified stepwise procedure of Paine[25].

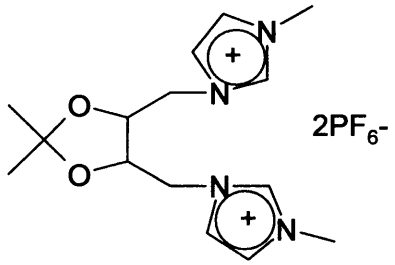
2.4.1.2 Synthesis of Bis Imidazolium Salts

Synthesis of (-)-*trans*-4,5-bis[tosyloxymethyl]-2,2-dimethyl-1,3-dioxolan:



(-)-*trans*-4,5-bis[tosyloxymethyl]-2,2-dimethyl-1,3-dioxolan was made according to a literature method[43].

Synthesis of (-)*trans*-4,5-Bis(methylimidazolium hexaflurophosphate)-2,2-dimethyl-1,3-dioxolan (2.27):



(-)-*trans*-4,5-bis[tosyloxymethyl]-2,2-dimethyl-1,3-dioxolan (5g, 10.6mmol) was stirred with 1-methylimidazole (15ml) overnight at 90°C to give a brown/red solution. 100ml of water was then added followed by an excess of KPF_6 (4.57g) to give a white precipitate. This was then filtered and recrystalized from acetone and Et_2O to give white crystals of the bis-imidazolium salt (5.2g, 84%). Crystals suitable for X-ray determination were grown by the slow evaporation of an acetone solution. **^{1}H NMR** (CD_3CN, 400MHz, δ): 8.3 (s, 2H, NCHN), 7.2-7.25 (m, 4H, HCCH), 4.3 (m, 2H, OCH), 4.1 (m, 2H, CH_2), 3.9 (m, 2H, CH_2), 3.65 (s, 6H, NCH_3), 1.15 (s, 6H, CCH_3). **^{13}C NMR** (CD_3CN, 250MHz, δ): 136.4 (NCN), 123.5 (NCCN), 123.2 (NCCN), 111.1 (OCC_2H_6) 75.2 (OCH), 50 (CH_2), 35.7 (NCH_3), 25.8 (CH_3). **MS** (ES) m/z (%): 437.2 (82) [M-PF_6]+, 281.3 (24), 151.0 (100).

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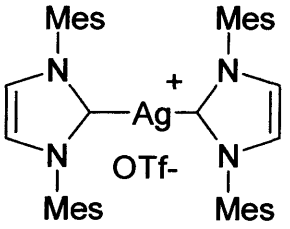
Chapter Three
Silver (I) Complexes Of Chelating Carbene Ligands

3.1 Introduction.

3.1.1 Ag(I)(NHC) As A Transmetallation Agent

Due to the catalytic importance of palladium NHC complexes, and more importantly Pd(hydrocarbyl)(NHC), the main aim of this work is the synthesis of novel complexes of these types. The last few years however have shown the importance of Ag(I)(NHC) complexes as intermediates in the synthesis of their related Pd complexes. In particular, Ag intermediates have been shown to be extremely useful when the desired complex contains a functionalised carbene ligand[1]. It is therefore appropriate to discuss some of the history behind Ag(NHC)s and why they can play such a pivotal role in Pd(NHC) synthesis.

Early synthetic procedures for Ag carbenes followed the standard routes as for any other metals at that time, the first being reported by Arduengo[2] in 1993. Arduengo displaced the weakly coordinated triflate ligand from Ag(OTf) with 1,3-dimethylimidazolin-2-ylidine and formed the homoleptic complex (**3.1**). (Figure 3.1)

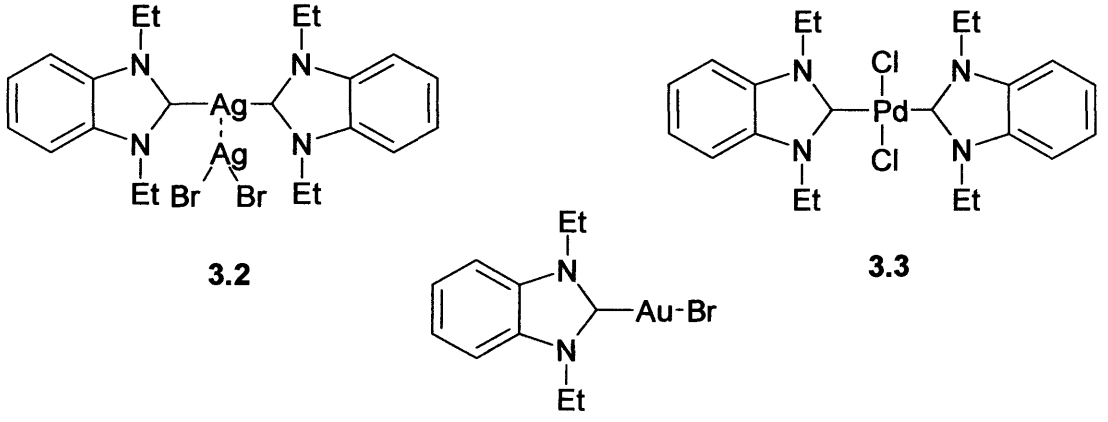


3.1

Mes = Mesityl

Figure 3.1: Arduengo's homoleptic Ag complex.

In the late 1990's Lin and Wang were conducting work on the molecular recognition of coinage metals and were investigating possible ligand-unsupported AgI-AgI interactions in Ag-carbene compounds. They published a paper[3] that demonstrated the ability of these Ag(NHC)s to act as transmetallation agents, and in doing so, offering a potentially easily accessible route to form palladium complexes. In particular early reports have since shown this to be a valuable and easy synthetic route to Pd(II)(hydrocarbyl)functionalized carbene complexes. The report concerned the synthesis of Ag(I) complexes of 1,3-diethylbenzimidazol-2-ylidene and the subsequent transfer of the carbene ligand onto Pd and Au. This was achieved by stirring the imidazolium salt with Ag_2O in DCM, or with AgBr and NaOH under phase transfer conditions, which afforded the Ag complex **(3.2)** (Figure 3.2) in high yields. Ligand transfer was achieved simply by stirring the Ag complexes with $Pd(MeCN)_2Cl_2$ to give **3.3** (Figure 3.2) or with $Au(SMe_2)Cl$ to give **3.4** (Figure 3.2). The silver halide by-products were shown to be recycled back in to the Ag(NHC) by phase transfer conditions. Importantly the silver complexes were shown to be stable towards air and, as water is a by-product of the reaction, the complexes were also stable towards moisture.

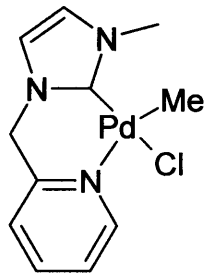


3.2 **3.3** **3.4**

Figure 3.2: Lin and Wang's Ag complex (**3.2**) and its related transmetallation products.

Realising this method's potential for the use in group 10 metal carbene complex synthesis, several groups have employed it as a reliable synthetic strategy[1,4-12]. Amongst these groups, Cavell successfully synthesised hydrocarbylpalladium

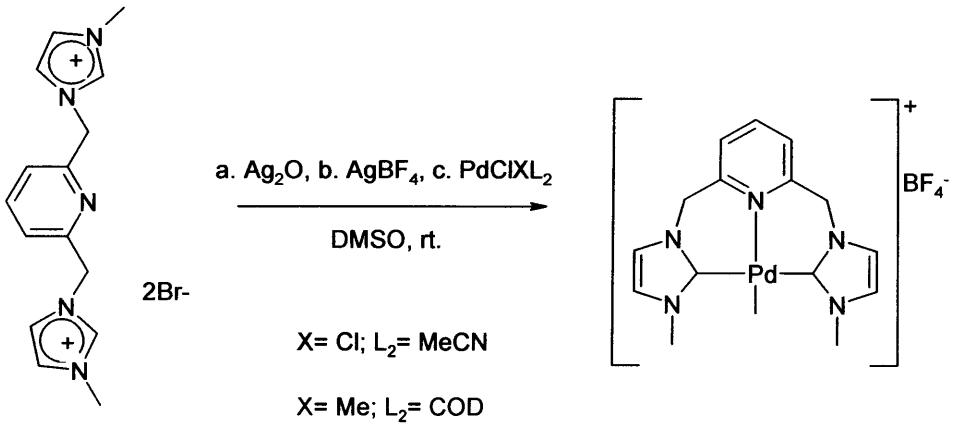
complexes with functionalised carbenes such as **3.5**[1] (Figure 3.3). The traditional routes to synthesise this type of ligand would have required strong bases with which to deprotonate the imidazole C2-H for the formation of the free carbene, often leading to abstraction of acidic (or 'active') protons on the CH_2 linker. In the case of **3.5**, both deprotonation to form the free carbene as well as reaction with $Pd(OAc)_2$ as a direct route to the Pd complex was unsuccessful. However, by simply reacting the Ag complex with PdMeCl(COD), the desired Pd complex was synthesised.



3.5

Figure 3.3: Cavell's hydrocarbylpalladium complex.

Further to the successful application of a Ag method with functionalised mono-imidazolium salts, the same group also implemented the Ag route for the formation of functionalised pincer complexes[5]. A one-pot reaction method was also developed that produced high yields of the desired Pd(II) complex. (Scheme 3.1)[9]

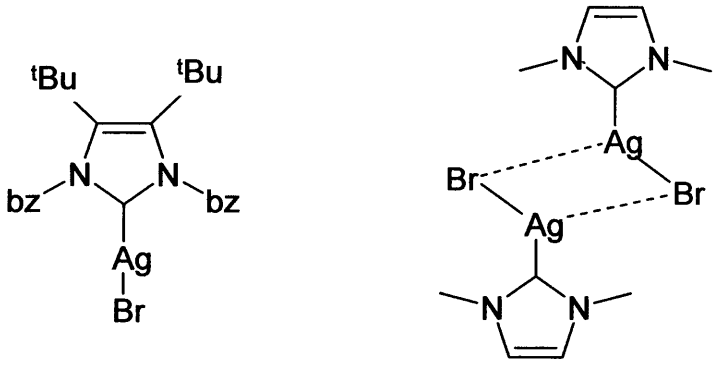


Scheme 3.1: Cavell's 'one pot' synthesis of Pd hydrocarbyl species via the Ag route.

The relative ease of formation of Ag(I) functionalised NHC's and their valuable ability to act as transmetallation agents, in particular for the formation of hydrocarbyl species, led to the method being adopted as the route for which to form the Pd complexes within this work.

3.1.2 Structural characteristics of Ag(I) Carbene complexes.

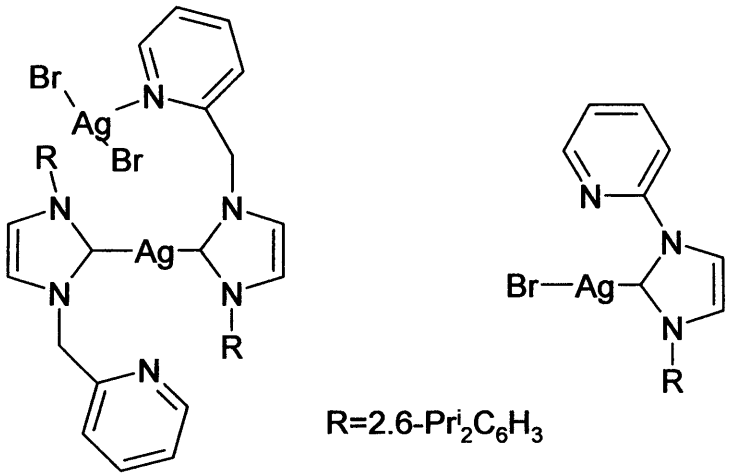
On reviewing the current literature with respect to solid state crystal structures of Ag(I)(NHC) complexes, it is apparent that it is difficult to predict the exact structure of any given complex. This is due to the ability of Ag(I) to form complex anions of the formula $[AgX_2]^-$ (X = Halogen), to be able to coordinate to either one or two NHC moieties and engage in AgI·····AgI interactions in the solid state[13]. This has led to a number of different structural arrangements, such as **3.2** (Figure 3.2), **3.6**[10] and **3.7**[8] (Figure 3.4) amongst others.



3.6 **3.7**

Figure 3.4: Examples of structural diversity seen within Ag NHC complexes

As an illustration of the unpredictability of Ag complexes the crystal structural evidence of Danopoulos for complexes **3.8** and **3.9** (Figure 3.5) are examined. **3.9** has the carbene moiety directly attached to the pyridine making it a more rigid ligand than that of **3.8.** Introducing a second ligand to **3.9** to form the $Ag(carbene)_2$ complex would most likely increase unfavourable steric interligand interactions. However Danopoulos also observed that when the Ag NHC preparations were carried out at higher temperatures (refluxing 1,2-dichloroethane), by-products were formed which were concluded to be the isostoichiometric Ag(ligand)Br (for **3.8**) and $[Ag(ligand)_2][AgBr_2]$ for **3.9**. The reasons why the different structures were adopted were therefore inconclusive[4].



3.8 **3.9**

Figure 3.5: Danopoulos's structurally characterised Ag NHC complexes.

It is important to note that in the examples in the literature, with the exception of complexes prepared in the absence of coordinating halide ions, the stoichiometry is mostly always 1:1:1 (NHC:Ag:X). Complexes prepared without the presence of coordinating halide ions show a stoichiometry of 1:2 (Ag:NHC).

3.2 Results And Discussion.

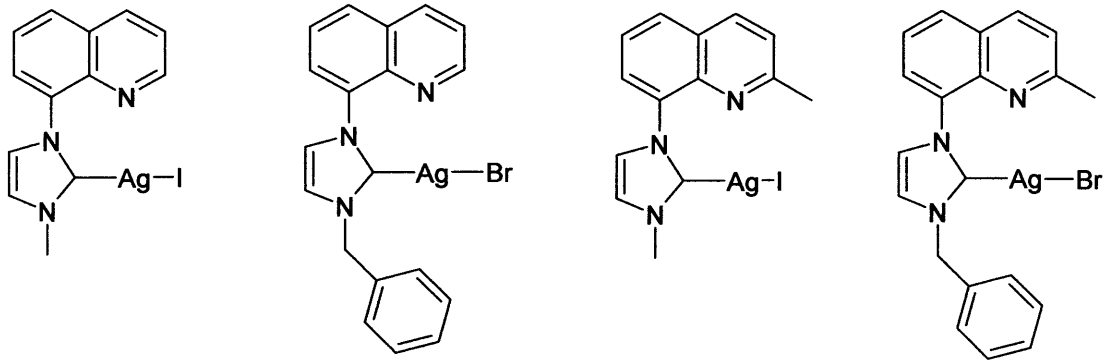
3.2.1 Ag(I) Complexes Of Quinoline Functionalised Carbenes.

