UNIVERSITY OF SOUTHAMPTON

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SCHOOL OF CHEMISTRY

Functionalised and Cyclometallated *N*-Heterocyclic Carbene

Complexes of Pd, Ni, Rh and Ir:

Synthesis and Applications

by

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ABSTRACT

New imidazolinium salts have been synthesised with the following substitution: (i) 2-(3-methylpyridyl), 2-pyridyl; (ii) alkoxyphenyl (*o*-OMe-phenyl, *p*-OMe-phenyl, *o,p*-(OMe)$_2$-phenyl, *o,p,o*-(OMe)$_3$-phenyl, *o*-O^{i}Pr-phenyl, *p*-O^{i}Pr-phenyl); (iii) substituted aryl (*o*-Et-phenyl, *o*-^{i}Pr-phenyl); (iv) fluoroaryl (*m,m*-(CF$_3$)$_2$-phenyl, *o*-F-phenyl, *o,p*-F$_2$-phenyl). In addition, novel pyridyl functionalised imidazolium salts have been synthesised. The targeted imidazol(in)ium salts were hoped to give rise to metal complexes with hemilabile coordination sites (pyridine functionalised species) or to cyclometallated complexes which on heating may generate active catalysts. Deprotonation of two of the imidazolium salts led to the isolation of the corresponding free carbenes. Five novel pyridyl functionalised imidazolin-2-ylidene complexes of palladium, three novel imidazolin-2-ylidene palladacycle complexes, four novel aryl substituted imidazolin-2-ylidene palladium complexes and two novel alkoxyphenyl imidazolin-2-ylidene palladacycle complexes have been synthesised by reacting the *in situ* deprotonated salt with various palladium precursors or by transmetallation reactions from silver carbene complexes. The complexes were characterised by analytical, spectroscopic and diffraction techniques. Interestingly, the first palladium 'C–C–C pincer' type complex (**3.14**) has been isolated after facile double cyclometallation succeeding the ligand complexation. Selected palladium imidazolin-2-ylidene complexes have been tested as catalysts for Heck coupling reactions. [1,3-Bis(4-methoxyphenyl)imidazolin-2-ylidene] {2-[3-(4-methoxyphenyl) imidazolin-2-ylidene] -5- methoxy phenyl-$\kappa^2 C,C'$} methyl palladium(II) (**3.16**) and [1,3-bis(2,4-dimethoxyphenyl)imidazolin-2-ylidene] {2-[3-(2,4-dimethoxy phenyl) imidazolin-2-ylidene] -3,5- dimethoxy phenyl-$\kappa^2 C,C'$} methyl palladium(II) (**3.15**) have been found to be excellent catalysts for the Heck couplings of aryl bromides, deactivated aryl bromides and activated aryl chlorides, while moderate results for the Heck coupling of chlorobenzene have been achieved. These complexes surpass the activity of standard palladium phosphine complexes and are amongst the most active palladium NHC complexes reported to date. Five novel picolyl-functionalised imidazol-2-ylidene complexes of Rh(I) and Ir(I) have been prepared and characterised by the reaction of [M(COD)Cl]$_2$ (M = Rh, Ir) with 1-[2-(3-methyl)pyridyl]-3-[(2,6-diisopropyl)phenyl]imidazol-2-ylidene (**2.1b**). When M = Rh the nature of the products was found to be dependent on the reactant ratio. Furthermore, one novel Ir(III) picolyl

functionalised imidazolin-2-ylidene complex featuring a 1-κ-4,5,6-η-C_8H_{12} moiety (**5.6**) has been synthesised by reacting $[Ir(COD)Cl]_2$ with, *in situ* formed, 1-[2-(3-picolyl)]-3-(2,6-diisopropylphenyl) imidazolin-2-ylidene. (Cycloocta-1,5-diene)-κ^2-{1-[2-(3-picolyl)]-3-(2,6-diisopropylphenyl) imidazol-2-ylidene} rhodium tetrakis- [3,5-bis (trifluoromethylphenyl)] borate (**5.2**) and (cycloocta-1,5-diene)-κ^2-{1-[2-(3-picolyl)]-3-(2,6-diisopropylphenyl) imidazol-2-} iridium tetrakis -[3,5-bis (trifluoromethylphenyl)] borate (**5.4**) have been extensively tested as catalysts in olefin hydroformylations, olefin molecular hydrogenations and transfer hydrogenation reactions of carbonyl compounds. Complex **5.2** was found to be a good catalyst in the hydroformylation of styrene, giving high activities and relatively good selectivities even at low catalyst loadings. Complex **5.4** performed as an excellent catalyst for the hydrogenation (by transfer) of β-citronellal and 4-methoxybenzaldehyde giving activities of up to 3000 moles of converted substrate per mole of catalyst per hour. Finally, two novel picolyl functionalised imidazol-2-ylidene complexes of nickel have been synthesised by the reaction of nickel precursor complexes with the free ylidene ligand **2.1b**. These complexes show high activities for the vinyl-type polymerisation of norbornene with MAO used as co-catalyst. Furthermore, one novel diimine ligand (*N*,*N'*-bis(2,4,6-trimethoxyphenyl) ethylenediamine) (**7.3**) has been synthesised. The diimine ligand has successfully displaced labile ligands from nickel precursor complexes to yield two novel nickel diimine complexes. Preliminary catalytic results indicated that these diimine complexes might be good catalysts for several reactions including ethylene polymerisation or other polymerisation reactions.

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LIST OF ABBREVIATIONS

BARF: tetrakis-[3,5-bis(trifluoromethyl) phenyl]borate

bp: boiling point

br.s: broad singlet

^{t}Bu: tertiary butyl

COD: cyclo-octa-1,5-diene

conc: concentrated

d: doublet

DBA: dibenzylidenacetone

DCM: dichloromethane

dd: doublet of doublets

Dipp: diisopropylphenyl

DME: dimethoxyethane

ES$^+$: positive ion electrospray

ES$^-$: negative ion electrospray

Et: ethyl

h: hours

Ipp: isopropylphenyl

m: multiplet

m-H: meta positioned H

MAO: Methylaluminoxane

Me: methyl

MeCN: acetonitrile

Mes: 2,4,6-trimethylphenyl

mp: melting point

MS: mass spectrometry

NHC: N-heterocyclic carbene

NMR: Nuclear Magnetic Resonance

o-H: ortho positioned H

p-H: para positioned H

Ph: phenyl

ppt: precipitate

^{i}Pr: isopropyl

py: pyridyl

q: quartet

r.b.f.: round bottom flask

rt: room temperature

s: singlet

sept: septet

t: triplet

THF: tetrahydrofuran

TMEDA: N,N,N',N'-tetramethylethylene -1,2-diamine

TON: turn-over number

tt: triplet of triplets

ACKNOWLEDGEMENTS

To my Mum and Dad

Chapter 1:

Introduction to

N-Heterocyclic Carbenes

Following Arduengo's isolation and characterisation of the first free NHC,[1] an increased interest in such ligands has been observed in the last few years. This is partially because NHCs are strong σ-donors with little or no π-back-bonding character, making them perfect substitutes to classical 2e$^-$ donor ligands (such as amines, ethers and especially phosphines) in metal coordination chemistry.[2]

NHCs have been referred to as "phosphine mimics", because of the striking similarity with trialkylphosphines (PR$_3$) in terms of their σ-donating ability on coordination to the metal.[3] But the fact that they present more attractive features, compared to trialkylphosphines, can not be ignored. NHCs are versatile, easy to prepare and easily tuneable ligands that, when coordinated to transition metals, have great potential in homogeneous catalysis.[2]

1.1 Carbenes

Carbenes (general formula: :CR^{1}R^2) are highly reactive neutral molecules with a divalent carbon atom that has only six valence electrons.[4] A pair of unshared electrons can be assigned to two non-bonding orbitals in different ways, giving the possibility of two types of carbenes: singlet and triplet state carbenes. Typically carbenes are very short-lived intermediates, but since 1991 many stable carbenes have been reported.[2]

| singlet carbene | stabilised singlet carbene | triplet carbene | triplet carbene |
| sp^2 hybrid | sp^2 hybrid | sp hybrid | sp^2 hybrid |
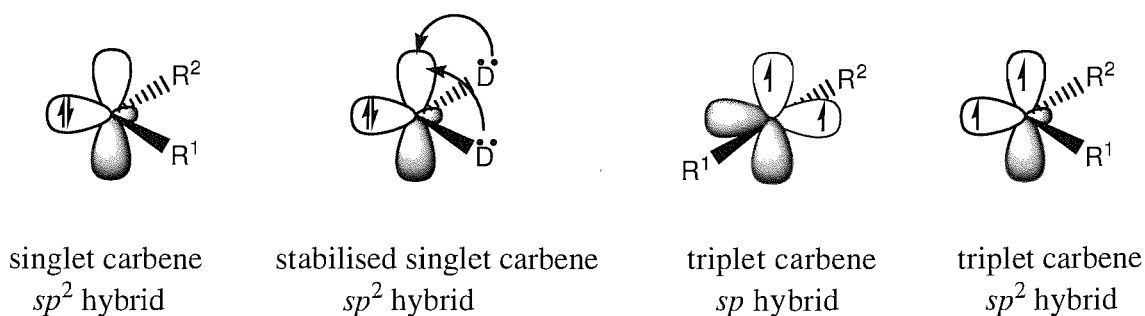
Figure 1.1: Singlet and triplet state carbenes (D = donor atom)

Singlet and triplet carbenes are named so because of the electronic spin multiplicities they possess (S =1 for singlet and S = 3 for triplet). In singlet carbenes, the carbon atom adopts a bent geometry and it is sp^2 hybridised, while a pair of electrons is occupying one of the sp^2 hybrids. In triplet carbenes however, the :C carbon may adopt either a bent (sp^2 hybridised) or a linear (sp hybridised) geometry while the two unpaired electrons, each

occupying a different orbital. The ground state spin multiplicity determines the reactivity of a carbene. Singlet carbenes possess one filled and one empty orbital and therefore are expected to act as either nucleophiles or electrophiles, while triplet carbenes possess two singly occupied orbitals and therefore are expected to have a radical (diradical) type of reactivity.[5]

Substituents that are σ-electron-attractors and π-electron-donors, denoted D (groups such as –F, –Cl, –Br, –I, –NR$_2$, –PR$_2$, –OR, –SR...) may stabilize singlet state carbenes by donating electron density into the empty p-orbital (Figure 1.1). Good examples are diaminocarbenes (Figure 1.2) in which the carbene electron deficiency is reduced by the donation of the two nitrogen lone pairs, whilst the carbene lone-pair is stabilized by the inductive effect of two electronegative nitrogen atoms.[6] However, most types of carbenes are kinetically stabilised by bulky substituents and if electronic effects are negligible, steric effects may also determine the ground-state spin multiplicity.[6]

cyclic
diaminocarbenes
n= 1, 2 or 3

imidazol-
2-ylidenes

1,2,4-triazol-
3-ylidenes

1,3-thiazol-
2-ylidenes

acyclic
diaminocarbenes

acyclic
aminooxycarbenes

acyclic
aminothiocarbenes

acyclic
diborylcarbenes
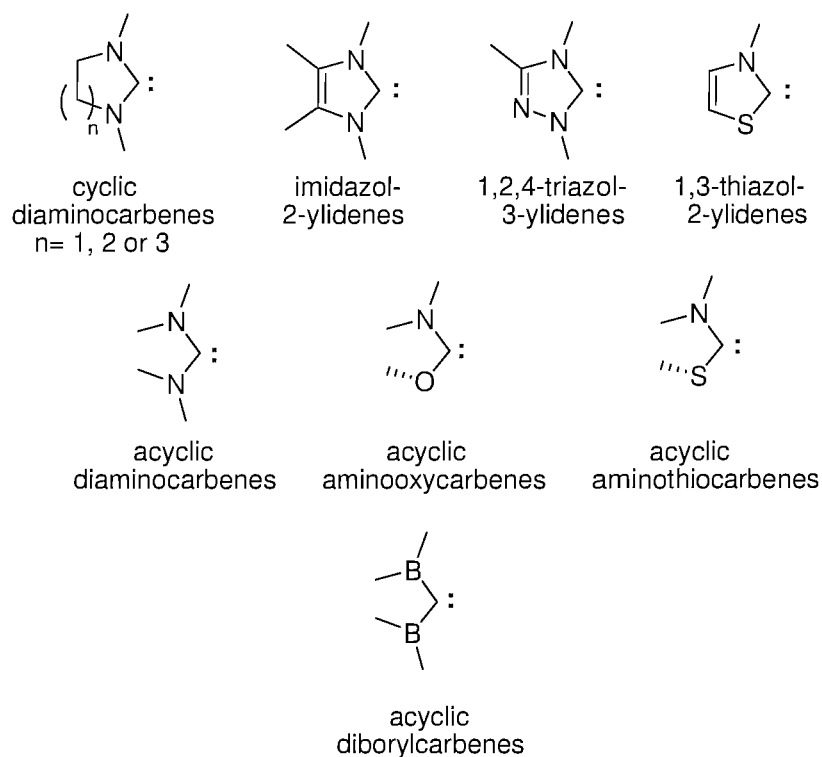
Figure 1.2: Some examples of singlet carbenes

In singlet carbenes (:CR^{1}R^2), the substituents of the carbene carbon are typically heteroatom donor groups (R^1, R^2 = –OR, –SR, –NR$_2$, –PR$_2$) and the carbenes are considered to be very strong nucleophiles due to the low electronegativity of the carbene

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carbon. Many examples of such carbenes exist[7] (Figure 1.2). On the other hand, substituents on triplet carbenes are not electron donors. These species are very unstable and their isolation is achieved by steric protection of the carbene carbon, in order to suppress its reactivity.[8]

Furthermore, singlet and triplet carbenes do not demonstrate the same reactivity. Singlet carbenes generally participate in reactions as either electrophiles or nucleophiles, whilst triplet carbenes are diradicals and participate in stepwise radical additions. The reactivity of a particular carbene depends on the substituent groups. For example, if a substituent is an electron-donating group, it is likely that the carbene will not be a good electrophile.

1.2 Stable Carbenes

A stable (or persistent) carbene is a neutral divalent carbon centre which may be isolated under suitable conditions and characterised by standard analytical methods. A stable carbene will typically have a lifetime of at least hours in the solid state at 0 °C. Instability in these carbenes involves reactivity with substrates, or formation of Wanzlick[9] type dimers (Scheme 1.1).
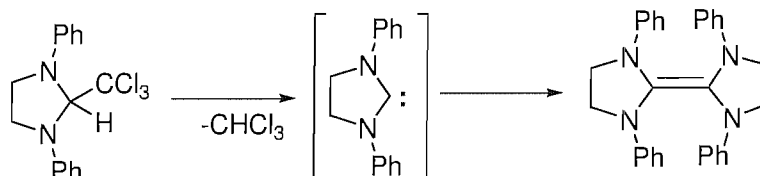
Scheme 1.1: Wanzlick-type dimerisation of carbenes

The first stable carbene was proposed by Breslow in 1957.[10] The proposal claimed a thiazol-2-ylidene being involved in the catalytic cycle of vitamin B1. This was the first example of a nucleophilic carbene being implicated in a reaction mechanism. In 1960 Wanzlick proposed that imidazolin-2-ylidenes were generated from 2-trichloromethyl dihydroimidazoles (Scheme 1.1), after the loss of chloroform by vacuum pyrolysis.[11]
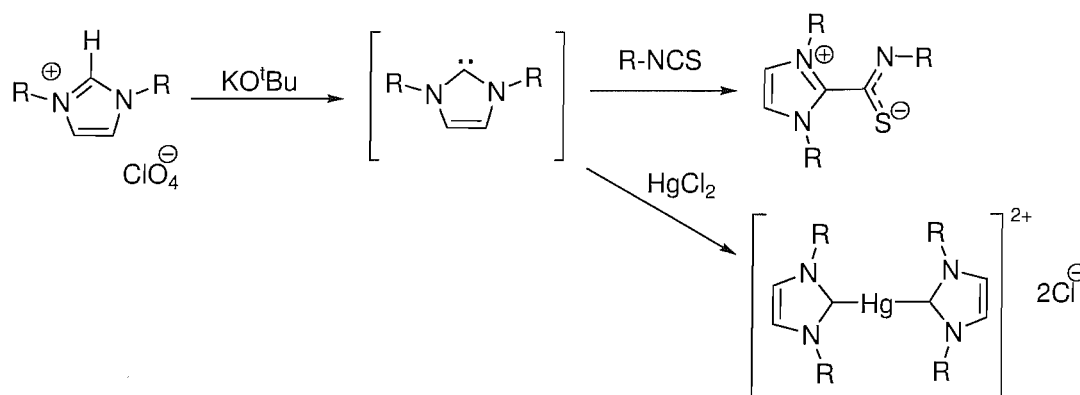
Scheme 1.2: Preparation and trapping of imidazol-2-ylidene (R = Ph)[12]

In 1970 Wanzlick prepared (but did not isolate) the first *N*-heterocyclic carbene by the deprotonation of an imidazolium salt.[13] Both Wanzlick[14] and Hoffmann[15] believed that these imidazole-based carbenes, with a $4n + 2\pi$-electron ring system (n= 1, 2, 3,… might be more stable than the 4,5-dihydro analogues, due to Hückel-type aromaticity. Instead of isolating the carbenes, Wanzlick[12] trapped them with reagents such as mercury chloride and isothiocyanates (Scheme 1.2).

It was not until twenty years later (in 1989) that Bertrand[16] isolated the first stable phosphinocarbene by the thermolysis of (trimethylsilyl)[bis(diisopropylamino)-phosphino]diazomethane at 250 °C under vacuum. The isolated red oil can be represented as either a λ^3-phosphinocarbene or λ^5-phosphaacetylene (Figure 1.3) and at the time of its publication some doubt remained as to if these phosphorus substituted "carbenes" are actually carbenes or not since they seem to exhibit some alkyne properties.[16b]
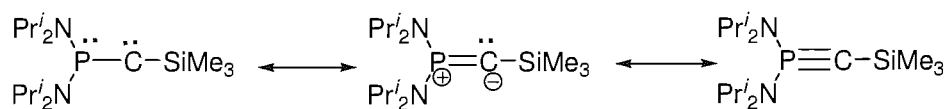
Figure 1.3: Alkyne and carbene resonances structures of Bertrand's carbene[16]

Finally in 1991 Arduengo isolated the first free *N*-heterocyclic carbene[1] and most importantly determined its molecular structure by X-ray crystallography (Scheme 1.3). Arduengo's success was a big surprise since up to that time it was believed that all carbenes existed only as highly reactive intermediates. On the contrary, a simple

deprotonation of the imidazolium chloride gave the free carbene that was found to be indefinitely stable at room temperature, in the absence of oxygen and moisture.
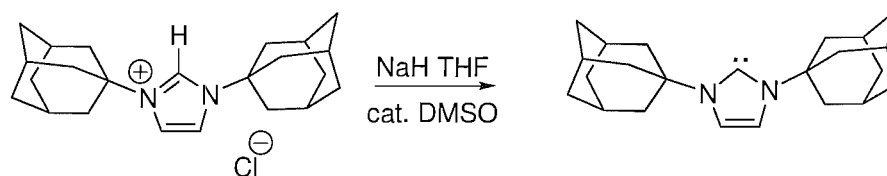
Scheme 1.3: Preparation of 1,3-diadamantylimidazol-2-ylidene[1]

1.3 *N*-Heterocyclic Carbenes (NHCs)

NHCs are singlet state carbenes. Their main characteristic is that the carbene carbon is flanked by two heteroatoms one of which must be nitrogen. Although most NHCs are derived from 5-membered heterocycles, 4-, 6- and 7-membered analogues have recently been reported[7b, 17] (Figure 1.4).
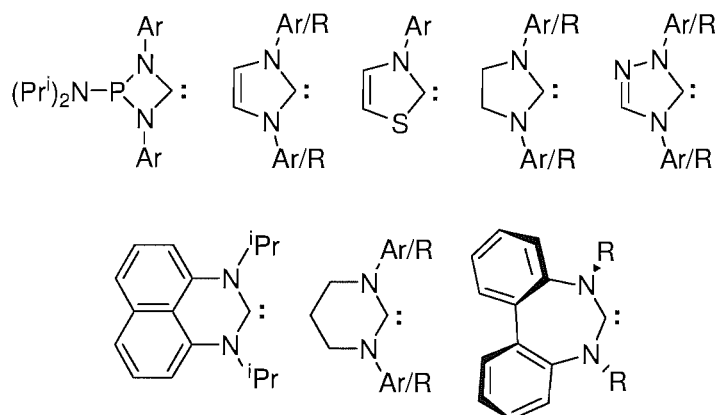
Figure 1.4: NHC frameworks reported in the literature[7b, 17]

1.3.1 Electronic properties of NHCs

The majority of the research attention has been focused on imidazol-2-ylidenes and imidazolin-2-ylidenes. Investigation of these systems began in the early 1960s, when Wanzlick initiated research into the formation of imidazolin-2-ylidenes (Scheme 1.1).[11] Unfortunately, instead of the desired carbene, only the electron-rich olefin (Wanzlick dimer) was isolated. Furthermore, no equilibrium between the 'monomeric' carbene and the dimer was experimentally observed at that time. However, quite recently, Hahn and

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co-workers were able to provide evidence for the existence of the equilibrium (Scheme 1.4) between NHCs and their corresponding dibenzotetraazafulvalenes (Wanzlick type dimmers) in solution.[18] Electron-rich (Wanzlick) olefins were later utilised by Lappert for the development of a general synthetic route for the isolation of metal-NHC complexes.[19]
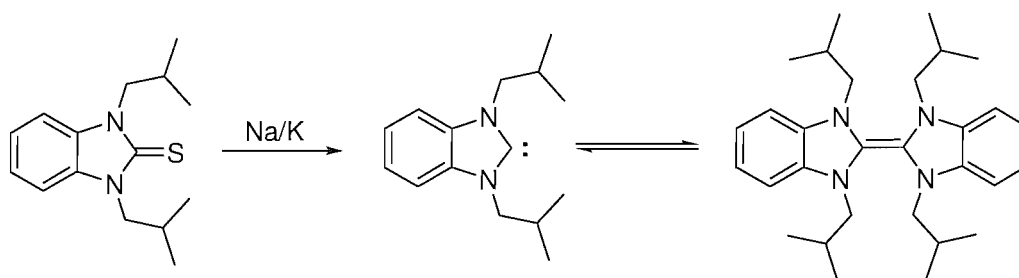
Scheme 1.4: Equilibrium between NHCs and its corresponding dibenzotetraazafulvalene

Following the isolation of the first crystalline carbene,[1] many examples of free NHCs have emerged and some of them are shown in Figure 1.5.[6] The steric bulk around the carbene carbon was initially thought to be crucial for their isolation.[1] Shortly after, this speculation (regarding imidazol-2-ylidenes) was overthrown by the isolation of ylidenes without bulky substituents attached to the nitrogen heteroatoms.[20]
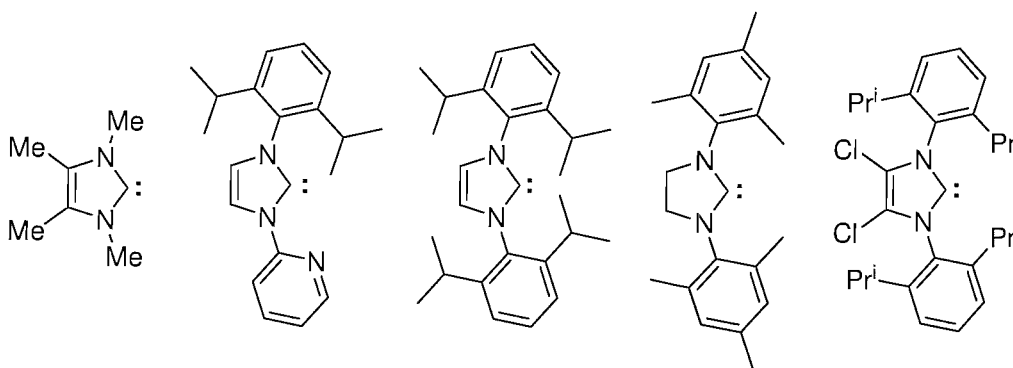
Figure 1.5: Examples of isolated free NHCs

The isolation of sterically unencumbered NHCs (*e.g.* 1,3,4,5-tetramethyl imidazol-2-ylidene,[20] Figure 1.5) showed that thermodynamic (electronic) rather than kinetic (steric hindrance) stabilisation was the key factor in imidazol-2-ylidenes. The electronic effects that should be taken into consideration are: i) the difference in electronegativity between the carbene carbon and the nitrogen substituents and ii) the further stabilisation achieved

by the donation of electron-density from the nitrogen heteroatoms to the unoccupied p-orbital of the carbene carbon (+M effect). These electronic effects are illustrated in Figure 1.6. Although the electronic situation in the N–C–N moiety is crucial, steric hindrance is also responsible for stability, especially in the case of imidazolin-2-ylidenes.[5]
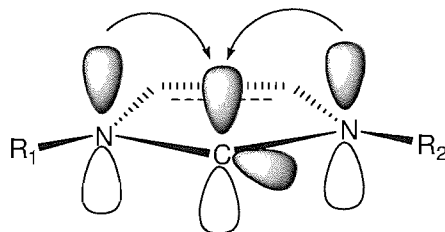
Figure 1.6: Thermodynamic stabilisation of NHCs

1.3.2 Reactivity of NHCs

NHCs react poorly with unsaturated nucleophiles, such as alkenes, allenes, acetylenes or arenes. They are prone to dimerisation, which can be considered as a nucleophilic attack of one singlet carbene at the vacant p-orbital of another singlet carbene.[5] NHCs can be utilized as catalysts to promote many organic transformations because of their nucleophilic character. Imidazol-2-ylidenes and triazol-2-ylidenes have been found to be excellent catalysts for organic syntheses such as a) the benzoin condensation of higher aldehydes to α-hydroxyketones,[21] b) the Michael-Stetter reaction,[22] c) the formoin reaction,[23] d) transesterifications[24] and e) macromolecular chemistry.[25] Furthermore, a thiazolylidene was found to be involved in biological systems as an active catalyst by Breslow in 1957.[10]

1.4 Metal carbene complexes

Carbene complexes (M = CR^1R^2) fall into two categories: a) Fischer carbenes; in which carbenes are complexed to a low oxidation state, late transition metal and one or both of the substituents R^1, R^2 are π-donors (the bonding of the carbene ligand is reminiscent to that of CO) and b) Schrock carbenes (described by Schrock as alkylidene complexes), in which carbenes are complexed to a high oxidation state, early transition metal and have an alkyl or hydrogen as substituents R^1, R^2 on the carbene carbon.[26]
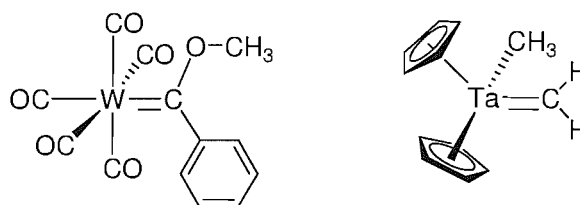
Figure 1.7: Examples of a Fischer[27] and a Schrock[28] carbene

The chemical reactivity of these two classes of carbenes is also different from each other. Fischer-type carbenes bear an electrophilic carbon, whilst Schrock-type carbenes bear a nucleophilic carbon. In either case common carbenes $:CR^1R^2$ (R^1, $R^2 =$ H, alkyl, alkoxy, amino, aryl) are not considered as spectator ligands, as the reactions of metal-carbene complexes proceed either *via* metal-carbon bond cleavage or by transfer of the carbene moiety to one of the substrates.[29]

1.5 Metal NHC complexes

Since NHCs became universal ligands in organometallic and inorganic coordination chemistry, the research interest in this field has dramatically increased and therefore new NHC ligands and NHC complexes are being prepared and reported tactically by research groups from all over the world.

1.5.1 Synthesis of NHCs

Well-established and reliable synthetic routes exist to form imidazolium and imidazolinium salts, the precursors to NHCs. The most widely used methods (Scheme 1.5) for preparing imidazolium salts are: a) one-pot synthesis of symmetrically substituted imidazolium salts, using glyoxal, the desired primary amine and formaldehyde; b) alternative method to (a) for symmetrically substituted salts, using glyoxal and the desired primary amine, followed by the cyclisation of the prepared diimine; c) preparation of a substituted imidazole followed by a quaternisation with a halogenated substrate for forming non-symmetrically substituted imidazolium salts and d) an alternative method for preparing a substituted imidazole, followed by a quaternisation with a halogenated substrate. The available methods for preparing the saturated analogues (imidazolinium salts) are: e) synthesis of symmetrically substituted imidazolinium salts by preparing a bis-ammonium salt (from glyoxal and the required

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amine) that can be then cyclised with the use of orthoformate and f) modification of method (e) for preparing non-symmetrically substituted imidazolinium salts by reacting the required primary amines with ethyl oxalyl chloride.[30]
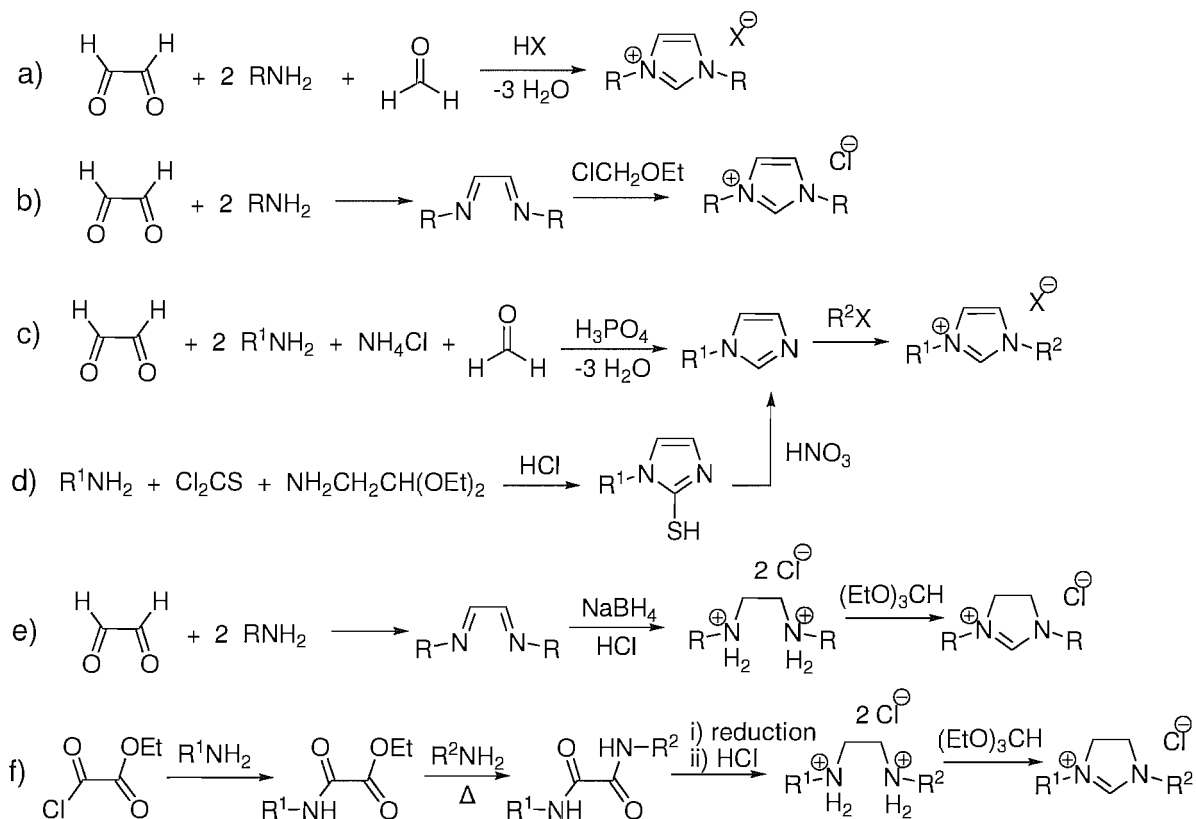
Scheme 1.5: Preparation of imidazolium (**a**, **b**, **c** and **d**) and imidazolinium (**e** and **f**) salts

The free carbenes can be then prepared by the deprotonation of the imidazolium or imidazolinium salt with a base. They are strongly basic (the pK_a value of the conjugate acid of an imidazol-2-ylidene was measured at *ca.* 24 in $(CD_3)_2SO)^{[31]}$ and react with oxygen and water. Therefore, reactions must be performed under a dry, inert atmosphere, avoiding protic solvents or compounds of even moderate acidity. Furthermore, one must also consider the relative stability of the starting materials.

An array of bases and reaction conditions have been tested with varying success and applicability. Success has been principally dependent on the nature of the precursor being deprotonated. Bases that are traditionally used include (but are not limited to): a) sodium or potassium hydride;[32] b) potassium *tert*-butoxide;[33] c) lithium amides;[34] d) alkali metals in liquid ammonia[35] e) metal hexamethyldisilazides.[17c, 36] Other reported methods for preparing NHCs include (but are not limited to): a) desulfurisation of thioureas with molten potassium in boiling THF;[37] b) vacuum pyrolysis, with the removal of neutral volatile by-products;[11, 38] c) electrochemical or chemical reduction[39]

and d) reaction of bis(trimethylsilyl)mercury with chloroiminium or amidinium salts to give a metal free carbene and elemental mercury[40]

It is worth noting that care should be taken when choosing the deprotonating agent, as undesired products obtained by side reactions have been reported.[41]

1.5.2 Tunability of NHCs

The thermal stability and chemical inertness of the metal-carbene bond makes NHC ligands ideal as ancillary anchors in organometallic catalysis.[42] NHCs also have many possibilities for electronic and steric tuning as is shown in Figure 1.8.
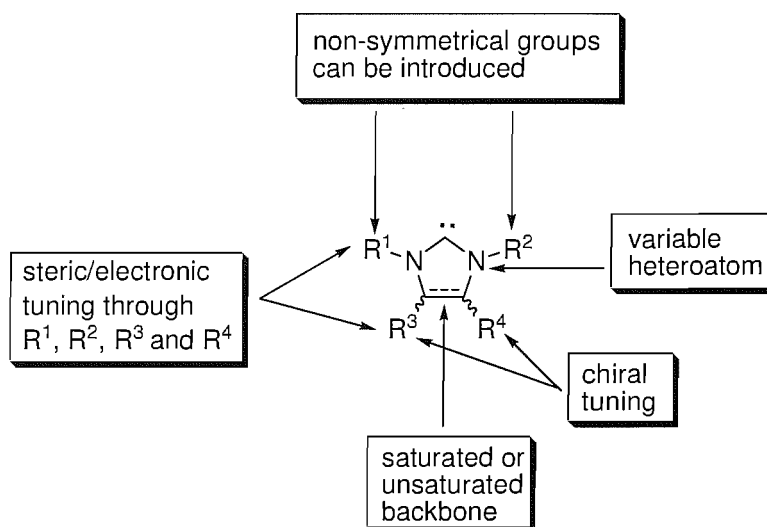
Figure 1.8: Tuning opportunities in NHCs

Variation of the R^1, R^2 substituents on the nitrogen heteroatoms can alter the steric and electronic characteristics around the metal centre. Introduction of electron-donating or electron-withdrawing groups on the backbone (R^3, R^4 substituents) or moving from imidazol-2-ylidenes (unsaturated backbone) to imidazol-2-ylidenes (saturated backbone) the electronic environment of the metal centre can be altered.