All of the quinoline functionalised imidazolium salts described in Chapter two were successfully reacted with Ag_2O to form the corresponding Ag(I) complexes. In a typical reaction, two equivalents of the salt was taken up in DCM and stirred with one equivalent of Ag_2O for several hours at ~40°C, until the black suspension of Ag_2O was replaced with the beige/grey coloured silver halide precipitate. Molecular sieves were added to the reaction mixture as water is formed as a by product. The addition of molecular sieves has also been shown to facilitate the formation of the Ag carbene complex[4]. As silver complexes are light sensitive with respect to decomposition, the reaction mixture was also protected from light. After the reaction was complete the

solutions were filtered to remove the silver halide, the solvents removed under reduced pressure, and the beige Ag product washed with Et_2O. The residues were recrystallised from DCM and hexane and characterised by ^1H and ^{13}C NMR. ^1H NMR data clearly shows an absence of the characteristic C2 proton peak with no residual signal remaining, which is a good indication that the reaction has proceeded. The ^{13}C NMR also shows the C-Ag peak within the 180ppm region. All of the complexes showed good stability to air and moisture, though decomposition occurred in solution over a period of time when exposed to light, again a good indication of Ag content. Crystals suitable for X-ray diffraction were attempted by using a layering method of DCM and hexane, though no suitable crystals could be grown.

Using the data collected thus far it is not possible to give the exact structure of the silver complexes of these ligands. For illustrative purposes only, the structures of the quinoline based Ag complexes are represented in a similar manner to the octahydroacridine based complex which was crystalographically analysed, i.e one of a mono NHC Ag complex with a coordinated anion.

The following complexes (**3.10-3.13**) were therefore synthesised and characterized by ^1H and ^{13}C NMR (Figure 3.6).

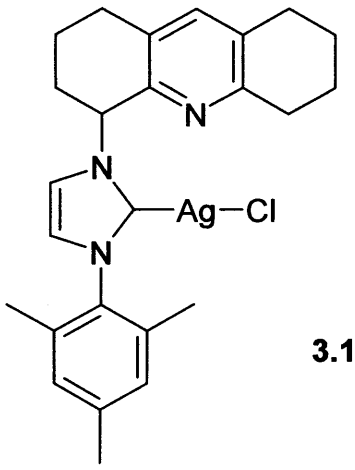


3.10 **3.11** **3.12** **3.13**

Figure 3.6: Ag complexes of the quinoline functionalised NHCs.

3.2.2 Ag(I) Complex Of Octahydroacridine Functionalised Imidazolium Salt

The Ag_2O route was successfully applied to the octahydroacridine functionalised imidazolium salt to give the Ag(I) complex. Again the reaction was carried out in a similar manner to the quinoline functionalised salts, though a higher temperature was used (~45°C) overnight. The tan coloured Ag complex proved to have similar stabilities to the quinoline functionalised ones, with slow decomposition in solution. ^{1}H NMR revealed an absence of the imidazolium C2-H proton at 10.15ppm, with no residual signal remaining, thus concluding that complex **3.14** (Figure 3.7) was successfully synthesised. Crystals suitable for X-ray diffraction were grown by adding hexane onto a DCM solution of the complex (protected from light). The structure and numbering scheme of **3.14** is given in Figure 3.8. Selected bond lengths and angles are given in Table 3.1.



3.14

Figure 3.7: Ag complex of the octahydroacridine functionalised NHC.

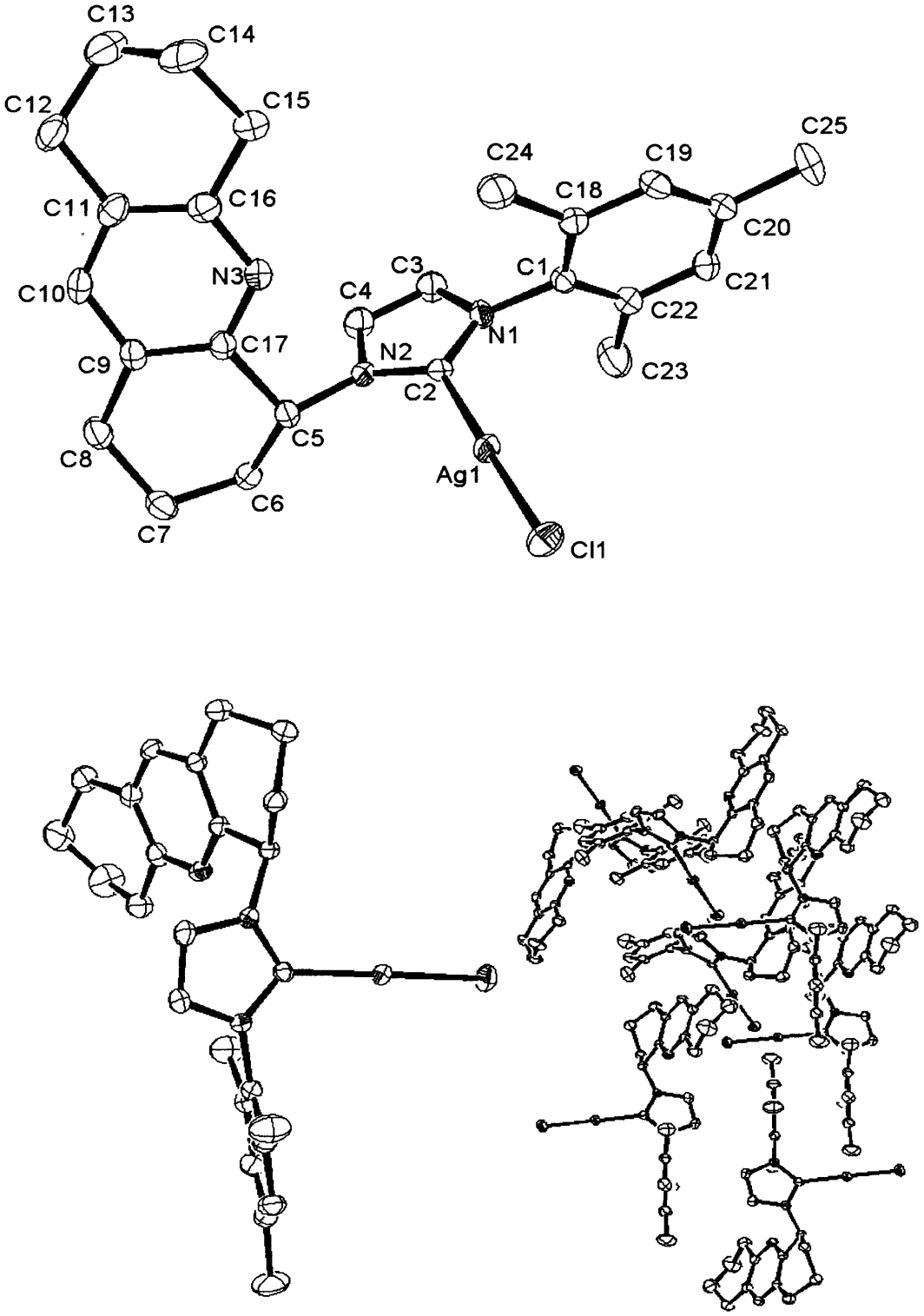


Figure 3.8: ORTEP representations of **3.14** (50% probability of thermal ellipsoids). Hydrogen atoms omitted for clarity.

C1	N1	1.446(4)	C4	N2	1.382(4)	N2	C2	N1	104.0(2)
C2	N2	1.344(4)	C5	N2	1.471(4)	N2	C2	Ag1	126.3(2)
C2	N1	1.355(4)	C5	C17	1.526(4)	N1	C2	Ag1	129.3(2)
C2	Ag1	2.084(3)	C17	N3	1.345(4)	C2	N1	C1	124.8(3)
C3	C4	1.343(5)	Ag1	Cl1	2.3395(8)	C2	N2	C5	123.8(2)
C3	N1	1.384(4)				C2	Ag1	Cl1	177.21(8)

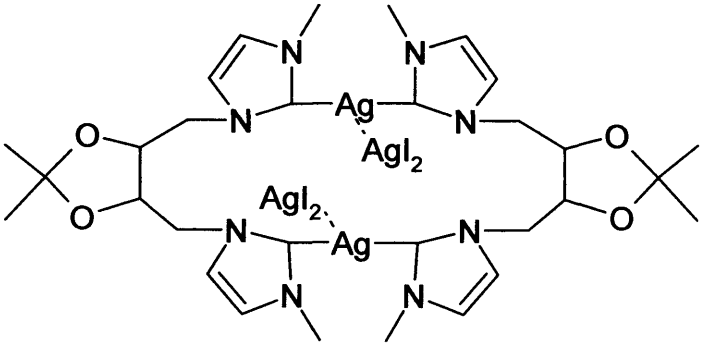
Table 3.1: Selected bond lengths (Å) and angles (°) for **3.14**.

Complex **3.14** is shown to be a monomer with a silver atom coordinated by a carbene carbon and a chloride in a quasi-linear geometry. The C2-Ag-Cl bond angle of 177.21(8)° is comparable to **3.9** (176.1(2)°). The Ag-C2 bond length (2.084(3)Å) is also similar to that of **3.9** (2.075(7)). Like the parent imidazolium salt, the plane of the NHC ring adopts a position perpendicular to the planes of the octahydroacridine and mesityl moieties thereby minimising steric interactions. The dihedral angle between the plane of the NHC and the octahydroacridine is approximately 107.1°, this is in contrast to the angle of 31.5(3)° formed by the imidazole against the pyridine of **3.9** and reflects the greater steric demands of the octahydroacridine. The N1-C2-N2 bond length and angles are all within the range of other NHC Ag complexes[2,3,4].

3.2.3 Ag(I) Complex of the Bis-imidazolium Salt DIOP Analogue (2.27)

Initial attempts to synthesis the Ag complex of the bis-carbene were unsuccessful and the unreacted salt was recovered. Exchanging the hexafluorophosphate counter ion for iodide by the addition of two equivalents of KI to the reaction mixture however, promoted the reaction to proceed. One equivalent of the salt was reacted with one equivalent of Ag_2O in acetonitrile at 40°C overnight and the resulting beige precipitate was filtered off and the solvent removed under reduced pressure to leave an off white solid. The product was then washed with Et_2O and recrystallised from acetonitrile. The complex was characterized by ^1H and ^{13}C NMR and crystals were grown by cooling an acetonitrile solution of the complex though a crystal structure

was not obtained. The main evidence for Ag carbene formation is the absence of the characteristic imidazolium C2 proton and the appearance of a peak at 179.2ppm in the ^{13}C spectra corresponding to C-Ag. The ^{1}H NMRs for the imidazolium salt and corresponding Ag complex are given in Figure 3.10. The complex showed slow decomposition in solution when exposed to light, again further evidence of Ag content. For illustrative purposes and in the absence of a crystal structure, the complex is shown to be a dinuclear Ag bridging complex such as **3.15** (Figure 3.9). This is based around other examples[9,14-17] where linkers connecting the NHC functions are sufficiently long and flexible to allow for this arrangement.



3.15

Figure 3.9: Proposed dinuclear Ag bridging NHC structure.

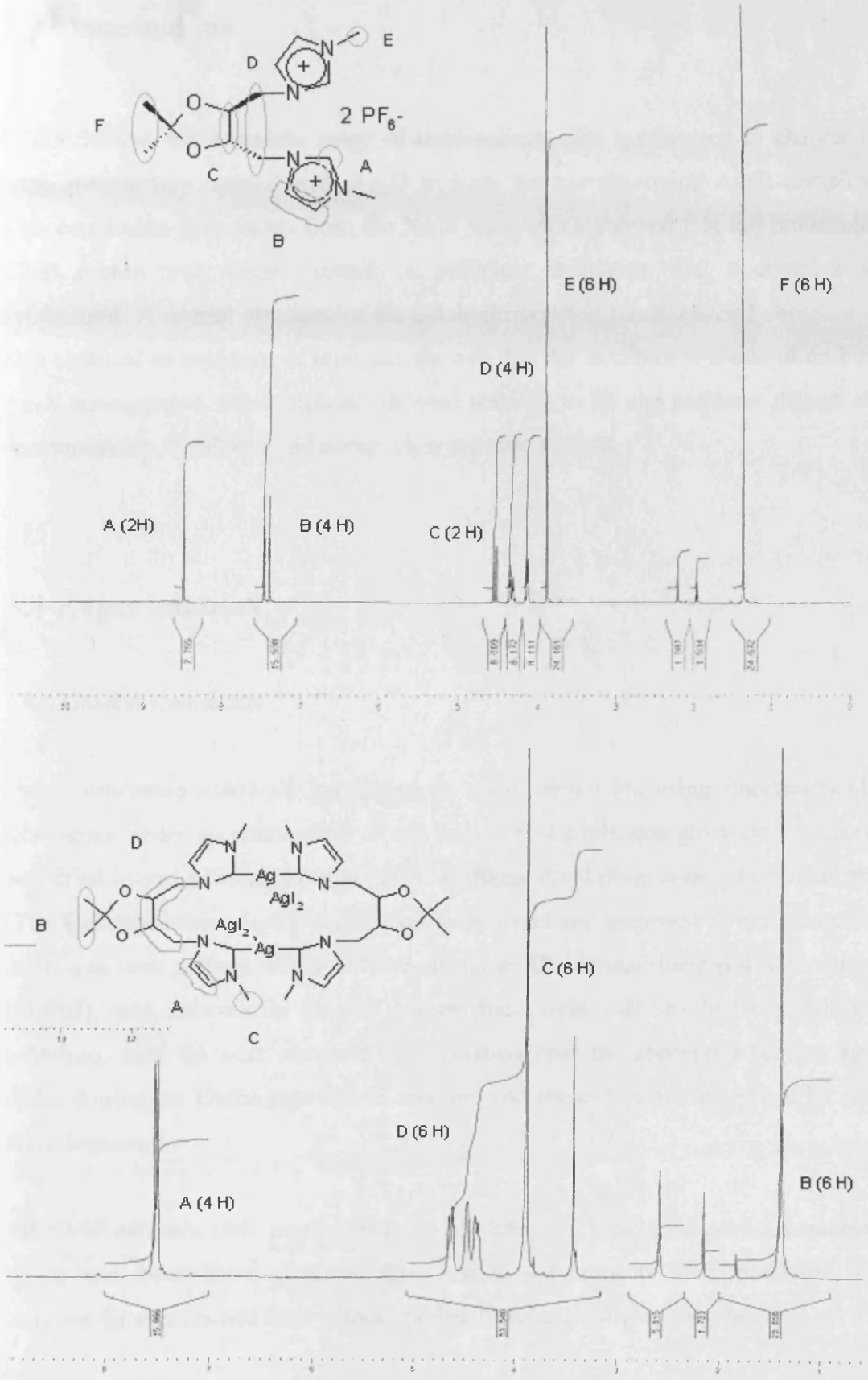


Figure 3.10: ^{1}H NMR spectra for the DIOP analogue imidazolium salt and its Ag(I) complex.

3.3 Conclusions

In conclusion, the complete range of imidazolium salts synthesised in chapter two were successfully reacted with Ag_2O to form the corresponding Ag(I) complexes. This conclusion was drawn from the NMR data which showed that the imidazolium C2-H proton was absent, usually a sufficient indication that a complex was synthesised. A crystal structure of the octahydroacridine functionalised complex was also obtained as evidence of this, and showed that the structure was one of an NHC-Ag-X arrangement. All complexes showed stability to air and moisture though slow decomposition in solution did occur when exposed to light.

3.4 Experimental

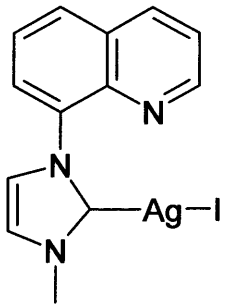
3.4.1 General Comments

Unless otherwise stated all manipulations were carried out using standard Schlenk techniques, under an atmosphere of dry argon or in a nitrogen glove box. Glassware was 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 degassed by refluxing under dinitrogen over sodium wire and benzophenone. Dichloromethane (DCM), methanol (MeOH), and acetonitrile (MeCN) were dried over calcium hydride. All other anhydrous solvents were obtained by distillation from the appropriate drying agents 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.

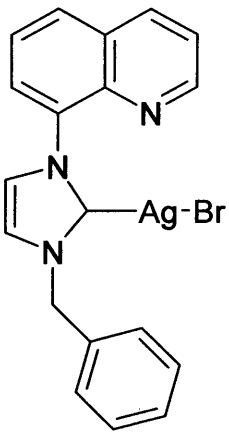
All NMR data are quoted in δ/ppm. ^{1}H and ^{13}C spectra were recorded on a Bruker 400 MHz DPX Avance, unless otherwise stated, and referenced to $SiMe_4$. Elemental analysis was carried out by Warwick Analytical Service Ltd, Coventry (UK).

Synthesis of [Ag(1-methyl-3-quinoline-imidazolin-2-ylidene).I] (3.10):



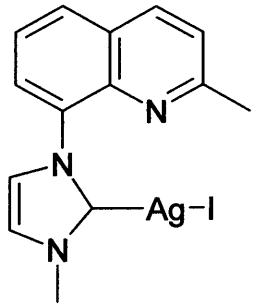
Ag_2O (0.152g, 0.66mmol) was added to a mixture of 1-methyl-3-quinoline-imidazolium iodide (0.444g 1.31mmol) and 4Å molecular sieves in 10ml DCM to give a black suspension. The mixture was protected from light and stirred overnight at 40°C. The resulting AgI was removed by filtration through celite and the solvent removed under reduced pressure to leave a tan coloured solid which was washed with Et_2O (2x10ml). The solid was then recrystallised from DCM/Hexane to give the desired Ag complex **3.10** (0.26g, 63%). **^{1}H NMR** (d_2-DCM, 250MHz, δ) 8.80 (m, 2H, Quin H2), 8.20 (m, 2H, Quin H4), 7.95 (m, 2H, Quin H6), 7.80 (m, 2H, Quin H8), 7.4-7.5 (m, 4H, QuinH3,7), 7.35 (m, 2H, HCCH), 7.15 (m, 2H, HCCH), 3.85 (s, 6H, NCH_3) **^{13}C NMR** (d_2-DCM, 100MHz, δ): 182.0 (*C*-Ag) , 163.2, 151.3, 147.6, 145.2, 139.4, 138.5, 138.1, 136.9, 134.7, 133.2, 131.8, 44.0 (CH_3).

Synthesis of [Ag(1-benzyl-3-quinoline-imidazolin-2-ylidene)Br] (3.11):



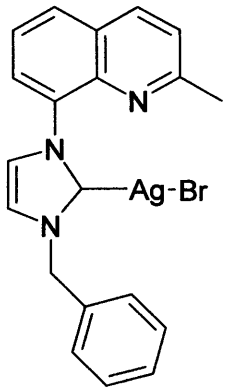
To a mixture of 1-benzyl-3-quinolinimidazolium bromide (2.69g, 0.787mmol) and 4Å molecular sieves in 10ml DCM, Ag_2O (0.091g, 0.394mmol) was added to give a black suspension which was protected from light and stirred overnight at 40°C. The resulting beige precipitate was removed by filtration through celite and the solvent removed under reduced pressure to leave a brown coloured solid. The solid was washed with Et_2O (3x10ml) and recrystallised from DCM/Hexane to give the desired Ag complex (**3.11**). (0.132g, 47%). **^{1}H NMR** ($CDCl_3$, 250MHz, δ): 8.85 (m, 2 H, Quin H2), 8.25 (m, 2H, Ar H), 7.90 (m, 4H, ArH), 7.55 (m, 2H, ArH), 7.45 (m, 4H, HCCH), 7.25-7.35 (m, 10H, ArH), 7.10 (2H, m, ArH), 5.35 (s, 4H, CH_2-Ph). **^{13}C NMR** (d_2-DCM, 100MHz, δ): 183 (NCAg) 151.7, 142.9, 137.1, 136.9, 136.3, 130.0, 129.8, 129.7, 129.5, 129.2, 128.8, 128.4, 126.5, 125.9, 122.8, 120.9, 56.1(CH_2)

Synthesis of [Ag(1-methyl-3-(2-methyl-quinoline)-imidazolin-2-ylidene)I] (3.12):



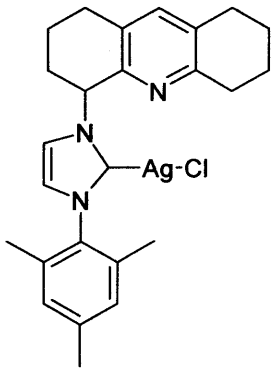
1-methyl-3-(2-methyl-quinoline)-imidazolium iodide (0.3g, 0.85mmol) was dissolved in 10ml DCM with 4Å molecular sieves. Ag_2O (0.1g, 0.43mmol) was added to the mixture to give a black suspension that was protected from light and stirred at 40°C overnight. The resulting beige precipitate was removed by filtration and the solvent removed under reduced pressure to leave a brown coloured solid. The solid was washed with Et_2O (2x10ml) and recrystallised from DCM/Hexane to give the desired Ag complex (**3.12**) (0.12, 43%). **^{1}H NMR**($CDCl_3$, 500MHz, δ): 8.10 (m, 2H, Quin H), 7.65-7.85 (m, 4H, Quin H), 7.35-7.45 (m, 4H, Quin H), 7.15-7.25 (m, 4H, HCCH), 3.75 (s, 3H, NCH_3), 2.55 (s, 3H, Quin CH_3). **^{13}C NMR** ($CDCl_3$, 100MHz, δ): 184.0 (NCN), 161.0, 142.0, 137.5, 137.0, 129.0, 128.0, 127.0, 125.0, 124.8, 123.5, 122.0, 39.5 (NCH3), 25.5 (Quin CH_3).

Synthesis of [Ag(1-benzyl-3-(2-methyl-quinoline)-imidazolin-2-ylidene)Br] (3.13):



Ag_2O (0.095g, 0.41mmol) was suspended in a solution of 1-benzyl-3-(2-methyl-quinoline)-imidazolium bromide (0.350g, 0.82mmol) in 10ml DCM with 4Å molecular sieves. The black suspension was protected from light and stirred overnight at 40°C. The resulting precipitate was removed by filtration and the solvent removed under reduced pressure to leave a brown coloured solid. The solid was washed with Et_2O and recrystalised from DCM/Hexane to give the desired Ag complex **3.13**. (0.19g, 56%). **^{1}H NMR** ($CDCl_3$, 250MHz, δ): 8.10(m, 2H, ArH), 7.85 (m, 4H, ArH), 7.55 (m, 4H, ArH), 7.45 (m, 2H, ArH), 7.35 (m, 10H, ArH), 7.10(m, 2H, ArH), 5.4 (4H, CH_2-Ph), 2.65 (s, 6H, Quin CH_3). **^{13}C NMR** (DCM, 100MHz, δ): 178.5 (NCN), 159.7, 141.2, 137.1, 135.6, 135.2, 135.1, 128.3, 128.2, 127.8, 127.2, 127.1, 126.7, 125.8, 124.8, 124.2, 122.4, 119.3, 55.0 (CH_2-Ph), 24.7 (Quin CH_3).

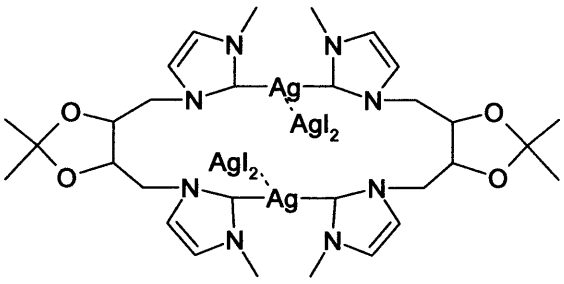
Synthesis of [Ag(1-mesityl-3-octahydroacridinimidazolin)Cl] (3.14):



Ag_2O (0.255g, 0.97mmol) was suspended in a solution of a 1-mesityl-3-octahydroacridinimidazolium chloride (0.79g, 1.94mmol) and 4Å molecular sieves in 10ml DCM. The reaction mixture was protected from the light and stirred at 45°C overnight. The resulting AgCl was filtered off and the solvent removed under reduced pressure to leave a yellow-brown powder. This was repeatedly washed with Et_2O (3x10ml) and recrystallized from DCM/Hexane to give the silver complex (**3.14**).

(3.8g, 44%). Crystals suitable for X-ray diffraction were grown by layering DCM and Hexane. **^{1}H NMR** ($CDCl_3$, 400MHz, δ) 7.1 (m, 1H, ArH), 6.9 (m, 3H, ArH), 6.85 (m, 1H, ArH), 1.5-2.95 (m, 24H, CH_2, CH_3). **^{13}C NMR** ($CDCl_3$, 100MHz, δ):185.9(NCN), 148.9, 139.2, 137.9, 135.9, 135.0, 134.7, 132.4, 130.3, 129.3, 121.6, 120.7, 61.8, 40.2, 32.6, 32.1, 28.5, 27.9, 23.1, 22.6, 21.1, 19.9, 17.7.

Synthesis of chiral DIOP analogue Ag complex (3.15):



4,5-Bis(methylimidazolium hexaflurophosphate)-2,2-dimethyl-1,3-dioxolan (0.246g, 0.42mmol) was dissolved in CH_3CN with 4Å molecular sieves. Ag_2O (0.097g, 0.42mmol) and KI (0.069g, 0.42mmol) was added to the mixture giving a black suspension which was protected from light and stirred at 40°C overnight. The solution was then filtered through celite to remove precipitated AgX and the solvent removed under reduced pressure to give a solid. This was washed with Et_2O to give **3.15** as an off white solid. (0.21g, 39%). **^{1}H NMR**(d_6-DMSO, 400MHz, δ): 7.5 (m, 8H, HCCH), 4.6 (m, 4H, OCH), 4.45 (m, 4H, CH_2), 4.35 (m, 4H, CH_2), 3.85 (s, 12H, NCH_3), 1.35 (s, 12H, CCH_3). **^{13}C NMR** (d_6-DMSO 100MHz, δ): 179.2 (NCN), 122.0 (NCCN), 121.6 (NCCN), 109.5 (OCC_2H_6), 76.8 (OCH), 51.8 (CH_2), 37.1 (NCH_3) 26.10 (CH_3). Elemental Anal. Calc. $C_{30}H_{44}N_4O_4Ag_2I_2$ (1280.9): C 28.1, H 3.4, N 8.7. Found: C 29.2, H 3.6, N 8.3.

3.5 References

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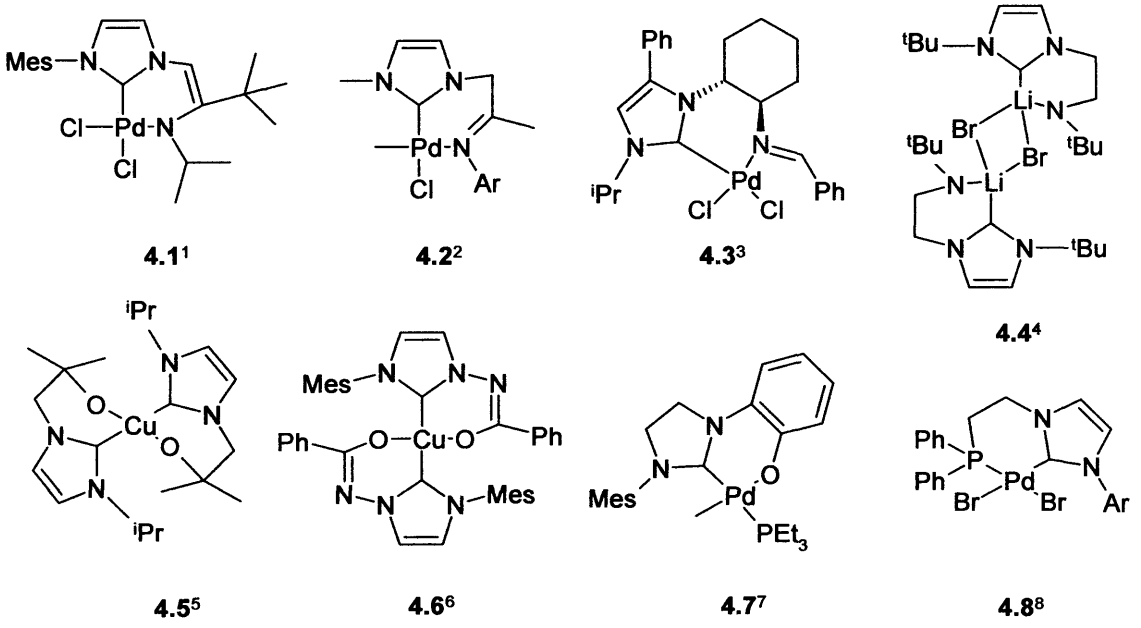
Chapter Four

Palladium Carbene Complexes

4.1 Introduction- NHC metal complexes.

A multitude of mixed donor NHC metal complexes have been synthesised by various groups, tethering a range of secondary donors to the NHC including amines, alkoxides and phosphines amongst others. These have all been synthesised with similar aims to those of this work, such as the ability to vary the steric bulk, chelate rigidity and electronic asymmetry. A number of examples of these mixed donor complexes are given in Figure 4.1.