In terms of sterics, a monodentate NHC ligand is expected to orientate itself in such a way in order to minimise the steric interference between the ligand and the coordination sphere about the metal. However, depending on the desired application of the NHC ligand in question, sterics can be controlled by the use of sterically demanding substituents R^1 and R^2 or not.

Chiral NHCs (or azolium precursors) have been also synthesised, by either the introduction of chiral substituents R^1, R^2 or, in the case of imidazolin-2-ylidines, introduction of stereogenic centres on the backbone (Figure 1.9).[43]
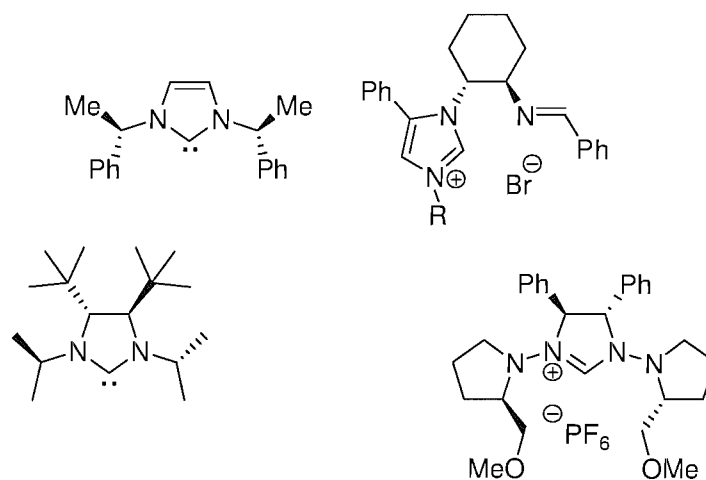
Figure 1.9: Examples of chiral NHCs and azolium precursors

Monodentate NHC complexes do not favour dissociation–association reactions, which are important for the generation of active species in homogeneous catalysis, due to the strength of the metal–NHC bonding. As a result, the use of classical donor ligands as substituents (R^1 and R^2) on the NHCs was employed in order to develop functionalised NHC complexes and to tailor the coordination sphere around the metal centres.[44]

Therefore, bidentate, tridentate and pincer tridentate heterocyclic carbenes have been isolated or introduced to metals after *in situ* generation (Figure 1.10). Such types of carbenes offer a variety of bite angles making carbene ligands even more suitable for homogeneous catalysts.
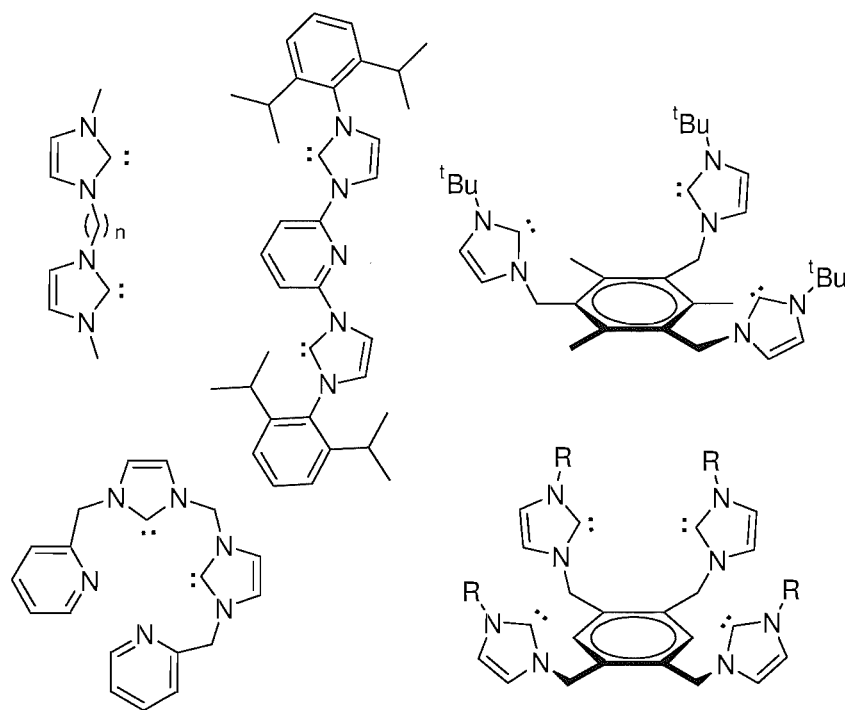
Figure 1.10: Bidentate (n = 1 [45] or 2 [46]), pincer tridentate,[47] tridentate,[48] helical tetradentate[49] and tetradentate[50] NHCs

Ligand hemilability is also possible for an NHC, by the incorporation of labile donors as the substituents R^1 and R^2. These type of ligands are expected to chelate to the metal centre and when electronic and coordinative unsaturation is required, the labile 'sidearm' can depart from the metal centre thus providing a vacant coordination site (Scheme 1.6).[51] The concept of ligand hemilability has gained in popularity and has been widely used in designing new ligand systems for molecular activation, homogeneous catalysis, functional materials, or small-molecule sensing.[52]
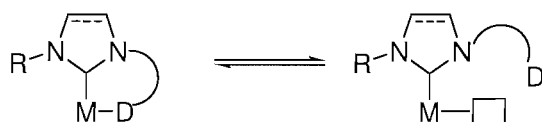
Scheme 1.6: Chelating and non-chelating modes of an NHC ligand

M = metal, D = labile donor group, □ = vacant coordination site

It is only fair to say that all these modification possibilities offered for NHCs make them desirable ligands for stereoelectronic tuning of the metal centres.

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1.5.3 Preparation of NHC complexes

Several synthetic pathways for preparing metal NHC complexes have been developed over the last few years. Amongst these, the most commonly used methods (Scheme 1.7) are: a) reaction of the isolated free carbene with a suitable metal precursor[53] — a simple substitution reaction offering control and eliminating the possibility of base-induced side reactions; b) *in situ* deprotonation of the azolium salt followed by reaction with a metal precursor[54] — again this is a substitution reaction but the possibility of base induced side reactions is higher; c) reaction of the azolium salt with metal amides/alkoxides/hydrides/alkyls/carboxylates[55] and d) transmetallation of the NHC from an appropriate silver NHC precursor[56] — silver carbene bonds are weaker than the product metal carbene bond therefore giving clean and high yielding reactions.
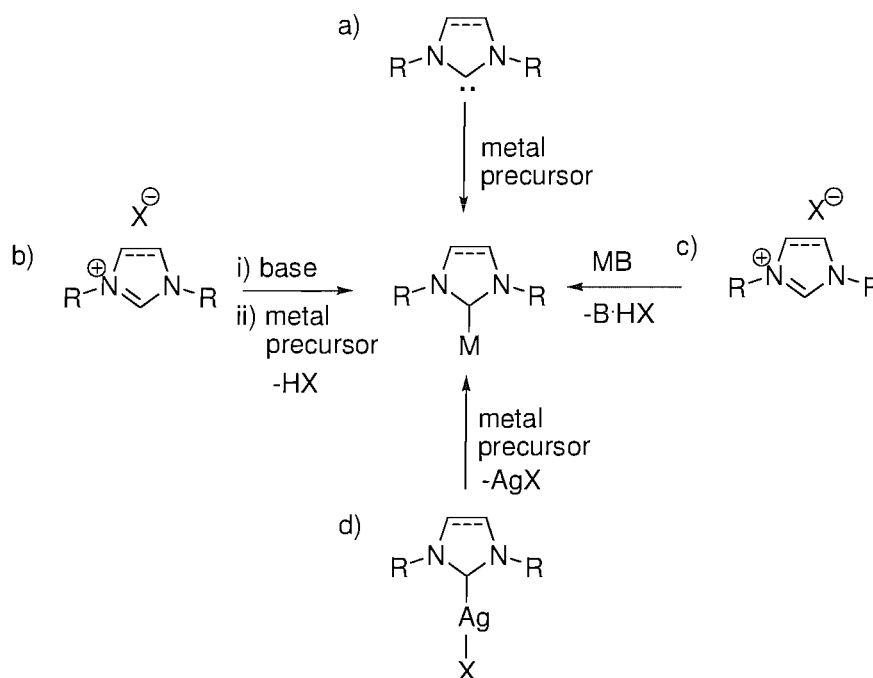
Scheme 1.7: Synthetic methods for NHC metal complexes

(B = amide, alkoxide, hydride, alkyl or carboxylate).

Using the synthetic methods outlined above, many NHC metal complexes have been prepared and characterised. Such is the interest in NHC metal complexes that, following a recent report on technetium NHC complexes,[57] all d-block transition metals have reported NHC complexes. Currently there are several hundred NHC metal complexes reported on the Cambridge Structural Database.[58] Many recent reviews cover this area.[2, 5, 6, 59, 60] Finally, it is worth noting that from the lanthanides and actinides, lanthanum,

14

cerium, samarium, europium, ytterbium and uranium have NHC complexes that have been characterised.[61]
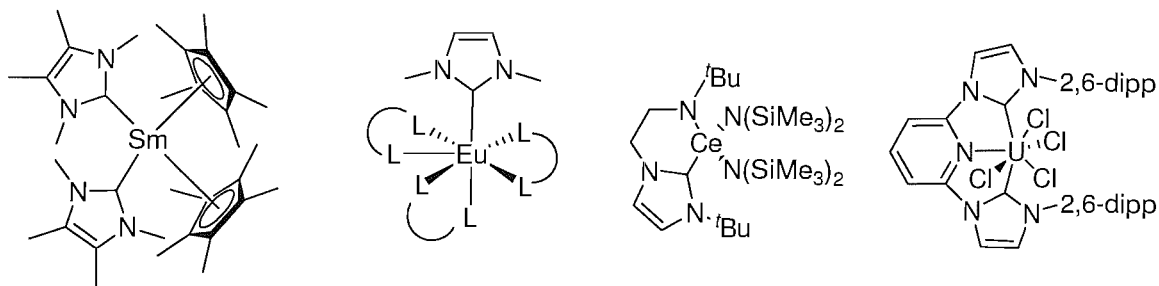
Figure 1.11: Examples of NHC complexes of lanthanides and actinides[61]

(L–L = 2,2,6,6-tetramethyl-3,5-heptanedione)

1.5.4 Electronic properties of NHC complexes

The nature of bonding of NHC ligands to metals is significantly related to the electronic properties of the NHCs. NHC ligands bond to metals primarily through σ-donation of the carbene lone pair to the metal. Although the bonding of the carbene was believed to have been purely σ-donation, recent theoretical and structural evidence suggests that some degree of back donation (depending on the metal in question) may occur.[62] Interestingly, in a recent study[63] it was found that the most frequently used imidazol-2-ylidenes and imidazolin-2-ylidenes 'belong to the more electron-rich C-donors among the congeners hitherto known.'

However, NHC complexes do not fall in any of the two metal carbene categories (Fischer or Schrock type) mentioned before, and this has been also validated by the X-ray single crystal diffraction studies of many NHC complexes. Due to the minimal back bonding present in metal-NHC bonds, the metal-NHC bond length is longer compared to typical carbene-metal bond lengths found in Fischer or Schrock type complexes.[2] Due to their chemical behaviour NHC ligands can be considered as spectator ligands in organometallic catalytic reactions.

1.6 Heck coupling reactions

As briefly mentioned earlier, metal NHC complexes are very good catalysts for an array of synthetic organic reactions. This is because NHC ligands both stabilise and activate metal centres in different catalytic steps of the synthetic reactions, due to their unique coordination chemistry.[5]

NHC transition metal complexes have been reported as excellent catalysts for an array of organic synthesis reactions such as aryl aminations,[64] hydrosilylations,[65] amide α-arylations, [66] olefin metathesis,[67] Sonogashira couplings,[68] hydrogenations and hydroformylations[69] and Heck and Suzuki couplings[70] to name a few, of which olefin metathesis[71] and palladium catalysed coupling reactions[72, 73] being the most important. For example, the substitution of a phosphine with an NHC ligand in the well established Grubbs' first generation catalyst, to give the second generation catalyst (Figure 1.12), gave astonishing improvements in activity for a range of olefin metathesis reactions.[71b]
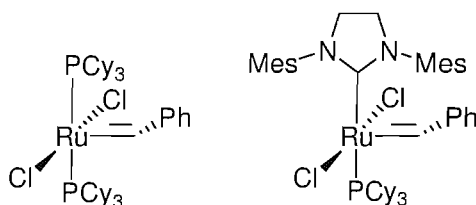
Figure 1.12: Grubbs' first and second generation catalysts

A very important synthetic organic reaction is the Mizoroki-Heck[74, 75] reaction (mostly referred to as Heck reaction). It is a powerful, stereoselective C–C bond forming reaction that has many industrial applications,[76] for example the production of Naproxen™ [77] — a non-steroidal anti-inflammatory drug — that involves a coupling between a brominated naphthalene derivative with ethylene (Scheme 1.8).
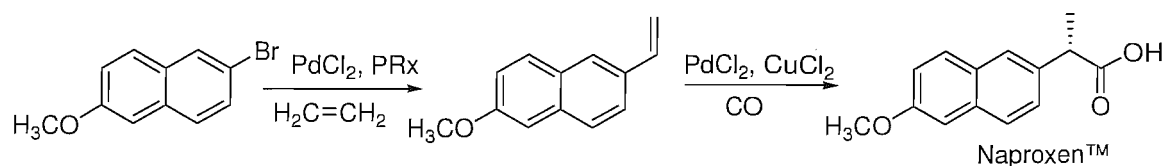
Scheme 1.8: The Heck reaction in the production of Naproxen™ [77]

The Heck reaction is the formation of a new C–C bond between a carbon of an aryl/vinyl reagent and a carbon of an olefin by the reaction of an aryl/vinyl halide (or triflate) with an olefin in the presence of a strong base and a transition metal (most commonly palladium) catalyst, to form a substituted olefin.[78]

Traditionally, phosphine-based catalysts give excellent results in the majority of cases with tris(*tert*-butyl)phosphine being the best catalyst for the Heck reaction of aryl chlorides, including chlorobenzene itself and even deactivated *p*-methoxy-chlorobenzene and *o*-chlorotoluene.[79] On the other hand though, phosphine ligands are expensive, toxic and cannot be recovered, making them a serious economical burden.[80] Additionally, it has been reported that the cleavage of the P–C bond of aryl phosphines at higher temperatures is a major disadvantage of the phosphine ligands.[80] Therefore alternative ligands had to be investigated and NHCs seemed to be perfect candidates since they resemble phosphines in the sense of being strong σ-donors that lack π-acceptor back-bonding properties featuring less steric bulkiness.[81] They differ in one important aspect though: NHC complexes have an extremely strong Pd–C bond and so cleavage is unlikely in solution.[82]

Mono-, bis-, and chelated carbene complexes have been found to be good catalysts in Heck couplings of aryl bromides, with the use of very low catalyst loadings (10^{-4} mol %) and achieve high TON values (100–300 thousands).[80] Furthermore, good yields for the coupling of activated aryl chlorides using NHC complexes (Figure 1.13) have been also reported.[83]
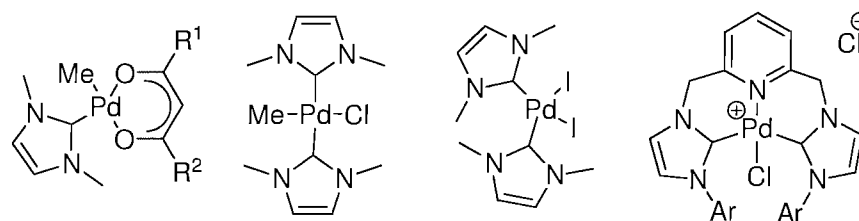
Figure 1.13: Successful NHC precatalysts for coupling activated aryl chlorides

$(R^1$ and R^2 = Me or CF$_3$, Ar = 2,4,6-trimethylphenyl or 2,6-di-*iso*propylphenyl).

It is worth noting that Pd(II) carbene complexes of the type L$_2$PdX$_2$ or (L-L)PdX$_2$ need to be pre-reduced in order to enter the Heck catalytic cycle (Scheme 1.9), while the respective methyl palladium complexes L$_2$Pd(Me)X and Pd(0) carbene complexes enter the reaction without the induction period. The pre-reduction is normally achieved either by external reducing agents (hydrazine or formates) or by using tetraalkylammonium salts.[83b] Modified mechanisms, where X is non-coordinating, but rather an anionic intermediate species is involved, have been also proposed.[84]
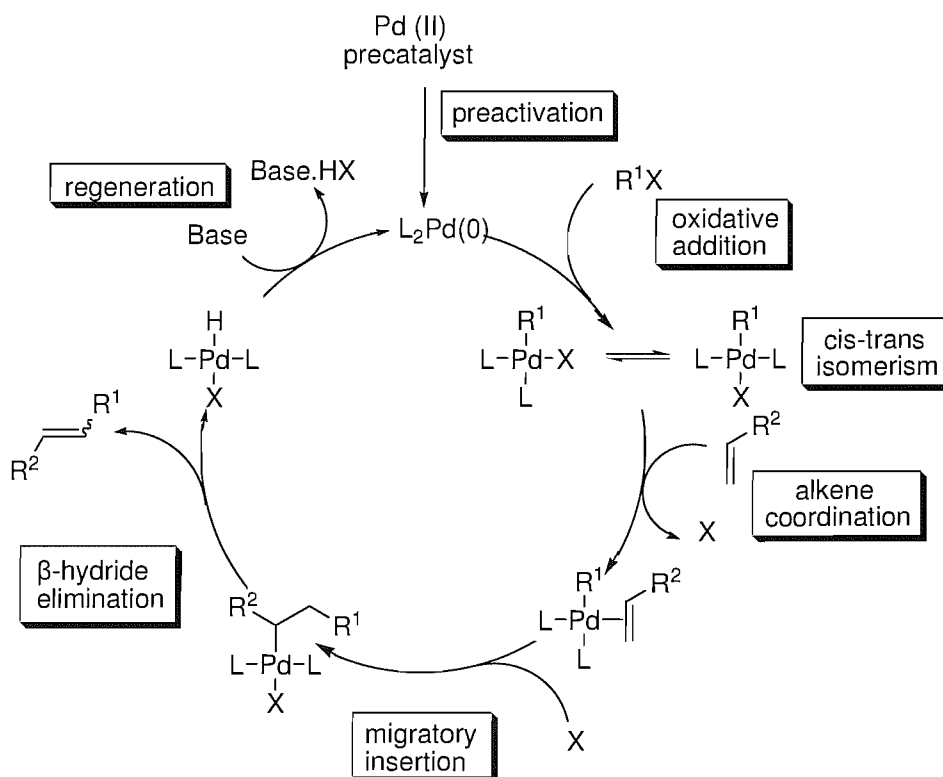
Scheme 1.9: Traditional mechanism of the Heck reaction

$(R^1$ = aryl or vinyl; R^2 = electron withdrawing group; L = NHC ligand; X = I, Br or Cl).

1.7 Background to this project

At the outset of this project, no catalyst had been successful in catalysing the Heck coupling of non-activated aryl chlorides as substrates. Since palladium (imidazol-2-ylidene) complexes have been proved to be good catalysts for the Suzuki coupling of activated aryl chlorides,[83] it was believed that a Pd carbene complex bearing an imidazolin-2-ylidene ligand might have been an active catalyst for this sort of coupling. The proposal was backed by the fact that saturated NHCs (imidazolin-2-ylidenes) are believed to be better σ-donors than the unsaturated analogues (imidazol-2-ylidenes),[85] making the metal centre of the complex more nucleophilic. A nucleophilic metal centre accelerates the oxidative addition of the aryl/vinyl halides in the Heck reaction (Scheme 1.9).

Insertion of the olefin into the metal-aryl bond is favoured by an under-ligated complex, while the β-hydride elimination step is accelerated by an over-ligated complex. Therefore these present different ligand requirements. A possible solution for this problem is the use of hemi-labile ligands *i.e.* able to coordinate on the metal centre of the complex only when desired (offering an over-ligated species able to accelerate the hydride elimination step), while remaining un-coordinated at other times (under-ligated species able to accelerate the olefin insertion on the metal centre). This way, the sterics of the cycle can be kept under control and make the contradicting steps to work in favour of the reaction. The choice of the nature of the 'classical' donor is very crucial permitting alkene coordination and coordinating after the insertion step. Bite angle effects may also influence the dynamic behaviour of a hemilabile ligand.

1.8 Aims

Although imidazol-2-ylidenes have been widely used in the past by many research groups around the globe, their saturated analogues, imidazolin-2-ylidenes, have not been studied as much. Since our interest was the development of a Heck coupling catalysts bearing imidazolin-2-ylidenes as ligands, the targets set for this project were:

a) The development of successful synthetic routes for preparing pyridine functionalised imidazolinium salts.

b) The synthesis of a preligand library consisting of pyridine, aryl, alkoxyphenyl, fluoro-phenyl and trifluoromethylphenyl functionalised imidazolinium salts based on the guidelines outlined earlier.

c) The complexation of the carbenes of the prepared pre-ligands to palladium and other platinum group metals.

d) The catalytic study of the prepared palladium complexes in Heck coupling reactions, while rhodium and iridium complexes were tested in olefin hydroformylation reactions, olefin molecular hydrogenation reactions and transfer hydrogenation reactions of carbonyl compounds. Nickel NHC complexes were tested as catalysts in norbornene polymerisations.

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Chapter 2:

Imidazolium and

Imidazolinium salts

2.1 Introduction

It has been almost 40 years since pioneers Öfele[1] and Wanzlick[2] prepared the first *N*-heterocyclic carbene metal complexes. But it was not until Arduengo[3] isolated and crystallised the first free *N*-heterocyclic carbene, in 1991, that the research interest in NHCs was reignited. Arduengo's paper was just the prelude to a vast amount of publications that followed,[4] proving the importance of NHCs in several catalytic reactions.

The strong binding and low reactivity[5] of NHCs make them ideal ligands for complexes to be used in homogeneous catalytic reactions and possible alternatives for the widely used phosphine ligands.[6] Although NHCs have been referred to as 'phosphine mimics', because of the striking similarity with the trialkylphosphines (PR$_3$) in terms of their σ-donating ability on coordination to the metal,[7] they present more attractive features. They are versatile, easy to prepare and easily tuneable ligands and have great potential when used (once co-ordinated to transition metal centres) in homogeneous catalysis.[4a]

The most easily available NHCs are the imidazole derived carbenes, the main reason being that numerous imidazolium precursor compounds can be made along various reliable routes, like the one-pot synthesis of symmetrically substituted imidazolium salts, using glyoxal, the desired primary amine and formaldehyde.[4a] This and other synthetic routes for the preparation of imidazolium and imidazolinium salts have been covered briefly in Chapter 1.

In the case of functionalised NHCs, the strong spectator ligand characteristics of the NHCs and the control over the coordination environment of the metal, provided by the hemilability of the other 'classical' heteroatom donors, could give rise to stabilised catalytic centres, while creating a degree of coordinative and electronic unsaturation. Therefore, mixed donor carbene complexes have been targeted and successfully synthesised by former members of the group[8] and other groups worldwide.[9]

First generation   Second generation
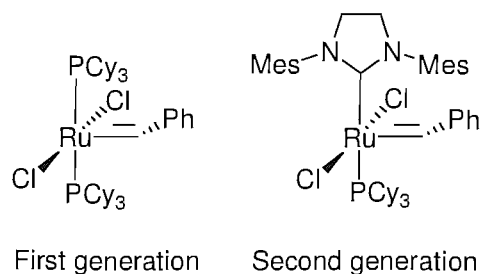
Figure 2.1: Grubbs' first and second generation catalysts[10]

On the other hand, aryl substituted NHCs offer steric bulk and possible chirality and extensive studies on the catalytic performance of NHC metal complexes bearing such ligands, have helped the scientific community to realise the advantages that NHC ligands have over classic phosphine ligands. Grubbs for example, replaced one phosphine ligand in a ruthenium alkylidene complex (known as first generation Grubbs catalyst) with a saturated aryl substituted NHC to synthesise a far better catalyst (known as second generation Grubbs catalyst) for olefin metathesis reactions (both catalysts are shown in Figure 2.1).[10]

Pyridine functionalised NHCs have also already been investigated and the catalytic testing of complexes involving such ligands showed that such systems are very promising.[11] Many such NHC ligands have been synthesised by former and current members of the group[12] and therefore an ongoing investigation and scientific interest is present from our part, in such functionalised NHCs. However, alkoxyphenyl functionalised NHCs is a relatively unexplored field and it is believed that such ligand moieties (when coordinated on metals) could provide a stronger σ-donation to the metal centre compared to aryl substituted NHCs, since alkoxy groups are electron donors and tend to provide electron density towards the heterocycle. This stronger σ-donation might in turn affect the catalytic performance of such NHC metal complexes.

In an effort to further investigate the effects that NHC substituents have on catalytic reactions (when complexes bearing such ligands are used as catalysts), a range of pyridyl and alkoxyphenyl functionalised imidazol(in)-2-ylidenes along with aryl substituted imidazol(in)-2-ylidenes have been targeted.
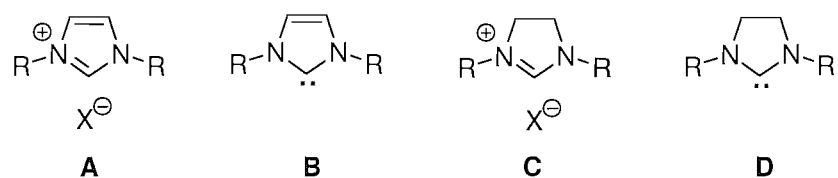
Figure 2.2: NHC precursors and free NHCs

R = pyridyl or aryl or alkoxyphenyl or fluorinated aryl

In this chapter the synthesis and characterisation of a range of imidazolium (**A**, Figure 2.2) and imidazolinium salts (**C**), the precursors to imidazol-2-ylidenes (**B**) and imidazolin-2-ylidenes (**D**) respectively, are described. Furthermore, the synthesis and isolation of two imidazol-2-ylidenes is described.

2.2 Results and Discussion

The novel pyridyl functionalised imidazolium salts, and the novel pyridyl, alkoxyphenyl, aryl, trifluoromethylphenyl and fluorophenyl functionalised imidazolinium salts that have been synthesised are shown in Figure 2.3.
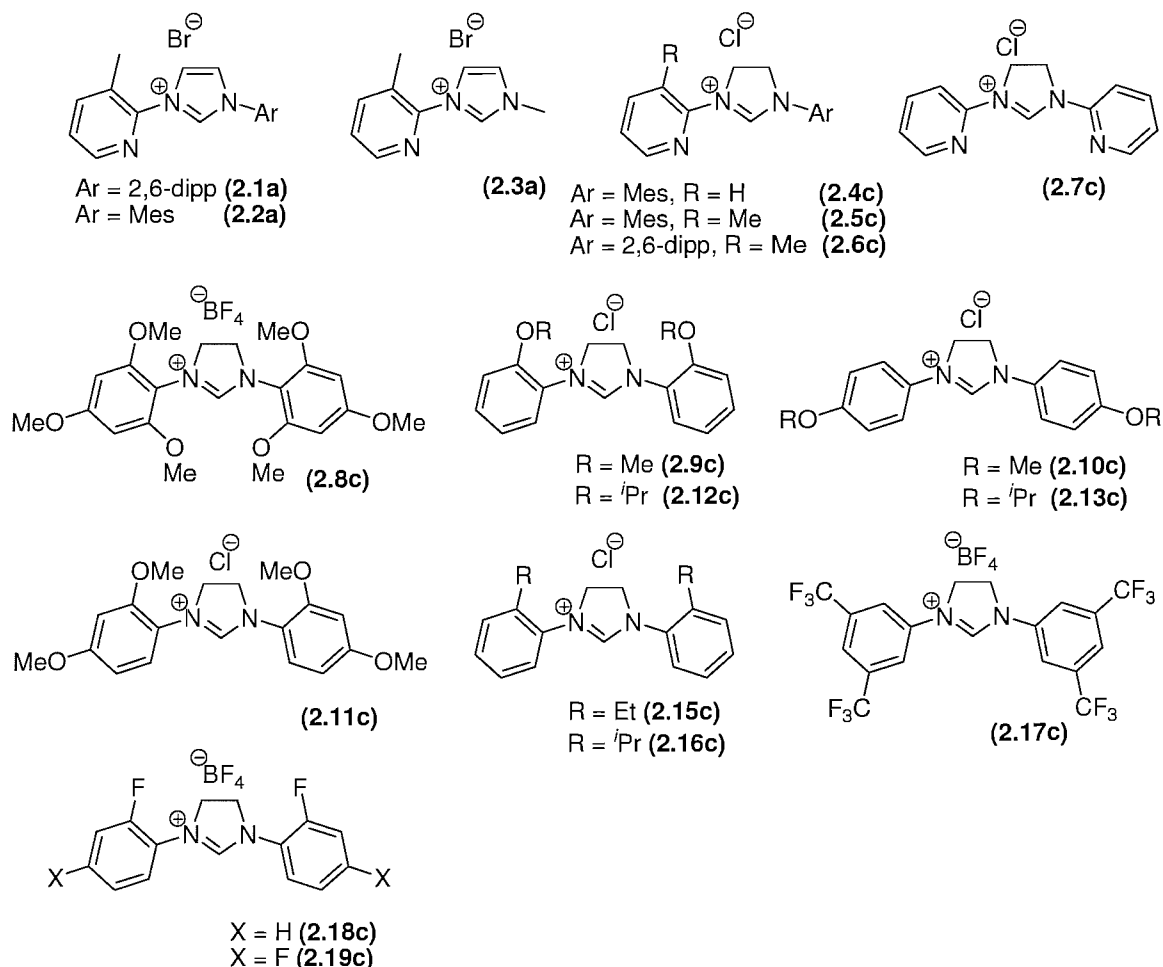
Figure 2.3: Novel imidazolium and imidazolinium salts

2.2.1 Pyridyl functionalised imidazolium salts and carbenes

Pyridyl-NHC metal complexes (Figure 2.4) that have been prepared by former members of the group featured unexpected binding.[13] In particular, in one case C–H activation took place and therefore the pyridine ring was not co-ordinated on the metal *via* the nitrogen but *via* a carbon, giving rise to an Ir(III) complex. In the other case the pyridine remained uncoordinated, but there was a close contact between the Rh centre and one of the hydrogens of the pyridine ring.
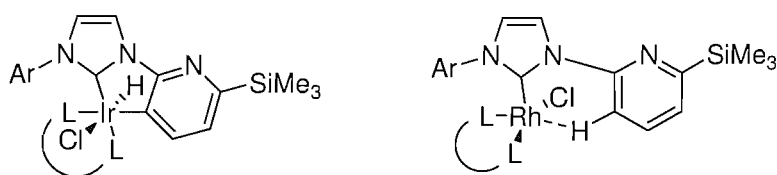
Figure 2.4: Reported NHC complexes featuring unexpected binding

(Ar = 2,6-diisopropylphenyl, L-L = η^4-cycloocta-1,5-diene) [13]

Therefore, in an effort to avoid this type of interactions or C–H activations and study the effect of the nature of the pyridine ring substituents on the electronic properties of the pyridyl functionalised NHC ligands, two analogues bearing a 3-methyl substituted pyridine ring were synthesised. Although there is a selection of methods for synthesising imidazolium salts (covered in Chapter 1), for these salts the quaternisation as a melt was chosen since it has been successful with most of the imidazolium salts prepared previously in the group.[14]

Ar = 2,6-dipp **(2.1a)** 96%   Ar = 2,6-dipp **(2.1b)** 76%
Ar = Mes   **(2.2a)** 95%   Ar = Mes   **(2.2b)** 78%
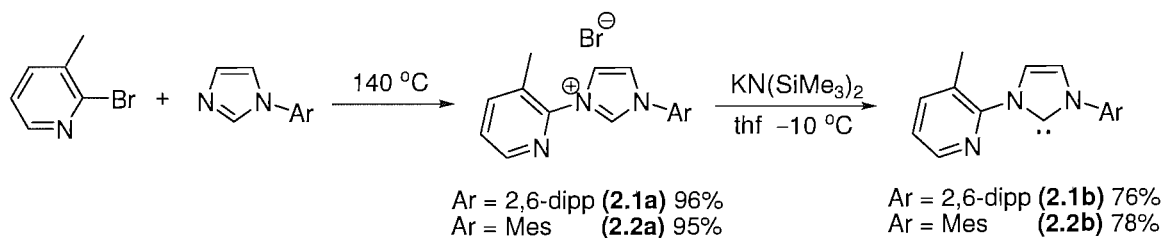
Scheme 2.1: Synthesis of imidazolium salts **2.1a**, **2.2a** and the related carbenes **2.1b**, **2.2b**

Following the general method described previously[12a] the imidazolium salts **2.1a** and **2.2a** (Scheme 2.1) were then deprotonated using KN(SiMe₃)₂ to give high yields of the

free pyridyl functionalised NHCs (**2.1b** and **2.2b**), which were characterised by spectroscopic, analytical and — in the case of **2.1b** — diffraction methods. A diagram of the free carbene molecule is given in Figure 2.5; this can be compared with the structure of the unsubstituted pyridine analogue that was synthesised by past members of the group.[12e] Both ligands show very similar metrical data with almost anti-arrangement of the pyridine and the NHC lone pairs [the average dihedral angle between the aromatic rings is 21° for the methyl substituted pyridyl NHC and 18.5° for the unsubstituted pyridyl NHC].[15]
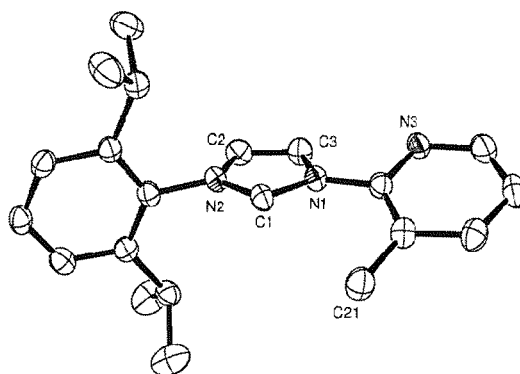
Figure 2.5: ORTEP representation of the structure of **2.1b** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: N1–C1: 1.381(4), N1–C3: 1.391(4), N2–C1: 1.357(4), C2–C3: 1.330(4).