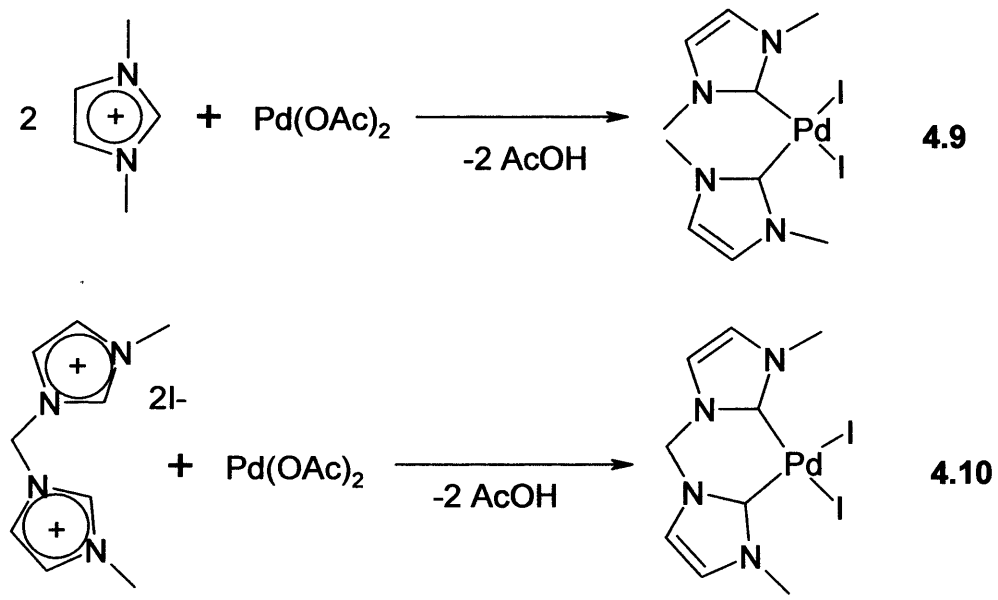


4.1[1] 4.2[2] 4.3[3] 4.4[4]

4.5[5] 4.6[6] 4.7[7] 4.8[8]

Figure 4.1: Examples of functionalised NHC metal complexes.

The first Pd(II) carbene complexs were reported by Herrmann in 1995[9] by the reaction of $Pd(OAc)_2$ with 1,3-dimethylimidazolium iodide to give **4.9** and 3,3-dimethyl-1,1-methylenediimidazloium diiodide to give **4.10** (Scheme 4.1). Herrmann showed that these new Pd complexes were 'extraordinarily stable to heat, oxygen and moisture'.

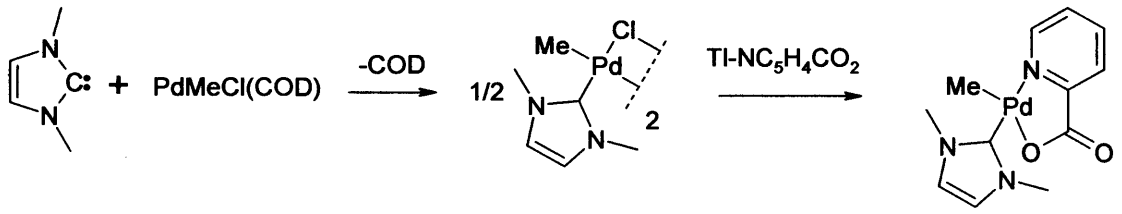


Scheme 4.1: Herrmann's synthesis of **4.9** and **4.10**

Further to this, Herrmann also demonstrated these Pd carbene complexes to be excellent catalysts in the Heck reaction, and in turn offered a viable alternative to the ubiquitous phosphines.

Depending on the nature of the ligand precursor there are a number of routes to synthesise Pd(NHC) complexes and these have been outlined in Chapter one along with other metals. The classical route is by reaction of an imidazolium salt with $Pd(OAc)_2$ (Scheme 4.1). For many simple mono and bis imidazolium salts this procedure is usually satisfactory and produces the Pd complex in moderate to high yields. However it suffers draw backs in that this route doesn't allow access to the catalytically interesting Pd-hydrocarbyl species and the solvent of choice is usually DMSO which can prove to be problematic. The high temperatures often associated with this route can also be disadvantageous in some systems where thermal stability is an issue. Another common route is via the free carbene which can be generated from imidazolium salts via a number of different bases including NaH with catalytic amounts of KO^tBu and amides such as $K[N(SiMe_3)_2]$. It can also be prepared from imidazole-2-thiones via abstraction of the sulphur atom with potassium. Once formed, the free carbene can be directly reacted with an appropriate metal source such as $PdCl_2(COD)$. Cavell demonstrated this method to be of use in the formation of the

important Pd-hydrocarbyl species. Methylating Pd carbene complexes with various alkylating agents had previously proved unsuccessful and so it was shown that reaction of 1,3-dimethylimidazolin-2-ylidene with PdMeCl(COD) led to the formation of a methylpalladium carbene chloro-bridged dimer (**4.11**)[10] (Scheme 4.2). This was found to be a valuable precursor for the preparation of a range of other methylpalladium complexes, both neutral and cationic. Cavell for example, reacted **4.11** with thallium 2-pyridinecarboxylate to give **4.12** in 100% yield[10].



4.11 **4.12**

Scheme 4.2: Cavell's route to Methylpalladium(II) complexes.

Where NHCs do not posses sufficiently bulky aryl or alkyl groups on the 1 and 3 positions of the ring, the free carbene route may be unsuitable as these provide stability to the free carbene and thereby aid complexation. It has also been found that the use of strong bases may cause problems if functionalised carbenes are used, due to acidic protons commonly associated with the functional group and any CH_2 linkers. Oxidative addition of low valent metal precursors to a carbon-hydrogen bond has also been shown[11,12] and has successfully been applied with $Pd_2(dba)_3$ and imidazolium salts[13].

As mentioned in Chapter three, the Ag_2O route was seen as the most appropriate route for functionalised carbene hydrocarbyl-Pd complex formation and was applied to the salts synthesised in this work. Alternative routes were attempted and will be discussed later.

4.2 Results and Discussion

4.2.1 Quinoline Functionalised Carbene Complexes Of Pd

In a typical reaction, the quinoline functionalised Ag(I)(NHC) was reacted with one equivalent of PdMeCl(COD) in DCM for several hours, the PdMeCl(COD) being synthesised by standard procedures. The Pd complexes were characterised by ^{1}H and ^{13}C NMR. The characteristic peak in the ^{1}H NMR is the appearance of a singlet at ~0.55-0.75ppm corresponding to the Pd-Methyl protons. The appearance of the imidazolium C2 protons was not observed. The following Pd(II)NHC complexes based around a quinoline system were synthesised (**4.13-4.16**, Figure 4.2). Crystals suitable for X ray diffraction were grown for complex **4.13** by layering hexanes on to a DCM solution of the complex. The structure and labelling scheme of complex **4.13** is given in Figure 4.3 with selected bond lengths and angles in Table 4.1. All of the complexes synthesised showed good stability to air and moisture.

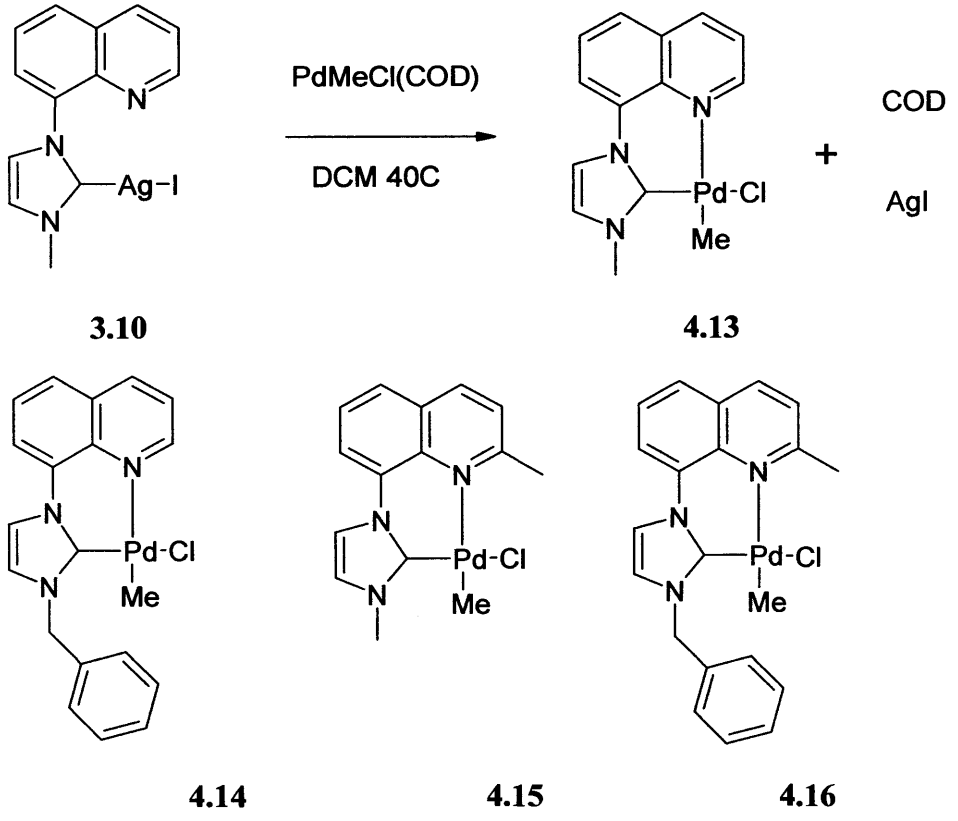


Figure 4.2: Palladium complexes of the quinoline functionalised carbene's

Complex **4.13** exhibits a square planar geometry that is slightly distorted where the chelating ligand occupies the two cis positions. The six membered ring formed by the chelate is slightly twisted with a dihedral angle between the plane of the quinoline and

the plane of the imidazolium ring of approximately 35.5°. This is consistent with the observation made in Chapter two from the crystal structure of imidazolium salt **2.8**. Similar six membered chelates such as Danopoulos's (**4.17**, Figure 4.4)[14] have been shown to form a puckered confirmation in order to minimise conformational strain, which is achievable due to the sp_3 hybridized CH_2 linker. The rigidity of **4.13** imposed by the aromatic ring system minimises deviations from overall ligand planarity and is therefore more comparable to five membered chelates such as **4.18**[14] where the chelate is relatively planar. The inclusion of the methyl group in the C12 position of complexes **4.15** and **4.16** should cause the chelate to be more strained. The carbene moiety of **4.13** is trans to the chloride which is consistent with other examples. The bond lengths around the metal centre are not unusual for this type of complex[14,16]. The ligand forms a bite angle of 86.9(2)°, slightly larger than that of the six membered chelate (**4.17**, 85.22(13)Å) and the five membered chelate (**4.18**, 79.15(3)Å)

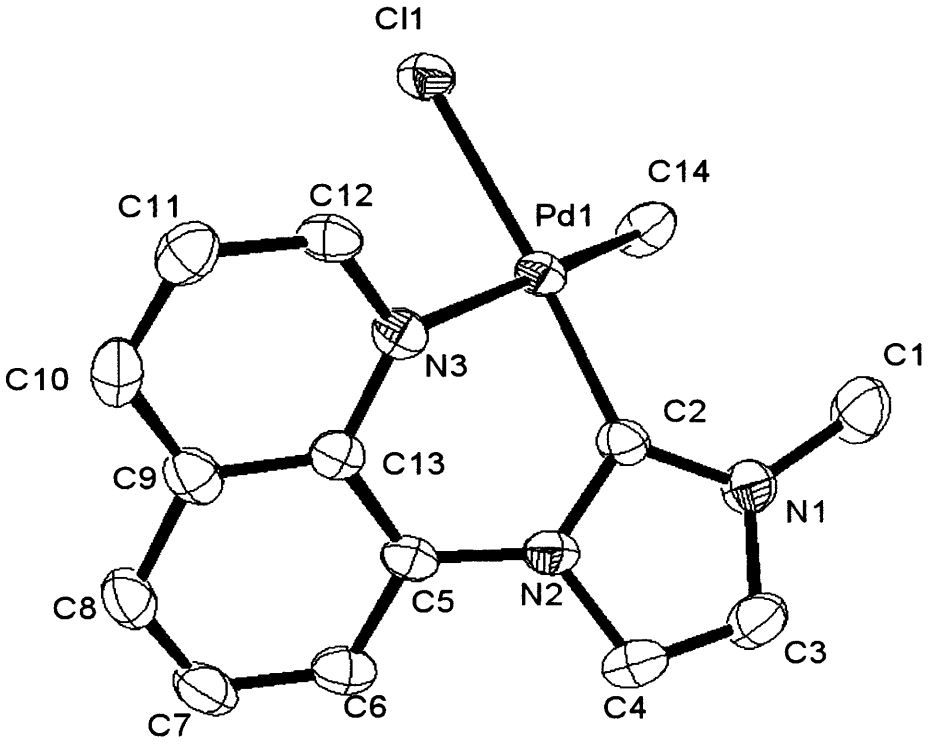


Figure 4.3: ORTEP representation of the quinoline functionalised carbene complex **4.13**, (50% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity.

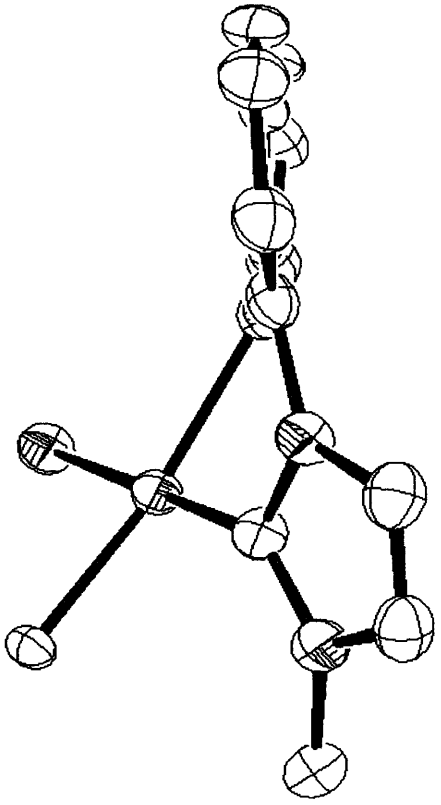
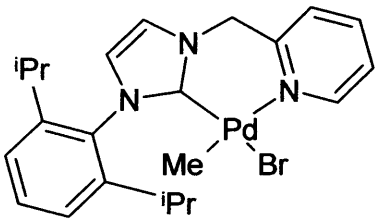


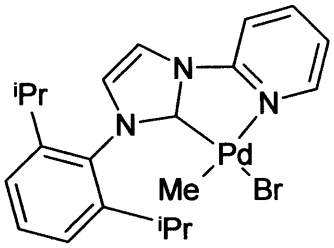
Figure 4.3 *cont.*: ORTEP representation of the quinoline functionalised carbene complex **4.13**, (50% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity.

C2	N1	1.366(8)	C13	C5	1.410(8)	C2	N1	C1	125.9(5)
C2	N2	1.380(7)	C13	N3	1.376(7)	C2	N2	C5	125.8(5)
C4	C3	1.321(9)	Pd1	C2	1.943(6)	C2	Pd1	Cl1	176.15(17)
C4	N2	1.412(8)	Pd1	N3	2.169(5)	C14	Pd1	N3	173.7(2)
C3	N1	1.392(8)	Pd1	C14	2.050(6)	C2	Pd1	C14	93.7(2)
C1	N1	1.443(8)	Pd1	Cl1	2.3763(14)	C2	Pd1	N3	86.9(2)
C5	N2	1.427(8)	N1	C2	N2	103.5(5)	C14	Pd1	Cl1	88.88(17)
						N3	Pd1	Cl1	90.28(13)

Table 4.1: Selected bond lengths (Å) and angles (°) for complex **4.13**



4.17

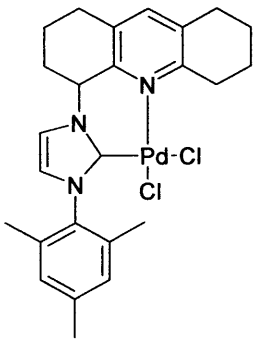


4.18

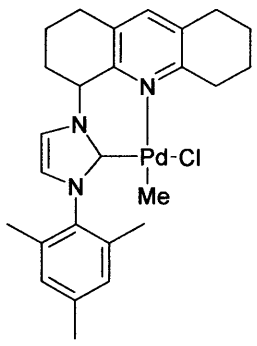
Figure 4.4: Danopoulos's five and six membered chelating ligands[14].