A less sterically demanding imidazolium salt (**2.3a**) was also synthesised by following a similar procedure as with compounds **2.1a** and **2.2a** using 1-methyl-1H-imidazole as shown in Scheme 2.2 below. The preparation of the free carbene of **2.3a** was not attempted since it was not directly involved in the current project.

(**2.3a**) 92%
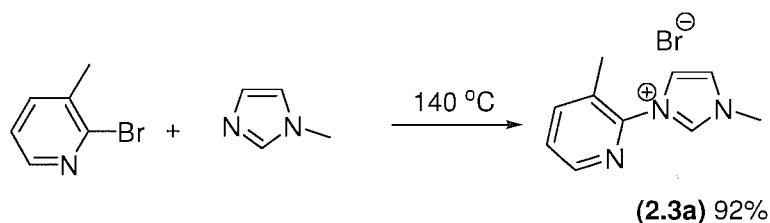
Scheme 2.2: Synthesis of imidazolium salt **2.3a**

2.2.2 Pyridyl functionalised imidazolinium salts

Saturated NHCs are considered to be better σ-donors compared to the more widely used unsaturated NHCs,[16] and therefore, when coordinated to a metal, make the metal centre of the complex more nucleophilic. This in turn might affect the catalytic properties of the complex, making it a better catalyst.

The preparation of non-symmetrically substituted imidazolinium salts has been a relatively unexplored area with the exception to a recent paper by Grubbs[17] dealing with o-hydroxylaryl substituted NHCs that provides a 'versatile synthetic method for the preparation of NHC ligands with nearly any substitution pattern imaginable.' Based on Grubbs' guidelines some new methods have been developed, each providing a useful synthetic route for different types of imidazolinium salts.

We have developed a different synthetic strategy based on Pd(0) (synthesised in situ[18]) catalysed aminations. Amination of 2-bromopyridine with N-(2,4,6-trimethylphenyl)ethylene diamine (**2.4a**),[19] produced the diamine **2.4b** (Scheme 2.3), while amination with 2-bromo-3-methylpyridine gave diamine **2.5b**. The aminations were highly selective (>98%) and gave good yields (60–70%). The diamine **2.6b** was synthesised following the same method using 2-bromo-3-methylpyridine and N-(2,6-diisopropylphenyl)ethylene-diamine (**2.6a**).[19]
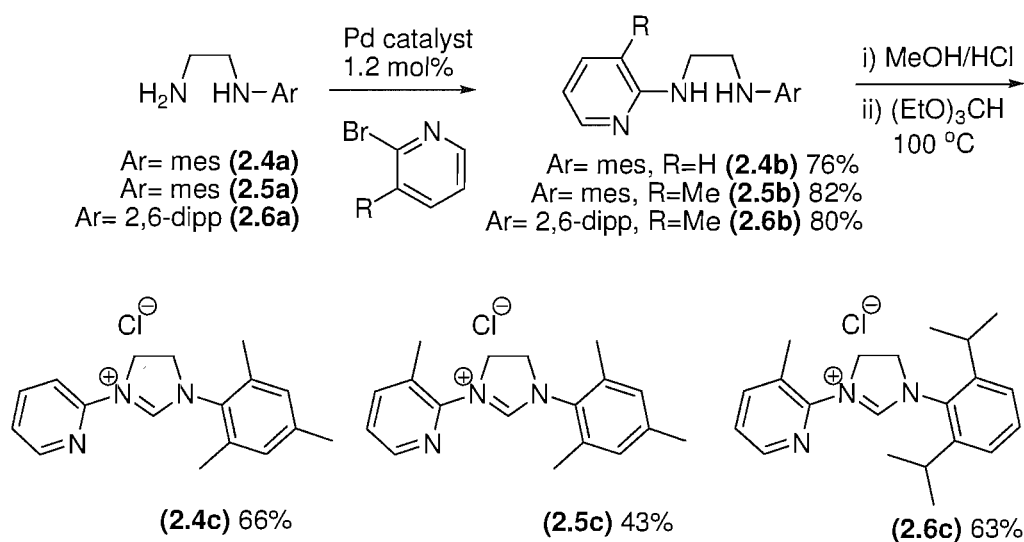
Scheme 2.3: Synthesis of pyridyl functionalised imidazolinium salts **2.4c–2.6c**

We have also adopted the method published by Grubbs[17] for the synthesis of the pyridyl functionalised imidazolinium salts **2.4c**, **2.5c** and **2.6c** in low yields. However, the yields can be noticeably increased by following a more detailed method reported by Hoveyda and co-workers.[20] The overall yields of these three pyridyl functionalised imidazolinium salts are moderate due to the limiting yields of the cyclisation step.

On the other hand, symmetrically substituted imidazolinium salts can be prepared much more easily, using fewer synthetic steps and provide higher total yields, when compared to the non-symmetrically substituted imidazolinium salts.

N,*N*'-Bis(2-pyridyl)oxalamide **2.7a** was prepared by reacting 2-aminopyridine with oxalyl chloride in the presence of triethylamine (Scheme 2.4). Reduction of **2.7a** with LiAlH₄ followed by acidification in methanol gives *N*,*N*'-bis(2-pyridyl)ethylene bis(ammonium) dichloride **2.7b**. This was then heated in neat triethyl orthoformate with catalytic amounts of formic acid[21] to give imidazolinium salt **2.7c** in good yield.
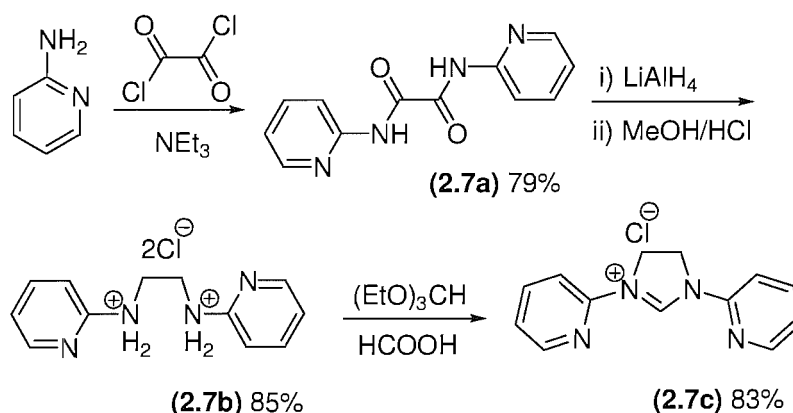
Scheme 2.4: Synthesis of bis(2-pyridyl) functionalised imidazolinium salt **2.7c**

2.2.3 Alkoxy-phenyl functionalised imidazolinium salts

Alkoxy groups tend to donate electron density to the aromatic rings, which in turn provide the electron density to the heterocycle and can promote ligand hemilability. Alkoxyphenyl functionalised NHCs (when coordinated on metals) will probably provide a stronger σ-donation to the metal centre, compared to aryl substituted NHCs, and therefore making the metal centre more nucleophilic. This in turn, might have a beneficial effect on the catalytic activity of such metal complexes. Therefore, a series of alkoxyphenyl functionalised imidazolinium salts was prepared.

2,4,6-Trimethoxyaniline[22] was reacted with oxalyl chloride to synthesise oxalamide **2.8a** which was reduced to the corresponding diamine **2.8b**. The desired imidazolinium salt **2.8c** was then prepared by the cyclisation of the diamine[23] using triethyl orthoformate in the presence of equivalent amounts of ammonium tetrafluoroborate.
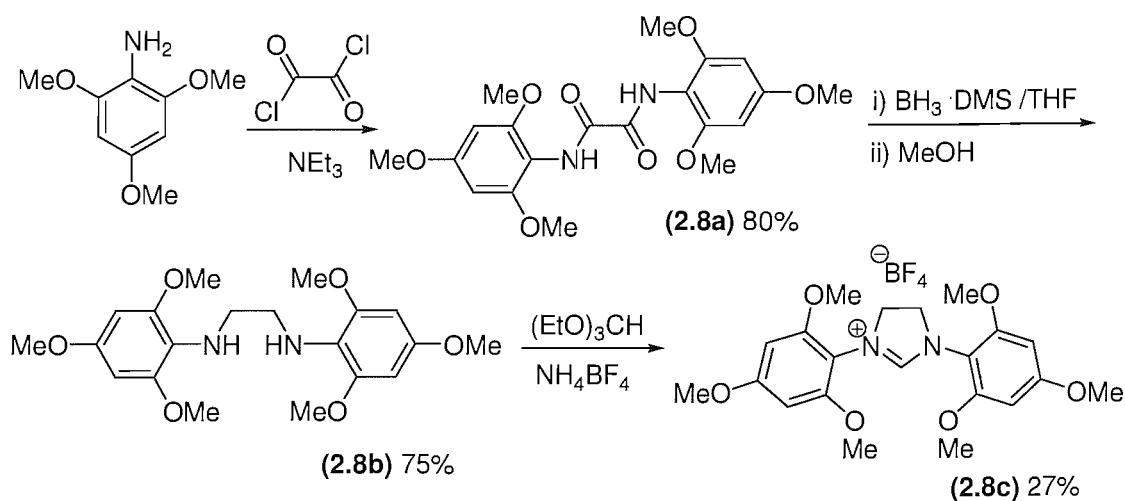
Scheme 2.5: Synthesis of 2,4,6-trimethoxyphenyl functionalised imidazolinium salt **2.8c**

Since imidazolinium salt **2.8c** was almost insoluble in all common deuterated solvents, only ^{1}H NMR data could be collected. On the other hand, the identity of the compound was confirmed by X-ray crystallography (Figure 2.6), high resolution mass spectrometry and elemental analysis.
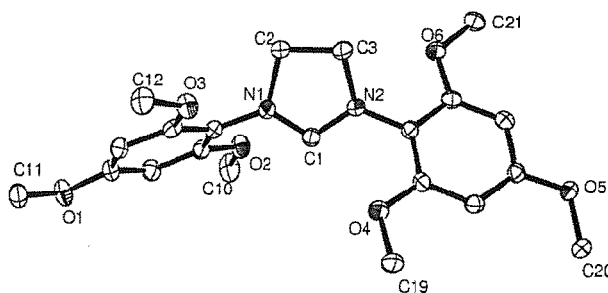
Figure 2.6: ORTEP representation of the structure of **2.8c** showing 50% probability ellipsoids. H atoms and a [BF$_4$]$^-$ molecule are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: C1–N2: 1.315(4), C1–N1: 1.324(4), C2–C3: 1.526(4), C18–O6: 1.362(3), C19–O4: 1.437(3), C20–O5: 1.427(3),

C9–O3: 1.364(3), C10–O2: 1.432(4), C11–O1: 1.435(4), N2–C1–N1: 112.8(3), N1–C2–C3: 102.8(2), N2–C3–C2: 102.6(2), C7–O1–C11: 116.6(2), C5–O2–C10: 116.6(2), C9–O3–C12: 117.3(2), C14–O4–C19: 117.1(2), C16–O5–C20: 117.4(2), C18–O6–C21: 117.6(2).

As it is portrayed in Figure 2.6, one of the phenyl rings is perpendicular to the plane formed by the heterocycle and the other phenyl ring. All four *ortho* positioned methoxy groups are pointing away from the heterocyclic ring in order to avoid steric congestion.

Slight modifications of some of the steps were found to be necessary in order to increase the total yield of the method. As a result, LiAlH$_4$ was used as a reducing agent and the acidification of the diamine prior the cyclisation was found to be necessary. The modified synthetic route, outlined in Scheme 2.6, was found to produce higher yields and be less time consuming.

R_1 = OMe, R_2 = H, R_3 = H (**2.9a**) 81%
R_1 = H, R_2 = OMe, R_3 = H (**2.10a**) 83%
R_1 = OMe, R_2 = OMe, R_3 = H (**2.11a**) 83%
R_1 = O^{i}Pr, R_2 = H, R_3 = H (**2.12a**) 85%
R_1 = H, R_2 = O^{i}Pr, R_3 = H (**2.13a**) 83%
R_1 = OMe, R_2 = OMe, R_3 = OMe (**2.14a**) 80%

R_1 = OMe, R_2 = H, R_3 = H (**2.9b**) 85%
R_1 = H, R_2 = OMe, R_3 = H (**2.10b**) 85%
R_1 = OMe, R_2 = OMe, R_3 = H (**2.11b**) 81%
R_1 = O^{i}Pr, R_2 = H, R_3 = H (**2.12b**) 85%
R_1 = H, R_2 = O^{i}Pr, R_3 = H (**2.13b**) 84%
R_1 = OMe, R_2 = OMe, R_3 = OMe (**2.14b**) 75%

R_1 = OMe, R_2 = H, R_3 = H (**2.9c**) 86%
R_1 = H, R_2 = OMe, R_3 = H (**2.10c**) 91%
R_1 = OMe, R_2 = OMe, R_3 = H (**2.11c**) 92%
R_1 = O^{i}Pr, R_2 = H, R_3 = H (**2.12c**) 90%
R_1 = H, R_2 = O^{i}Pr, R_3 = H (**2.13c**) 93%
R_1 = OMe, R_2 = OMe, R_3 = OMe (**2.14c**) 83%

Scheme 2.6: Synthesis of alkoxyphenyl functionalised imidazolinium salts **2.9c–2.14c**

As shown in Scheme 2.6 the corresponding anilines were reacted with oxalyl chloride in the presence of NEt₃ as the base, to synthesise the bis-amides **2.9a–2.14a**. These reactions gave yields of around 70%, while the rest of the steps gave a total yield of around 85%. Most of the prepared bis-amide compounds were almost insoluble in all common deuterated solvents and therefore ¹³C NMR data could not be collected. However, analytical and diffraction methods were employed for characterisation. The molecular structures of **2.9a** and **2.11a** are portrayed in Figure 2.7 and Figure 2.8 respectively.
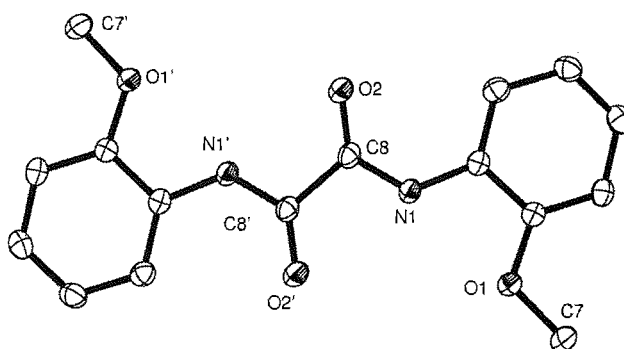
Figure 2.7: ORTEP representation of the structure of **2.9a** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: C8–O2: 1.2247(12), C8–N1: 1.3430(12), C8–C8': 1.541(2), C6–O1: 1.3687(12), C7–O1: 1.4287(13), C1–N1: 1.4055(12), C8–N1–C1: 129.08(8), C6–O1–C7: 116.92(8).
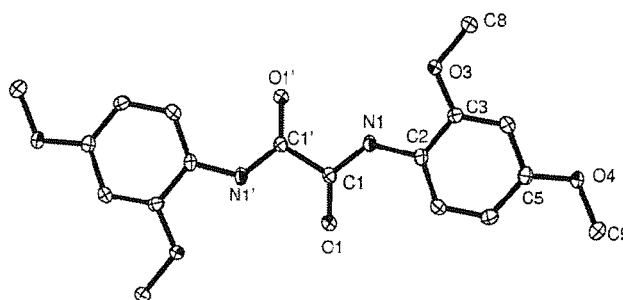
Figure 2.8: ORTEP representation of the structure of **2.11a** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: O1–C1: 1.228(2), O3–C3: 1.368(2), O3–C8: 1.431(2), O4–C5: 1.364(2), O4–C9: 1.434(2), N1–C1: 1.346(2), N1–C2: 1.416(2), C1–C1':

1.536(4), C3–O3–C8: 116.17(14), C5–O4–C9: 116.73(15), C1–N1–C2: 128.10(16), O1–C1–N1: 127.42(17), O1–C1–C1': 121.6(2), N1–C1–C1': 110.97(19).

Both **2.9a** and **2.11a** are planar and symmetric molecules, bearing a vertical C_2 axis between C8 and C8' for compound **2.9a** (Figure 2.7) or C1 and C1' for compound **2.11a** (Figure 2.8). All bond lengths and angles are within the expected ranges.

The bis-amides were then reduced to the diamines (which were not isolated) using LiAlH$_4$ and these were reacted with acid to make the bis-ammonium salts, that were easily cyclised to the corresponding imidazolinium salts **2.9c–2.14c** by refluxing them in triethyl orthoformate with catalytic amounts of formic acid.[21] All imidazolinium salts, being hydroscopic, were dried azeotropically before storing in a glovebox to avoid exposure to moisture.

X-ray diffraction quality crystals of 1,3-bis(2-isopropoxyphenyl)imidazolinium chloride (**2.12c**) were obtained by the slow solvent evaporation of an aqueous solution of the salt. The cation of the molecule (shown in Figure 2.9) is almost planar and all bond lengths and angles are within the expected ranges. The methyl groups of each of the two isopropyl groups are positioned one above and one below the plane of the molecule.
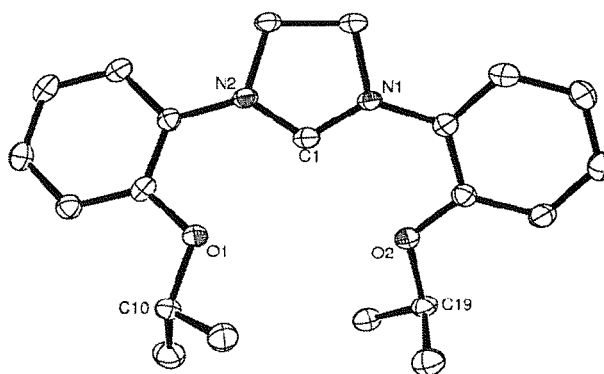
Figure 2.9: ORTEP representation of the structure of **2.12c** showing 50% probability ellipsoids. H atoms, three water molecules and a chloride anion are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: O1–C9: 1.369(2), O1–C10: 1.460(2), O2–C18: 1.366(2), O2–C19: 1.464(2), N1–C1: 1.321(2), N1–C13: 1.424(2), N1–C2: 1.483(2), N2–C1: 1.323(2), N2–C4: 1.425(2), N2–C3: 1.484(2), C2–C3: 1.521(3), N1–C1–N2: 113.46(15), C9–O1–C10: 118.18(14), C18–O2–

C19: 119.10(14), C1–N1–C13: 128.87(14), C1–N1–C2: 109.60(14), C13–N1–C2: 120.99(14), C1–N2–C4: 128.88(15), C1–N2–C3: 109.52(14), C4–N2–C3: 120.92(14).

2.2.4 Aryl-substituted imidazolinium salts

Aryl-substituted imidazol-2-ylidene ligands (bearing an unsaturated backbone) were first investigated some years ago,[24] but imidazolin-2-ylidenes have been preferred in many applications (e.g. second generation Grubb's catalyst[24b] shown in Figure 2.1). A recent extensive study[25] of aryl substituted imidazol-2-ylidenes and imidazolin-2-ylidenes as ligands in ring opening metathesis polymerisation of cyclooctene, outlined the preparation of their precursors, the imidazolium and imidazolinium salts. Following the reported synthetic method[25] (shown in Scheme 2.7) two new *ortho* substituted aryl substituted imidazolinium salts (**2.15c** and **2.16c**) have been synthesised.
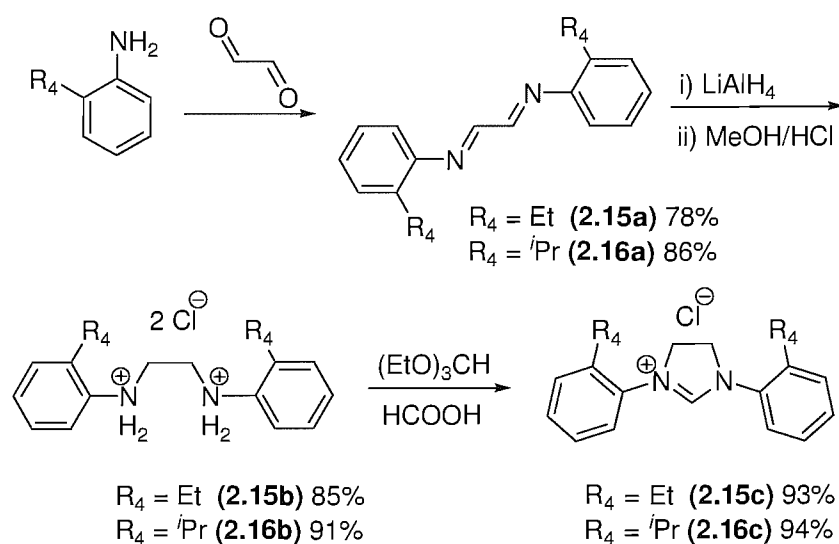
Scheme 2.7: Synthesis of aryl substituted imidazolinium salts **2.15c** and **2.16c**

2.2.5 Fluorinated-aryl functionalised imidazolinium salts

1,3-Bis[3,5-bis(trifluoromethyl)phenyl]imidazolinium tetrafluoroborate (**2.17c** in Scheme 2.8) was synthesised by using a similar synthetic method as outlined earlier in Scheme 2.6.
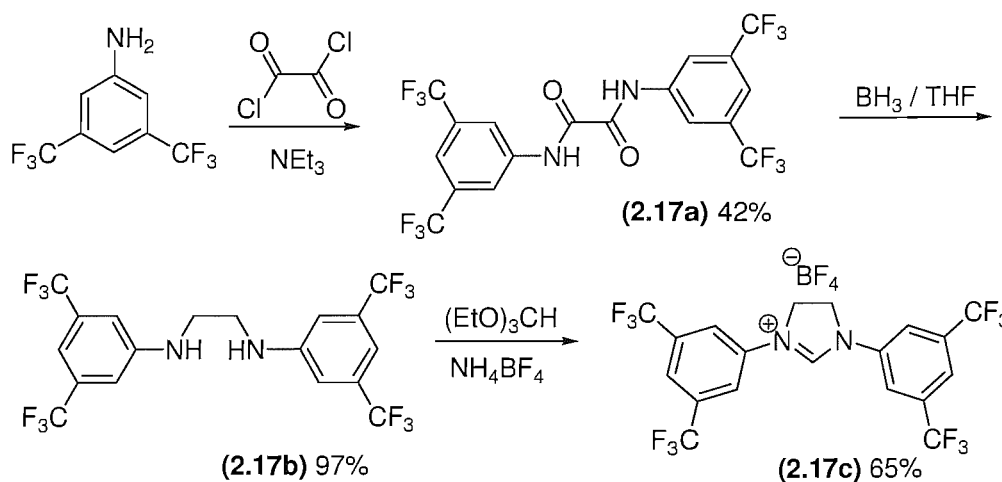
Scheme 2.8: Synthesis of trifluoromethylphenyl functionalised imidazolinium salt **2.17c**

A milder reducing agent ($BH_3 \cdot THF$) was selected for the reduction of the bis-amide **2.17a** since $LiAlH_4$ that was used for other bis-amides (**2.9a–2.14a**), was found[26] to react with trifluoromethyl substituted aromatic rings. Diamine **2.17b** was then heated along with stoichiometric quantities of NH_4BF_4 at 100 °C in neat triethyl orthoformate to give the desired imidazolinium tetrafluoro borate **2.17c** in good yield. The molecular structure of the cation of the salt is shown in Figure 2.10.
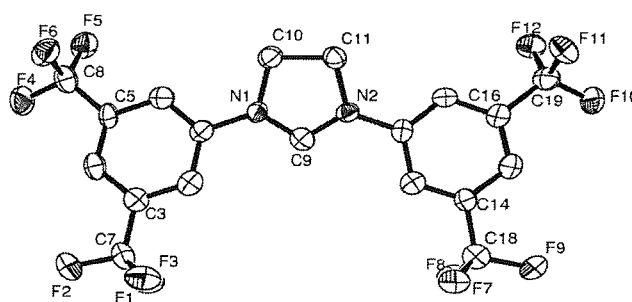
Figure 2.10: ORTEP representation of the structure of **2.17c** showing 50% probability ellipsoids. H atoms and a $[BF_4]^-$ molecule are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: C9–N2: 1.302(9), C9–N1: 1.312(9), C7–F2: 1.321(9), C7–F1: 1.335(9), C7–F3: 1.340(9), C8–F5: 1.334(9), C8–F4:

41

1.339(9), C8–F6: 1.363(9), N2–C9–N1: 114.2(6), F2–C7–F1: 107.4(7), F2–C7–F3: 106.2(7), F1–C7–F3: 105.6(7).

The cation of **2.17c** (shown in Figure 2.10) is not planar. The angle between the plane of the aromatic ring (connected through N1) and the plane of the heterocycle is 20.5 °, while the angle between the plane of the other aromatic ring (connected through N2) and the plane of the heterocycle is 16.3 °. All bond lengths and angles are within the expected ranges.

Furthermore, 1,3-bis(2-fluorophenyl)imidazolinium tetrafluoroborate (**2.18c**) and 1,3-bis(2,4-difluorophenyl)imidazolinium tetrafluoroborate (**2.19c**) were prepared by following similar methodology (Scheme 2.9). In these cases, LiAlH₄ was used for the reduction of the bis-amides (**2.18a** and **2.19a**). The molecular structure of the cation of **2.19c** is shown in Figure 2.11.

X= H (**2.18a**) 78%
X= F (**2.19a**) 83%

X= H (**2.18b**) 87%
X= F (**2.19b**) 97%

X= H (**2.18c**) 53%
X= F (**2.19c**) 61%
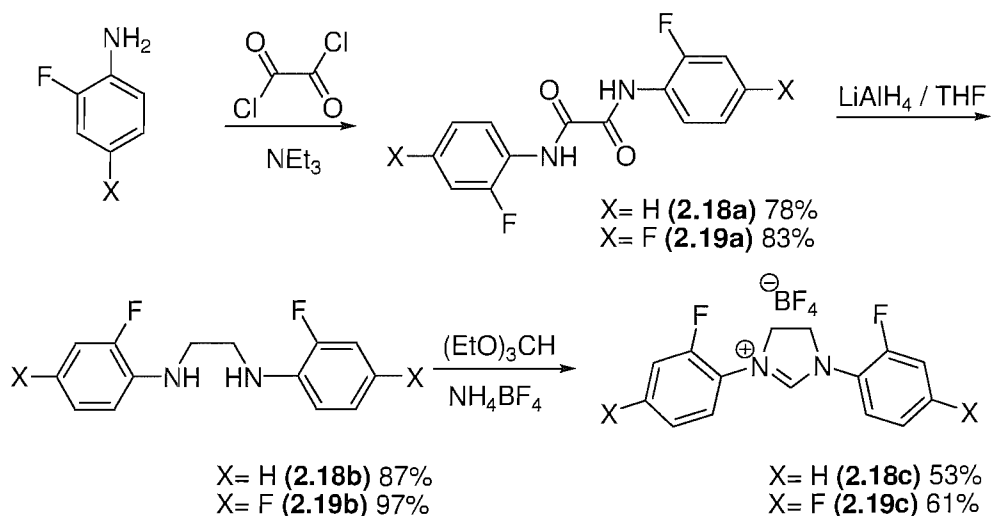
Scheme 2.9: Synthesis of fluorophenyl functionalised imidazolinium salts **2.18c** and **2.19c**
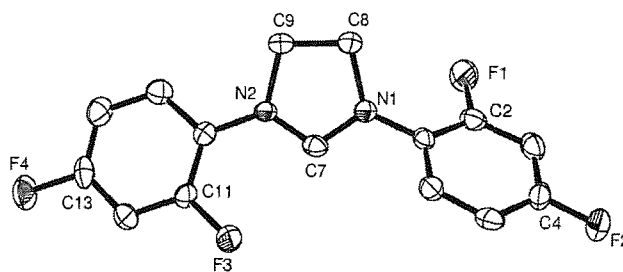
Figure 2.11: ORTEP representation of the structure of **2.19c** showing 50% probability ellipsoids. H atoms and a $[BF_4]^-$ molecule are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: C7–N1: 1.315(5), C7–N2: 1.315(5), C2–F1: 1.345(4), C4–F2: 1.353(4), C11–F3: 1.348(4), C13–F4: 1.358(4), N1–C7–N2: 113.3(3).

The cation of **2.19c** (shown in Figure 2.11) has all bond lengths and angles lying within the expected ranges. The *ortho* positioned fluorine atoms point to almost opposite directions to each other, in order to eliminate electronic and steric repulsions. The angle between the plane of the aromatic ring (connected through N2) and the plane of the heterocycle is 17.8 °, while the angle between the plane of the aromatic ring (connected through N1) and the plane of the heterocycle is 52.9 °.

Although the majority of the imidazolinium salts prepared in this chapter are soluble in water, all three fluorinated imidazolinium tetrafluoroborates (**2.17c**, **2.18c** and **2.19c**) are not, due to the lipophilic groups (-F and $-CF_3$) present. Furthermore they are insoluble in the majority of common solvents with the exception of acetone.

2.3 NMR Spectroscopy

The identity of the imidazolium or imidazolinium salts was confirmed by the presence of the acidic imidazol(in)ium proton of each of the compounds in the ^{1}H-NMR spectra. Depending on the nature of the salt (saturated or unsaturated backbone and functional groups present) and the solvent used, the characteristic peak of the proton appears in the region approximately between 8 and 11 ppm. In the majority of literature cases[12e, 14, 20, 23a, 27] this appears as a singlet, but some exceptions have also been reported.[12e] The ^{13}C{^{1}H}-NMR spectra of the salts also support the formation of the imidazol(in)ium salts, from the existence of the imidazol(in)ium carbon in the region of 140–160 ppm

approximately. The ^{1}H-NMR and ^{13}C{^{1}H}-NMR shifts of the imidazol(in)ium protons and carbons of the ligand precursors that have been synthesised, are given in Table 2.1.

Imidazolium / Imidazolinium salt	Solvent	^{1}H-NMR shift (ppm)	^{13}C{^{1}H}-NMR shift (ppm)
2.1a	CDCl$_3$	10.70	147.06
2.2a	CDCl$_3$	10.69	146.95
2.3a	CDCl$_3$	10.18	146.29
2.4c	CDCl$_3$	10.64	156.38
2.5c	CDCl$_3$	10.06	159.08
2.6c	CDCl$_3$	10.10	159.10
2.7c	D$_2$O	8.85	165.13
2.8c	(CD$_3$)$_2$SO	9.30	see note
2.9c	(CD$_3$)$_2$SO	9.52	157.19
2.10c	(CD$_3$)$_2$SO	9.90	151.68
2.11c	(CD$_3$)$_2$SO	9.24	157.06
2.12c	(CD$_3$)$_2$SO	10.28	151.34
2.13c	(CD$_3$)$_2$SO	10.16	150.51
2.14c	CDCl$_3$	7.90	160.20
2.15c	D$_2$O	8.65	158.10
2.16c	CDCl$_3$	8.20	157.42
2.17c	(CD$_3$)$_2$CO	10.36	155.85
2.18c	(CD$_3$)$_2$CO	9.40	157.92
2.19c	(CD$_3$)$_2$CO	9.36	161.42

Table 2.1: ^{1}H-NMR and ^{13}C{^{1}H}-NMR chemical shifts of imidazol(in)ium protons and carbons. Note: ^{13}C NMR data could not be collected for compound **2.8c** since it was almost insoluble in all common deuterated solvents

As shown in Table 2.1 all imidazolium and imidazolinium proton signals appear as singlets in the region between 8 and 11 ppm, while the imidazol(in)ium carbon signals appear in the region between 145 and 165 ppm. These chemical shifts are in agreement with other similar functionalised imidazol(in)ium salts.[12e, 14, 20, 23a, 27]

The characterisation of the free carbenes **2.1b** and **2.2b** was achieved by spectroscopic methods. The absence of the imidazolium protons in their ^{1}H-NMR spectra, as well as the appearance of the electron deficient carbene carbon in the ^{13}C-$\{^1$H$\}$-NMR spectra of **2.2b**, at 221.17 ppm, was of important diagnostic value. We were unable to locate the carbene carbon in the ^{13}C-$\{^1$H$\}$-NMR spectra of **2.1b**.

2.4 Conclusions

Three novel pyridyl functionalised imidazolium salts have been synthesised and characterised. Deprotonation of two of these imidazolium salts lead to the isolation of their free carbenes that were characterised by spectroscopic methods and X-ray single crystal diffraction (for **2.1b**).

New synthetic methods for preparing imidazolinium salts have been developed. Using these new methodologies, four novel pyridyl functionalised imidazolinium salts, six novel alkoxyphenyl imidazolinium salts, two novel aryl substituted imidazolinium salts and three fluorinated aryl functionalised imidazolinium salts have also been synthesised and characterised.

The co-ordination chemistry of these new ligand precursors along with the reactivity of their complexes will be the subject of the following chapters.

2.5 Experimental Details

General Materials

The synthetic methods for 2-methoxyaniline, 4-methoxyaniline, 2,4-dimethoxyaniline, 2,4,6-trimethoxyaniline, 2-isopropoxyaniline, 4-isopropoxyaniline, 2-fluoroaniline and 2,4-difluoroaniline can be found in Appendix 1. 2,4,6-Trimethylphenyl-1H-imidazole,[28] 2,6-diisopropyl-1H-imidazole,[29] compounds **2.4a**,[19] **2.5a**[19] and **2.6a**[19] were prepared according to the literature methods. 2-Bromo-3-methylpyridine, 2-aminopyridine, 2-ethylaniline, 2-isopropylaniline, 3,5-bis(trifluoromethyl) aniline, oxalyl chloride, glyoxal (40% aqueous solution) and all other materials used were purchased from Aldrich or Lancaster and were used without any further purification.

(2.1a) 3-(2,6-Diisopropylphenyl)-1-[2-(3-methylpyridyl)]imidazolium bromide
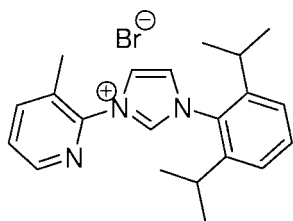
3-(2,6-Diisopropylphenyl)-1H-imidazole (5.90 g, 26.00 mmol) and 2-bromo-3-methylpyridine (4.00 g, 23.00 mmol) were heated and stirred in a sealed ampoule in an oil bath at 150 °C for 5 days. The resulting solid was dissolved in chloroform and transferred to a round bottom flask. The solvent was removed and the solid was washed with ether. The creamy-white solid was azeotropically dried using toluene as the solvent and a Dean-Stark apparatus. It was then stored in a glovebox.

Yield: 8.80 g (22.10 mmol), 96%.

ES$^+$MS m/z (%): 320.2 and 321.2 [M]$^+$.

HRMS (ES$^+$): calcd for [$C_{21}H_{26}N_3$]$^+$: 320.2127, found: 320.2129.

^{1}H NMR (300 MHz, CDCl$_3$), δ: 10.70 (1H, s, imidazolium C$\underline{H}$), 8.25 (1H, d, J = 4.5 Hz, 6-pyridyl C$\underline{H}$), 8.25 and 7.10 (2 × 1H, d, J = 1.8 Hz, imidazole backbone C$\underline{H}$), 7.71 (1H, m, 5-pyridyl C$\underline{H}$), 7.46 (1H, t, J = 7.3 Hz, p-aromatic C$\underline{H}$), 7.30 (2H, d, J = 7.3 Hz, m-aromatic C$\underline{H}$), 6.65 (1H, t, J = 4.5 Hz, 4-pyridyl C$\underline{H}$), 2.67 (3H, s, pyridyl C$\underline{H}_3$), 2.37 (2H, sept. J = 6.9 Hz, C$\underline{H}$(CH$_3$)$_2$), 1.20 and 1.15 (2 × 6H, d, J = 6.9 Hz, CH(C$\underline{H}_3$)$_2$).

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$), δ: 147.06 (o-$\underline{C}$H pyridine), 145.43 (o-$\underline{C}$ pyridine), 145.08 (o-$\underline{C}$ pyridine), 142.25 (p-$\underline{C}$H pyridine), 138.14 (m-$\underline{C}$H pyridine), 131.98 (p-$\underline{C}$H aromatic), 130.01 and 128.31 (2 × $\underline{C}$-CH(CH$_3$)$_2$), 126.10 and 124.73 (2 × $\underline{C}$H imidazolium backbone), 124.62 (2 × m-$\underline{C}$H aromatic), 28.93 (2 × $\underline{C}$H(CH$_3$)$_2$), 24.36 and 24.03 (4 × CH($\underline{C}$H$_3$)$_2$), 18.68 (-$\underline{C}$H$_3$ pyridine).

(2.1b) 3-(2,6-Diisopropylphenyl)-1-[2-(3-methylpyridyl)]imidazol-2-ylidene
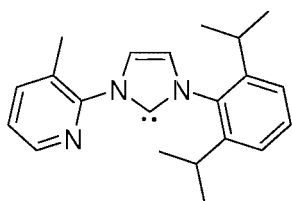
1-[2-(3-Methyl)pyridyl]-3-(2,6- diisopropylphenyl)imidazolium bromide (2.1a) (3.12 g, 7.80 mmol) and KN(SiMe$_3$)$_2$ (1.71 g, 8.60 mmol, 1.2 equiv.) were placed together under nitrogen. The solids were cooled to –78 °C. Pre-cooled THF (30 mL) was added via cannula and the mixture was stirred until the bath temperature rose to –20 °C, and held at this temperature for 3 h. The solution was then allowed to warm to room temperature, and after evaporating the volatiles under reduced pressure, the pale residue was washed with petroleum (2 × 15 mL). The product was extracted into toluene (2 × 30 mL), filtered through Celite and the solvent removed under vacuum to yield a light yellow crystalline product. For crystallographic data of the compound see Table 2.2.

Yield 2.37 g (5.90 mmol), 76%.

m.p. 150-155 °C.

^{1}H NMR (300MHz, C_6D_6), δ: 8.30 (1H, d, J = 4.5 Hz, 6-pyridyl C$\underline{H}$), 8.05 and 6.71(2 ×

1H, d, J = 1.8 Hz, imidazole backbone C$\underline{H}$), 7.81 (1H, m, 5-pyridyl C$\underline{H}$), 7.42 (1H, t, J =

7.3 Hz, p-aromatic C$\underline{H}$), 7.38 (2H, d, J = 7.3 Hz, m-aromatic C$\underline{H}$), 6.65 (1H, t, J = 4.5 Hz,

4-pyridyl C$\underline{H}$), 3.0 (2H, sept. J = 6.9 Hz, C$\underline{H}$(CH$_3$)$_2$), 2.90 (3H, s, pyridyl C$\underline{H}_3$) 1.40 and

1.20 (2 × 6H, d, J = 6.9 Hz, CH(C$\underline{H}_3$)$_2$).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6), δ: 145.01 (o-$\underline{C}$ pyridine), 144.33 (quaternary $\underline{C}$–N

pyridine), 137.50 (quaternary $\underline{C}$–N aromatic), 139.64 (m-$\underline{C}$H pyridine), 130.56 (p-$\underline{C}$H

aromatic), 122.34 (o-$\underline{C}$H aromatic), 120.08 (2 × m-$\underline{C}$H aromatic), 119.80 and 118.38 (2 ×

$\underline{C}$-CH(CH$_3$)$_2$), 27.21 (2 × $\underline{C}$H(CH$_3$)$_2$), 23.12 and 22.45 (4 × CH(C$\underline{H}_3$)$_2$), 20.32 (-$\underline{C}$H$_3$

pyridine).

(2.2a) 3-(2,4,6-Trimethylphenyl)-1-[2-(3-methylpyridyl)]imidazolium bromide
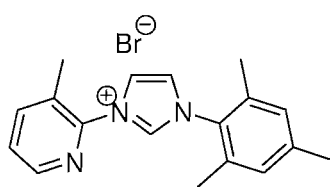
This was prepared in the same way as **2.1a** using 3-(2,4,6-trimethylphenyl)-1H-imidazole (4.84 g, 26.00 mmol) and 2-bromo-3-methylpyridine (4.00 g, 23.00 mmol). Yield: 7.9 g (22.10 mmol), 96%.

ES$^+$MS m/z (%): 278.2 and 279.2 [M]$^+$.

HRMS (ES$^+$): calcd for [$C_{18}H_{20}N_3$]$^+$: 218.1657, found: 218.1659.

^{1}H NMR (300MHz, CDCl$_3$), δ: 10.69 (1H, s, 2-imidazolium C$\underline{H}$), 8.34 (1H, dd, J = 1.2,

4.5 Hz, m-pyridyl C$\underline{H}$), 8.20 and 7.46 (2 × 1H, d, J = 1.8 Hz, imidazole backbone C$\underline{H}$),

7.76 (1H, dd, J = 0.9, 4.5 Hz, m-pyridyl C$\underline{H}$), 7.40 (1H, m, p-pyridyl C$\underline{H}$), 6.94 (2H, s, m-

aromatic C$\underline{H}$), 2.59 (3H, s, pyridyl C$\underline{H}_3$), 2.26 (3H, s, p-aromatic C$\underline{H}_3$), 2.09 (6H, s, o-

aromatic C$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$), δ: 146.95 (imidazolium $\underline{C}$H), 145.42 (quaternary $\underline{C}$–N

pyridine), 141.97 (p-$\underline{C}$H pyridine), 141.11 (quaternary $\underline{C}$–N aromatic), 137.70 (m-$\underline{C}$H

pyridine), 133.86 (pyridyl $\underline{C}$-CH$_3$), 130.33 (aromatic $\underline{C}$-CH$_3$), 129.71 (2 × aromatic $\underline{C}$–

H), 128.20 (aromatic $\underline{C}$-CH$_3$), 125.97 (pyridyl $\underline{C}$H), 123.89 and 123.41 (backbone $\underline{C}$H),

20.92 (-$\underline{C}$H$_3$ pyridine), 18.47 (p-$\underline{C}$H$_3$ aromatic), 17.62 (2 × o-$\underline{C}$H$_3$ aromatic).

(2.2b) 3-(2,4,6-trimethylphenyl)-1-[2-(3-methylpyridyl)]imidazol-2-ylidene
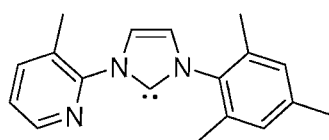
This was prepared in the same way as compound **2.1b** using 1-[2-(3-methyl)pyridyl]-3-(2,4,6-trimethylphenyl)-imidazolium bromide (**2.2a**) (2.79 g, 7.80 mmol) and

KN(SiMe$_3$)$_2$ (1.71 g, 8.60 mmol, 1.2 equiv.). Yield 1.68 g (6.08 mmol), 78%.

^{1}H NMR (300MHz, C_6D_6), δ: 8.35 (1H, dd, J = 0.9, 4.8 Hz, 6-pyridyl C$\underline{H}$), 8.05 and 6.63 (2 × 1H, d, J = 1.8 Hz, imidazole backbone C$\underline{H}$), 7.30 (1H, dd, J = 1.2, 6.9 Hz, pyridyl C$\underline{H}$), 6.90 (2H, s, m-C$\underline{H}$ aromatics), 6.82 (1H, dd, J = 4.8, 7.5 Hz, pyridyl C$\underline{H}$), 2.87 (3H, s, pyridyl C$\underline{H}_3$) 2.27 (3H, s, p-C$\underline{H}_3$ aromatic), 1.20 (6H, s, o-C$\underline{H}_3$ aromatic).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6), δ: 221.17 (carbene $\underline{C}$), 152.87 (quaternary $\underline{C}$–N), 145.70, 141.03 and 121.55 (pyridyl $\underline{C}$H), 139.03 (quaternary $\underline{C}$–N), 137.32 (pyridyl quaternary $\underline{C}$–CH$_3$), 135.38 (aromatic quaternary o-$\underline{C}$-CH$_3$), 129.10 (aromatic m-$\underline{C}$H), 127.30 (aromatic quaternary p-$\underline{C}$-CH$_3$), 119.99 and 119.93 (imidazole backbone $\underline{C}$H), 21.68 (pyridyl $\underline{C}$H$_3$), 21.01 (aromatic p-$\underline{C}$H$_3$), 18.07 (aromatic o-$\underline{C}$H$_3$).

(2.3a) 3-Methyl-1-[2-(3-methylpyridyl)]imidazolium bromide
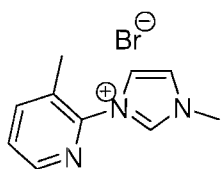
1-Methyl-1H-imidazole (2.12 g, 26.00 mmol) and 2-bromo-3-methyl-pyridine (4.00 g, 23.00 mmol) were heated and stirred in a sealed ampoule in an oil bath at 110 °C for 5 days. The resulting oil was triturated in ether to solidify the product. This was then dissolved in chloroform and transferred to a round bottom flask. The solvent was removed and the solid was washed with ether. The creamy-white solid was azeotropically dried using toluene as the solvent and a Dean- Stark apparatus. It was then stored in a glovebox. Yield: 5.37 g (21.16 mmol), 92%.

ES$^+$MS m/z (%): 174.1 and 175.1 [M]$^+$.

HRMS (ES$^+$): calcd for [$C_{10}H_{12}N_3$]$^+$: 174.1031, found: 174.1028.

^{1}H NMR (300MHz, CDCl$_3$), δ: 10.18 (1H, s, imidazolium C$\underline{H}$), 8.01 (1H, d, J = 4.8 Hz, backbone C$\underline{H}$), 7.75, 7.50 and 7.10 (3 × H, s, aromatic C$\underline{H}$), 7.47 (1H, d, J = 4.8 Hz, backbone C$\underline{H}$), 3.96 (3H, s, pyridyl -C$\underline{H}_3$), 2.19 (3H, s, imidazolium -C$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$), δ: 146.29 (imidazolium $\underline{C}$H), 141.21, 126.33 and 124.93 (aromatic $\underline{C}$H), 135.85 (quaternary $\underline{C}$-N), 123.32 and 122.74 (backbone $\underline{C}$H), 121.00 (quaternary $\underline{C}$-CH$_3$), 36.28 (-$\underline{C}$H$_3$), 17.50 (-$\underline{C}$H$_3$).

(2.4b) N-(2,4,6-Trimethylphenyl)-N'-(2-pyridyl)ethylenediamine

In an ampoule, 2-bromopyridine (0.42 g, 2.80 mmol), N-(2,4,6-trimethylphenyl)ethylene diamine (0.55 g, 2.50 mmol), Pd(dba)$_2$ (30 mg, 5.00 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (42 mg, 1.00 mmol) and KO^{t}Bu (0.46 g, 4.10 mmol) were suspended in dioxane (20 mL). The mixture was heated at 100 °C under partial vacuum for 20 h. The resulting mixture was then quenched with water and extracted with chloroform (3 × 15 mL). The combined organic layers were treated with

brine, then dried over $MgSO_4$ and filtered through Celite. The solvent was removed and the resulting brown oil was distilled using a Kugelröhr distillation apparatus, to give a light yellow oil. Yield 0.48 g (1.90 mmol), 76%.

ES^+MS m/z (%): 256.0 and 257.0 $[M+H]^+$.

^1H NMR (300MHz, $CDCl_3$), δ: 8.11 (1H, dd, J = 0.9, 5.1 Hz, pyridyl C$\underline{H}$), 7.41 (1H, dt, J = 1.8, 6.9 Hz, pyridyl C$\underline{H}$), 6.82 (2H, s, aromatic C$\underline{H}$), 6.59 (1H, dt, J = 0.9, 5.1 Hz, pyridyl C$\underline{H}$), 6.41 (1H, d, J = 8.4, pyridyl C$\underline{H}$), 4.88 (2H, br.s, -N$\underline{H}$), 3.51 and 3.19 (2 × 2H, t, J = 5.7 Hz, ethylene C$\underline{H}_2$), 2.25 (6H, s, -C$\underline{H}_3$), 2.24 (3H, s, -C$\underline{H}_3$).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$), δ: 158.82 and 143.00 (2 × quaternary $\underline{C}$-N), 148.11, 137.29, 113.00 and 107.12 (4 × pyridyl $\underline{C}$H), 131.45, 117.11 and 114.65 (quaternary $\underline{C}$-CH$_3$), 129.43 (2 × $\underline{C}$H aromatic), 48.02 and 42.71 (2 × ethylene $\underline{C}$H$_2$), 20.48 (p-$\underline{C}$H$_3$ aromatic) 18.25 (2 × o-$\underline{C}$H$_3$ aromatic).

(2.4c) 1-(2-Pyridyl)-3-(2,4,6-trimethylphenyl)imidazolinium chloride
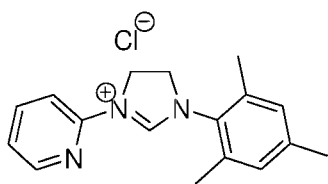
N-(2,4,6-Trimethylphenyl)-N'-(2-pyridyl)ethylenediamine (0.10 g, 0.40 mmol), was dissolved in methanol (10 mL). To the solution, conc. HCl (1.5 mL) was added. All solvents were then removed under vacuum to give a light orange solid.

The solid was suspended in triethyl orthoformate and heated at 100 °C. As the temperature rose, the solid dissolved, and after a while, a light beige precipitate was formed. The reaction mixture was let to cool to room temperature, was filtered and the solid obtained was washed with ether. Yield 0.09 g(0.26 mmol), 66%.

ES^+MS m/z (%): 266.2 and 267.2 $[M]^+$.

HRMS (ES^+): calcd for $[C_{17}H_{20}N_3]^+$: 266.1657, found: 266.1656.

^1H NMR (300MHz, $CDCl_3$), δ: 10.64 (1H, s, imidazolinium C$\underline{H}$), 8.27 (1H, dd, J = 4.8, 1.5 Hz, pyridyl-C$\underline{H}$), 8.23 (1H, d, J = 8.4 Hz, pyridyl-C$\underline{H}$), 7.77 (1H, m, pyridyl-C$\underline{H}$), 7.15 (1H, m, pyridyl-C$\underline{H}$), 6.88 (2H, s, aromatic-C$\underline{H}$), 4.86 (2H, t, J = 10.5 Hz, backbone C$\underline{H}_2$), 4.44 (2H, t, J = 10.5 Hz, backbone C$\underline{H}_2$), 2.30 (6H, s, o-aromatic C$\underline{H}_3$), 2.22 (3H, s, p-aromatic C$\underline{H}_3$).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$), δ: 156.38 (imidazolinium $\underline{C}$H), 148.07, 139.42, 122.12 and 113.23 (pyridyl-$\underline{C}$H), 140.53 (quaternary $\underline{C}$-N), 129.87 (aromatic $\underline{C}$H), 51.96 and 47.45 (backbone $\underline{C}$H$_2$), 20.88 ($\underline{C}$H$_3$), 17.91 (2 × $\underline{C}$H$_3$).

(2.5b) *N*-(2,4,6-Trimethylphenyl)-*N'*-[2-(3-picolyl)]ethylenediamine

This was prepared following the same procedure as for compound **2.4b** using the following amounts: 2-bromo-3-methylpyridine (0.86 g, 5.00 mmol), *N*-(2,4,6-trimethylphenyl)ethylene diamine (0.90 g, 5.00 mmol), Pd(dba)$_2$ (60 mg, 0.10 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (90 mg, 0.21 mmol) and KO^{t}Bu (0.72 g, 47.50 mmol). Yield: 1.10g (4.10 mmol), 82%.

ES$^+$MS *m/z* (%): 270.0 and 271.1 [M+H]$^+$.

^{1}H NMR (300MHz, CDCl$_3$), δ: 8.02 (1H, d, *J* = 5.1 Hz, picolyl C$\underline{H}$), 7.22 (1H, d, *J* = 6.3 Hz, picolyl C$\underline{H}$), 6.82 (2H, s, *m*-C$\underline{H}$ aromatic), 6.53 (1H, dd, *J* = 5.1, 7.2 Hz, picolyl C$\underline{H}$), 4.63 (2H, br.s, N-$\underline{H}$), 3.70 (2H, q, *J* = 5.4 Hz, ethylene C$\underline{H}_2$), 3.24 (2H, t, *J* = 5.4 Hz, ethylene C$\underline{H}_2$), 2.25 (6H, s, 2 × *o*-C$\underline{H}_3$ aromatic), 2.23 (3H, s, *p*-C$\underline{H}_3$ aromatic), 2.07 (3H, s, picolyl C$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$), δ: 156.96 (quaternary $\underline{C}$–N), 145.37, 136.73 and 112,72 (picolyl $\underline{C}$H), 143.27 (quaternary picolyl $\underline{C}$-CH$_3$), 131.47 (quaternary $\underline{C}$–N), 129.75 (2 × aromatic quaternary $\underline{C}$–CH$_3$), 129.48 (2 × *m*-$\underline{C}$H aromatic), 116.69 (aromatic quaternary $\underline{C}$-CH$_3$), 48.38 (ethylene $\underline{C}$H$_2$), 42.44 (ethylene $\underline{C}$H$_2$), 20.49 (*p*-$\underline{C}$H$_3$ aromatic), 18.31 (2 × *o*-$\underline{C}$H$_3$ aromatic), 16.83 (picolyl $\underline{C}$H$_3$).

(2.5c) 1-[2-(3- Picolyl)]-3-(2,4,6-trimethylphenyl)imidazolinium chloride
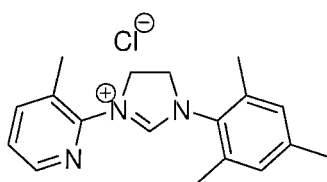
This was prepared following the same procedure as for compound **2.4c** using *N*-(2,4,6-trimethylphenyl)-*N*-[2-(3-picolyl)]ethylenediamine (1.00 g, 3.70 mmol). Yield: 0.50 g (1.59 mmol), 43%.

ES$^+$MS *m/z* (%): 280.2 and 281.2 [M]$^+$.

HRMS (ES$^+$): calcd for [C$_{18}$H$_{22}$N$_3$]$^+$: 280.1814, found: 280.1814.

^{1}H NMR (300MHz, CDCl$_3$), δ: 10.06 (1H, s, imidazolinium C$\underline{H}$), 8.22 (1H, d, *J* = 3.3 Hz, picolyl C$\underline{H}$), 7.61 (1H, dd, *J* = 7.5, 0.9 Hz, picolyl C$\underline{H}$), 7.19 (1H, dd, *J* = 7.8, 4.5 Hz, picolyl C$\underline{H}$), 6.90 (2H, s, 2 × *m*-aromatic C$\underline{H}$), 4.89 and 4.45 (2 × 2H, t, *J* = 10.5 Hz, backbone C$\underline{H}_2$), 2.63 (3H, s, picolyl C$\underline{H}_3$), 2.34 (6H, s, 2 × *o*-aromatic C$\underline{H}_3$), 2.25 (3H, s, *p*-aromatic C$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$), δ: 159.08 (imidazolinium $\underline{C}$H), 147.13 (quaternary $\underline{C}$–N),146.06, 141.76 and 123.72 (picolyl $\underline{C}$H), 140.44 (quaternary $\underline{C}$–N), 134.72 and 126.61 (2 × quaternary aromatic-$\underline{C}$-CH$_3$), 129.88 (2 × aromatic $\underline{C}$H), 126.61 (*p*-aromatic-$\underline{C}$-CH$_3$), 51.78 and 50.22 (2 × backbone $\underline{C}$H$_2$), 20.95 (picolyl-$\underline{C}$H$_3$), 18.89 (2 × *o*-aromatic-$\underline{C}$H$_3$), 17.99 (*p*-aromatic-$\underline{C}$H$_3$).

(2.6b) *N*-(2,6-Diisopropylphenyl)-*N'*-[2-(3-picolyl)]ethylenediamine

This was prepared following the same procedure as for compound **2.4b** using the following amounts: 2-bromo-3-methylpyridine (0.86 g, 5.00 mmol), *N*-(2,6-diisopropylphenyl)ethylene diamine (1.10 g, 5.00 mmol), Pd(dba)$_2$ (60 mg, 0.10 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (9 mg, 0.21 mmol) and KO^{t}Bu (0.72 g, 47.50 mmol). Yield: 1.25 g (4.00 mmol), 80%.

ES$^+$MS *m/z* (%): 312.2 and 313.2 [M+H]$^+$.

^{1}H NMR (300MHz, CDCl$_3$), δ: 8.02 (1H, d, *J* = 3.6 Hz, picolyl C$\underline{H}$), 7.12 (2H, m, picolyl C$\underline{H}$), 7.03 (2H, m, aromatic C$\underline{H}$), 6.52 (2H, dd, *J* = 5.1, 7.2 Hz, aromatic C$\underline{H}$), 5.40 and 4.70 (2 × 1H, s, N$\underline{H}$), 3.70 and 3.10 (2 × 2H, dd, *J* = 5.7 Hz, ethylene C$\underline{H}_2$), 3.15 and 3.05 (2 × 1H, sept., *J* = 6.9 Hz, C$\underline{H}$(CH$_3$)$_2$), 2.15 (3H, s, picolyl C$\underline{H}_3$), 1.12 and 1.10 (2 × 6H, d, *J* = 6.9 Hz, CH(C$\underline{H}_3$)$_2$).

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$), δ: 156.86 (quaternary $\underline{C}$-N), 146.10, 123.92 and 113.31 (aromatic $\underline{C}$H), 142.58 (quaternary $\underline{C}$-N), 136.78, 127.45 and 112. 78 (picolyl $\underline{C}$H), 118.47 and 116.72 (quaternary $\underline{C}$-^{i}Pr), 51.28 (ethylene $\underline{C}$H$_2$), 42.26 (ethylene $\underline{C}$H$_2$), 28.64 and 27.59 ($\underline{C}$H(CH$_3$)$_2$), 24.17 (picolyl $\underline{C}$H$_3$), 17.30 and 16.80 (CH($\underline{C}$H$_3$)$_2$).

(2.6c) 1-[2-(3-Picolyl)]-3-(2,6-diisopropyl-phenyl)imidazolinium chloride
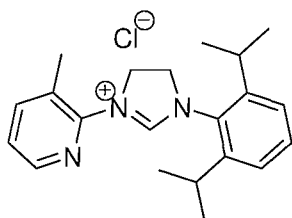
This was prepared following the same procedure as for compound **2.4c** using *N*-(2,6-diisopropylphenyl)-*N'*-[2-(3-picolyl)]ethylenediamine (1.00 g, 0.32 mmol). Yield: 0.70g (2.0 mmol), 63%.

ES$^+$MS *m/z* (%): 322.2 and 323.2 [M]$^+$.

HRMS (ES$^+$): calcd for [C$_{21}$H$_{28}$N$_3$]$^+$: 322.2283, found: 322.2280.

^{1}H NMR (300MHz, CDCl$_3$), δ: 10.10 (1H, s, imidazolinium C$\underline{H}$), 8.23 (1H, d, *J* = 3.3 Hz, picolyl C$\underline{H}$), 7.64 (1H, d, *J* = 6.9 Hz, picolyl C$\underline{H}$), 7.42 (1H, t, *J* = 7.8 Hz, picolyl C$\underline{H}$), 7.22 (3H, m, aromatic C$\underline{H}$), 4.98 (2H, t, *J* = 9.9, 11.4 Hz, C$\underline{H}_2$ backbone), 4.47 (2H, t, *J* = 9.9, 11.4 Hz, C$\underline{H}_2$ backbone), 3.00(2H, sept, *J* = 6.9 Hz, C$\underline{H}$(CH$_3$)$_2$), 2.70 (3H, s, picolyl C$\underline{H}_3$), 1.30 (6H, d, *J* = 2.1 Hz, CH(C$\underline{H}_3$)$_2$), 1.28 (6H, d, *J* = 2.1 Hz, CH(C$\underline{H}_3$)$_2$).

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$), δ: 159.10 (imidazolinium $\underline{C}$H), 147.22 (quaternary $\underline{C}$-N), 146.20 (quaternary $\underline{C}$-CH$_3$), 146.04, 141.99 and 131.35 (picolyl–$\underline{C}$H), 129.85 (aromatic quaternary $\underline{C}$-N), 126.65 (2 × quaternary $\underline{C}$-^{i}Pr), 124.95 and 123.85 (aromatic-$\underline{C}$H), 54.50 and 50.48 (backbone $\underline{C}$H$_2$), 28.95 ($\underline{C}$H(CH$_3$)$_2$), 25.09 (CH($\underline{C}$H$_3$)$_2$), 24.11 (CH($\underline{C}$H$_3$)$_2$), 18.98 (picolyl $\underline{C}$H$_3$).

(2.7a) N,N'-Bis(2-pyridyl)oxalamide

A solution of oxalyl chloride (2.74 mL, 16.00 mmol) in Et$_2$O (50 mL) was added dropwise to a solution of 2-aminopyridine (3.08 g, 32.00 mmol) and Et$_3$N (8.76 mL, 32.00 mmol) in Et$_2$O (350 mL) at 0 °C. The mixture turned bright red on the addition. It was then stirred at r.t. overnight. The mixture was filtered and the resulting precipitate was triturated in methanol. The solid was then filtered, washed with acetone and then ether. It was then dried under vacuum. Yield: 3.05 g (12.60 mmol), 79%.

ES$^+$MS m/z (%): 242.9 and 243.9 [M]$^+$

^{1}H NMR (300MHz, d_6-DMSO), δ: 10.45 (2H, s, 2 × N$\underline{H}$), 8.41 (2H, d, J = 3.6 Hz, 2 × o-pyridine C$\underline{H}$), 8.08 (2H, d, J = 8.1 Hz, 2 × m-pyridine C$\underline{H}$), 7.90 (2H, m, 2 × m- pyridine C$\underline{H}$), 7.24 (2H, m, 2 × p- pyridine C$\underline{H}$).

^{13}C{^{1}H} NMR (75 MHz, d_6-DMSO), δ: 158.40 (2 × $\underline{C}$=O), 150.04 (2 × quaternary $\underline{C}$), 148.44 (2 × o- pyridine $\underline{C}$), 138.56 (2 × m-pyridine $\underline{C}$), 120.87 (2 × p-pyridine $\underline{C}$), 114.22 (2 × m-C pyridine).

(2.7b) N,N'-Bis(2-pyridyl)ethylenebis(ammonium) dichloride

N,N'-Bis(2-pyridyl)oxalamide (**2.7a**) (1.93 g, 8.00 mmol) was dissolved in THF and then was added dropwise to a pre-cooled (0 °C) LiAlH$_4$ (0.61 g, 16.00 mmol) THF suspension (10 mL). The mixture was refluxed overnight. After cooling to 0 °C, methanol was added dropwise until the bubbling ceased. The mixture was then hydrolysed with a solution of NaOH (2.0 g) and MgSO$_4$ (2.0 g) in water (10 mL). The resulting slurry was filtered and the solid was washed with THF. The filtrate's solvents were removed and the resulting oil was dissolved in methanol. Concentrate HCl was then added and the solvents were removed to get a solid. The solid was collected, washed with acetone and dried under vacuum. Yield 1.96 g (6.89 mmol), 85%.

^{1}H NMR (300MHz, D$_2$O), δ: 8.34 (2H, d, J = 4.8 Hz, pyridyl C$\underline{H}$), 7.98 (2H, m, pyridyl C$\underline{H}$), 7.86 (2H, m, pyridyl C$\underline{H}$), 7.14 (2H, m, pyridyl C$\underline{H}$), 4.30 (4H, s, ethylene C$\underline{H}_2$).

^{13}C{^{1}H} NMR (75 MHz, D$_2$O), δ: 152.31 (quaternary $\underline{C}$–N), 148.76, 140.92, 135.43 and 125.84 (pyridyl $\underline{C}$H), 38.02 (ethylene $\underline{C}$H$_2$).

(2.7c) 1,3-Bis(2-pyridyl)imidazolinium chloride
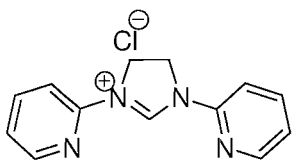
This was prepared following the same procedure as for compound **2.4c** using N,N'-bis(2-pyridyl)ethylene bis(ammonium) dichloride (1.00 g, 0.35 mmol). Yield: 0.76 g (2.92 mmol), 83%.

ES$^+$MS m/z (%): 225.1 and 226.1 [M]$^+$.

^{1}H NMR (300MHz, D$_2$O), δ: 8.85 (1H, s, imidazolinium C<u>H</u>), 8.39 (1H, d, J = 4.8 Hz, pyridyl C<u>H</u>), 7.93 (2H, m, pyridyl C<u>H</u>), 7.81 (1H, d, J = 4.8 Hz, pyridyl C<u>H</u>), 7.39 (2H, m, pyridyl C<u>H</u>), 6.94 (2H, m, pyridyl C<u>H</u>), 4.32 (2H, t, J = 6.0 Hz, backbone C<u>H</u>$_2$), 3.74 (2H, t, J = 6.0 Hz, backbone C<u>H</u>$_2$).

^{13}C{^{1}H} NMR (75 MHz, D$_2$O), δ: 165.13 (imidazolinium <u>C</u>H), 152.67 and 152.28 (quaternary <u>C</u>–N), 148.46, 144.10, 140.29, 135.26, 122.42, 115.82 112.95 and 111.37 (pyridyl <u>C</u>H), 40.83 and 39.79 (backbone <u>C</u>H$_2$).

(2.8a) N,N'-Bis(2,4,6-trimethoxyphenyl)oxalamide

To a diethyl ether solution (200 mL) of 2,4,6-trimethoxyaniline (4.00 g, 22.00 mmol) and Et$_3$N (2.90 mL), a solution of oxalyl chloride (0.90 mL, 10.00 mmol) in ether (50 mL) was added dropwise at 0 °C. The mixture was then let to stir at r.t. overnight. The precipitate was filtered and triturated in methanol to remove triethylammonium chloride. The solid was then filtered, washed with ether and dried under vacuum. Yield 3.40 g (8.00 mmol), 80%.

Anal. Calcd for C$_{20}$H$_{24}$N$_2$O$_8$: C, 57.14; H, 5.75; N, 6.66 % Found: C, 57.2; H, 5.7; N, 6.6%

^{1}H NMR (300MHz, d_6-DMSO), δ: 9.30 (2H, s, -N<u>H</u>), 6.30 (4H, s, m-<u>H</u> aromatics), 3.81 (6H, s, p-OC<u>H</u>$_3$), 3.79 (12H, s, o-OC<u>H</u>$_3$).

^{13}C NMR data could not be collected since the compound was almost insoluble in all common deuterated solvents.

(2.8b) N,N'-Bis(2,4,6-trimethoxyphenyl)ethylene diamine

N,N'-Bis(2,4,6-trimethoxyphenyl)oxalamide (**2.8a**) (3.40 g, 8.00 mmol) was dissolved in THF and to this a BH$_3$·THF solution (10 mL) was added. The mixture was refluxed overnight. Methanol was then added dropwise, after cooling, until the bubbling ceased. The solvents were removed and methanol was added again and removed under vacuum. This was repeated three times. The methanol-insoluble solid was then filtered and dried under vacuum. Yield 2.35 g (6.00 mmol), 75%.

ES$^+$MS m/z (%): 391.9, 393.0 and 394.0 [M+H]$^+$.

^{1}H NMR (300MHz, d_6-DMSO), δ: 9.30 (2H, s, -N$\underline{H}$), 6.30 (4H, s, m-$\underline{H}$ aromatics), 6.10 (4H, s, C$\underline{H}_2$ ethylene), 3.90 (6H, s, p-OC$\underline{H}_3$), 3.80 (12H, s, o-OC$\underline{H}_3$).

^{13}C NMR data could not be collected since the compound was almost insoluble in all common deuterated solvents.

(2.8c) 1,3-Bis(2,4,6-trimethoxyphenyl)imidazolinium tetrafluoroborate
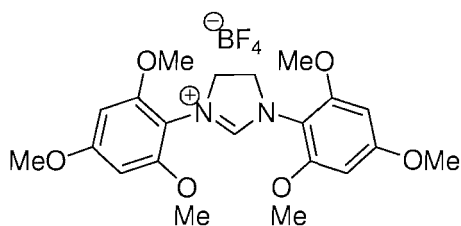
N-N'-Bis(2,4,6-trimethoxyphenyl)ethylene diamine **2.8b**) (0.30 g, 0.74 mmol) and ammonium tetrafluoro borate (0.10 g, 0.90 mmol) were suspended in triethyl orthoformate (5 mL) and refluxed overnight at 120 °C. The mixture was cooled to r.t., the product was precipitated, filtered, washed with ether and dried under vacuum. Yield 0.10 g (0.20 mmol), 27%.

ES$^+$MS m/z (%): 403.2 and 404.2 [M]$^+$.

HRMS (ES$^+$): calcd for [C$_{21}$H$_{27}$N$_2$O$_6$]$^+$: 403.1869, found: 403.1872.

Anal. Calcd for C$_{21}$H$_{27}$BF$_4$N$_2$O$_6$: C, 51.45; H, 5.55; N, 5.71% Found: C, 51.4; H, 5.5; N, 5.7%.

^{1}H NMR (300MHz, d_6-DMSO), δ: 9.30 (1H, s, imidazolinium $\underline{H}$), 6.30 (4H, s, aromatic C$\underline{H}$), 3.85 (4H, s, backbone C$\underline{H}_2$), 3.80 (6H, s, p-OC$\underline{H}_3$), 3.35 (12H, s, o-OC$\underline{H}_3$).