4.2.2 Pd Complexes Of An Octahydroacridine Functionalised Carbene.

The Ag_2O route was again used for synthesising the Pd complexes of the octahydroacridine functionalised carbene. In a similar manner to the quinoline functionalised complexes, the Ag(I) complex of the octahydroacridine carbene was reacted with one equivalent of either PdMeCl(COD) or $PdCl_2$(COD) in DCM and stirred for several hours at room temperature. The solution was filtered to remove the precipitated AgCl and the solvent removed under reduced pressure. The yellow solids were washed with Et_2O to remove any residual COD and were recrystallised from DCM and Hexane. Both the dichloro (**4.19**) and methyl chloro (**4.20**) Pd complexes were synthesised (Figure 4.5) and characterized by ^1H and ^{13}C NMR. Crystals suitable for X-ray diffraction were grown by layering hexane onto a DCM solution of both complexes. Both complexes showed good stability to air and moisture, the crystals of **4.20** being exposed to air for several months with little decomposition. The crystal structures and numbering schemes for complexes **4.19** and **4.20** are given in Figure 4.6 and 4.7, with selected bond lengths in tables 4.2 and 4.3 respectively.



4.19



4.20

Figure 4.5: Pd complexes of the octahydroacridine functionalised NHC

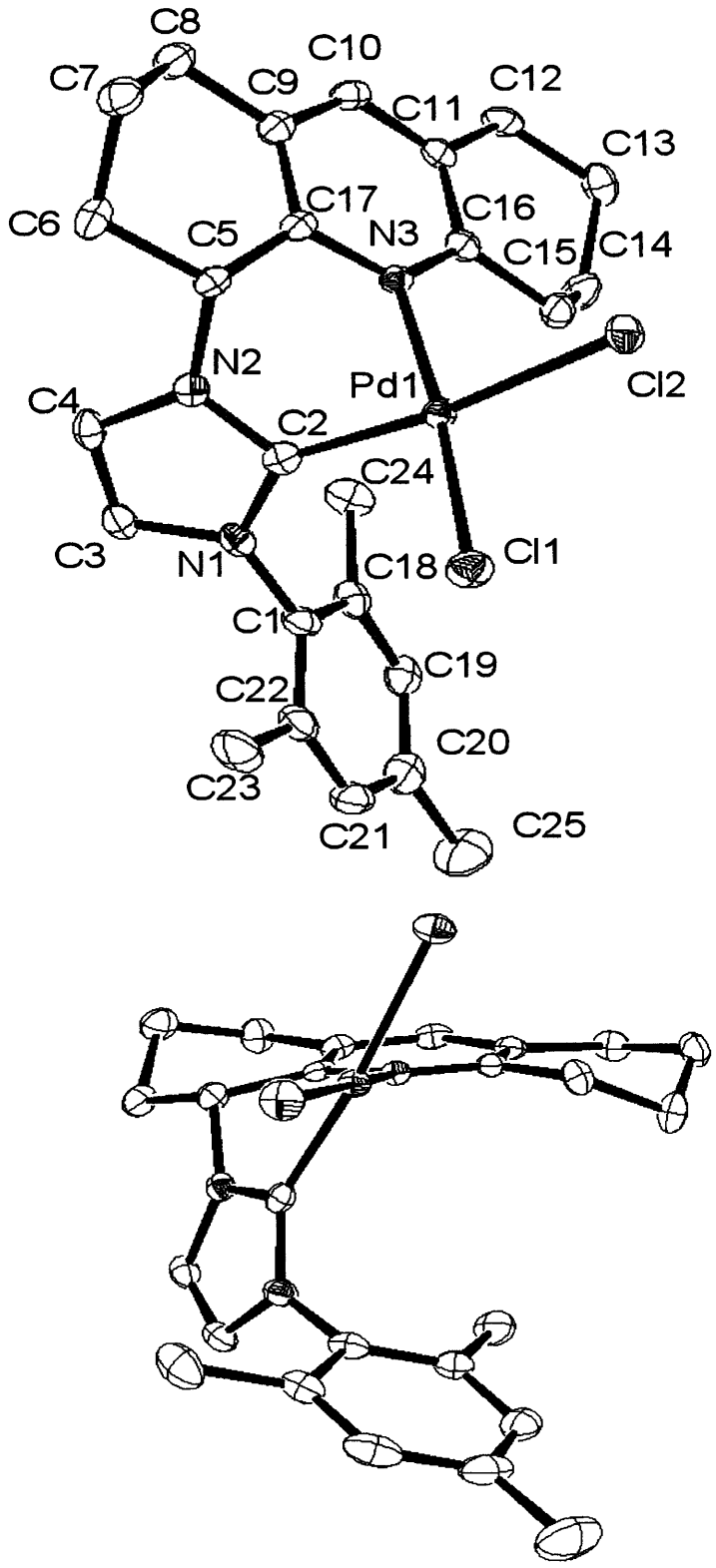


Figure 4.6: ORTEP representations of complex **4.19** (50% probability of thermal ellipsoids). Hydrogen atoms are omitted for clarity.

C2	N1	1.352(4)	C17	N3	1.357(5)		C2	Pd1	Cl2	172.17(11)
C2	N2	1.347(5)	C2	Pd1	1.949(4)		N3	Pd1	Cl1	173.63(9)
C3	N1	1.395(5)	N3	Pd1	2.060(3)		C2	Pd1	N3	83.40(13)
C4	N2	1.400(4)	Cl1	Pd1	2.3036(9)		C2	Pd1	Cl1	92.10(11)
C3	C4	1.334(5)	Cl2	Pd1	2.3748(9)		N3	Pd1	Cl2	91.68(8)
C1	N1	1.445(5)	N2	C2	N1	106.3(3)	Cl1	Pd1	Cl2	92.30(3)
C5	N2	1.488(5)	C2	N1	C1	127.3(3)				
C5	C17	1.524(5)	C2	N2	C5	120.4(3)				

Table 4.2: Selected bond lengths (Å) and angles (°) for complex **4.19**.

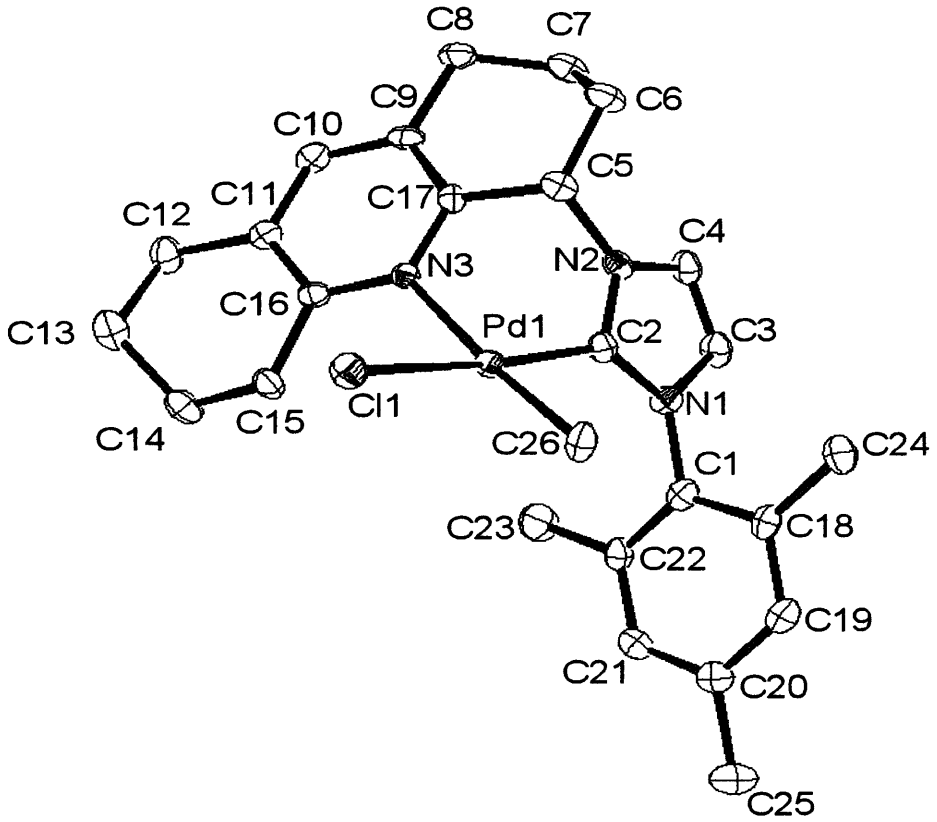


Figure 4.7: ORTEP representation of complex **4.20** (50% probability of thermal ellipsoids). Hydrogen atoms omitted for clarity.

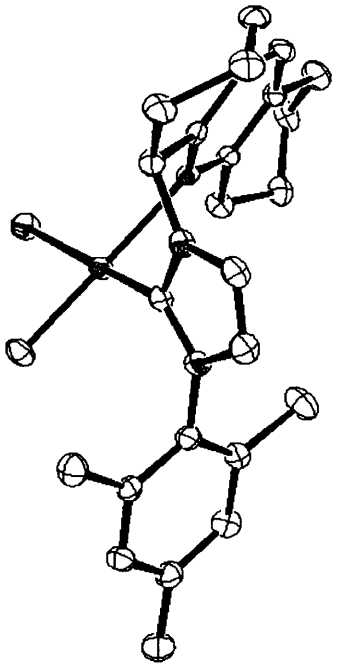


Figure 4.7 *cont.*: ORTEP representation of complex **4.20** (50% probability of thermal ellipsoids). Hydrogen atoms omitted for clarity.

C2	- N1	1.354(4)	C17 - N3	1.355(4)	C2	- Pd1 - Cl1	174.06(10)
C2	- N2	1.354(4)	C2 - Pd1	1.975(3)	C26	- Pd1 - N3	174.96(12)
C3	- N1	1.403(4)	N3 - Pd1	2.224(3)	C2	- Pd1 - C26	91.49(14)
C4	- N2	1.384(4)	C26 - Pd1	2.030(4)	C2	- Pd1 - N3	84.73(13)
C3	- C4	1.325(5)	Cl1 - Pd1	2.3814(8)	C26	- Pd1 - Cl1	88.46(10)
C1	- N1	1.448(5)	N2 - C2 - N1	104.80(3)	N3	- Pd1 - Cl1	94.96(7)
C5	- N2	1.496(5)	C2 - N1 - C1	126.3(3)			
C5	- C17	1.514(5)	C2 - N2 - C5	119.8(3)			

Table 4.3: Selected bond lengths (Å) and angles (°) for complex **4.20**.

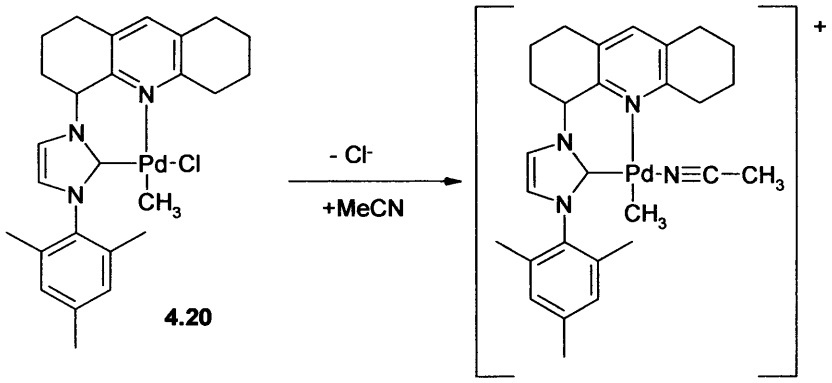
Complexes **4.19** and **4.20** both exhibit square planar geometries which are slightly distorted around the Pd Centres. The chelating ligands occupy the cis positions in both cases. The unit cell contains the R and S isomers in both cases. Figure 4.6 illustrates complex **4.19** containing the R enantiomer of the carbene ligand whilst figure 4.7 shows complex **4.20** containing the S. Both six membered chelate rings adopt a boat

configuration which is made possible by the sp^3 hybridized linker and is comparable to **4.17**. **4.19** has a bite angle of 83.40(13)° and **4.20** has an angle of 84.73(13)°. Both are smaller than the quinoline functionalised complex (**4.13**) and Danopoulos's (**4.17**) and are an indication of how different linkers can effect bite angle. The plane of the imidazolium ring and the plane of the octahydroacridine rings form a dihedral angle of approximately 60.7° in complex **4.19** and approximately 69.1° for complex **4.20**. The larger angle for **4.20** has an effect of reducing interligand steric interactions by increasing the distance between the Pd-Methyl group (C26) and the methyl groups of the mesityl moiety, the closest in the solid state structure being C24 with a distance of 3.748Å. The distance between Cl1 and C23 in **4.19** is 3.646Å. The N3-Pd1 bond lengths of complexes **4.19** and **4.20** are 2.060(3)Å and 2.224(3)Å respectively the latter being longer due to the stronger trans influence of the methyl group on **4.20** compared to Cl. Again the Pd-Methyl group is cis to the NHC in complex **4.20**. In complex **4.19**, the plane of the imidazole forms an angle of approximately 89.6° with the plane of the mesityl moiety, and an angle of 49.8° with the plane of the four coordinate Pd centre. The plane of the octahydroacridine function forms an angle of 57.1° with the plane of the four coordinate Pd centre. In complex **4.20** these angles are approximately 83.3°, 53.1° and 50.7° respectively.

4.2.3 Electrospray Mass Ionisation (ESI) Spectroscopy of 4.14 & 4.20

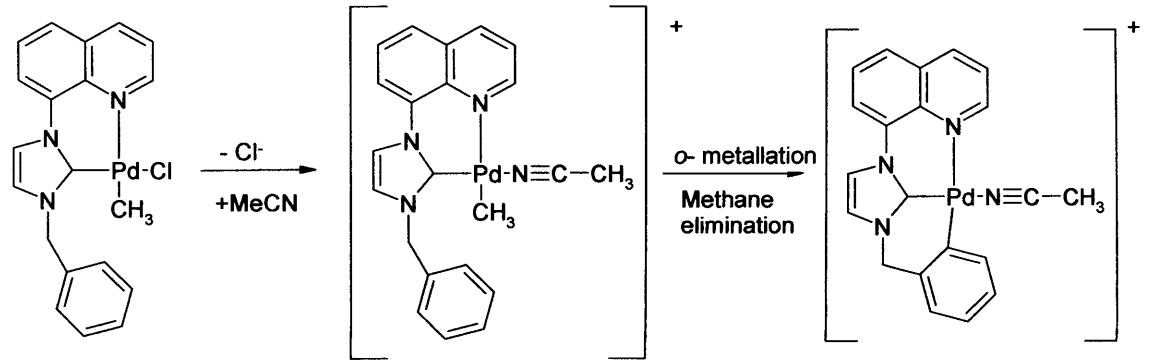
High resolution electrospray mass spectrometry was carried out on **4.14** and **4.20** in order to confirm their identity which also provided an insight into their reactivity. The mass spectroscopy of these ligands was undertaken in the presence of an acetonitrile mobile phase and in both cases chloride displacement by acetonitrile afforded cations observable in the ESI +ve mode. Two types of ion products were observed, firstly those in which acetonitrile simply displaces a coordinated chloride ligand and secondly those which involved chloride displacement and subsequent metallation of the carbene ligand framework. The later class of ion product, by necessity, requires oxidative addition and reductive elimination steps and thus provides indirect evidence for the potential for catalytic activity. The composition of the ligand precursors **2.7** and **2.14** were verified by the observation of the imidazolium parent cations and requires no further discussion.