^{13}C NMR data could not be collected since the compound was almost insoluble in all common deuterated solvents.

(2.9a) N,N'-Bis(2-methoxyphenyl)oxalamide

This was prepared in the same way as compound **2.8a** using the following: 2-methoxyaniline (2.58g, 21.00 mmol), oxalyl chloride (0.90 mL, 10.00 mmol) and NEt$_3$ (2.90 mL). Yield 2.43 g (8.10 mmol), 81%.

Anal. Calcd for C$_{16}$H$_{16}$N$_2$O$_4$: C, 63.99; H, 5.37; N, 9.33 % Found: C, 64.0; H, 5.4; N, 9.3%.

^{1}H NMR (300MHz, d_6-DMSO), δ: 9.89 (2H, br. s, -N$\underline{H}$), 8.16 (2H, m, aromatic C$\underline{H}$), 7.18 (4H, m, aromatic C$\underline{H}$), 7.05 (2H, m, aromatic C$\underline{H}$), 3.92 (6H, s, OC$\underline{H}_3$).

^{13}C NMR data could not be collected since the compound was almost insoluble in all common deuterated solvents.

(2.9b) *N*,*N'*-Bis(2-methoxyphenyl)ethylenebis(ammonium) dichloride

N,*N'*-Bis(2-methoxyphenyl)oxalamide (**2.9a**) (2.43 g, 8.10 mmol) was dissolved in THF and it was added dropwise to a pre-cooled (0 °C) LiAlH₄ (0.61 g, 16.00 mmol) THF suspension (10 mL). The mixture was refluxed overnight. After cooling to 0 °C, methanol was added dropwise until the bubbling ceased. The mixture was then hydrolysed with a solution of NaOH (2.0 g) and MgSO₄ (2.0 g) in water (10 mL). The resulting slurry was filtered and the solid was washed with THF. The filtrate was evaporated and the resulting oil was dissolved in methanol. Concentrate HCl was then added and the solvents were removed to yield a solid. The solid was collected, washed with acetone and dried under vacuum. Yield 2.35 g (6.89 mmol), 85%.

¹H NMR (300MHz, D₂O), δ: 7.45 (2H, dt, *J* = 1.8, 7.5 Hz, aromatic C<u>H</u>), 7.29 (2H, dd, *J* = 1.8, 8.1 Hz, aromatic C<u>H</u>), 7.19 (2H, d, *J* = 8.1 Hz, aromatic C<u>H</u>), 7.13 (2H, dt, *J* = 1.8, 7.8 Hz, aromatic C<u>H</u>), 3.93 (6H, s, OC<u>H</u>₃), 3.79 (4H, s, ethylene C<u>H</u>₂).

¹³C{¹H} NMR (75 MHz, D₂O), δ: 151.13 (quaternary <u>C</u>–N), 129.18, 121.55, 121.13 and 112.78 (<u>C</u>H aromatics), 124.65 (quaternary <u>C</u>–OMe), 56.10 (O–<u>C</u>H₃), 44.10 (ethylene <u>C</u>H₂).

(2.9c) 1,3-Bis(2-methoxyphenyl)imidazolinium chloride
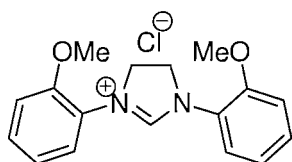
N-*N'*-Bis(2-methoxyphenyl)ethylenebis(ammonium) dichloride (**2.9b**) (2.35 g, 6.89 mmol) was suspended in triethyl orthoformate (5 mL) along with formic acid (two drops) and was refluxed at 120 °C for 2 hrs. The mixture was allowed to cool to r.t. and ether was added. The precipitated product was filtered, washed with ether and was azeotropically dried using toluene as the solvent before storing in a glovebox. Yield 1.89 g (5.92 mmol), 86%.

ES⁺MS *m/z* (%): 283.2 and 284.2 [M]⁺.

HRMS (ES⁺): calcd for [C₁₇H₁₉N₂O₂]⁺: 283.1447, found: 283.1445.

¹H NMR (300MHz, *d*₆-DMSO), δ: 9.52 (1H, s, imidazolinium C<u>H</u>), 7.55 (2H, dd, *J* = 7.8, 1.5 Hz, aromatic C<u>H</u>), 7.43 (2H, td, *J* = 1.5, 8.4 Hz, aromatic C<u>H</u>), 7.30 (2H, dd, *J* = 0.9, 8.4 Hz, aromatic C<u>H</u>), 7.12 (2H, td, *J* = 7.8, 1.2 Hz, aromatic C<u>H</u>), 4.56 (4H, s, backbone C<u>H</u>₂), 3.94 (6H, s, OC<u>H</u>₃).

¹³C{¹H} NMR (75 MHz, *d*₆-DMSO), δ: 157.19 (imidazolinium <u>C</u>H), 151.73 (quaternary <u>C</u>-N), 124.66 (quaternary <u>C</u>–O), 129.24, 123.47, 120.97 and 112.87 (aromatic <u>C</u>H), 56.23 (O<u>C</u>H₃), 49.95 (backbone <u>C</u>H₂).

(2.10a) *N,N'*-Bis(4-methoxyphenyl)oxalamide

This was prepared in the same way as compound **2.8a** using the following: 4-methoxyaniline (2.58 g, 21.00 mmol), oxalyl chloride (0.90 mL, 10.00 mmol) and NEt_3 (2.90 mL). Yield 2.49 g (8.30 mmol), 83%.

Anal. Calcd for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33 % Found: C, 64.0; H, 5.4; N, 9.4 %

^{1}H NMR (300MHz, d_6-DMSO), δ: 10.79 (2H, br. s, N$\underline{H}$), 7.64 and 7.16 (2 × 4H, m, aromatic C$\underline{H}$), 3.90 (6H, s, OC$\underline{H}_3$).

^{13}C NMR data could not be collected since the compound was almost insoluble in all common deuterated solvents.

(2.10b) *N,N'*-Bis(4-methoxyphenyl)ethylenebis(ammonium) dichloride

This was prepared in the same way as compound **2.9b** using the following: *N,N'*-bis(4-methoxyphenyl)oxalamide (2.43 g, 8.10 mmol) and $LiAlH_4$ (0.61 g, 16.00 mmol). Yield 2.35 g (6.89 mmol), 85%.

^{1}H NMR (300MHz, D_2O), δ: 7.34 (4H, d, *J* = 9.0 Hz, aromatic C$\underline{H}$), 7.09 (4H, d, *J* = 9.0 Hz, aromatic C$\underline{H}$), 3.89 (6H, s, OC$\underline{H}_3$), 3.81 (4H, s, ethylene C$\underline{H}_2$).

^{13}C{^{1}H} NMR (75 MHz, D_2O), δ: 159.33 (quaternary $\underline{C}$–N), 127.48 (quaternary $\underline{C}$–OMe), 123.23, and 115.73 (aromatic $\underline{C}$H), 55.82 (O-$\underline{C}H_3$), 45.45 (ethylene $\underline{C}H_2$).

(2.10c) 1,3-Bis(4-methoxyphenyl)imidazolinium chloride
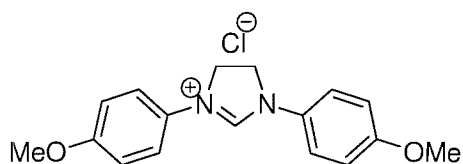
This was prepared in the same way as compound **2.9c** using the following: *N,N'*-bis(4-methoxyphenyl) ethylenebis(ammonium) dichloride (2.35 g, 6.89 mmol). Yield 2.00 g (6.27 mmol), 91%.

ES$^+$MS *m/z* (%): 283.2 and 284.2 [M]$^+$.

HRMS (ES$^+$): calcd for $[C_{17}H_{19}N_2O_2]^+$: 283.1447, found: 283.1448.

^{1}H NMR (300MHz, d_6-DMSO), δ: 9.90 (1H, s, imidazolinium $\underline{H}$), 7.70 and 7.10 (2 × 4H, d, *J* = 9.0 Hz, aromatic C$\underline{H}$), 4.55 (4H, s, backbone C$\underline{H}_2$), 3.80 (6H, s, OC$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, d_6-DMSO), δ: 155.13 (aromatic quaternary $\underline{C}$-N), 151.68 (imidazolinium $\underline{C}$), 127.73 (aromatic quaternary $\underline{C}$-O), 123.39 (aromatic $\underline{C}$H), 119.82 (aromatic $\underline{C}$H), 48.50 (imidazolinium backbone $\underline{C}H_2$), 38.34 (O$\underline{C}H_3$).

(2.11a) *N,N'*-Bis(2,4-dimethoxyphenyl)oxalamide

This was prepared in the same way as compound **2.8a** using the following: 2,4-dimethoxyaniline (3.22 g, 21.00 mmol), oxalyl chloride (0.90 mL, 10.00 mmol) and NEt_3 (2.90 mL). Yield 3.00 g (8.30 mmol), 83%.

Anal. Calcd for $C_{42}H_{52}N_4Pd$: C, 70.13; H, 7.29; N, 7.79 % Found: C, 69.7; H, 7.2; N, 7.9%.

^{1}H NMR (300MHz, d_6-DMSO), δ: 10.28 (2H, br. s, -N$\underline{H}$), 7.38 (2H, m, C$\underline{H}$ aromatics), 7.01 and 6.85 (2 × 2H, m, C$\underline{H}$ aromatics), 3.90 (6H, s, OC$\underline{H}_3$), 3.68 (6H, s, OC$\underline{H}_3$).

^{13}C NMR data could not be collected since the compound was almost insoluble in all common deuterated solvents.

(2.11b) *N,N'*-Bis(2,4-dimethoxyphenyl)ethylenebis(ammonium) dichloride

This was prepared in the same way as compound **2.9b** using the following: *N,N'*-bis(2,4-dimethoxyphenyl)oxalamide (2.91 g, 8.10 mmol) and $LiAlH_4$ (0.61g, 16.00 mmol). Yield 2.65 g (6.56 mmol), 81%.

^{1}H NMR (300MHz, D_2O), δ: 7.21 (2H, d, J = 9.3 Hz, aromatic C$\underline{H}$), 6.64 (4H, m, aromatic C$\underline{H}$), 3.92 (6H, s, OC$\underline{H}_3$), 3.88 (6H, s, OC$\underline{H}_3$), 3.80 (4H, s, ethylene C$\underline{H}_2$).

^{13}C{^{1}H} NMR (75 MHz, D_2O), δ: 160.82 (quaternary $\underline{C}$-N), 152.69 and 115.28 (quaternary $\underline{C}$–OMe), 123.83, 105.84 and 99.64 (aromatic $\underline{C}$H), 56.06 (O–$\underline{C}H_3$), 55.89 (O–$\underline{C}H_3$), 43.79 (ethylene $\underline{C}H_2$).

(2.11c) 1,3-Bis(2,4-dimethoxyphenyl)imidazolinium chloride
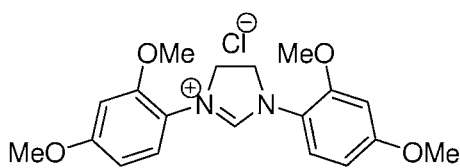
This was prepared in the same way as compound **2.9c** using the following: *N,N'*-bis(2,4-dimethoxyphenyl)ethylenebis(ammonium) dichloride (2.65 g, 6.56 mmol). Yield 2.29 g (6.04 mmol), 92%.

ES$^+$MS *m/z* (%): 343.2 and 344.2 [M]$^+$.

HRMS (ES$^+$): calcd for $[C_{19}H_{23}N_2O_4]^+$: 343.1658, found: 343.1660.

^{1}H NMR (300MHz, d_6-DMSO), δ: 9.24 (1H, s, imidazolinium C$\underline{H}$), 7.48 (2H, d, J = 9.0 Hz, aromatic C$\underline{H}$), 6.80 (2H, d, J = 2.7 Hz, aromatic C$\underline{H}$), 6.66 (2H, dd, J = 2.7, 9.0 Hz, aromatic C$\underline{H}$), 4.64 (4H, s, backbone C$\underline{H}_2$), 3.92 (6H, s, OC$\underline{H}_3$), 3.82 (6H, s, OC$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, d_6-DMSO), δ: 160.16 (quaternary $\underline{C}$–N), 157.06 (imidazolinium $\underline{C}$H), 153.29 and 117.88 (quaternary $\underline{C}$-O), 125.09, 105.25 and 99.69 (aromatic $\underline{C}$H), 56.28 (O$\underline{C}H_3$), 55.65 (O$\underline{C}H_3$), 50.43 (backbone $\underline{C}H_2$).

(2.12a) N,N'-Bis(2-isopropoxyphenyl)oxalamide

This was prepared in the same way as compound **2.8a** using the following: 2-isopropoxyaniline (2.55 g, 21.00 mmol), oxalyl chloride (0.90 mL, 10.00 mmol) and NEt$_3$ (2.90 mL). The final product is soluble in ether; the solvent was removed under vacuum from an etherial solution of the product and the resulting solid was recrystallysed from a saturated ether solution to get a light yellow solid. Yield 3.03 g (8.50 mmol), 85%. Anal. Calcd for $C_{20}H_{24}N_2O_4$: C, 67.40; H, 6.79; N, 7.86 % Found: C, 67.4; H, 6.8; N, 7.9%.

^{1}H NMR (300MHz, CDCl$_3$), δ: 10.04 (2H, br. s, N$\underline{H}$), 8.44 (2H, dd, J = 1.5, 8.1 Hz, aromatic C$\underline{H}$), 7.11 (2H, m, aromatic C$\underline{H}$), 6.96 (4H, m, aromatic C$\underline{H}$), 4.63 (2H, sept., J = 6.0 Hz, C$\underline{H}$(CH$_3$)$_2$), 1.43 (12H, d, J = 6.0 Hz, CH(C$\underline{H}_3$)$_2$).

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$), δ: 157.44 (quaternary. $\underline{C}$–N), 147.17 (quaternary. $\underline{C}$–O^{i}Pr), 127.25 (quaternary. $\underline{C}$=O), 125.06, 120.94, 119.79 and 113.15 (aromatic $\underline{C}$H), 71.76 ($\underline{C}$H(CH$_3$)$_2$), 22.11 (CH($\underline{C}$H$_3$)$_2$).

(2.12b) N,N'-Bis(2-isopropoxyphenyl)ethylenebis(ammonium) dichloride

This was prepared in the same way as compound **2.9b** using the following: N,N'-bis(2-isopropoxyphenyl)oxalamide (2.89 g, 8.10 mmol) and LiAlH$_4$ (0.61 g, 16.00 mmol). Yield 2.76 g (6.89 mmol), 85%.

^{1}H NMR (300MHz, D$_2$O), δ: 7.44 (2H, t, J = 7.8 Hz, aromatic C$\underline{H}$), 7.32 (2H, dd, J = 1.5, 7.8 Hz, aromatic C$\underline{H}$), 7.18 (2H, d, J = 8.4 Hz, aromatic C$\underline{H}$), 7.07 (2H, dd, J = 1.5, 8.4 Hz, aromatic C$\underline{H}$), 4.73 (2H, sept., J = 6.0 Hz, C$\underline{H}$(CH$_3$)$_2$), 3.76 (4H, s, ethylene C$\underline{H}_2$), 1.27 (12H, d, J = 6.0 Hz, CH(C$\underline{H}_3$)$_2$).

^{13}C{^{1}H} NMR (75 MHz, D$_2$O), δ: 149.64 (quaternary $\underline{C}$–N), 130.45, 122.52, 121.20 and 114.60 (aromatic $\underline{C}$H), 123.43 (quaternary $\underline{C}$–O^{i}Pr), 71.81 ($\underline{C}$H(CH$_3$)$_2$), 44.06 (ethylene $\underline{C}$H$_2$), 20.93 (CH($\underline{C}$H$_3$)$_2$).

(2.12c) 1,3-Bis(2-isopropoxyphenyl)imidazolinium chloride
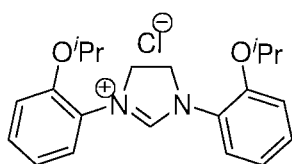
This was prepared using the same way as compound **2.9c** using the following: N,N'-bis(2-isopropoxyphenyl)ethylene bis(ammonium) dichloride (2.76 g, 6.89 mmol). Yield 2.33 g (6.20 mmol), 90%.

ES$^+$MS m/z (%): 339.2 and 340.2 [M]$^+$.

HRMS (ES$^+$): calcd for [$C_{21}H_{27}N_2O_2$]$^+$: 339.2073, found: 339.2077.

^{1}H NMR (300MHz, d_6-DMSO), δ: 10.28 (1H, s, imidazolinium C$\underline{H}$), 7.83 (2H, t, J = 7.8 Hz, aromatic C$\underline{H}$), 7.51 (2H, dd, J = 1.5, 7.8 Hz, aromatic C$\underline{H}$), 7.19 (2H, d, J = 8.4 Hz, aromatic C$\underline{H}$), 6.98 (2H, dd, J = 1.5, 8.4 Hz, aromatic C$\underline{H}$), 4.51 (2H, sept., J = 6.0 Hz, C$\underline{H}$(CH$_3$)$_2$), 3.89 (4H, s, backbone C$\underline{H}_2$), 1.54 (12H, d, J = 6.0 Hz, CH(C$\underline{H}_3$)$_2$).

^{13}C{^{1}H} NMR (75 MHz, d_6-DMSO), δ: 156.81 (quaternary $\underline{C}$–N), 151.34 (imidazolinium $\underline{C}$H), 132.31, 123.12, 120.89 and 115.71 (aromatic $\underline{C}$H), 128.34 (quaternary $\underline{C}$–O^{i}Pr), 69.13 ($\underline{C}$H(CH$_3$)$_2$), 46.09 (ethylene $\underline{C}$H$_2$), 21.33 (CH($\underline{C}$H$_3$)$_2$).

(2.13a) *N,N'*-Bis(4-isopropoxyphenyl)oxalamide

This was prepared in the same way as compound **2.8a** using the following: 4-isopropoxy aniline (2.55 g, 21.00 mmol), oxalyl chloride (0.90 mL, 10.00 mmol) and NEt$_3$ (2.90 mL) Yield 2.96 g (8.30 mmol), 83%.

Anal. Calcd for C$_{20}$H$_{24}$N$_2$O$_4$: C, 67.40; H, 6.79; N, 7.86 % Found: C, 67.4; H, 6.8; N, 7.9%.

^{1}H NMR (300MHz, d_6-DMSO), δ: 10.66 (2H, s, N$\underline{H}$), 7.74 (4H, d, J = 9.0 Hz, aromatic C$\underline{H}$), 6.90 (4H, d, J = 9.0 Hz, aromatic C$\underline{H}$), 4.58 (2H, sept., J = 6.0 Hz, C$\underline{H}$(CH$_3$)$_2$), 1.25 (12H, d, J = 6.0 Hz, CH(C$\underline{H}_3$)$_2$).

^{13}C NMR data could not be collected since the compound was almost insoluble in all common deuterated solvents.

(2.13b) *N,N'*-Bis(4-isopropoxyphenyl)ethylenebis(ammonium) dichloride

This was prepared in the same way as compound **2.9b** using the following: *N,N'*-bis(4-isopropoxyphenyl)oxalamide (2.89 g, 8.10 mmol) and LiAlH$_4$ (0.61 g, 16.00 mmol). Yield 2.76 g (6.89 mmol), 85%

^{1}H NMR (300MHz, D$_2$O), δ: 7.31 and 6.82 (2 × 4H, d, J = 9.0 Hz, aromatic C$\underline{H}$), 4.32 (2H, sept., J = 6.9 Hz, 2 × C$\underline{H}$(CH$_3$)$_2$), 3.72 (4H, s, ethylene C$\underline{H}_2$), 1.18 (12H, d, J = 6.9 Hz, 2 × CH(C$\underline{H}_3$)$_2$).

^{13}C{^{1}H} NMR (75 MHz, D$_2$O), δ: 154.92 (quaternary $\underline{C}$–N), 130.12 (2 × quaternary $\underline{C}$–O^{i}Pr), 118.35 (aromatic $\underline{C}$H), 115.53 (aromatic $\underline{C}$H), 69.50 ($\underline{C}$H(CH$_3$)$_2$), 43.12 (ethylene $\underline{C}$H$_2$), 20.09 (CH($\underline{C}$H$_3$)$_2$).

(2.13c) 1,3-Bis(4-isopropoxyphenyl)imidazolinium chloride
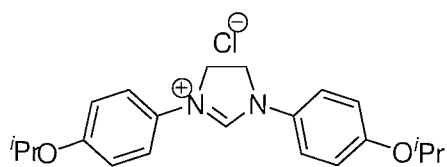
This was prepared in the same way as compound **2.9c** using the following: N,N'-bis-(4-isopropoxyphenyl)ethylenebis(ammonium) dichloride (2.76 g, 6.89 mmol). Yield 2.40 g (6.41 mmol), 93%.

ES$^+$MS m/z (%): 339.2 and 340.2 [M]$^+$.

HRMS (ES$^+$): calcd for [$C_{21}H_{27}N_2O_2$]$^+$: 339.2073, found: 339.2071.

^{1}H NMR (300MHz, d_6-DMSO), δ: 10.16 (1H, s, imidazolinium C$\underline{H}$), 7.66 and 7.04 (2 × 4H, d, J = 9.0 Hz, aromatic C$\underline{H}$), 4.65 (2H, sept., J = 6.0 Hz, 2 × C$\underline{H}$(CH$_3$)$_2$), 4.53 (4H, s, backbone C$\underline{H}_2$), 1.26 (12H, d, J = 6.0 Hz, 2 × CH(C$\underline{H}_3$)$_2$).

^{13}C{^{1}H} NMR (75 MHz, d_6-DMSO), δ: 155.97 (quaternary $\underline{C}$–N), 150.51 (imidazolinium $\underline{C}$H), 129.06 (2 × quaternary $\underline{C}$–O^{i}Pr), 119.99 (aromatic $\underline{C}$H), 116.20 (aromatic $\underline{C}$H), 69.53 ($\underline{C}$H(CH$_3$)$_2$), 48.44 (backbone $\underline{C}$H$_2$), 21.59 (CH($\underline{C}$H$_3$)$_2$).

(2.14a) N,N'-bis(2,4,6-trimethoxyphenyl) oxalamide

See compound **2.8a**

(2.14b) N,N'-Bis(2,4,6-trimethoxyphenyl)ethylenebis(ammonium) dichloride

This was prepared in the same way as compound **2.9b** using the following: N,N'-bis(2,4,6-trimethoxyphenyl)oxalamide (3.77 g, 8.10 mmol) and LiAlH$_4$ (0.61 g, 16.00 mmol). Yield 2.83 g (6.08 mmol), 75%.

^{1}H NMR (300MHz, CDCl$_3$), δ: 6.90 (4H, s, aromatic C$\underline{H}$), 4.53 (4H, s, ethylene C$\underline{H}_2$), 3.56 (12H, s, o-OC$\underline{H}_3$), 2.69 (6H, s, p-OC$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$), δ: 161.20 (aromatic quaternary $\underline{C}$–N), 152.87 (aromatic quaternaries o-$\underline{C}$–OCH$_3$), 101.16 (aromatic quaternary p-$\underline{C}$–OCH$_3$), 90.16 (aromatic $\underline{C}$H), 56.41 (o-O$\underline{C}$H$_3$), 55.50 (p-O$\underline{C}$H$_3$), 42.63 (ethylene $\underline{C}$H$_2$).

(2.14c) 1,3-Bis(2,4,6-trimethoxyphenyl)imidazolinium chloride
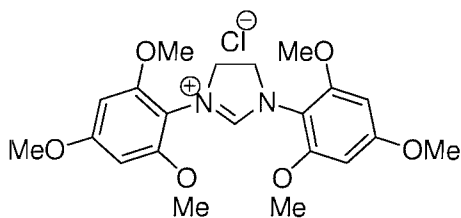
This was prepared in the same way as compound **2.9c** using the following: N,N'-bis(2,4,6-trimethoxyphenyl)ethylenebis(ammonium) dichloride (2.83g, 6.08 mmol). Yield 2.22 g (5.05 mmol), 83%.

ES$^+$MS m/z (%): 403.2 and 404.2 [M]$^+$.

HRMS (ES$^+$): calcd for [C$_{21}$H$_{27}$N$_2$O$_6$]$^+$: 403.1869, found: 403.1864.

^{1}H NMR (300MHz, CDCl$_3$), δ: 7.90 (1H, s, imidazolinium C$\underline{H}$), 6.11 (4H, s, aromatic C$\underline{H}$), 4.40 (4H, s, backbone C$\underline{H}_2$), 3.83 (12H, s, o-OC$\underline{H}_3$), 3.78 (6H, s, p-OC$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$), δ: 161.97 (aromatic quaternary $\underline{C}$-N), 160.20 (imidazolinium $\underline{C}$H), 155.77 (aromatic quaternaries o-$\underline{C}$-OCH$_3$), 105.61 (aromatic quaternary p-$\underline{C}$-OCH$_3$), 90.87 (aromatic $\underline{C}$H), 56.31 (o-O$\underline{C}$H$_3$), 55.69 (p-O$\underline{C}$H$_3$), 51.25 (backbone $\underline{C}$H$_2$).

(2.15a) N,N'-Bis(2-ethylphenyl)ethylenediimine

Glyoxal (0.39 g of 40% aq. solution, 2.50 mmol) was dissolved in a mixture of -propan-2-ol (30 mL) and water (10 mL) and was slowly added to a solution of 2-ethylaniline (0.61 g, 5.00 mmol) in propan-2-ol (100 mL). The mixture was stirred overnight. The resulting yellow precipitate was then filtered, washed with cold water and dried under vacuum. Yield: 0.52 g (1.95 mol), 78%.

ES$^+$MS m/z (%): 265.3 and 266.3 [M]$^+$.

^{1}H NMR (300MHz, CDCl$_3$), δ: 8.35 (2H, s, ethylene C$\underline{H}$), 7.27 (6H, m, aromatic C$\underline{H}$), 7.02 (2H, m, aromatic C$\underline{H}$), 2.84 (4H, q, J = 7.5 Hz, C$\underline{H}_2$CH$_3$), 1.23 (6H, d, J = 7.5 Hz, CH$_2$C$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$), δ: 159.71 (ethylene $\underline{C}$H), 148.98 (quaternary $\underline{C}$-N), 138.94 (quaternary aromatic $\underline{C}$-Et), 128.97, 127.93, 126.76 and 117.29 (aromatic $\underline{C}$H), 24.62 ($\underline{C}$H$_2$CH$_3$), 22.21 (CH$_2$$\underline{C}H_3$).

(2.15b) N,N'-Bis(2-ethylphenyl)ethylenebis(ammonium) dichloride

N-N'-Bis(2-ethylphenyl)ethylenediimine (2.15a) (2.14 g, 8.10 mmol) was dissolved in THF and added dropwise to a pre-cooled (0 °C) LiAlH$_4$ (0.61 g, 16.00 mmol) THF suspension (10 mL). The mixture was refluxed overnight. After cooling to 0 °C, methanol was added dropwise until the bubbling ceased. The mixture was then hydrolysed with an aqueous solution of NaOH (2.0 g) and MgSO$_4$ (2.0 g). The resulting slurry was filtered and the solid was washed with THF. The filtrate was evaporated and the resulting oil was dissolved in methanol. Concentrate HCl was then added and the solvents were removed to yield a solid. The solid was collected, washed with acetone and dried under vacuum. Yield 2.35 g (6.89 mmol), 85%.

^{1}H NMR (300MHz, d_6-DMSO), δ: 7.32 (4H, br.s, N$\underline{H}_2$), 7.21 (8H, m, aromatic C$\underline{H}$), 3.63 (4H, s, ethylene C$\underline{H}_2$), 2.72 (4H, q, J = 7.2 Hz, C$\underline{H}_2$CH$_3$), 1.15 (6H, t, J = 7.2 Hz, CH$_2$C$\underline{H}_3$).

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$^{13}C\{^{1}H\}$ NMR (75 MHz, d_6-DMSO), δ: 137.35 (quaternary $\underline{C}$–N), 134.47 (quaternary. $\underline{C}$-CH$_2$CH$_3$), 129.46, 127.05, 125.17 and 118.73 (aromatic $\underline{C}$H), 44.99 (ethylene $\underline{C}$H$_2$), 22.72 ($\underline{C}$H$_2$CH$_3$), 14.21 (CH$_2\underline{C}$H$_3$).

(2.15c) 1,3-Bis(2-ethylphenyl)imidazolinium chloride

This was prepared in the same way as compound **2.9c** using the following: N,N'-bis(2-ethylphenyl)ethylenebis(ammonium) dichloride (2.08 g, 6.08 mmol). Yield 1.78 g (5.65 mmol), 93%

ES$^+$MS m/z (%): 279.2 and 280.2 [M]$^+$.

HRMS (ES$^+$): calcd for [C$_{21}$H$_{23}$N$_2$]$^+$: 279.1861, found: 279.1859.

^{1}H NMR (300MHz, D$_2$O), δ: 8.65 (1H, s, imidazolinium $\underline{C}$H), 7.60 and 7.51 (8H, m, aromatic $\underline{C}$H), 4.67 (4H, s, backbone $\underline{C}$H$_2$), 2.86 (4H, q, J = 7.5 Hz, $\underline{C}$H$_2$CH$_3$), 1.38 (6H, t, J = 7.5 Hz, CH$_2\underline{C}$H$_3$).

$^{13}C\{^{1}H\}$ NMR (75 MHz, D$_2$O), δ: 158.10 (imidazolinium $\underline{C}$H), 140.43 (quaternary $\underline{C}$–N), 133.85 (quaternary $\underline{C}$–CH$_2$CH$_3$), 130.67, 130.40, 127.74 and 126.49 (aromatic $\underline{C}$H), 53.12 (backbone $\underline{C}$H$_2$), 23.71 ($\underline{C}$H$_2$CH$_3$), 14.55 (CH$_2\underline{C}$H$_3$).

(2.16a) N,N'-Bis(2-isopropylphenyl)ethylenediimine

This was prepared in the same way as compound **2.15a** using the following: glyoxal (0.39 g of 40% aq. solution, 2.50 mmol) and 2-isopropylaniline (0.68 g, 5.00 mmol). Yield 0.63 g (2.15 mmol), 86%

ES$^+$MS m/z (%): 293.2 and 294.2 [M]$^+$.

^{1}H NMR (300MHz, CDCl$_3$), δ: 8.36 (2H, s, ethylene $\underline{C}$H), 7.30 (6H, m, aromatic $\underline{C}$H), 7.01 (2H, dd, J = 1.2, 7.8 Hz, aromatic $\underline{C}$H), 3.61 (2H, sept., J = 6.9 Hz, $\underline{C}$H(CH$_3$)$_2$), 1.28 (12H, d, J = 6.9 Hz, CH($\underline{C}$H$_3$)$_2$).

$^{13}C\{^{1}H\}$ NMR (75 MHz, CDCl$_3$), δ: 159.63 (ethylene $\underline{C}$H), 148.36 (quaternary $\underline{C}$–N), 143.26 (quaternary aromatic $\underline{C}$-^{i}Pr), 126.66, 119.03, 117.46 and 115.89 (aromatic $\underline{C}$H), 27.58 ($\underline{C}$H(CH$_3$)$_2$), 22.21 (CH($\underline{C}$H$_3$)$_2$).

(2.16b) N,N'-Bis(2-isopropylphenyl)ethylenebis(ammonium) dichloride

This was prepared in the same way as compound **2.15b** using the following: N,N'-bis(2-isopropylphenyl)ethylenediimine (1.78 g, 6.08 mmol). Yield 2.04 g (5.53 mmol), 91%.

^{1}H NMR (300MHz, d_6-DMSO), δ: 9.75 (4H, br.s, N$\underline{H}$$_2$), 7.35 (2H, dd, J = 1.5, 7.5 Hz, aromatic $\underline{C}$H), 7.18 (4H, m, aromatic $\underline{C}$H), 3.58 (4H, s, ethylene $\underline{C}$H$_2$), 3.24 (2H, sept., J = 6.9 Hz, $\underline{C}$H(CH$_3$)$_2$), 1.14 (12H, d, J = 6.9 Hz, CH($\underline{C}$H$_3$)$_2$).

$^{13}C\{^1H\}$ NMR (75 MHz, d_6-DMSO), δ: 138.97 (quaternary $\underline{C}$-N), 136.67 (quaternary $\underline{C}$–CH(CH$_3$)$_2$), 126.93, 126.78, 124.94 and 118.52 (aromatic $\underline{C}$H), 45.28 (ethylene $\underline{C}$H$_2$), 26.36 ($\underline{C}$H(CH$_3$)$_2$), 23.47 (CH($\underline{C}$H$_3$)$_2$).

(2.16c) 1,3-Bis(2-isopropylphenyl)imidazolinium chloride
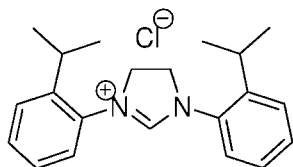
This was prepared in the same way as compound **2.9c** using the following: N,N'-bis(2-isopropylphenyl)ethylenebis(ammonium) dichloride (1.85 g, 5.00 mmol). Yield 1.61 g (4.70 mmol), 94% ES$^+$MS m/z (%): 307.3 and 308.3 [M]$^+$.

HRMS (ES$^+$): calcd for [C$_{21}$H$_{27}$N$_2$]$^+$: 307.2174, found: 307.2175.

^{1}H NMR (300MHz, CDCl$_3$), δ: 8.20 (1H, s, imidazolinium C$\underline{H}$), 8.10 (2H, dd, J = 7.2 Hz, aromatic C$\underline{H}$), 7.40 (4H, m, aromatic C$\underline{H}$), 7.20 (2H, m, aromatic C$\underline{H}$), 4.70 (4H, s, C$\underline{H}_2$ backbone), 3.00 (2H, sept., J = 6.9 Hz, 2 × C$\underline{H}$(CH$_3$)$_2$), 1.30 (12H, d, J = 6.9 Hz, 2 × CH(C$\underline{H}_3$)$_2$).

$^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$), δ: 157.42 (imidazolinium $\underline{C}$H), 144.40 (aromatic quaternary $\underline{C}$–N), 132.76 (aromatic quaternary $\underline{C}$–CH(CH$_3$)$_2$), 130.67, 128.33, 127.80 and 126.66 (aromatic $\underline{C}$H), 54.41 ($\underline{C}$H$_2$ backbone), 28.27 ($\underline{C}$H(CH$_3$)$_2$), 24.06 (CH($\underline{C}$H$_3$)$_2$).

(2.17a) N,N'-Bis[3,5-bis(trifluoromethyl)phenyl]oxalamide

This was prepared in the same way as compound **2.8a** using the following: 3,5-bis(trifluoromethyl)aniline (9.10 g, 40.00 mmol), oxalyl chloride (1.65 mL, 20.00 mmol) and NEt$_3$ (6.40 mL). After stirring overnight, all solvents were removed. The resulting solid was triturated in acetone and the precipitate (triethylammonium chloride) was filtered off. The solution obtained was collected and the solvent was removed. The resulting slurry was dissolved in petrol and filtered. The white solid obtained was washed with chloroform and dried under vacuum. Yield 4.42 g (8.30 mmol), 42%.

ES$^+$MS m/z (%): 511.2 and 512.2 [M]$^+$.

^{1}H NMR (300MHz, (CD$_3$)$_2$CO), δ: 10.62 (2H, br.s, N$\underline{H}$), 8.58 (4H, s, o-aromatic C$\underline{H}$), 7.73 (2H, s, p-aromatic C$\underline{H}$).

$^{13}C\{^1H\}$ NMR (75 MHz, (CD$_3$)$_2$CO), δ: 159.18 (2 × quaternary $\underline{C}$=O), 140.29 (2 × quaternary $\underline{C}$–N), 132.76 (q, J = 33.2 Hz, 4 × $\underline{C}$F$_3$), 124.26 (br. q, J = 270.3 Hz 4 × quaternary $\underline{C}$–CF$_3$) 121.23 (4 × o-aromatic $\underline{C}$H), 118.81 (2 × p- aromatic $\underline{C}$H).

$^{19}F\{^1H\}$ NMR (282 MHz, (CD$_3$)$_2$CO), δ: –62.97 (C$\underline{F}_3$).

(2.17b) N,N'-Bis[3,5-bis(trifluoromethyl)phenyl]ethylenediamine

Compound **2.17a** (1.00 g, 1.95 mmol) was dissolved in THF. To this a BH_3·THF solution (1.0 M, 10.00 mL, 10.00 mmol) was added dropwise. The mixture was refluxed at 70 °C overnight. After cooling to r.t., water was added dropwise until the bubbling ceased. The solvents were removed under vacuum and the aqueous solution was worked up with ether. The organic layer was washed with $NaHCO_3$ (aq.) solution, brine and finally dried over $MgSO_4$. Solvents were removed and the white solid was dried under vacuum. Yield 0.91g (1.90 mmol), 97%.

ES^+MS m/z (%): 484.2 and 485.2 $[M]^+$.

^1H NMR (300MHz, $CDCl_3$), δ: 7.12 (2H, s, p-aromatic C$\underline{H}$), 6.87 (4H, s, o-aromatic C$\underline{H}$), 4.28 (2H, br.s, N$\underline{H}$), 4.45 (4H, s, C$\underline{H}_2$ ethylene).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$), δ: 147.30 (2 × quaternary $\underline{C}$-N), 131.78 (q, J = 32.7 Hz, 4 × $\underline{C}F_3$), 122.43 (br. q, J = 271.1 Hz, 4 × quaternary $\underline{C}$-CF3) 111.13 (4 × o-aromatic $\underline{C}$H), 110.15 (2 × p-aromatic $\underline{C}$H), 41.68 (2 × ethylene $\underline{C}$H2).

$^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$), δ: -63.55 (C$\underline{F}_3$).

(2.17c) 1,3-Bis[3,5-bis(trifluoromethyl)phenyl]imidazolinium tetrafluoro borate
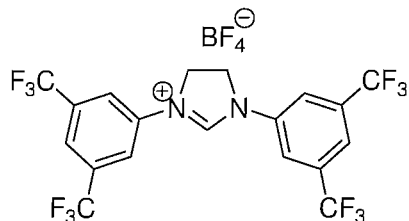
Compound **2.17b** (1.00 g, 2.06 mmol), was dissolved in triethyl orthoformate (20 mL) and to this NH_4BF_4 (0.22 g, 2.06 mmol) was added. The mixture was then heated at 100 °C for approx. 5 hrs. The white solid obtained was then collected and washed with ether and then washed with chloroform before it was dried under vacuum. Yield: 0.78g (1.34 mmol), 65%.

ES^+MS m/z (%): 495.1 and 496.1 $[M]^+$.

HRMS (ES^+): calcd for $[C_{19}H_{11}F_{12}N_2]^+$: 495.0731, found: 495.0729.

^1H NMR (300MHz, $(CD_3)_2CO$), δ: 10.36 (1H, s, imidazolinium C$\underline{H}$), 8.38 (4H, s, o-aromatic C$\underline{H}$), 8.13 (2H, s, p-aromatic C$\underline{H}$), 5.12 (4H, s, imidazolinium backbone C$\underline{H}_2$).

$^{13}C\{^1H\}$ NMR (75 MHz, $(CD_3)_2CO$), δ: 155.85 (imidazolinium $\underline{C}$H), 139.02 (2 × quaternary $\underline{C}$-N), 133.68 (q, J = 33.8 Hz, 4 × $\underline{C}F_3$), 123.85 (br. q, J = 271.2 Hz, 4 × quaternary $\underline{C}$-CF3) 122.02 (2 × p-aromatic $\underline{C}$H), 121.45 (4 × o-$\underline{C}$H aromatic), 50.89 (backbone $\underline{C}$H2).

$^{19}F\{^1H\}$ NMR (282 MHz, $(CD_3)_2CO$), δ: -62.97 (C$\underline{F}_3$), -151.25 (B$\underline{F}_4$).

(2.18a) *N,N'*-Bis(2-fluorophenyl)oxalamide

This was prepared in the same way as compound **2.8a** using the following: 2-fluoroaniline (2.00 g, 18.00 mmol), oxalyl chloride (0.90 mL, 9.00 mmol) and NEt$_3$ (3.70 mL). Yield 1.93 g (7.00 mmol), 78%.

ES$^+$MS m/z (%): 276.1 and 277.1 [M]$^+$.

^{1}H NMR (300MHz, d_6-DMSO), δ: 10.50 (2H, br.s, N$\underline{H}$), 7.71 (2H, t, J = 8.1 Hz, C$\underline{H}$ aromatic), 7.27 (6H, m, C$\underline{H}$ aromatics).

^{13}C{^{1}H} NMR (75 MHz, d_6-DMSO), δ: 158.21 (2 × quaternary $\underline{C}$=O), 155.14 (d, J = 246.0 Hz, $\underline{C}$F), 127.47 ($\underline{C}$H aromatic), 125.84 (aromatic $\underline{C}$H), 124.39 (aromatic $\underline{C}$H), 124.28 (2 × quaternary $\underline{C}$–N) 115.85 (d, J = 19.2 Hz, aromatic $\underline{C}$H).

^{19}F{^{1}H} NMR (282 MHz, d$_6$-DMSO), δ: –121.95 ($\underline{C}$F).

(2.18b) *N,N'*-Bis(2-fluorophenyl)ethylenediamine

To a solution of LiAlH$_4$ (0.40 g, 10.50 mmol) in THF (20 mL), cooled to 0 °C, compound **2.18a** (1.45 g, 5.30 mmol) in THF (20 mL) was added dropwise. The mixture was refluxed at 80 °C overnight. After cooling to 0 °C, methanol was added dropwise until the bubbling ceased. The mixture was then hydrolysed with an aqueous solution of NaOH (2.0g) and MgSO$_4$ (2.0g). The resulting slurry was filtered and the solid was washed with THF. The filtrate was evaporated and the resulting white solid was collected. Yield 1.14 g (4.60 mmol), 87%.

ES$^+$MS m/z (%): 248.1 and 249.1 [M]$^+$.

^{1}H NMR (300MHz, CDCl$_3$), δ: 7.00 (4H, m, aromatic C$\underline{H}$), 6.71 (4H, m, aromatic C$\underline{H}$), 4.13 (2H, br.s, N$\underline{H}$), 3.45 (4H, s, ethylene C$\underline{H}_2$).

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$), δ: 151.76 (d, J = 237.0 Hz, $\underline{C}$F), 136.40 (quaternary $\underline{C}$-N), 124.63 (aromatic $\underline{C}$H), 117.21 (aromatic $\underline{C}$H), 114.61 (d, J = 19.2 Hz, aromatic $\underline{C}$H) 112.20 (aromatic $\underline{C}$H), 42.94 (ethylene $\underline{C}$H$_2$).

^{19}F{^{1}H} NMR (282 MHz, CDCl$_3$), δ: –136.33 ($\underline{C}$F).

(2.18c) 1,3-Bis(2-fluorophenyl)imidazolinium tetrafluoroborate
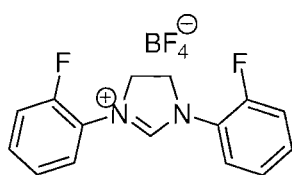
This was prepared as compound **2.17c** using the following: *N,N'*-bis(2-fluorophenyl)ethylenediamine (**2.18b**) (9.00 g, 36.30 mmol) and NH$_4$BF$_4$ (3.82 g, 36.30 mmol). Yield: 6.65 g (19.20 mmol), 53%.

ES$^+$MS m/z (%): 259.1 and 260.1 [M]$^+$.

HRMS (ES$^+$): calcd for [C$_{15}$H$_{13}$F$_2$N$_2$]$^+$: 259.1047, found: 259.1047.

^{1}H NMR (300MHz, (CD$_3$)$_2$CO), δ: 9.40 (1H, s, imidazolinium C$\underline{H}$), 7.79 (2H, m, aromatic C$\underline{H}$), 7.52 (4H, m, aromatic C$\underline{H}$), 7.41 (2H, m, aromatic C$\underline{H}$), 4.91 (4H, s, imidazolinium backbone C$\underline{H}_2$).

^{13}C{^{1}H} NMR (75 MHz, (CD$_3$)$_2$CO), δ: 157.92 (imidazolinium $\underline{C}$H), 156.00 (d, J = 248.0 Hz, $\underline{C}$F), 137.13 (quaternary $\underline{C}$-N), 131.25 (aromatic $\underline{C}$H), 126.58 (aromatic $\underline{C}$H), 125.39 (aromatic $\underline{C}$H), 117.91 (d, J = 19.8 Hz, aromatic $\underline{C}$H), 51.97 (backbone $\underline{C}$H$_2$).

^{19}F{^{1}H} NMR (282 MHz, (CD$_3$)$_2$CO), δ: –123.01 (C$\underline{F}$) and –151.95 (B$\underline{F}_4$).

(2.19a) *N,N'*-Bis(2,4-difluorophenyl)oxalamide

This was prepared in the same way as compound **2.8a** using the following: 2,4-difluoro aniline (3.50 g, 22.00 mmol), oxalyl chloride (0.90 mL, 10.00 mmol) and NEt$_3$ (2.90 mL). Yield 2.59 g (8.30 mmol), 83%.

ES$^+$MS *m/z* (%): 312.1 and 313.1 [M]$^+$.

^{1}H NMR (300MHz, d_6-DMSO), δ: 10.60 (2H, br.s, N$\underline{H}$), 7.65 (2H, m, aromatic C$\underline{H}$), 7.38 (2H, m, aromatic C$\underline{H}$), 7.16 (2H, m, aromatic C$\underline{H}$).

^{13}C{^{1}H} NMR (75 MHz, d_6-DMSO), δ: 160.02, (d, J = 232.5 Hz, $\underline{C}$F), 158.40 (2 × quaternary $\underline{C}$=O), 155.76 (d, J = 248.9 Hz, $\underline{C}$F), 127.71 (*o*-aromatic $\underline{C}$H), 120.82 (2 × quaternary $\underline{C}$–N), 111.40 (d, J = 19.0 Hz, *m*-aromatic $\underline{C}$H), 104.49 (t, J = 26.5 Hz, *m*-aromatic $\underline{C}$H).

^{19}F{^{1}H} NMR (282 MHz, d_6-DMSO), δ: –111.87 and –116.06 (2 × C$\underline{F}$).

(2.19b) *N,N'*-Bis(2,4-difluorophenyl)ethylenediamine

Compound **2.19a** (2.00 g, 6.40 mmol) was dissolved in THF (20 mL) and cooled to 0 °C. To this a LiAlH$_4$ (0.97 g, 25.00 mmol) in THF (20 mL) solution was added dropwise. The mixture was refluxed at 80 °C overnight. After cooling to 0 °C, methanol was added dropwise until the bubbling ceased. The mixture was then hydrolysed with a solution of NaOH (2.0g) and MgSO$_4$ (2.0g) in water(10 mL). The resulting slurry was filtered and the solid was washed with THF. The filtrate's solvents were removed and the resulting white solid was collected. Yield 1.76 g (6.19 mmol), 97%.

ES$^+$MS *m/z* (%): 284.1 and 285.1 [M]$^+$.

^{1}H NMR (300MHz, CDCl$_3$), δ: 7.73 (2H, m, aromatic C$\underline{H}$), 7.21 (2H, m, aromatic C$\underline{H}$), 6.99 (2H, m, aromatic C$\underline{H}$), 4.31 (2H, br.s, N$\underline{H}$), 3.56 (4H, s, ethylene C$\underline{H}_2$).

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$), δ: 157.34, (d, J = 238.6 Hz, $\underline{C}$F), 155.76 (d, J = 245.2 Hz, $\underline{C}$F), 136.40 (quaternary $\underline{C}$–N) 123.93 (aromatic $\underline{C}$H), 122.49 (2 × quaternary $\underline{C}$–N)

115.37 (d, J = 20.7 Hz, aromatic C$\underline{\text{H}}$), 108.71 (t, J = 26.1 Hz, aromatic C$\underline{\text{H}}$) 43.46 (ethylene C$\underline{\text{H}}_2$).

^{19}F{^{1}H} NMR (282 MHz, CDCl$_3$), δ: –110.32 and –117.10 (2 × C$\underline{\text{F}}$).

(2.19c) 1,3-Bis(2,4-difluorophenyl)imidazolinium tetrafluoroborate
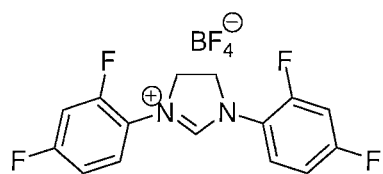
This was prepared like compound **2.17c** using the following: N,N'-bis(2,4-difluorophenyl)ethylenediamine (**2.19b**) (1.00 g, 3.52 mmol) and NH$_4$BF$_4$ (0.37 g, 3.52 mmol). Yield: 0.82 g (2.15 mmol), 61%.

ES$^+$MS m/z (%): 295.1 and 296.1 [M]$^+$.

HRMS (ES$^+$): calcd for [C$_{15}$H$_{11}$F$_4$N$_2$]$^+$: 295.0858, found: 295.0860.

^{1}H NMR (300MHz, (CD$_3$)$_2$CO), δ: 9.36 (1H, s, imidazolinium C$\underline{\text{H}}$), 7.88 (2H, m, aromatic C$\underline{\text{H}}$), 7.40 (2H, m, aromatic C$\underline{\text{H}}$), 7.24 (2H, m, aromatic C$\underline{\text{H}}$), 4.38 (4H, s, imidazolinium backbone C$\underline{\text{H}}_2$).

^{13}C{^{1}H} NMR (75 MHz, (CD$_3$)$_2$CO), δ: 161.42 (imidazolinium C$\underline{\text{H}}$), 158.58 (d, J = 236.8 Hz, C$\underline{\text{F}}$), 155.81 (d, J = 244.6 Hz C$\underline{\text{F}}$), 135.90 (quaternary $\underline{\text{C}}$-N), 127.60 (aromatic C$\underline{\text{H}}$), 113.52 (d, J = 22.9 Hz, aromatic C$\underline{\text{H}}$), 106.35 (t, J = 23.6 Hz, aromatic C$\underline{\text{H}}$), 52.42 (backbone C$\underline{\text{H}}_2$).

^{19}F{^{1}H} NMR (282 MHz, (CD$_3$)$_2$CO), δ: –108.49 and –117.81 (2 × C$\underline{\text{F}}$), –150.79 (B$\underline{\text{F}}_4$).

X-ray Crystallography

All data sets were collected on an Enraf-Nonius Kappa CCD area detector diffractometer with an FR591 rotating anode (Mo/Ka radiation) and an Oxford Cryosystems low temperature device operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. The programs used for control and integration were Collect, Scalepack, and Denzo.[30] The crystals were mounted on a glass fiber with silicon grease, from Fomblin vacuum oil. All solutions and refinements were performed using the WinGX package[31] and all software packages within. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogens were added using a riding model. Crystallographic data collected are presented in Table 2.2.

Table 2.2: Crystallographic data for compounds **2.1b**, **2.8c**, **2.9a**, **2.11a** and **2.12c**

	2.1b	2.8c	2.9a	2.11a	2.12c	2.17c	2.19c
Chemical formula	$C_{21}H_{25}N_3$	$C_{21}H_{27}BF_4N_2O_6$	$C_{16}H_{16}N_2O_4$	$C_{18}H_{18}N_2O_6$	$C_{21}H_{33}ClN_2O_5$	$C_{19}H_{11}BF_{16}N_2$	$C_{15}H_{11}BF_8N_2$
Formula weight	319.44	490.26	300.31	358.34	428.94	582.11	382.07
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P\,2_1/c$	$P\,2_1/c$	$P\,2_1/c$	P-1	$P\,2_1/n$	$Pbca$	$P2_1/c$
a / Å	8.319(3)	17.4391(12)	7.7065(15)	6.7934(3)	15.4360(6)	11.3248(8)	7.3769(3)
b / Å	10.787(5)	7.6873(7)	14.748(3)	7.8529(4)	6.7896(2)	12.6176(9)	30.8938(15)
c / Å	20.628(14)	16.8172(13)	6.8468(14)	7.9298(4)	21.5079	29.299(2)	7.0308(4)
α / °	90	90	90	95.656(3)	90	90	90
β / °	105.22(5)	102.049(5)	113.61(3)	99.510(3)	94.6060(10)	90	107.679(2)
γ / °	90	90	90	98.477(3)	90	90	90
V / Å^3	1786.2(16)	2204.8(3)	713.1(2)	409.38(3)	2246.84(14)	4186.6(5)	1526.65(13)
Z	4	4	2	1	4	8	4
T / K	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
μ / mm^{-1}	0.071	0.128	0.102	0.111	0.203	0.209	0.167
No. data collected	20952	23563	7471	8594	23885	25843	10931
No. unique data	3522	5041	2114	1887	5157	3682	2667
R_{int}	0.1669	0.0644	0.0223	0.0601	0.0543	0.1252	0.0779
Final $R(|F|)$ for $F_o > 2\sigma(F_o)$	0.0829	0.0799	0.0398	0.0567	0.0460	0.1102	0.0693
Final $R(F^2)$ for all data	0.1422	0.1152	0.0488	0.0756	0.0715	0.2022	0.1326

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Chapter 3:

Palladium imidazolin-2-ylidene

complexes

3.1 Introduction

Since the first report of a stable carbene by Arduengo in 1991,[1] the use of *N*-heterocyclic carbenes in organic synthesis has increased dramatically. This is principally due to their unique properties covered earlier in Chapters 1 and 2. Most importantly, NHCs are known to form strong bonds with late transition metals, since they are excellent σ-donors and possess minimal π-back donation.[2]

In situ generated palladium NHC complexes, prepared from the corresponding imidazolium salt precursors, have been shown to offer a significant advantage as catalysts for a range of synthetically valuable coupling reactions.[3] The first use of palladium(II) NHC complexes in the Heck reaction was reported by Herrmann *et al.* in 1995[4] and currently there are a number of reports describing structures of four-coordinate Pd(II) carbene species.[5] It has been postulated that the Pd(II) species, a stable catalyst precursor, must be converted into a Pd(0) complex for the coupling to occur.[4] Since then, carbene complexes of Pd(II) or Pd(0) have been widely used as catalysts or catalyst precursors for many reactions.[2]

As briefly mentioned in Chapter 1, palladium NHC complexes (mainly imidazol-2-ylidene complexes) can be easily synthesised by one of the following methods: a) Reaction of a palladium precursor complex with a silver carbene reagent, resulting in a mild and almost quantitative transmetallation; b) Interaction of a palladium precursor complex with the free carbene in an inert solvent; c) Reaction of the palladium precursor complex with the free carbene generated *in situ* from the corresponding imidazol(in)ium salt and lithium or potassium amide bases in THF.[6]

In this chapter, the synthesis and characterisation of a range of palladium imidazolin-2-ylidene complexes is described.

3.2 Results and Discussion

The novel pyridyl-functionalised imidazolin-2-ylidene complexes of palladium, imidazolin-2-ylidene palladacycle complexes, aryl substituted imidazolin-2-ylidene palladium complexes and alkoxyphenyl imidazolin-2-ylidene palladacycle complexes that have been synthesised and characterised during this project are summarised in Figure 3.1 below.

Ar = Mes, R = H   (3.2)
Ar = 2,6-dipp, R = Me (3.4)

Ar = Mes (3.3)

Ar = 2,6-dipp (3.5)

Ar = 2,6-dipp (3.6)

(3.8)

Ar = 2-ipp (3.9)

Ar = Mes (3.10)
Ar = 2-ipp (3.13)

Ar = Mes (3.11)

Ar = 2-ipp (3.12)

Ar = 2-ipp (3.14)

R = H, Ar = 4-methoxyphenyl   (3.15)
R = OMe, Ar = 2,4-dimethoxyphenyl (3.16)
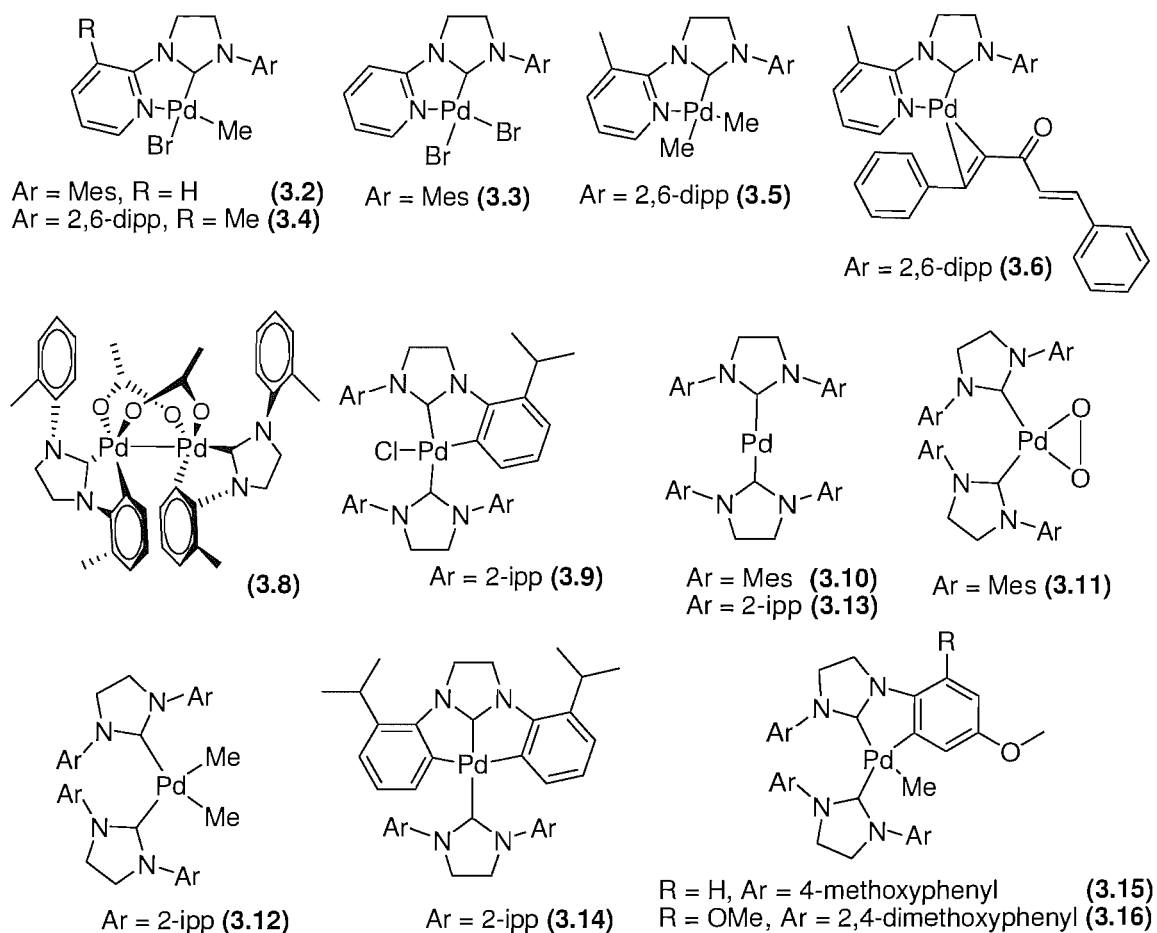
Figure 3.1: Novel palladium imidazolin-2-ylidene complexes

3.2.1 Palladium pyridyl functionalised NHC complexes

N-Functionalised NHCs are a relatively recent development in successful ligand design.[2] Their synthesis originated from the need to generate a tailor-made co-ordination sphere at the metal using chelating ligands offering a strongly bound, robust functional group (the N-heterocyclic carbene) with additional moieties carrying labile donors.[7] These moieties

can temporarily dissociate during catalytic reactions creating free co-ordination sites and electronic unsaturation, which is believed to be important for catalysis.
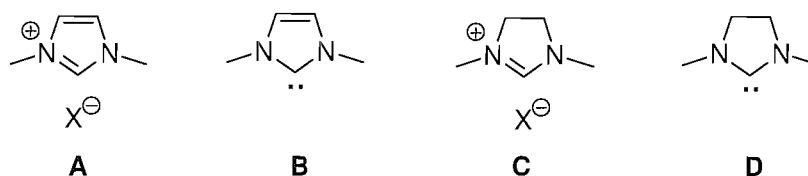
Figure 3.2: NHC precursors and free NHCs

In an effort to prepare such tailor-made ligands, our group[8] and others[9] have synthesised a number of NHC precursors (imidazolium salts, type **A** in Figure 3.2) functionalised with substituted pyridine rings. All of these prepared precursors feature an unsaturated NHC backbone, while a wide range of NHC precursors (imidazolinium salts, type **C** in Figure 3.2) prepared during the present project (Chapter 2) feature a saturated backbone.

Saturated NHCs (type **D** in Figure 3.2) are considered to be better σ-donors compared to the more widely used unsaturated NHCs (type **B** in Figure 3.2),[10] and therefore, when co-ordinated to a metal, make the metal centre of the complex more nucleophilic. This in turn might affect the catalytic properties of the complex, making it a better catalyst.
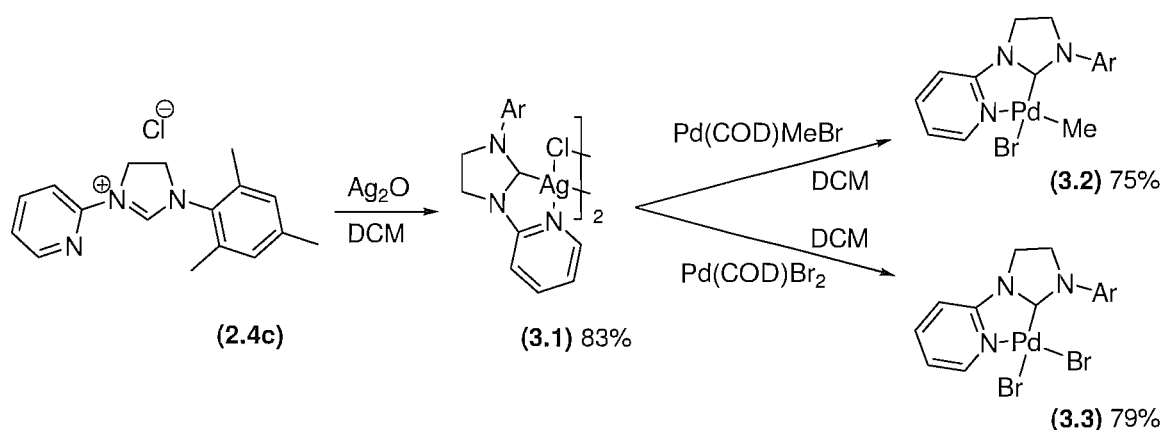
Scheme 3.1: Synthesis of palladium NHC complexes **3.2** and **3.3** *via* transmetallation of silver imidazolin-2-ylidene **3.1** Ar = 2,4,6-trimethylphenyl

Based on the modified method reported by past members of the group,[8a] 1-(2-pyridyl)-3-(2,4,6-trimethylphenyl)imidazolinium chloride (**2.4c**) was reacted with silver(I) oxide

as outlined in Scheme 3.1 to produce the silver imidazolin-2-ylidene **3.1**. Although the molecular structure of **3.1** has not been confirmed *via* X-ray crystallography, analytical data (MS[+]ES) support the proposed ratio of Ag to NHC to Cl in each molecule. Interaction of **3.1** with Pd(COD)MeBr or Pd(COD)Br$_2$ lead to the almost quantitative transmetallation,[6] yielding palladium imidazolin-2-ylidene complexes **3.2** and **3.3** respectively. The molecular structures of complexes **3.2** and **3.3** are displayed in Figures 3.3 and 3.4 respectively.
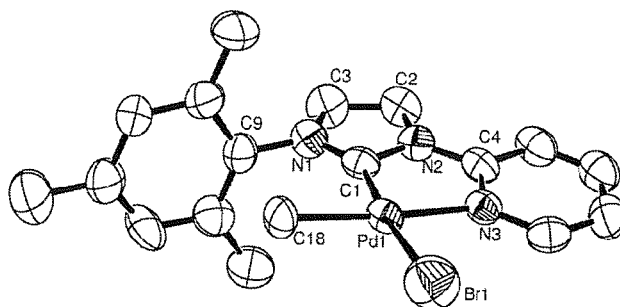
Figure 3.3: ORTEP representation of the structure of **3.2** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Pd1–C18: 2.116(8), Pd1–Br: 2.4311(15), Pd1–N3: 2.146(7), Pd1–C1: 1.984(8), C1–Pd1–C18: 97.0(3), C1–Pd1–N3: 79.6(3), C18–Pd1–N3: 175.8(3), C1–Pd1–Br1: 173.6(2), C18–Pd1–Br1: 88.8(2), N3–Pd1–Br1: 94.54(19).

Complex **3.2** adopts a slightly distorted square planar geometry around the Pd metal centre. The plane of the mesityl moiety is almost perpendicular (81.0 °) to the plane formed by the heterocyclic and the pyridyl rings in order to eliminate steric repulsions. The methyl group is situated *trans* to the pyridine ring, while the bromide atom is *trans* to the carbene. The palladium carbene bond length (Pd1–C1) is 1.984(8) Å, while the ligand bite angle is 79.6(3) °.

Figure 3.4: ORTEP representation of the structure of **3.3** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Pd1–C2: 1.962(5), Pd1–Br1: 2.397(9), Pd1–Br2: 2.422(16), Pd1–N1: 2.041(4), C2–Pd1–N1: 80.39(19), C2–Pd1–Br1: 97.9(3), N1–Pd1–Br1: 177.0(2), C2–Pd1–Br2: 173.3(3), N1–Pd1–Br2: 94.6(4), Br1–Pd1–Br2: 87.2(5).

Complex **3.3** also adopts a distorted square planar geometry. The two halide sites show mixed chloride and bromide occupancy. This was caused by the two different halides present in the reaction mixture (Cl anion of the imidazolinium salt and Br from the metal complex precursor). The plane of the mesityl moiety is perpendicular to the plane formed by the heterocyclic and the pyridyl rings. The bond distance between Pd and Br1, which is *trans* to the pyridine, is shorter than the bond distance of Pd and Br2, which is *trans* to the NHC (2.397(9) and 2.422(16) respectively), due to the *trans* ligand influence. The palladium carbene bond length in this case is 1.962(5) Å while the ligand bite angle is 80.39(19) ° which is almost equal to that of complex **3.2** within the observed estimated standard deviations.

A very popular method for preparing metal imidazolin-2-ylidene complexes is the *in situ* deprotonation of the imidazolinium salt using a base, followed by reaction with a metal precursor.[11] Based on this method, imidazolinium chloride **2.6c** was deprotonated *in situ* using KN(SiMe3)2[12] as the deprotonation base and the resulting free ylidene was reacted with Pd(COD)MeBr, Pd(TMEDA)Me2 or Pd(DBA)2 to yield the palladium imidazolin-2-ylidene complexes **3.4**, **3.5** and **3.6** respectively in good yields. All three novel complexes were purified by crystallisation and were then isolated as crystalline solids.

Scheme 3.2: Synthesis of palladium NHC complexes **3.4**, **3.5** and **3.6**

by *in situ* deprotonation of imidazolinium salt **2.6c**

Ar = 2,6-diisopropylphenyl

The molecular structures of complexes **3.4**, **3.5** and **3.6** were determined by single crystal X-ray diffraction studies and are displayed in Figures 3.5, 3.6 and 3.8 respectively.

Figure 3.5: ORTEP representation of the structure of **3.4** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Pd1–C1: 1.972(4), Pd1–C22: 2.053(4), Pd1–N1: 2.130(3), Pd1–Br1: 2.4846(6), C1–Pd1–C22: 96.94(17), C1–Pd1–N1: 79.19(15), C22–Pd1–N1: 174.77(15), C1–Pd1–Br1: 173.75(12), C22–Pd1–Br1: 89.31(12), N1–Pd1–Br1: 94.58(9).

Complex **3.4** (Figure 3.5) adopts the preferred square planar geometry (slightly distorted) around the metal centre. As in complex **3.2**, the plane of the aryl moiety is perpendicular to the plane formed by the heterocyclic and the pyridyl rings. Furthermore, the methyl group of the palladium centre is situated *trans* to the pyridyl ring while the bromide is *trans* to the NHC exactly like complex **3.2**. The palladium carbene bond length (Pd1–C1) is 1.972(4) Å while the ligand bite angle is 79.19(15) °. Both values are almost equal (within the observed estimated standard deviations) to those of complex **3.2**.

Figure 3.6: ORTEP representation of the structure of **3.5** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Pd1–C2: 2.0294(18), Pd1–N1: 2.124(2), Pd1–C22: 2.0762(19), Pd1–C23: 2.034(2), C2–Pd1–C23: 101.92(8), C2–Pd1–C22: 173.20(7), C23–Pd1–C22: 84.89(9), C2–Pd1–N1: 77.63(8), C23–Pd1–N1: 176.49(6), C22–Pd1–N1: 95.58(8).