A different pattern of reactivity is observed for the Pd (II) complexes of the quinoline and octahydroacridine based ligands. In the case of the hydrocarbyl complex **4.20** simple displacement of the chloride by acetonitrile is observed (Scheme 4.3). In common with **4.20**, the quinoline based [Pd(II)(NHC)(Me)Cl] **4.14** undergoes chloride substitution to form a cationic Pd(II) complex $[Pd(NHC)(Me)(MeCN)]^+$ which is observed as the major ion product. In contrast to **4.20**, this $[Pd(II)(NHC)(Me)(MeCN)]^+$ further reacts to form the metallated one. Although it is not possible to comment on the sequence of reactions that occur within the mass spectrometer, a suggested sequence is given (Scheme 4.3).



4.20

Calculated for $C_{28}H_{35}N_4Pd$ ($M - Cl^- + MeCN$), 533.1897; observed, 533.1782 (100 %)



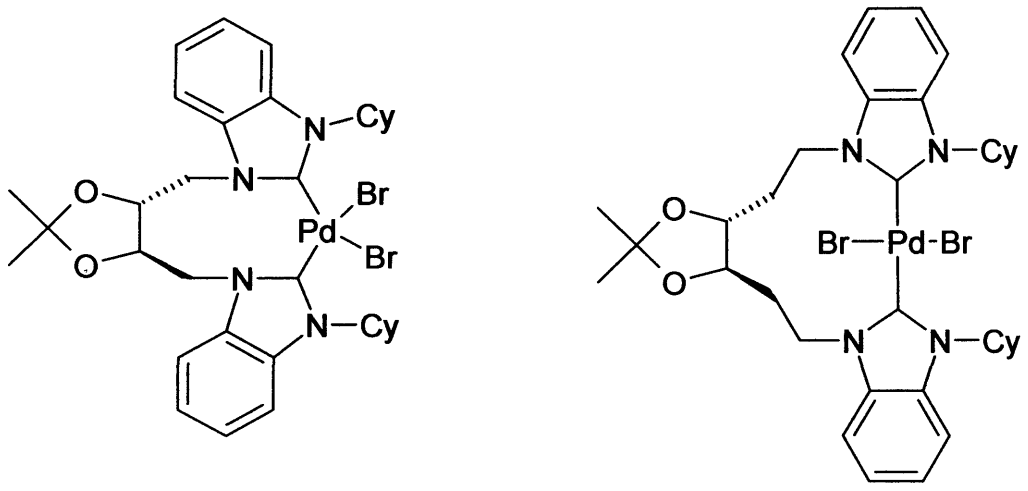
Calculated for $C_{22}H_{21}N_4Pd$ ($M - Cl^- + MeCN$), 447.0801; observed, 447.0771 (100 %). Calculated for $C_{21}H_{17}N_4Pd$, 431.0488 ($M - Cl^- + MeCN - CH_4$); observed, 431.0469 (39 %).

Scheme 4.3: Suggested reaction pathways for the Pd(II) based complexes.

4.2.4 Pd Complex Of A Carbene DIOP Analogue

In order to generate the free carbene, deprotonation of the bis-imidazolium salt (**2.23**) was attempted with a number of bases. None of the products however could be isolated and verified as the desired free carbene. Again the Ag_2O route was therefore seen as the best option for generating the Pd complex. While there were no major problems associated with generating the Ag(I) complex, transmetallation to form a stable Pd complex was not as successful. The silver complex was reacted with a solution of PdMeCl(COD) at room temperature for several hours. The resulting AgCl was removed by filtration and the solvents removed under reduced pressure to give a white solid. After a short period of time the solid began to darken with a rapid colour change towards a black/dark grey solid on washing with Et_2O. ^1H NMR gave consistently poorly resolved spectra in a number of different deuterated solvents, though the reappearance of the imidazolium C2-H was not observed. It is possible that the Pd complex forms but undergoes reductive elimination to form imidazolium salts and Pd black. Although chelating ligands have been shown to stabilise metal complexes from reductive elimination by reducing the bite angle this particular 9 membered ring chelate may be inefficient at providing a bite angle sufficient for this.

During the course of this work Harrison[17] had also synthesised an NHC DIOP analogue and had successfully formed the Pd(II) complex (**4.21**, Figure 4.8). **4.21** was formed in a 61% yield by reaction of the dibromo imidazolium salt with $Pd(OAc)_2$ in DMSO using a temperature gradient, and was found by crystal structure determination to be the cis bis-carbene. Further to this Harrison also synthesised a similar imidazolium salt with two extra CH_2 spacers, which upon coordination gave the eleven membered chelate *trans* bis-carbene (**4.22**, Figure 4.8) by the same method (also crystalographically determined). Reaction with $Pd(OAc)_2$ with our salt (2.23) was attempted using similar reaction conditions as well as the addition of KI to exchange the counter ion. ^1H NMR revealed only poorly resolved spectra of the imidazolium salt. Due to time constraints and in light of Harrison's work, the investigations into the formation of the desired Pd-hydrocarbyl species and its possible subsequent reductive elimination were abandoned.



4.21 **4.23**

Figure 4.8: Harrison's NHC DIOP analogue complexes.

4.3 Conclusions

Several Pd(II) complexes have been successfully synthesised using the Ag(I) complexes of Chapter Three as transmetallation agents, the majority of these being the catalytically interesting PdMeCl(NHC) species. All complexes showed good stability to air and moisture. All the complexes were characterized by various means including ^{1}H and ^{13}C NMR with three of the complexes being crystalographically determined.

The crystal structure of **4.13** indicates the quinoline based systems to be relatively planar chelates, with differences in the bond lengths of the Pd substituents reflecting the electronic asymmetry of the chelating ligand and the trans effect. Both of these features were targets in the ligand design. From the crystal structures of **4.19** and **4.20** the octahydroacridine system extends the ring bridging NHC-functional group system by introducing a greater extent of flexibility to the chelate as well as a chiral centre. Again electronic asymmetry is maintained for this ligand fulfilling some of the objectives of the ligand design.

The Pd complex of the chiral bis carbene was unfortunately not isolated, possibly due to a reductive elimination pathway. Performing the transmetallation procedure at

lower temperatures and maintaining these temperatures for NMR studies would be the first step in investigating any reductive elimination pathway.

4.4 Experimental

4.4.1 General Comments

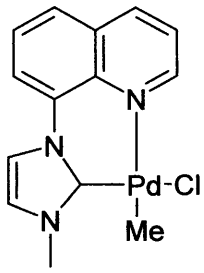
Unless otherwise stated all manipulations were carried out using standard Schlenk techniques, under an atmosphere of dry argon or in a nitrogen glove box. Glassware was dried overnight in an oven at 120°C or flame dried prior to use. Tetrahydrofuran (THF), diethyl ether (Et_2O), and hexane were dried and degassed by refluxing under dinitrogen and over sodium wire and benzophenone. Dichloromethane (DCM), methanol (MeOH), and acetonitrile (MeCN) were dried over calcium hydride. All other anhydrous solvents were obtained by distillation from the appropriate drying agents 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 in δ/ppm. ^{1}H and ^{13}C spectra were recorded on a Bruker 400 MHz DPX Avance, unless otherwise stated, and reference to $SiMe_4$. Electrospray mass spectrometry (ESMS) was performed on a VG Fisons Platform II instrument by the Department of Chemistry, Cardiff University. High accuracy electrospray mass spectra were recorded on a Waters Micromass Q-Tof Micro spectrometer and are referenced against a raffinose internal ion (lockspray) source. A Waters Acquity UHPLC with a MeCN: H_2O (90:10) mobile phrase was used as an autosampler with trace HCO_2H (0.001%) being added to the mobile phase promote positive ion formation. Elemental analysis was carried out by Warwick Analytical Service Ltd, Coventry (UK).

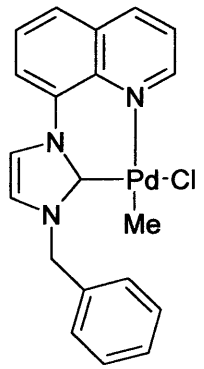
PdClMe(COD) and $PdCl_2$(COD) were prepared by standard methods in bulk[18]. $PdCl_2$ was supplied by Johnson Matthey.

Synthesis of [Pd(Me)(1-methyl-3-quinoline-imidazolin-2-ylidene)Cl] (4.13):



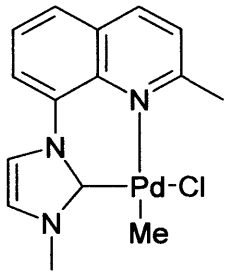
A solution of [Ag(1-methyl-3-quinoline-imidazolin-2-ylidene)I] (0.350g, 1.12mmol) and PdMeCl(COD) (0.316, 1.12mmol) was stirred together in DCM for 2 hours at room temperature. The mixture was filtered through celite to remove precipitated silver chloride and Pd black. The solvent was then reduced to ca. 10ml and hexanes added to precipitate a pale yellow powder. The solvent was removed by the use of a filterstick and the remaining solid was washed with Et_2O (3x10ml). The powder was recrystallized from DCM/Hexane to give the Pd complex (**4.13**) (0.18g, 44%). Crystals suitable for X-ray diffraction were grown by layering hexane on DCM. **^{1}H NMR** ($CDCl_3$, 400MHz, δ): 9.55 (m, 1H, Quin H2), 8.3 (m, 1H, Quin H), 7.8 (m, 2H, Quin H), 7.6 (m, 1H, Quin H), 7.50 (m, 1H, Quin H), 7.3 (m, 1H, HCCH), 7.10 (m, 1H, HCCH), 3.90 (s, 2H, NCH_3), 0.75 ($PdCH_3$) **^{13}C NMR** ($CDCl_3$, 100MHz, δ) 171.85 (NCN) 156.31, 139.0, 138.5, 135.0, 129.8, 128.8, 128.0, 126.6, 123.9, 122.3, 120.9, 38.5, -9.8. Elemental Anal. Calc. for $C_{14}H_{14}N_3ClPd$: C 45.8, H 3.8, N 11.4; found: C 44.6, H 3.8, N 10.35

Synthesis of [PD(Me)(1-benzyl-3-quinoline-imidazolin-2-ylidene)Cl] (4.14):



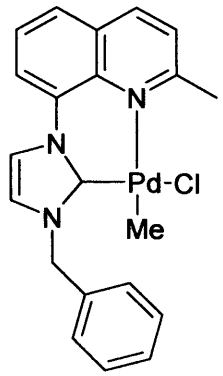
A solution of [Ag(1-benzyl-3 quinoline-imidazolin-2-ylidene)Br] (0.25g, 0.74mmol) and PdMeCl(COD) (0.195g, 0.74mmol) was stirred together in DCM for 2 hours at room temperature. The mixture was filtered through celite to remove precipitated silver chloride and any Pd black. The solvent was then reduced to ca. 10ml and hexanes added to precipitate a brown powder. This was filtered by use of a filter stick and washed with Et_2O (3x10ml). The powder was then recrystallized from DCM/Hexane to give the Pd complex (**4.14**). (0.14g, 43%). **1H NMR** ($CDCl_3$, 500MHz, δ): 9.5 (m. 1H, Quin H2), 8.25 (m, 1H, Quin H), 7.75 (m, 2H, Quin H),7.60 (m, 2H, HCCH), 7.55 (m, ^{1}H, Quin H), 7.30 (m, 5H, ArH), 6.95 (m, 1H, Quin H), 5.35 (s, 2H, CH_2-Ph), 0.75 (s, 3H, $PdCH_3$). **^{13}C NMR** (DCM, 100MHz, δ): 172.7 (NCN), 156.7, 139.4, 139.0, 136.71, 135.2, 130.1, 129.6, 129.4, 128.7, 128.5, 128.3, 127.2, 124.1, 123.1, 123.0, 122.4, 122.1, 54.9, -8.5. MS (ESI) m/z (%) Calculated for $C_{22}H_{21}N_4Pd$ (M – Cl^- + MeCN), 447.0801; observed, 447.0771 (100 %)

Synthesis of [Pd(Me)(1-methyl-3-(2-methyl-quinoline)-imidazolin-2-ylidene)Cl] (4.15):



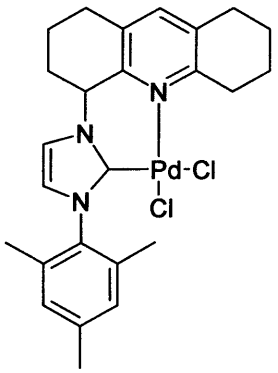
A solution of [Ag(1-methyl-3-(2-methyl-quinoline)-imidazolin-2-ylidene)I] (0.1g, 0.3mmol) and PdMeCl(COD) (0.079g, 0.3mmol) was stirred together in DCM for 2 hours at room temperature. The mixture was filtered through celite to remove the precipitated silver chloride and any Pd black. The solvent was then reduced to ca. 10ml and hexanes added to precipitate a brown powder. The solvent was removed with a filter stick and the solid washed with Et_2O (3x10ml). The solid was then recrystallized from DCM/Hexane to give the Pd complex (**4.15**). (0.12g, 86%) **^{1}H NMR** ($CDCl_3$, 500MHz, δ): 8.1 (m, 1H, Quin 4), 7.75 (m, 1H, Quin 6), 7.65 (m, 1H quin 8), 7.50 (m, 1H, Quin 7), 7.25 (m, 1H, Quin3), 7.2 (m, 1H, HCCH), 7.1 (m, 1H, HCCH), 3.85 (s, 3H, NCH_3), 3.0 (s, 3H, Quin CH_3), 0.65 (s, 3H, PdMe). **^{13}C NMR** ($CDCl_3$, 100MHz, δ): 179.0, 162.0, 144.2, 139.0, 138.8, 128.7, 128.4, 126.7, 124.6, 124.4, 123.3, 121.5, 38.6, 29.6, -9.8.