The structure of complex **3.5** (Figure 3.6) resembles the structure of complex **3.3**, although instead of bromides, methyl groups are co-ordinated on the palladium metal centre. The bond between of Pd1 and C23, which is *trans* to the pyridine, is shorter than the bond distance of Pd1 and C22, which is *trans* to the NHC (2.034(2) and 2.0762(19) respectively), due to the *trans* ligand influence effect. The bond length of the palladium carbene bond is considerably longer compared to that of complex **3.3** (2.0294(18) and 1.962(5) Å respectively). However, the ligand bite angle of complex **3.5** is smaller (77.63(8) °) than that of complex **3.3** (80.39(19) °).

Furthermore, the structure of complex **3.5** can be compared to the Pd-NHC complex shown in Figure 3.7 (denoted **3.5***) that was synthesised by former members of the group.[13] It features an unsaturated backbone NHC substituted with the same moieties (3-methylpyridyl and 2,6-diisopropylphenyl) as the NHC featured on **3.5**.

(3.5)   (3.5*)
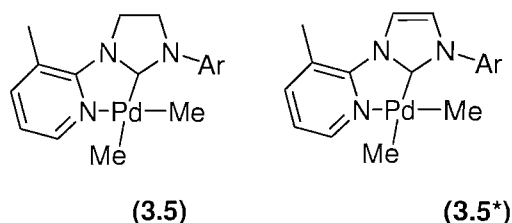
Figure 3.7: Pd-NHC complex **3.5** and Pd-NHC complex **3.5*** with unsaturated backbone
Ar = 2,6-diisopropylphenyl

A list of selected bond lengths and angles for both **3.5** and **3.5*** are shown in Table 3.1 for comparison purposes. The atom numbering used for both complexes is the same and can be found in Figure 3.6. As seen in Table 3.1, all bond lengths and angles around the palladium metal centre are almost equal within the estimated standard deviations. It can be therefore assumed that the electronics of the ligands do not differ greatly from one to another. Unfortunately, due to the high estimated standard deviations in the palladium carbene bond length in both complexes, it can not be clarified whether the palladium carbene bond length of complex **3.5** is shorter than that of **3.5***. Consequently, it can not be determined if the ligand of **3.5** is a stronger σ-donor compared to the ligand of **3.5*** (shorter bond length would have implied a stronger σ-donation).

	3.5	**3.5***
Pd1–C2	2.0294(18) Å	2.038(10) Å
Pd1–N1	2.124(2) Å	2.130(9) Å
Pd1–C22	2.0762(19) Å	2.082(11) Å
Pd1–C23	2.034(2) Å	2.017(11) Å
N2–C2–N3	106.90(14) Å	104.2(9) Å
C2–Pd1–C23	101.92(8) °	100.7(5) °
C2–Pd1–C22	173.20(7) °	172.2(5) °
C23–Pd1–C22	84.89(9) °	85.1(5) °
C2–Pd1–N1	77.63(8) °	76.8(4) °
C23–Pd1–N1	176.49(6) °	174.5(5) °
C22–Pd1–N1	95.58(8) °	97.8(4) °

Table 3.1: Comparison of selected bond lengths and angles of complexes **3.5** and **3.5***

The distorted square planar complex **3.6**, shown in Figure 3.8, features an even longer palladium carbene bond length (2.064(6) Å) compared to complexes **3.2** (1.984(8) Å), **3.3** (1.962(5) Å), **3.4** (1.972(4) Å) and **3.5** (2.0294(18) Å); therefore, the ligand bite angle is the shortest (76.7(2) °) compared to complexes **3.2** (79.6(3) °), **3.3** (80.39(19) °), **3.4** (79.19(15) °) and **3.5** (77.63(8) °). The steric congestion caused by the bulkiness of the DBA ligand is probably responsible for the longer palladium carbene bond observed in this complex.

The bond length between C22 and C23 of the DBA ligand is 1.448(8) Å, which is typical of an sp^2–sp^2 carbon–carbon bond[14] and it is significantly shorter than the uncoordinated double bond of the ligand. Similar ligand bond lengths, within the estimated standard deviations, have been reported for other complexes bearing a DBA ligand coordinated in the same way.[15]

Figure 3.8: ORTEP representation of the structure of **3.6** showing 50% probability ellipsoids. H atoms and two molecules of THF are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Pd1–C1: 2.064(6), Pd1–N1: 2.1444(5), Pd1–C22: 2.105(5), Pd1–C23: 2.099(5), C22–C23: 1.448(8), C1–Pd1–C23: 166.9(2), C1–Pd1–C22: 126.8(2), C23–Pd1–C22: 40.3(2), C1–Pd1–N1: 76.7(2), C23–Pd1–N1: 116.2(2), C22–Pd1–N1: 156.52(19).

3.2.2 Palladium complexes with aryl substituted NHCs

As mentioned earlier, $KN(SiMe_3)_2$ has successfully deprotonated the pyridyl functionalised imidazolinium salt **2.6c** to give the corresponding free carbene *in situ*, that was then reacted with metal complex precursors to yield palladium *N*-functionalised NHC complexes (see Scheme 3.2). However, attempts to deprotonate other imidazolinium salts using the same method were not successful.

As shown in Scheme 3.3, 1,3-bis(4-isopropoxyphenyl)imidazolinium chloride (**2.13c**) was reacted with stoichiometric amounts of $KN(SiMe_3)_2$ in THF followed by the reaction with $Pd(AcO)_2$ to yield complex **3.7**.
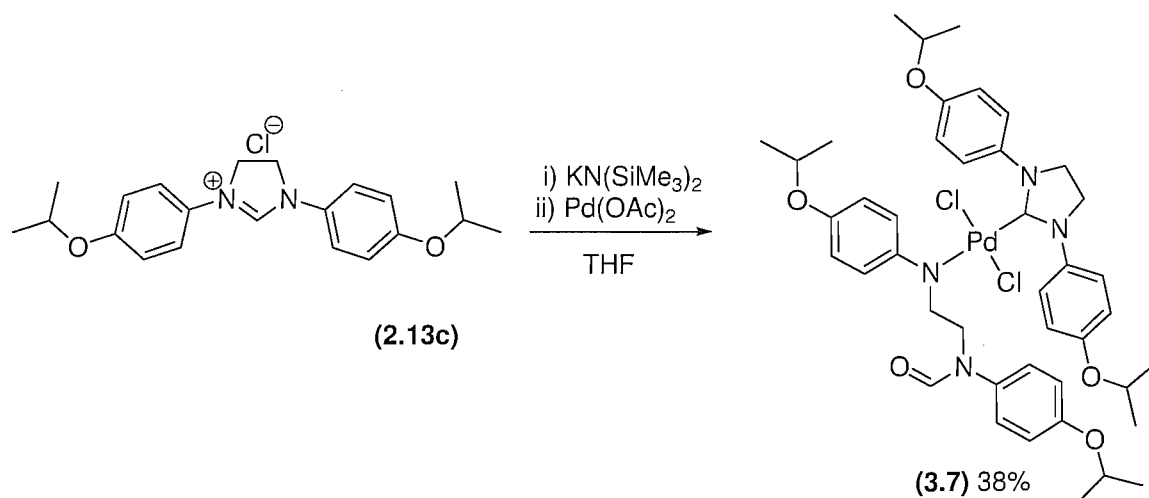
Scheme 3.3: C–N bond cleavage of NHC resulting in complex **3.7**

X-ray crystallographic studies of **3.7** (Figure 3.9) revealed that around the co-ordination sphere of the Pd(II) metal centre, one NHC and two chlorides are co-ordinated in an expected fashion, while another NHC molecule has had one of the C–N bonds cleaved, for unknown reasons, and was co-ordinated to the metal centre *via* one of the nitrogens. The terminal carbon, attached to the nitrogen heteroatom, has probably reacted with a water molecule present in the reaction mixture, due to insufficient drying of the imidazolinium salt, to give an aldehyde. Such C–N bond cleavage when using KN(SiMe₃)₂ as the deprotonation agent, has been also observed by others.[16]
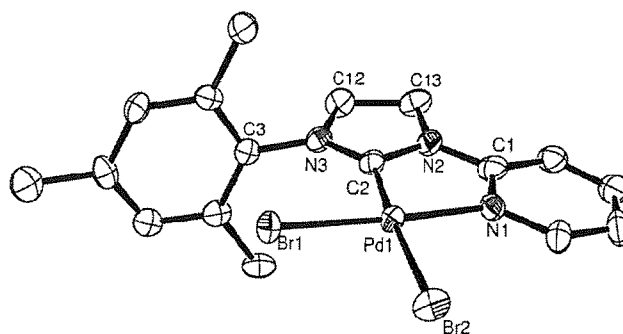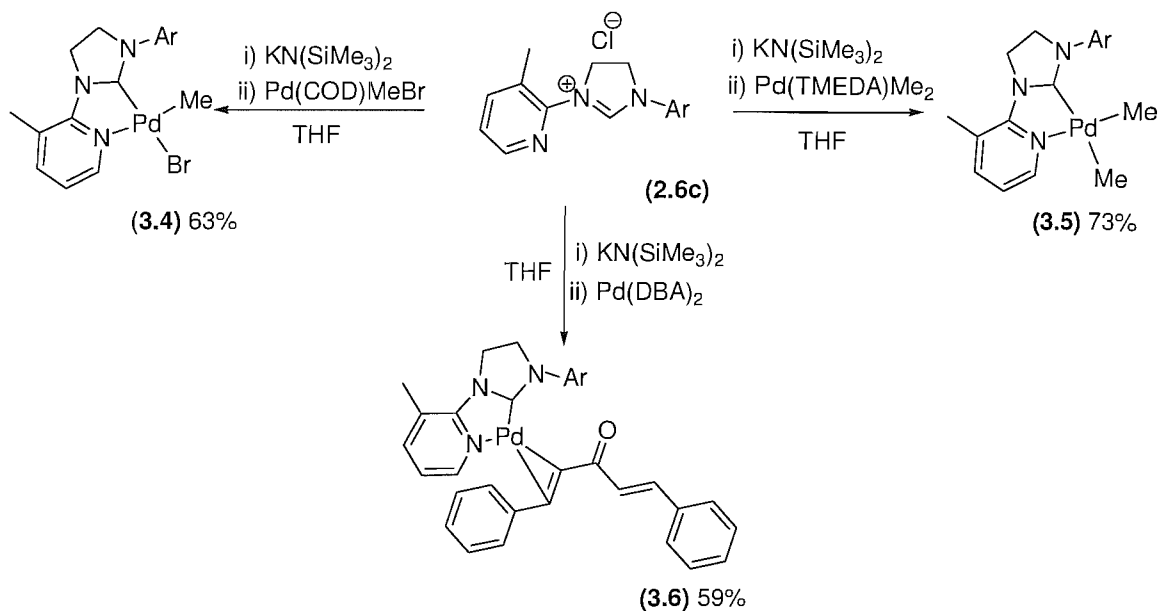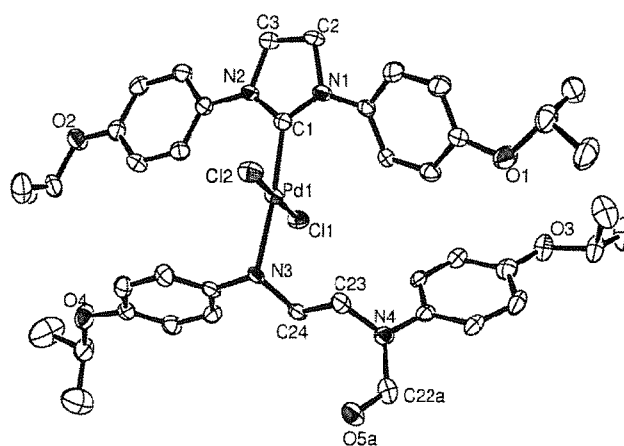

Figure 3.9: ORTEP representation of the structure of **3.7** showing 50% probability ellipsoids. H atoms are omitted for clarity.

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An in depth study of deprotonation agents was carried out by others, and it was found that KN(SiMe₃)₂ was responsible for this type of cleavage.[16b] The same study also suggested that the use of KO^{t}Bu or NaH as the deprotonation agents could avoid this type of unwanted reaction.
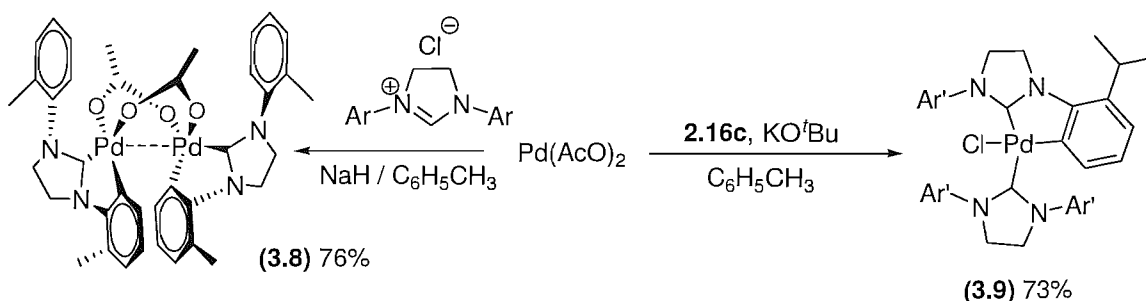
Scheme 3.4: 'One pot' synthesis of palladacycle NHC complexes **3.8** and **3.9**

Ar = 2-methylphenyl, Ar' = 2-isopropylphenyl

As shown in Scheme 3.4, Pd(AcO)₂ was reacted with aryl substituted imidazolinium salts, using NaH or KO^{t}Bu as deprotonation bases, to yield palladacycle complexes **3.8**, and **3.9**. The 'one pot' reaction of 1,3-bis(2-methylphenyl)imidazolinium chloride[17] with Pd(AcO)₂ and NaH as the deprotonation base, yielded the symmetric palladacycle NHC complex **3.8** (molecular structure displayed in Figure 3.10). Each Pd metal centre adopts a distorted square pyramidal geometry with the opposite Pd metal centre in the top apical position of the pyramid. The palladium carbene bond lengths are 1.946(5) and 1.934(5) Å, while the palladium metallated aromatic carbon bond lengths are 1.972(5) and 1.963(5) Å. The interaction between the two palladium metal centres has a length of 2.8688(6) Å, which is relatively normal and it slightly longer than the range observed for the bond distances of common Pd(I)–Pd(I) single bonds, i.e. 2.500(1)–2.823(1) Å.[18,19,20] The ligand bite angles around the two palladium centres are 79.5(2) and 79.6(2) °.

Figure 3.10: ORTEP representation of the structure of **3.8** showing 50% probability ellipsoids. H atoms and three molecules of toluene are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: O1–Pd2: 2.090(3), O2–Pd1: 2.123(4), O3–Pd2: 2.127(4), O4–Pd1: 2.094(3), Pd1–Pd2: 2.8688(6), C5–Pd2: 1.946(5), C7–Pd2: 1.963(5), C22–Pd1: 1.934(5), C33–Pd1: 1.972(5), C22–Pd1–C33: 79.5(2), C22–Pd1–O4: 173.32(19), C33–Pd1–O4: 93.91(18), C22–Pd1–O2: 98.78(19), C33–Pd1–O2: 178.29(18), O4–Pd1–O2: 87.77(13), C22–Pd1–Pd2: 101.06(15), C33–Pd1–Pd2: 103.02(14), O4–Pd1–Pd2: 81.59(10), O2–Pd1–Pd2: 77.56(10), C5–Pd2–C7: 79.6(2), C5–Pd2–O1: 173.48(19), C7–Pd2–O1: 93.89(18), C5–Pd2–O3: 99.72(19), C7–Pd2–O3: 178.46(19), O1–Pd2–O3: 86.72(13), C5–Pd2–Pd1: 95.26(14), C7–Pd2–Pd1: 97.93(15), O1–Pd2–Pd1: 84.78(10), O3–Pd2–Pd1: 80.72(10).

The 'one pot' reaction of 1,3-bis(2-isopropylphenyl)imidazolinium chloride (**2.16c**) with Pd(AcO)$_2$ and KO^{t}Bu yielded the cyclometallated palladium complex **3.9**. The molecular structure of **3.9** is shown in Figure 3.11.
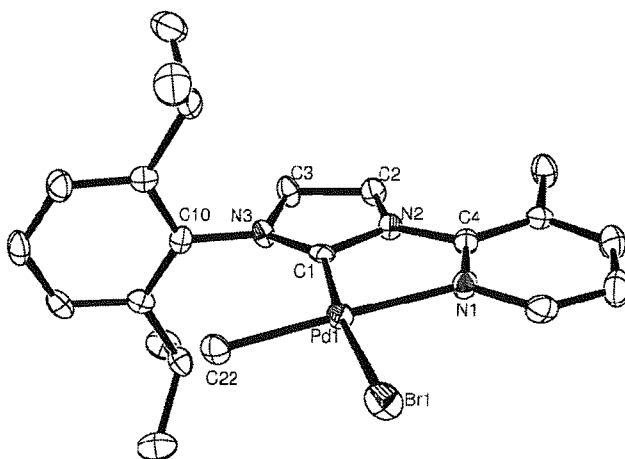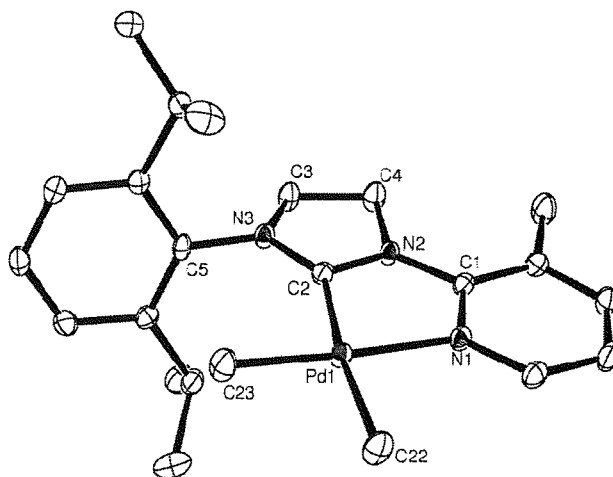
Figure 3.11: ORTEP representation of the structure of **3.9** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: C10–Pd1: 2.029(8), C31–Pd1: 1.93(6), C39–Pd1: 2.024(8), Cl1–Pd1: 2.366(4), C31–Pd1–C39: 83.1(16), C31–Pd1–C10: 168.7(16), C39–Pd1–C10: 91.9(3), C31–Pd1–Cl1: 96.0(16), C39–Pd1–Cl1: 179.1(2), C10–Pd1–Cl1: 89.0(2).

As shown in Figure 3.11, complex **3.9** adopts a distorted square planar geometry, with one co-ordinated NHC moiety, one cyclometallated NHC moiety and one chloride co-ordinated around the metal centre. The chloride atom is situated *trans* to the metallated carbon of the aromatic ring, while the two NHCs are *trans* to each other. The length of the bond between the palladium centre and the carbene of the co-ordinated NHC is longer than that of the palladium centre and the carbene of the cyclometallated NHC (2.029(8) and 1.93(6) Å respectively) while the ligand bite angle of the cyclometallated NHC is 83.1(16) °.
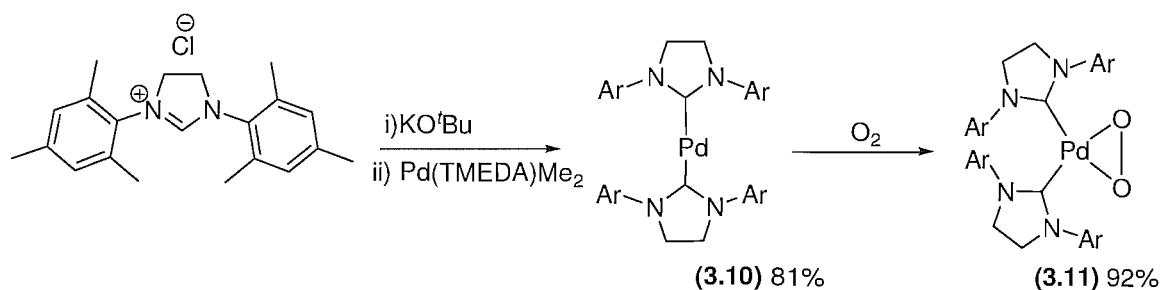
Scheme 3.5: Synthesis of palladium(0) NHC complex **3.10** and oxidation to

palladium(II) NHC complex **3.11**

Ar = 2,4,6-trimethylphenyl

As shown in Scheme 3.5, 1,3-bis-(2,4,6-trimethylphenyl)imidazolinium chloride[17] was deprotonated using KO^{t}Bu to prepare the free carbene *in situ* that was then reacted with Pd(TMEDA)Me$_2$ to yield the Pd(0) complex **3.10**, the molecular structure of which can be seen in Figure 3.12. The Pd(II) starting material was reduced to Pd(0) by the loss of the two methyl groups as gaseous ethane. Exposure of the bright orange coloured solution of **3.10** in petrol to atmospheric air results to the aerobic oxidation of the Pd-NHC complex to produce the η^2-peroxo Pd(II) complex **3.11**. The molecular structure of **3.11** is displayed in Figure 3.11. Interestingly, the same aerobic oxidation reaction was reported by others when bis[1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene]palladium(0), denoted **3.10*** (the unsaturated NHC version of complex **3.10**) was exposed to air to give bis [1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene]palladium dioxygen, denoted **3.11***.[21]

Figure 3.12: ORTEP representation of the structure of **3.10** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with

estimated standard deviations: Pd1–C22: 2.006(7), Pd1–C1: 2.024(7), C22–Pd1–C1: 173.4(3).

Complex **3.10** adopts an almost linear geometry (173.4(3) °) around the palladium metal centre. The two NHC moieties are staggered with respect to each other, while the planes of all mesityl groups are almost perpendicular to the planes of the heterocycles. It is believed that crystal packing is the major factor that determines the adopted conformation. The palladium carbene bond lengths are 2.006(7) and 2.024(7) Å while the palladium carbene bond lengths in **3.10*** are 1.990(3) and 1.997(3) Å.[21]
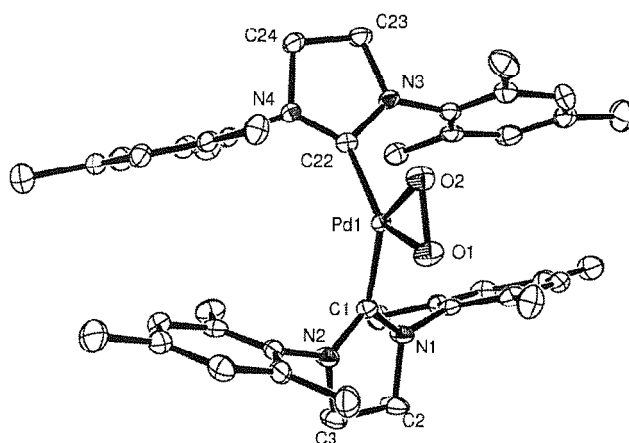
Figure 3.13: ORTEP representation of the structure of **3.11** showing 50% probability ellipsoids. H atoms and one toluene molecule are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: C1–Pd1: 2.026(4), C22–Pd1: 2.046(4), Pd1–O1: 2.011(3), Pd1–O2: 2.014(3), O1–O2: 1.439(5), O1–Pd1–O2: 41.89(14), O1–Pd1–C1: 102.61(16), O2–Pd1–C1: 144.48(16), O1–Pd1–C22: 144.30(16), O2–Pd1–C22: 102.41(15), C1–Pd1–C22: 113.09(17), O2–O1–Pd1: 69.16(18), O1–O2–Pd1: 68.95(18).

The geometry of **3.11** can be described as distorted trigonal planar, considering the dioxygen moiety as a single ligand situated at the middle of O1–O2. The major departure from the trigonal planar geometry is possibly due to sterics of the NHC ligand. The palladium carbene bond lengths are 2.046(4) and 2.011(3) Å while the palladium carbene bond lengths of **3.11***are 2.0414(16) and 2.0266(17).[21] The palladium-oxygen bond lengths are 2.011(3) and 2.014(3) Å, equal within the observed estimated standard deviations to the bond lengths of complex **3.11*** (2.0104(11) and 2.0104(12) Å). The

dioxygen bond lengths are again equal within the observed estimated standard deviations (1.439(5) ° for **3.11** and 1.4429(16) ° for **3.11***).[21]

As shown in Scheme 3.6, the *in situ* deprotonation of the imidazolinium salt **2.16c** followed by the reaction with Pd(TMEDA)Me$_2$ yielded the Pd(II) bis(NHC) dimethyl complex **3.12**, provided that the reaction temperature was maintained at around 0 °C. However, when the reaction was allowed to warm up to room temperature the Pd(0) bis(NHC) complex **3.13** was isolated, while if the reaction temperature was increased to 50 °C the dimetallated Pd(II) NHC complex **3.14** was isolated. Interestingly, when the isolated complex **3.12** was heated in THF at 30 °C, complex **3.13** was isolated as the sole product. When the isolated complex **3.13** was heated in THF at 50 °C, complex **3.14** was formed as the sole product.
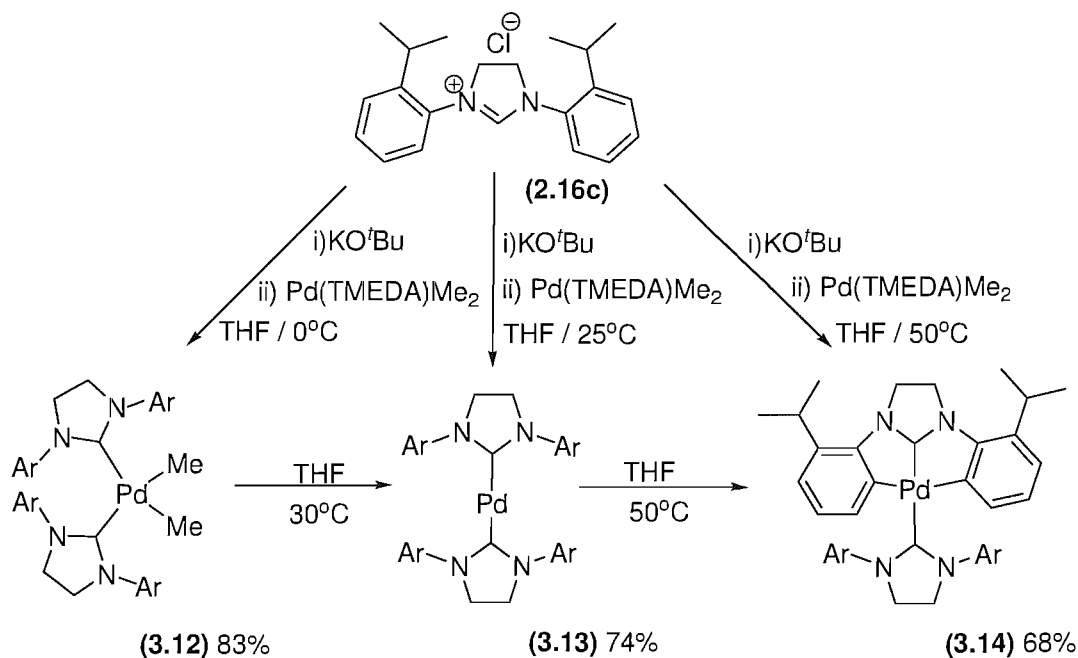
Scheme 3.6: Synthesis of palladium(II) NHC complex **3.12**, reduction to palladium(0) complex **3.13** and oxidation to palladium(II) 'pincer' NHC complex **3.14**

Ar = 2-isopropylphenyl

It is therefore believed that complex **3.12** is originally formed and depending on the temperature of the reaction, the reductive elimination of the two methyl groups as gaseous ethane leads to complex **3.13** or the reductive elimination of the two methyl groups as gaseous ethane followed by a double metallation and the loss of hydrogen leads to the 'C–C–C pincer' type complex **3.14**.

All three complexes **3.12**, **3.13** and **3.14** were isolated as crystalline solids and the molecular structures are displayed in Figures 3.14, 3.15 and 3.16 respectively.
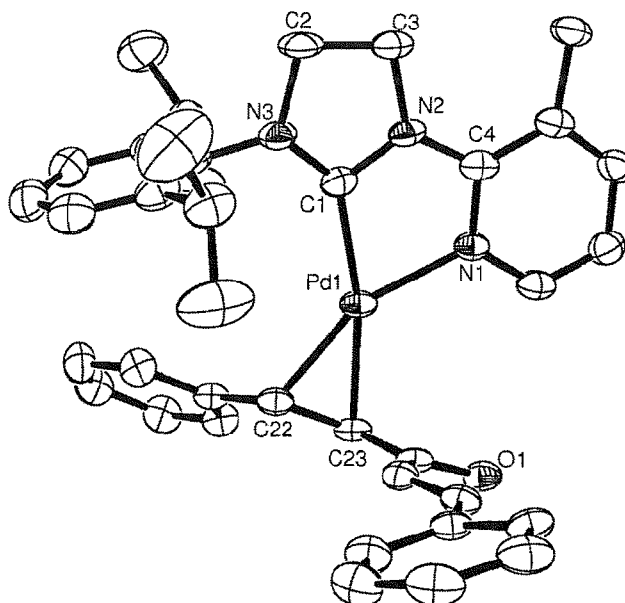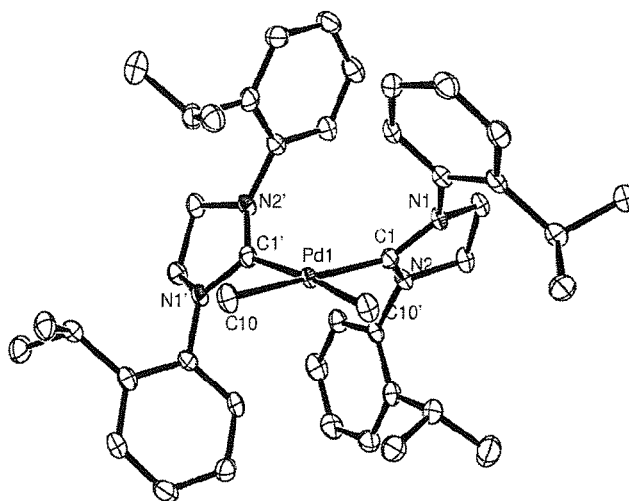

Figure 3.14: ORTEP representation of the structure of **3.12** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Pd1–C1: 2.045(3), Pd1–C10: 2.088(3), C1'–Pd1–C1: 97.09(14), C1'–Pd1–C10: 88.79(10), C1–Pd1–C10: 173.81(10), C10–Pd1–C10': 85.42(15).

Complex **3.12**, which is a C_{2v} symmetric molecule (symmetry in solution identified by NMR), adopts a slightly distorted square planar geometry with each of the methyl groups *trans* to each of the NHCs. The palladium carbene bond length is 2.045(3) Å while the palladium methyl bond length is 2.088(3) Å.

The reductive elimination of ethane from the Pd(II) complex **3.12**, may occur through a transition state complex **3.12a**[22] that eliminates the ethane molecule to yield the Pd(0) complex **3.13** as outlined in Scheme 3.7 below.

(3.12)   (3.12a)   (3.13)
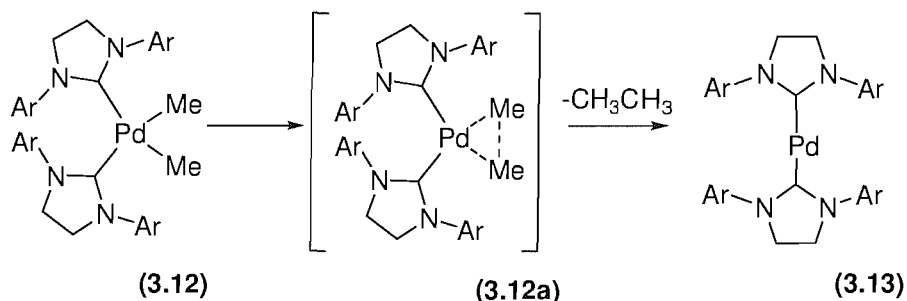
**Scheme 3.7**: Postulated mechanism for the formation of Pd(0) complex **3.13**

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Ar = 2-isopropylphenyl
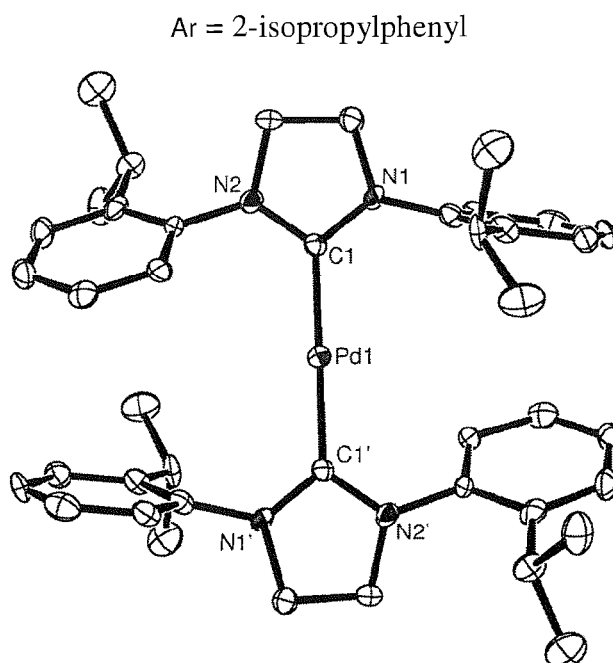
Figure 3.15: ORTEP representation of the structure of **3.13** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: C1–Pd1: 2.022(6), C1–Pd1–C1': 180.000(1).

The linear Pd(0) bis(NHC) complex **3.13** can be compared to Pd(0) bis(NHC) complex **3.10**. In the case of **3.10** the two NHC moieties are staggered to each other, while in the case of **3.13** the two NHC moieties are almost eclipsed. In both cases the planes of all aromatic groups are almost perpendicular to the planes of the heterocycles. The palladium carbene bond length of **3.13** is slightly longer (2.022(6) Å) compared to complex **3.10** (2.006(7) Å).