Synthesis of [Pd(Me)(1-benzyl-3-(2-methyl-quinoline)-imidazolin-2-ylidene)Cl] (4.16):



A solution of [Ag(1-benzyl-3-(2-methyl-quinoline)-imidazolin-2-ylidene)Br] (0.2g, 0.48mmol) and PdMeCl(COD) (0.127g, 0.48mmol) was stirred together in DCM for 2 hours at room temperature. The mixture was then filtered through celite to remove the precipitated silver chloride and Pd black. The solvent was reduced to ca. 10ml and hexanes added to precipitate a brown powder. The solvents were removed by a filter stick and the remaining powder washed with Et_2O (3x10ml). This was then recrystalized from DCM/Hexane to give the Pd complex (**4.16**). (0.18g, 76%). **^{1}H NMR** (DCM, 500MHz, δ): 8.15 (m, 1H, ArH), 7.75 (m, 2H, ArH), 7.55 (m, 1H, ArH), 7.45 (m, 2H, ArH), 7.35 (m, 5H, ArH), 7.0 (m, 1H, ArH), 5.25 (s, CH_2-Ph) 2.95 (s, 3H, Quin CH_3), 0.55 (s, 3H, $PdCH_3$). **^{13}C NMR** (DCM, 100MHz, δ): 177.5 (NCN), 152.5, 139.8, 137.6, 135.9, 135.7, 134.4, 128.1, 127.8, 127.6, 127.3, 127.2, 127.0, 125.1, 123.0, 122.8, 122.4, 121.1, 120.6, 53.42 (quin CH_3), -9.8 (PdMe).

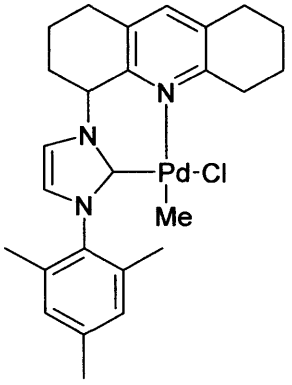
Synthesis of [Pd(1-mesityl-3-octahydroacridinimidazolin-2-ylidene)Cl_2] (4.19):



A solution of $PdCl_2$(COD) (0.123g, 0.434mmol) in 10ml DCM was added to a solution of [Ag(1-mesityl-3-octahydroacridinimidazolin)Cl] (0.4g, 0.434mmol) in

10ml DCM and stirred at room temperature for 2 hours. The solution was then filtered through celite to remove the precipitated silver chloride and the solvent removed until ca. 5ml remained. Hexane was then added, precipitating a yellow solid which was filtered with a filter stick. The solid was recrystalized from DCM/Hexane and washed with hexane to give a yellow powder of **4.19**. (1.6g, 67%). Crystals suitable for X-ray diffraction were grown by layering DCM and hexane. **^{1}H NMR** ($CDCl_3$, 400MHz, δ) 7.2 (m, 2H, ArH), 6.9 (m, 2H, ArH), 6.75 (m, 1H, ArH), 4.2 (m, 1H, CHN), 1.5-2.90 (m, 23H, CH_2, CH_3). Elemental Anal. Calc. for $C_{25}H_{29}N_3Cl_2Pd$ (548.85): C 53.6, H 5.3, N 7.5; found: C 51.4, H 5.3, N 6.3.

Synthesis of [Pd(Me)(1-mesityl-3-octahydroacridinimidazolin-2-ylidene)Cl] (4.20):



A solution of [Ag(1-mesityl-3-octahydroacridinimidazolin)Cl] (0.432g, 0.77mmol) and PdMeCl(COD) (0.203, 0.77mmol) was stirred together in DCM for 2 hours at room temperature. The mixture was filtered through celite to remove the precipitated silver chloride and any Pd black. The solvent was then reduced to ca. 10ml and hexanes added to precipitate a pale yellow powder. The solvents were removed with a filter stick and the solid washed with Et_2O (3x10ml). The powder was recrystalized from DCM/Hexane to give the Pd complex **4.20**. (0.27g, 66%). Crystals suitable for X-ray diffraction were grown by layering Hexanes onto a DCM solution of the complex. **^{1}H NMR** (DCM, 500MHz, δ) 7.25 (m, 2H, HCCH), 7.05 (m, 2H, ArH), 6.8 (m, 1H, ArH), 4.1 (m, 1H, CHN), 1.55-2.95 (m, 23H, CH_2, CH_3), 0.0 (s, 3H, $PdCH_3$). **^{13}C NMR** (DCM, 100MHz, δ):159.28 (NCN), 139.4, 139.2, 135.65, 135.6, 135.2, 134.4, 131.2, 129.5, 129.0, 122.3, 116.9, 59.5, 34.4, 29.2, 28.8, 27.5, 23.0, 22.6,

21.2, 20.4, 18.6, 18.2, -10.1 Elemental Anal. Calc. for $C_{26}H_{32}N_3ClPd$ (528.43): C 59.0, H 6.0, N 6.9; found: C 52.6, H 5.56, N 6.74. **MS** (ESI) m/z (%):Calculated for $C_{28}H_{35}N_4Pd$ ($M - Cl^- + MeCN$), 533.1897; observed, 533.1782 (100 %)

4.5 References:

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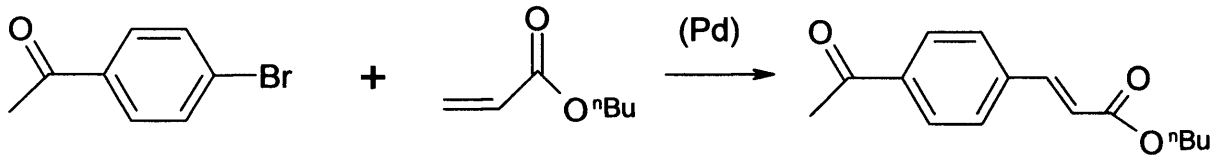
Chapter Five
Pd catalysed C-C Coupling reactions : The Heck Reaction

5.1 Introduction

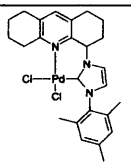
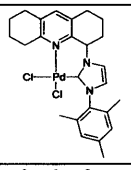
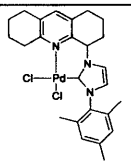
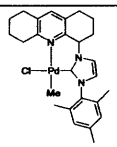
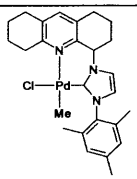
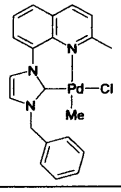
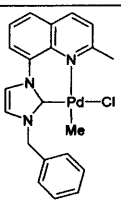
Due to time constraints, catalyst testing of the complexes synthesised in Chapter Four was confined to the Heck reaction. The Heck reaction was chosen due to its widespread use as 'one of the basic tools of organic preparations', and 'a natural way to assemble molecules'[1]. This chapter will focus on the Heck reaction with systems involving pyridine–carbene type ligands. Aryl bromides and chlorides were chosen to evaluate the necessary parameters to give high TONs (turn over number) and thus be viable catalysts, particularly for the aryl chlorides.

5.2 Results and Discussion

Catalytic testing of the Pd(II) complexes, described in Chapter Four, has focused on the Heck coupling of the activated aryl bromide 4-Bromoacetophenone with n-butyl acrylate (Scheme 5.1) which was likely to give positive results for comparison with other similar systems. A small selection of the complexes were also tested for their activity for the coupling of 4-chlorobenzaldehyde with n-butyl acrylate. Sodium acetate was chosen as the base due to its proven suitability in the Heck reaction with regard to a wide variety of substrates[2-8]. Tetrabutylammonium bromide was used as an additive, as it has previously been shown that ammonium salts have a positive effect on the Heck reaction[9,10]. All reactions were carried out under standardised conditions at 120°C for 16 hours. The results of the catalyst testing can be seen in Table 5.1, while Table 5.2 provides examples of other NHC complexes of various groups for comparison in the Heck reaction.



Scheme 5.1: Heck coupling of 4-bromoacetophenone with n-butyl acrylate.

Entry	Pre catalyst	Loading Mol%	Aryl halide	Coupling partner	Time (h)	Conversion (%)(GC)	TON
1		0.5	4-bromoacetophenone	n-butyl acrylate	16	32	64
2		0.1	4-bromoacetophenone	n-butyl acrylate	16	50	500
3		0.01	4-bromoacetophenone	n-butyl acrylate	16	86.4	8640
4		0.1	4-bromoacetophenone	n-butyl acrylate	16	47	470
5		0.01	4-bromoacetophenone	n-butyl acrylate	16	88	8800
6		0.1	4-bromoacetophenone	n-butyl acrylate	16	76	760
7		0.01	4-bromoacetophenone	n-butyl acrylate	16	74	7400

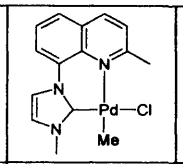
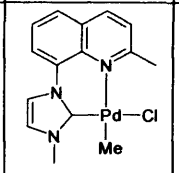
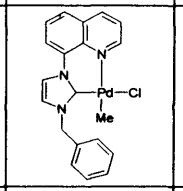
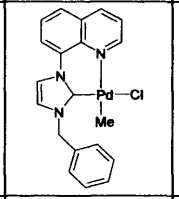
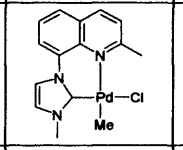
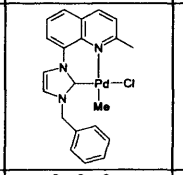
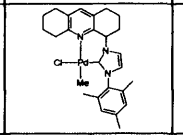
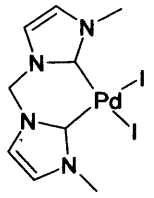
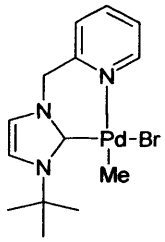
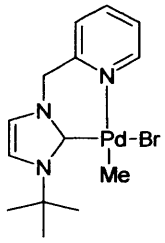
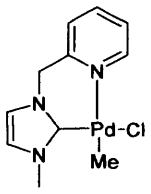
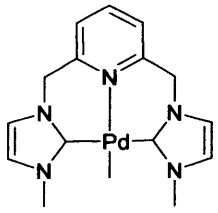
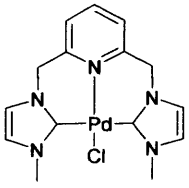
8		0.1	4-bromoacetophenone	n-butyl acrylate	16	60	600
9		0.01	4-bromoacetophenone	n-butyl acrylate	16	80	8000
10		0.1	4-bromoacetophenone	n-butyl acrylate	16	36	360
11		0.01	4-bromoacetophenone	n-butyl acrylate	16	40	4000
12		0.1	4-chlorobenzaldehyde	n-butyl acrylate	16	10	100
13		0.1	4-chlorobenzaldehyde	n-butyl acrylate	16	8	80
14		0.1	4-chlorobenzaldehyde	n-butyl acrylate	16	14	140

Table 5.1: Results from testing of a number of preformed Pd complexes as catalysts in the Heck reaction. (Reaction conditions: DMAc, 120°C, additive: Tetrabutylammonium bromide. Each result is the average of at least two catalytic runs.)

It can be seen from the table of results that the catalysts gave moderate conversions with yields ranging from 8-88%. The time of 16 hours was an arbitrary time and therefore the TONs stated do not necessarily represent the maximum turnovers, nor do they indicate in anyway that the catalyst had ceased to operate. Indeed Danopoulos's similar system (entry 16 and 17, Table 5.2), was shown to have no loss in activity with large increases in time, implying a high thermal stability under the reaction conditions in a number of Heck catalytic runs[11]. It can be seen from the results that

the higher catalytic loading has an effect on the conversions by lowering the yield. This is particularly evident for entries 1 to 3, with the 0.5, 0.1 and 0.01 mol% catalyst loading giving 32, 50 and 86.4% conversions respectively. The reasons for this are unclear though it may be possible that a decomposition pathway between two molecules exist, the low catalyst loading having an effect of decreasing the frequency of collisions. Both the dichloro- and methyl- chloro- complexes of the octahydroacridine functionalised carbene were tested in the Heck reaction to evaluate if the methyl group would have any significant advantages in this particular system. Pd hydrocarbyl complexes of pyridine functionalised carbenes have been used in the Heck reaction by both Danopoulos and Cavell in the coupling of BA and BAP (entries 17 and 18). It has been shown by Cavell that the methyl group has an activating influence on catalyst formation, possibly by providing a facile route to the catalytically active Pd(0) species through the insertion of the olefin and subsequent β-hydride elimination[4,9]. This however doesn't seem to have any significant effect in the case of this system with TONs of 8640 and 8800 for the dichloro- (entry 3) and methyl- chloro- (entry 5) systems respectively. The induction period was not measured for this reaction and so the catalytic superiority for the methyl complexes cannot be completely ruled out. Cavell also found the chloro complex of his 'pincer' complex (entry 20, Table 5.2) was consistently more active than the methyl derivative (entry 19), though activity for the chloro- complex was found to decrease as the catalytic cycle continued. On comparing entries 7 and 11, we can see the effect the extra steric bulk of the methyl group in the 2 position of the quinoline function has on the conversions. Complex **4.16** with the extra methyl group gave a 74% yield compared to 40% without this group. When comparing the results for the different N-substituents, i.e. the benzyl group and the methyl group, it can be seen that there is very little difference with respect to conversions. On examination of the data in Table 5.2 for NHC-pyridine systems it is evident that the preformed catalysts used within this work are comparable to those previously tested when factors such as reaction time (16 hours versus 120 of entry 18), and reaction temperature (120°C versus 140°C of entry 17) are taken into consideration.

Entry	Catalyst	Conditions/Additives	TON (TOF)	Coupling Reagents	Run Time (Hours)
15		100°C	>200	BAP & BA	-
16		140°C	1400,000 (1,000)	PhI & MA	18
17		140°C	200 (11) (100%)	BAP & BA	18
18		120°C	610,000 (5,080)	BAP & BA	120
19		120°C/Pr_4NBr	34,330 (1,720)	BAP & BA	20
20		120°C and $NH_2NH_2.H_2O$	40,160 (1,980)	BAP & BA	20

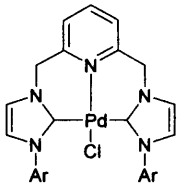
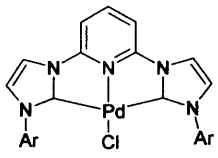
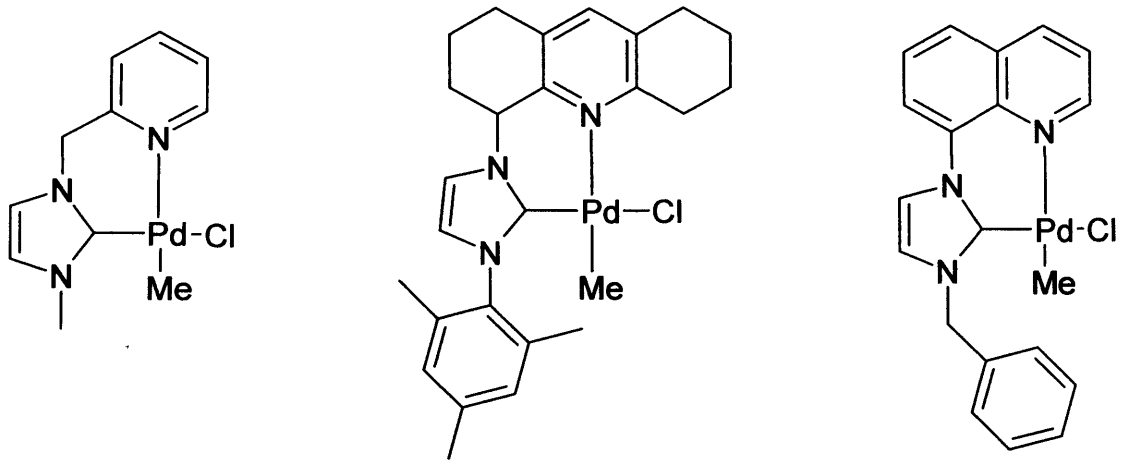
21		140°C	14,290 (793)	BAP & MA	18
22		140°C	14,290 (793)	BAP & MA	18

Table 5.2. Selected literature examples of Pd NHC complexes in the Heck reaction. (Adapted from the review by Crudden and Allen[12]).

Although none of the new complexes show particularly high activities for the coupling of the aryl bromide, it was decided to evaluate their performance with an activated aryl chloride. Entries 12 to 14 (Table 5.1) show the performance of complexes **4.15, 4.16** and **4.20** with 4- chlorobenzaldehyde. It can clearly be seen that the complexes tested have very low activities with respect to the coupling 4-chlorobenzaldehyde and butyl acrylate with conversion from 8-14%. There was no evidence of Pd black in any of the catalytic runs indicating that the complexes were stable throughout the length of the catalysis times.

The effect of rigidity of the chelating backbone in the Heck reaction can be compared using McGuinness's complex **5.3** (Figure 5.2) with those synthesised within this work such as **4.14** and **4.20**. Like those of this work, **5.3** forms a 6 membered chelate ring and contains a second donor separated from the NHC by a –C- linker. The order of rigidity should be **5.3**≤ **4.20**< **4.14**. Table 5.3 shows some selected catalytic data from McGuinness's work with **5.3**[9].



5.3 **4.20** **4.14**

Figure 5.2: The effect of rigidity should increase from left to right due to the nature of the linker between each donor.

Entry	Amount Mol%	Aryl halide	Coupling partner	Time	Conversion	TON
21	0.00016	4-Bromoacetophenone	Butyl acrylate	48	63	393800
22	0.021	4-Chlorobenzaldehyde	Butyl acrylate	24	75	360

Table 5.3: Selected catalytic data from McGuinness's work[13]. (120°C, DMAc)

The coupling of 4-bromoacetophenone and n-butyl acrylate with **5.3** and those synthesised within this work are comparable with respect to conversions, indicating that rigidity is not a key controlling factor for the Heck reaction. The high TON of entry 21 reflects the catalyst loading in comparison to those of Table 5.1. If time constraints were not an issue it would have been of interest to carry out the Heck reaction using the same catalyst loading as in entry 21 for the Pd complexes synthesised in Chapter Four, to see if the activities and hence TON's would be similar. The difference in reaction times must also be taken into consideration (48 hours compared to 16) and so again it would be interesting to see if in fact it is the nature of

the ligand, or of the catalyst loading coupled with the reaction times, that provided these similar conversions.

With respect to the coupling of 4-chlorobenzaldehyde it can be seen that McGuinness's complex out performed any of the complexes within this work, with a satisfactory conversion of 75%, compared to our highest of 14% (entry 14). Again this was achieved at lower catalyst loading (0.021mol% compared with 0.1mol%).

Further investigations with the complexes synthesised herein into the Heck reaction should include the use of a range of aryl chlorides and bromides, a probe of the induction time and a screening of the conditions with respect to reaction times and catalyst loading, in order to fine tune the system for optimum results.

5.3 Conclusions

The majority of the complexes synthesised in Chapter Four were catalytically tested in the Heck reaction in order to be benchmarked against the ever-growing number of existing Pd functionalised carbene complexes. All of the complexes tested showed low to satisfactory activities with respect to the coupling of 4-chlorobenzaldhyde and 4-bromoacetophenone with n-butyl acrylate, though are comparable to similar systems when reaction conditions are taken into consideration. In terms of ligand design it can be seen that the possession of a rigid, cyclic structure with delocalised electrons has no obvious benefits in the Heck coupling of the aforementioned substrates. In hindsight, it appears likely that Heck coupling was not the best catalytic process to study when reviewing the catalytic performance of these new ligands. Due to time constraints only the Heck reaction was investigated and so the successful application of these complexes in other catalytic reactions cannot be ruled out.

5.4 Experimental

5.4.1 General comments

All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. All complexes used were synthesised according to the procedures outlined in Chapter Four. Reagents were bought from commercial suppliers and used without further purification. DMAc was dried over molecular sieves prior to use. GC-MS analyses were carried out on a HP Agilent 5973, with an Agilent HPSMS column (50m x 0.25mm).

5.4.2 Analysis Method

For all catalytic Heck reactions the yields of the coupled products were determined by GC-MS based on the amount of aryl halide remaining after the allocated reaction time using internal standard methods. GC-MS was used to identify the identity of the desired product.

5.4.3 Procedure for the Heck Reaction

4-Bromoacetophenone (5mmol, 0.99g), sodium acetate (5.56mmol, 0.456g) and 20% tetrabutylammoniumbromide (0.198g) was suspended in 5mL DMAc. n-butyl acrylate (7mmol, 1mL) was then added followed by the Pd catalyst in a DMAc solution. The reaction mixture was then placed into a preheated oil bath at 120°C and allowed to stir for 16 hours. After cooling, n-dodecane (5mmol, 1.13mL) was added to the mixture as an internal standard. The mixture was then washed with water to remove inorganic salts, and the solution analysed by GC-MS. GC-MS indicated only one product was formed though selectivity was not measured.

5.5 References

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Appendix

X- Ray crystallography

Crystal structure determination.

All single crystal X-ray data were collected on a Bruker Nonius Kappa CCD diffractometer using graphite monochromated Mo-Kα radiation, equipped with an Oxford Cryostream cooling apparatus.

1-methyl-3-(2-methyl-quinoline)-imidazolium iodide (2.8)

Empirical formula	C14 H14 I N3	
Formula weight	351.18	
Temperature	150(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.523(5) Å	α= 90.000(5)°.
	b = 7.574(5) Å	β= 93.861(5)°.
	c = 17.237(5) Å	γ = 90.000(5)°.
Volume	1370.7(12) $Å^3$	
Z	4	
Density (calculated)	1.702 Mg/m^3	
Absorption coefficient	2.322 mm^{-1}	
F(000)	688	
Crystal size	0.23 x 0.23 x 0.15 mm^3	
Theta range for data collection	3.57 to 26.37°.	
Index ranges	-13<=h<=13, -9<=k<=9, -20<=l<=21	
Reflections collected	14387	
Independent reflections	2795 [R(int) = 0.1071]	
Completeness to theta = 26.37°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7220 and 0.6172	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2795 / 0 / 165
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0304, wR2 = 0.0642
R indices (all data)	R1 = 0.0398, wR2 = 0.0678
Largest diff. peak and hole	0.707 and -1.060 e.Å^{-3}

1-mesityl-3-octahydroacridinimidazolium chloride (2.14)

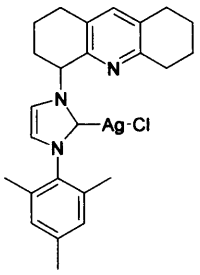
Empirical formula	C27 H35 Cl8 N3 O	
Formula weight	701.18	
Temperature	150(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	P 21/a	
Unit cell dimensions	a = 14.141(5) Å	α= 90.000(5)°.
	b = 16.458(5) Å	β= 92.359(5)°.
	c = 14.209(5) Å	γ = 90.000(5)°.
Volume	3304.1(19) Å^3	
Z	4	
Density (calculated)	1.410 Mg/m^3	
Absorption coefficient	0.708 mm^{-1}	
F(000)	1448	
Crystal size	0.20 x 0.15 x 0.05 mm^3	
Theta range for data collection	3.13 to 27.46°.	
Index ranges	-18<=h<=18, -21<=k<=21, -14<=l<=18	
Reflections collected	39529	
Independent reflections	7557 [R(int) = 0.1688]	
Completeness to theta = 27.46°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9655 and 0.8714	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7557 / 6 / 357	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0903, wR2 = 0.2034	

R indices (all data)	R1 = 0.1578, wR2 = 0.2374
Largest diff. peak and hole	1.534 and -1.020 e.Å^{-3}

4,5-Bis(methylimidazolium hexaflurophosphate)-2,2-dimethyl-1,3-dioxolan (2.23)

Empirical formula	C15 H24 F12 N4 O2 P2	
Formula weight	582.32	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2(1)	
Unit cell dimensions	a = 6.56670(10) Å	α= 90°.
	b = 14.9593(3) Å	β= 91.6244(11)°.
	c = 12.1524(2) Å	γ = 90°.
Volume	1193.29(4) Å^3	
Z	2	
Density (calculated)	1.621 Mg/m^3	
Absorption coefficient	0.296 mm^{-1}	
F(000)	592	
Crystal size	0.25 x 0.20 x 0.20 mm^3	
Theta range for data collection	3.10 to 27.46°.	
Index ranges	-8<=h<=8, -19<=k<=19, -15<=l<=15	
Reflections collected	20597	
Independent reflections	5354 [R(int) = 0.0790]	
Completeness to theta = 27.46°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9431 and 0.9296	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5354 / 1 / 320	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.1012	
R indices (all data)	R1 = 0.0498, wR2 = 0.1064	
Absolute structure parameter	-0.01(9)	
Largest diff. peak and hole	0.249 and -0.320 e.Å^{-3}	

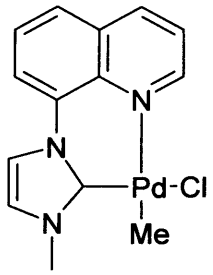
Ag(I) complex of Octahydroacridine functionalised carbene (3.12).



Empirical formula	C25 H29 Ag Cl N3	
Formula weight	514.83	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 15.5780(4) Å	α= 90°.
	b = 11.5620(3) Å	β= 104.6560(10)°.
	c = 25.8740(6) Å	γ = 90°.
Volume	4508.60(19) $Å^3$	
Z	8	
Density (calculated)	1.517 Mg/m^3	
Absorption coefficient	1.030 mm^{-1}	
F(000)	2112	
Crystal size	0.45 x 0.33 x 0.33 mm^3	
Theta range for data collection	2.95 to 27.51°.	
Index ranges	-20<=h<=20, -14<=k<=14, -27<=l<=31	
Reflections collected	10294	
Independent reflections	4937 [R(int) = 0.0447]	
Completeness to theta = 27.51°	95.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7275 and 0.6544	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4937 / 0 / 274	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0371, wR2 = 0.0809	
R indices (all data)	R1 = 0.0517, wR2 = 0.0876	

Largest diff. peak and hole	0.690 and -0.828 e.Å^{-3}

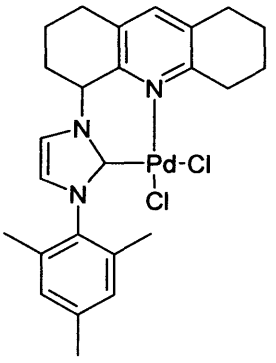
[Pd(Me)(1-methyl-3-quinoline-imidazolin-2-ylidene)Cl] (4.13):



Empirical formula	C14.50 H15 Cl2 N3 Pd	
Formula weight	408.60	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 15.8709(7) Å	α= 90°.
	b = 13.6114(5) Å	β= 117.075(2)°.
	c = 15.9427(6) Å	γ = 90°.
Volume	3066.6(2) Å^3	
Z	8	
Density (calculated)	1.770 Mg/m^3	
Absorption coefficient	1.552 mm^{-1}	
F(000)	1624	
Crystal size	0.18 x 0.15 x 0.03 mm^3	
Theta range for data collection	3.87 to 27.46°.	
Index ranges	-20<=h<=20, -17<=k<=17, -20<=l<=20	
Reflections collected	27046	
Independent reflections	6909 [R(int) = 0.1531]	
Completeness to theta = 27.46°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9549 and 0.7675	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6909 / 0 / 374	
Goodness-of-fit on F^2	1.048	

Final R indices [I>2sigma(I)]	R1 = 0.0591, wR2 = 0.1135
R indices (all data)	R1 = 0.0996, wR2 = 0.1276
Largest diff. peak and hole	0.799 and -0.758 e.Å^{-3}

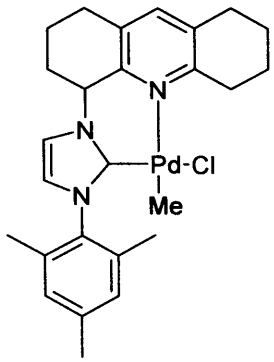
[Pd(1-mesityl-3-octahydroacridinimidazolin-2-ylidene)Cl_2] (4.19):



Empirical formula	C26 H30 Cl4 N3 Pd	
Formula weight	632.73	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 8.7030(2) Å	α= 90°.
	b = 17.6960(4) Å	β= 100.9000(10)°.
	c = 17.3720(5) Å	γ = 90°.
Volume	2627.16(11) Å^3	
Z	4	
Density (calculated)	1.600 Mg/m^3	
Absorption coefficient	1.134 mm^{-1}	
F(000)	1284	
Crystal size	0.40 x 0.38 x 0.20 mm^3	
Theta range for data collection	3.65 to 26.37°.	
Index ranges	-10<=h<=10, -22<=k<=22, -21<=l<=21	
Reflections collected	20389	
Independent reflections	5354 [R(int) = 0.0810]	
Completeness to theta = 26.37°	99.6 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8050 and 0.6597
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5354 / 0 / 310
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0431, wR2 = 0.0905
R indices (all data)	R1 = 0.0674, wR2 = 0.0991
Largest diff. peak and hole	0.990 and -0.950 e.$Å^{-3}$

[Pd(Me)(1-mesityl-3-octahydroacridinimidazolin-2-ylidene)Cl] (4.20):



Empirical formula	C27 H34 Cl3 N3 Pd	
Formula weight	613.32	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2(1)/n	
Unit cell dimensions	a = 9.6970(2) Å	α= 90°.
	b = 17.7540(5) Å	β= 96.6670(10)°.
	c = 15.5720(5) Å	γ = 90°.
Volume	2662.75(13) $Å^3$	
Z	4	
Density (calculated)	1.530 Mg/m^3	
Absorption coefficient	1.019 mm^{-1}	
F(000)	1256	
Crystal size	0.38 x 0.20 x 0.20 mm^3	
Theta range for data collection	3.12 to 27.45°.	

Index ranges	-12<=h<=12, -22<=k<=23, -19<=l<=20
Reflections collected	19490
Independent reflections	6048 [R(int) = 0.0850]
Completeness to theta = 27.45°	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8221 and 0.6981
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6048 / 0 / 311
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0475, wR2 = 0.0964
R indices (all data)	R1 = 0.0775, wR2 = 0.1087
Largest diff. peak and hole	0.565 and -0.871 e.$Å^{-3}$