The geometry around the metal centre of complex **3.14** can be described as distorted square planar. The co-ordinated NHC is almost perpendicular to the plane formed by the two metallated aromatic rings and the heterocycle of the pincer type co-ordinated NHC. The palladium carbene bond length of the pincer type co-ordinated NHC is shorter (1.901(3) Å) than that of the co-ordinated NHC (2.038(3) Å). It is worth noting that this type of double C–H activation leading to the 'C–C–C pincer' type complex **3.14** is the first to be reported to our knowledge.
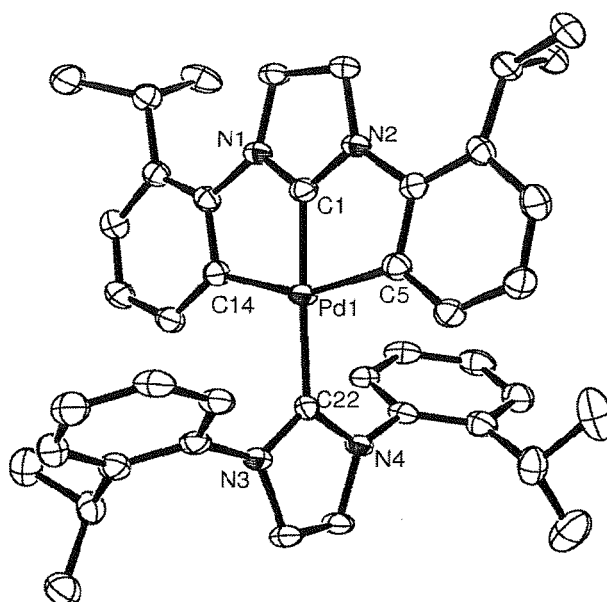
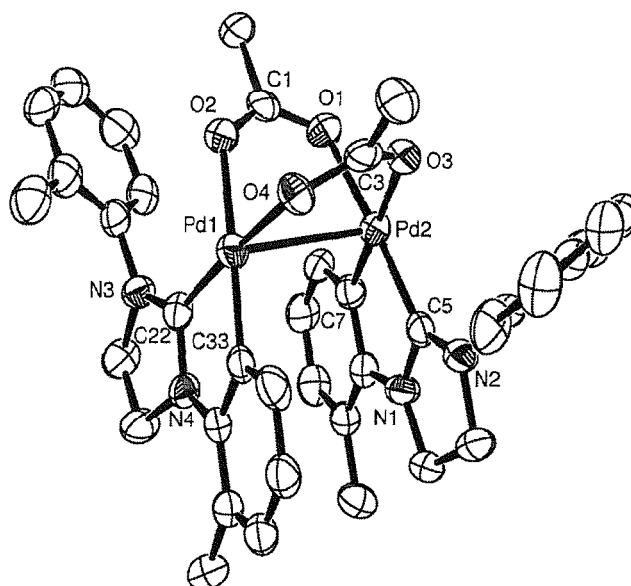**Figure 3.16**: ORTEP representation of the structure of **3.14** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: C1–Pd1: 1.901(3), C5–Pd1: 2.101(3), C14–Pd1: 2.092(3), C22–Pd1: 2.038(3), C1–Pd1–C22: 176.06(11), C1–Pd1–C14: 77.59(11), C22–Pd1–C14: 101.68(10), C1–Pd1–C5: 77.72(11), C22–Pd1–C5: 102.85(10), C14–Pd1–C5: 155.27(10).

It is believed that the formation of complex **3.14** from complex **3.13** goes through a Pd(0) to Pd(II) mechanism that is outlined in Scheme 3.8 below. The Pd(0) complex **3.13** is oxidised to the Pd(II) hydride complex **3.13a** that undergoes a σ-bond metathesis (intermediates **3.13b** and **3.13c**) leads to the Pd(II) C-C-C pincer type complex **3.14**. Such agostic interactions leading to σ-bond metathesis, present in intermediate **3.13b**, have been suggested in the past by others.[23]
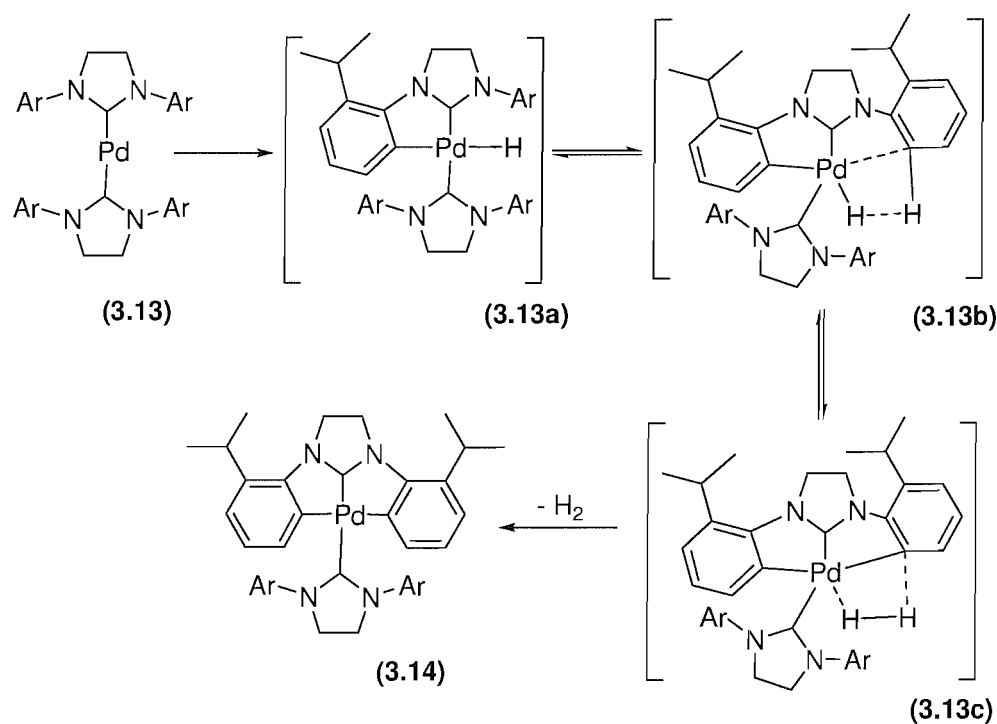
Scheme 3.8: Postulated mechanism for the formation of Pd(II) complex **3.14**

Ar = 2-isopropylphenyl

3.2.3 Palladium alkoxyphenyl functionalised NHC complexes

Alkoxy groups tend to donate electron density to the aromatic rings, which in turn provide the electron density to the heterocycle. Alkoxyphenyl functionalised NHCs (when co-ordinated to palladium) will probably provide a stronger σ-donation to the metal centre compared to aryl substituted NHCs. It is believed that this might have a beneficial effect on the catalytic activity of such Pd NHC complexes. Attempts for preparing Pd alkoxyphenyl functionalised NHC complexes were successful.

In situ deprotonation of alkoxyphenyl functionalised imidazolinium salts **2.10c** or **2.11c** with KO^{t}Bu, followed by the reaction with Pd(TMEDA)Me$_2$, yielded the palladacycle complex **3.15** or **3.16** respectively in good yields (Scheme 3.9). The structures of the complexes have been determined by single crystal X-ray diffraction studies and are displayed in Figures 3.17 and 3.18.

R = H   **(2.10c)**
R = OMe **(2.11c)**

i) KO^{t}Bu
ii) Pd(TMEDA)Me$_2$

THF

R = H   **(3.15)** 64%
R = OMe **(3.16)** 71%
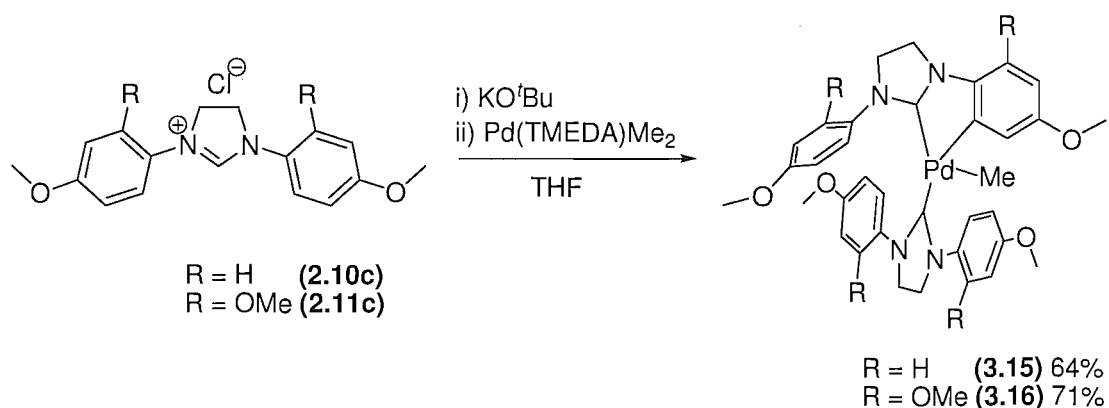
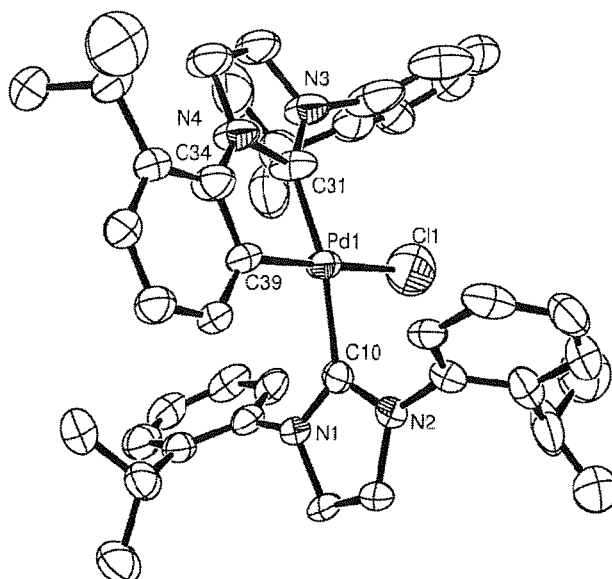**Scheme 3.9**: Synthesis of palladacycle NHC complexes **3.15** and **3.16**
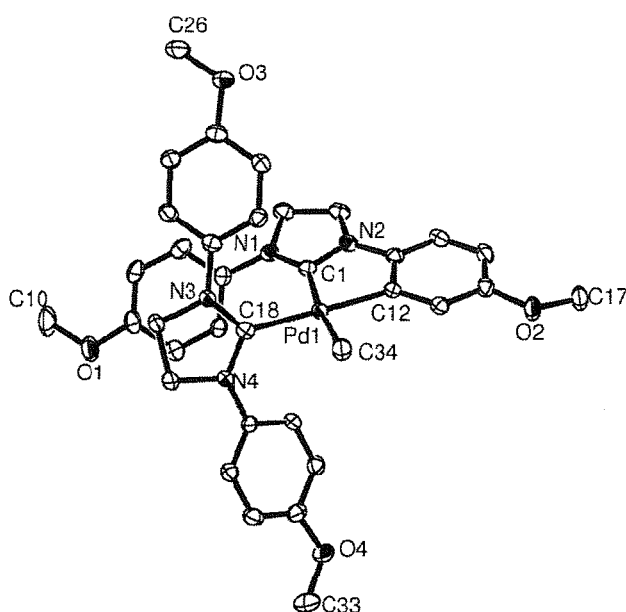

Figure 3.17: ORTEP representation of the structure of **3.15** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Pd1–C18 2.036(3), Pd1–C12 2.048(3), Pd1–C1 2.053(3), Pd1–C34 2.086(3), C18–Pd1–C12 178.53(10), C18–Pd1–C1 98.64(10), C12–Pd1–C1 80.26(11) C18–Pd1–C34 88.40(10), C12–Pd1–C34 92.61(11), C1–Pd1–C34 171.33(11).

Complexes **3.15** and **3.16** (Figures 3.17 and 3.18 respectively) adopt a slightly distorted square planar geometry around the palladium centre. Interestingly both complexes have very similar structures: two NHC moieties are co-ordinated, one of which has one of the aromatic rings activated at the *ortho* position. The methyl group is *trans* to the carbene of the NHC moiety with the activated aromatic ring while the co-ordinated NHC moiety is *trans* to the activated aromatic ring.

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The main difference between the two structures is that while the co-ordinated NHC in complex **3.15** has all three rings almost forming a plane, the plane of the one aromatic ring in complex **3.16** is almost perpendicular to the plane formed by the heterocyclic and the other aromatic ring.

Furthermore, the bond lengths and angles of the complexes are comparable. The bond length between the palladium centre and the carbene of the co-ordinated NHC is equal within the observed estimated standard deviations for both complexes (2.036(3) and 2.038(3) Å). The same is true for the bond length between the palladium centre and the carbene of the metallated NHC (2.053(3) and 2.054(4) Å) and the bond length between the palladium centre and the activated aromatic carbon (2.048(3) and 2.044(3) Å). However, the bond length between the palladium centre and the methyl group of complex **3.15** is shorter than that of **3.16** (2.086(3) and 2.095(4) Å respectively). The ligand bite angle of the metallated NHC moiety of complex **3.15** is slightly bigger than that of **3.16** (80.26(11) and 79.86(14) ° respectively).
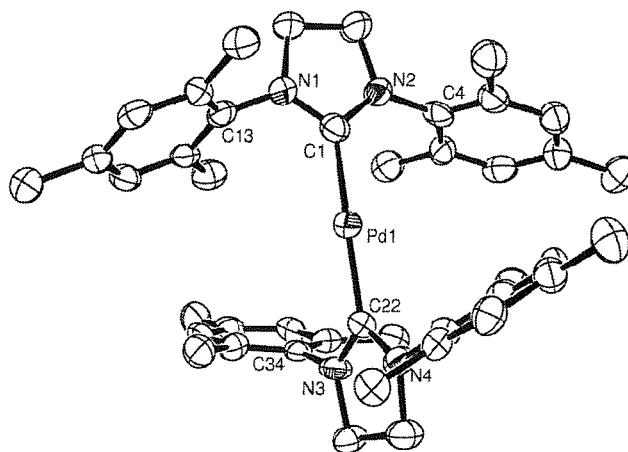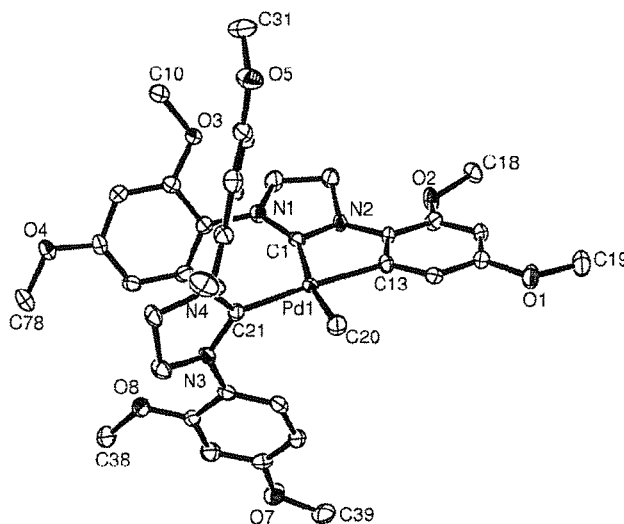

Figure 3.18: ORTEP representation of the structure of **3.16** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Pd1–C21: 2.038(3), Pd1–C13: 2.044(3), Pd1–C1: 2.054(4), Pd1–C20: 2.095(4), C21–Pd1–C13: 176.17(14), C21–Pd1–C1: 103.88(14), C13–Pd1–C1: 79.86(14), C21–Pd1–C20: 84.57(14), C13–Pd1–C20: 91.80(14), C1–Pd1–C20: 169.63(14).

Scheme 3.10 shows the postulated mechanism for the formation of complexes **3.15** and **3.16**. It is believed that once the *in situ* carbene is formed, it is co-ordinated to the palladium complex precursor (Pd(TMEDA)Me₂) to give the proposed Pd(II) complex **3.15a** or **3.16a**. The activation of the aryl group leads to the formation of the cyclometallated Pd(II) complex **3.15** or **3.16** through the intermediate complex **3.15b** or **3.16b**. The intermediate complex (**3.15b** or **3.16b**) is formed by an electrophilic aromatic substitution. As a result, the metal is attached to an sp^3 carbon centre with a M–C σ bond and therefore the former aromatic ring carries a positive charge and the metal centre carries a negative charge. Finally, the proton is released, along with the CH_3 group, as methane from the intermediate palladium to form the final product of the cyclometallation (complex **3.15** or **3.16**).[24]

(3.15a)   **(3.15b)**   **(3.15)**
(3.16a)   **(3.16b)**   **(3.16)**
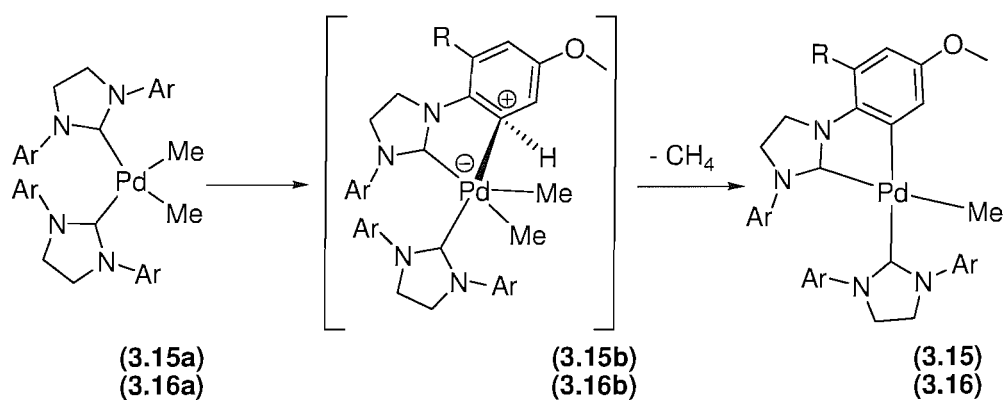
Scheme 3.10: Postulated mechanism for the formation of Pd(II) complexes **3.15** and **3.16**

Ar = 2-methoxyphenyl, R = H (for **3.15**)

Ar = 2,4-dimethoxyphenyl, R = OMe (for **3.16**)

3.3 NMR Spectroscopy

All prepared carbene complexes were characterised by ^{1}H and ^{13}C NMR spectroscopy. The absence of the characteristic singlet peak at 9–11 ppm, belonging to the corresponding imidazolinium proton, from all the ^{1}H spectra of the prepared complexes, confirms the formation of the free carbene and the co-ordination on the metal centre. The carbene C was observed by ^{13}C NMR spectroscopy only for complexes **3.2**, **3.4**, **3.5**, **3.8**, **3.9**, **3.10**, **3.11**, **3.12** and **3.14**. These characteristic singlet peaks were observed at 195–215 ppm. The limited stability of all complexes in chlorinated solvents precluded acquisition with long pulse delays which may have facilitated the observation of the slow relaxing carbene C.

Furthermore, only one of the two carbene carbons is visible in the ^{13}C NMR spectrum of complex **3.14** and it was not possible to identify the nature of the one observed.

Depending on the structure of the complex, the nature of the ^{1}H chemical shift for the imidazolinium backbone methylenic groups (CH_2), appeared as a singlet (in the case of complexes bearing symmetrically substituted NHC molecules, *i.e.* **3.7**, **3.9**, **3.10**, **3.11**, **3.12**, **3.13**, **3.14**, **3.15** and **3.16**), a triplet or a multiplet (in the case of complexes bearing non symmetrically substituted NHC molecules, *i.e.* **3.1**, **3.2**, **3.3**, **3.4**, **3.5**, **3.6** and **3.8**).

3.4 Conclusions

Five novel pyridyl functionalised NHC complexes of palladium, three novel NHC palladacycle complexes, four novel aryl substituted NHC palladium complexes and two novel alkoxyphenyl NHC palladacycle complexes have been synthesised and characterised. The catalytic activity for most of these complexes in the Heck couplings of aryl halides is described in Chapter 4.

3.5 Experimental Details

General Materials and Methods

All manipulations were performed under nitrogen in a M. Braun glove-box or using standard Schlenk techniques, unless otherwise stated. Solvents were dried using standard methods and distilled under nitrogen prior use (see Appendix 2). Pd(COD)MeBr,[25] Pd(COD)Br$_2$[26] and Pd(TMEDA)Me$_2$,[27] were prepared according to literature procedures. All other materials used were purchased from Aldrich or Lancaster and used without further purification.

(3.1)   **Bis{μ-chloro[1-(2-Pyridyl)-3-(2,4,6-trimethylphenyl)imidazolin-2-ylidene] silver(I)}**

Ar = Mes
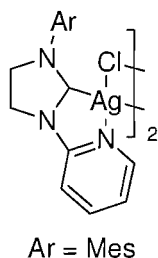
1-(2-Pyridyl)-3-(2,4,6-trimethylphenyl)imidazolinium   chloride   **(2.4c)** (0.12 g, 0.40 mmol), Ag$_2$O (0.07 g, 0.30 mmol) and molecular sieves were suspended in DCM (20 mL). The mixture was refluxed (48 °C) under nitrogen for 48 h. The resulting solution was filtered through Celite and the solvent was removed under vacuum to give a white-beige solid.

Yield 0.102 g (0.25 mmol), 83 %.

Anal. Calcd for C$_{17}$H$_{20}$AgClN$_3$: C, 49.84; H, 4.92; N, 10.26 %. Found: C, 50.0; H, 4.5; N, 10.2%.

ES$^+$MS: m/z (%): 408.4, 409.3, 410.4, 411.4, 412.3 and 413.4 [Ag(NHC)Cl]$^+$

^{1}H NMR (300MHz, CD$_2$Cl$_2$), δ: 8.38 (1H, d, J = 3.6 Hz, pyridyl-$\underline{H}$), 7.80 (1H, m, pyridyl-$\underline{H}$), 7.54 (1H, d, J = 8.4 Hz, pyridyl-$\underline{H}$), 7.18 (1H, dd, J = 8.4, 3.6 Hz, pyridyl-$\underline{H}$), 7.03 (2H, s, aromatic-$\underline{H}$), 4.38 (2H, t, J =10.5 Hz, backbone C$\underline{H}_2$), 4.06 (2H, t, J =10.5 Hz, backbone C$\underline{H}_2$), 2.36 (6H, s, o-C$\underline{H}_3$), 2.24 (3H, s, p-C$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$), δ: 165.02 (pyridyl quaternary $\underline{C}$–N), 153.11 (aromatic, quaternary $\underline{C}$–N), 148.79, 139.21, 121.08 and 111.67 (pyridyl $\underline{C}$H), 136.67 and 135.68 (2 × quaternary $\underline{C}$–CH$_3$), 130.24 (2 × aromatic $\underline{C}$H), 113.20 (quaternary $\underline{C}$–CH$_3$), 52.10 and 48.35 (backbone $\underline{C}$H$_2$), 21.40 (p-$\underline{C}$H$_3$) , 18.27 (2 × o-$\underline{C}$H$_3$).

(3.2) 1-(2-Pyridyl)-3-(2,4,6-trimethylphenyl)imidazolin-2-ylidene methyl bromide palladium(II)
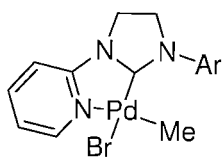
Pd(COD)MeBr (0.050 g, 0.16 mmol) was dissolved in DCM (10 mL) and to this a solution of compound **3.1** (0.065 g, 0.16 mmol) in DCM was added dropwise. After stirring for 18 h, it was then filtered through Celite and the solvent was reduced to the minimum. The saturated solution was layered with petroleum to give light yellow crystals. Yield 56 mg (0.12 mmol), 75 %.

Anal. Calcd for $C_{18}H_{22}BrN_3Pd$: C, 46.32; H, 4.75; N, 9.00 %. Found: C, 46.4; H, 4.6; N, 9.1%.

^{1}H NMR (300MHz, CD_2Cl_2), δ: 8.97 (1H, d, J = 4.8 Hz, pyridyl-$\underline{H}$), 7.92 (1H, dt, J = 8.1, 1.8 Hz, pyridyl-$\underline{H}$), 7.22 (1H, dt, J = 5.1, 1.8 Hz, pyridyl-$\underline{H}$), 7.01 (2H, s, aromatic-$\underline{H}$), 6.86 (1H, d, J = 8.1 Hz, pyridyl-$\underline{H}$), 4.11 (4H, m, 2 × backbone C$\underline{H}_2$), 2.36 (3H, s, p-C$\underline{H}_3$), 2.32 (6H, s, 2 × o-C$\underline{H}_3$), 0.02 (3H, s, Pd–C$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2), δ: 194.10 (carbene $\underline{C}$–Pd), 148.40 (pyridyl quaternary $\underline{C}$–N), 140.55,119.75 and 108.32 (pyridyl $\underline{C}$H), 139.56 (aromatic, quaternary $\underline{C}$–N), 135.34 (quaternary o-$\underline{C}$–CH$_3$), 129.98 (2 × aromatic $\underline{C}$H), 110.59 (quaternary p-$\underline{C}$–CH$_3$), 54.93 and 44.28 (backbone $\underline{C}$H$_2$), 21.40 (p-$\underline{C}$H$_3$) , 18.27 (2 × o-$\underline{C}$H$_3$).

(3.3) 1-(2-Pyridyl)-3-(2,4,6-trimethylphenyl)imidazolin-2-ylidene dibromide palladium(II)
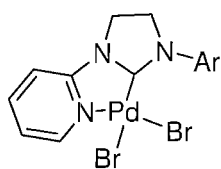
This was prepared in the same way as compound **3.2** using the following: Pd(COD)Br$_2$ (0.092 g, 0.24 mmol) and **3.1** (0.10 g, 0.24 mmol). The saturated solution was layered with petroleum to give light yellow crystals. Yield 0.10 g (0.19 mmol), 79 %.

Anal. Calcd for $C_{17}H_{19}Br_{0.65}Cl_{1.35}N_3Pd$: C, 43.30; H, 4.06; N, 8.91 %. Found: C, 43.4; H, 4.2; N, 9.0%.

^{1}H NMR (300MHz, d_6-DMSO), δ: 9.04 (1H, d, J = 7.5 Hz, pyridyl-$\underline{H}$), 8.19 (1H, t, J = 7.5, 8.1 Hz, pyridyl-$\underline{H}$), 7.33 (2H, m, 2 × pyridyl-$\underline{H}$), 6.90 (2H, s, 2 × aromatic-$\underline{H}$), 4.25 and 4.14 (2 × 2H, t, J = 9.2 Hz, 2 × backbone C$\underline{H}_2$), 2.25 (3H, s, p-C$\underline{H}_3$), 2.24 (6H, s, 2 × o-C$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, d_6-DMSO), δ: 153.99 (pyridyl quaternary $\underline{C}$–N), 147.98 (aromatic, quaternary $\underline{C}$–N), 142.02, 128.49 and 118.62 (pyridyl $\underline{C}$H), 137.61 (quaternary p-$\underline{C}$–CH$_3$), 134.91 and 134.01 (quaternary o-$\underline{C}$–CH$_3$), 110.08 (2 × aromatic $\underline{C}$H), 54.65 and 43.17 (backbone $\underline{C}$H$_2$), 20.54 (p-$\underline{C}$H$_3$) , 17.44 (2 × o-$\underline{C}$H$_3$).

(3.4) 1-[2-(3-Picolyl)]-3-(2,6-diisopropylphenyl)imidazolin-2-ylidene methyl bromide palladium(II)
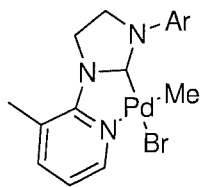
1-[2-(3-Picolyl)]-3-(2,6-diisopropylphenyl)imidazolinium chloride **(2.6c)** (0.11 g, 0.32 mmol) was dissolved in THF (20 mL) at –78 °C, to this a solution of $KN(SiMe_3)_2$ (0.07 g, 0.35 mmol) in THF (15 mL) at –78 °C was added. The mixture was allowed to warm up to –10 °C and stirred for 2 h. It was then cooled to –78 °C and added to a cold (–78 °C) solution of Pd(COD)MeBr (0.10 g, 0.32 mmol) in THF (10 mL). The reaction mixture was let to warm up to r.t. and stirred over night. The solvent was removed from the resulting solution and the solid obtained was dissolved in DCM. It was then filtered through Celite, the volume was reduced and the resulting saturated solution was layered with petroleum to give colourless crystals. Yield 0.10 g (0.20 mmol), 63 %.

Anal. Calcd for $C_{22}H_{30}BrN_3Pd$: C, 50.54; H, 5.78; N, 8.04 %. Found: C, 50.6; H, 5.8; N, 8.1%.

^{1}H NMR (300MHz, CD_2Cl_2), δ: 9.18 (1H, dd, J = 5.1, 1.2 Hz, pyridyl-H̲), 7.65 (1H, dd, J = 7.5, 0.9 Hz, pyridyl-H̲), 7.47 (1H, t, J = 8.1 Hz, aromatic-H̲), 7.30 (2H, d, J = 7.8 Hz, aromatic-H̲), 7.10 (1H, d, J = 5.4, 2.1 Hz, pyridyl-H̲), 4.57 and 4.08 (2 × 2H, t, J = 10.2 Hz backbone CH̲$_2$), 3.10 (2H, septet, J = 6.9 Hz, CH̲(CH$_3$)$_2$), 2.66 (3H, s, pyridyl CH̲$_3$), 1.40 and 1.29 (2 × 6H, d, J = 6.9 Hz, CH(CH̲$_3$)$_2$), 0.03 (3H, s, Pd–CH̲$_3$).

^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2), δ: 196.87 (carbene C̲–Pd), 152.96 (pyridyl quaternary C̲–N), 148.15, 144.09 and 130.40 (pyridyl C̲H), 145.97 (pyridyl quaternary C̲–CH$_3$), 135.69 (aromatic quaternary C̲–N), 125.06 (2 × aromatic m-C̲H), 120.23 (aromatic p-C̲H), 119.43 (2 × aromatic quaternary C̲–CH(CH$_3$)$_2$), 57.41 and 47.82 (2 × backbone C̲H$_2$), 29.11 (pyridyl C̲H$_3$), 25.48 and 24.26 (2 × –CH(C̲H$_3$)$_2$), 18.27 (C̲H(CH$_3$)$_2$), –1.41 (Pd–C̲H$_3$).

(3.5)   1-[2-(3-Picolyl)]-3-(2,6-diisopropylphenyl)imidazolin-2-ylidene   dimethyl palladium(II)

This was prepared in the same way as compound **3.4** using the following: 1-[2-(3-picolyl)]-3-(2,6-diisopropylphenyl)imidazolinium chloride **(2.6c)** (0.20 g, 0.56 mmol), $KN(SiMe_3)_2$ (0.12 g, 0.62 mmol) and Pd(TMEDA)Me$_2$ (0.14 g, 0.56 mmol). After stirring overnight, the solvent was removed; the solid obtained was dissolved in toluene,

filtered through Celite and concentrated by evaporating the excess solvent under vacuum. The saturated solution was placed in a freezer at $-30\ ^{\circ}C$ to yield colourless crystals. Yield 0.19 g (0.41 mmol), 73 %.

Anal. Calcd for $C_{23}H_{33}N_3Pd$: C, 60.32; H, 7.26; N, 9.18 %. Found: C, 60.1; H, 7.1; N, 9.0%.

^1H NMR (300MHz, C_6D_6), δ: 8.76 (1H, d, J = 4.2 Hz, pyridyl-$\underline{H}$), 7.28 (1H, m, aromatic p-C$\underline{H}$), 7.17 (2H, d, J = 7.2 Hz, aromatic m-C$\underline{H}$), 6.75 (1H, d, J = 6.9 Hz, aromatic-$\underline{H}$), 6.40 (1H, m, pyridyl-$\underline{H}$), 3.28 (4H, m, 2 × backbone C$\underline{H}_2$), 3.12 (2H, septet, J = 6.9 Hz, C$\underline{H}$(CH$_3$)$_2$), 1.75 (3H, s, pyridyl C$\underline{H}_3$), 1.58 and 1.21 (2 × 6H, d, J = 6.9 Hz, CH(C$\underline{H}_3$)$_2$), 0.79 and 0.39 (2 × 3H, s, Pd–C$\underline{H}_3$).

$^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6), δ: 214.90 (carbene Pd–$\underline{C}$), 154.37 (pyridyl quaternary $\underline{C}$–N), 145.90 (aromatic quaternary $\underline{C}$–N), 145.47, 141.60 and 118.77 (pyridyl $\underline{C}$H), 136.47 (pyridyl quaternary $\underline{C}$–CH$_3$), 129.70 (aromatic p-$\underline{C}$H), 124.53 (2 × aromatic m-$\underline{C}$H), 56.35 and 46.90 (2 × backbone $\underline{C}$H$_2$), 28.90 ($\underline{C}$H(CH$_3$)$_2$), 24.89 and 24.60 (2 × –CH($\underline{C}$H$_3$)$_2$), 20.32 (pyridyl $\underline{C}$H$_3$), -1.39 and -9.51 (2 × Pd–$\underline{C}$H$_3$).

(3.6) 1-[2-(3-Picolyl)]-3-(2,6-diisopropylphenyl)imidazolin-2-ylidene dibenzylidene acetone palladium(II)
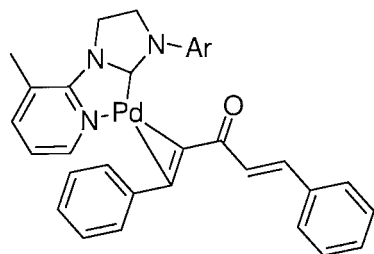
Ar = 2,6-dipp

This was prepared in the same way as compound **3.4** using the following: 1-[2-(3-picolyl)]-3-(2,6-diisopropylphenyl) imidazolinium chloride (**2.6c**) (0.12 g, 0.35 mmol), KN(SiMe$_3$)$_2$ (0.08 g, 0.40 mmol) and Pd(DBA)$_2$ (0.10 g, 0.17 mmol). After stirring overnight, the solvent was removed, the solid obtained was dissolved in toluene, filtered through celite and evaporated under vacuum. The solid was dissolved in the minimum amount of THF and was layered with petroleum to give dark orange crystals. Yield 0.06 g (0.10 mmol), 59 %.

Anal. Calcd for $C_{46}H_{57}N_3O_3Pd$: C, 68.51; H, 7.12; N, 5.21 %. Found: C, 68.4; H, 7.0; N, 5.1%.

^1H NMR (300MHz, CD_2Cl_2), δ: 8.39 (1H, s, pyridyl-$\underline{H}$), 7.54-7.36 (10H, m, DBA aromatic C$\underline{H}$), 7.10 (3H, m, 3 × aromatic C$\underline{H}$), 6.88 (2H, m, 2 × pyridyl-$\underline{H}$), 4.50 and 4.03 (2 × 1H, d, J = 9.3 Hz, C$\underline{H}$=CH), 4.31 and 3.71 (2 × 2H, m, 2 × backbone C$\underline{H}_2$), 3.27 and 2.64 (2 × 1H, septet, J = 6.9 Hz, C$\underline{H}$(CH$_3$)$_2$), 2.58 (3H, s, pyridyl C$\underline{H}_3$), 1.85, 1.70, 1.28 and 1.11 (4 × 3H, d, J = 6.9 Hz, CH(C$\underline{H}_3$)$_2$), 0.32 (2H, br.s, Pd–C$\underline{H}$=CH).

^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$), δ: 154.56 (pyridyl quaternary $\underline{C}$–N), 146.99 (aromatic quaternary $\underline{C}$–N), 146.37 and 145.96 (DBA aromatic quaternary $\underline{C}$), 143.45, 129.68 and 129.10 (pyridyl $\underline{C}$H), 137.54 (pyridyl quaternary $\underline{C}$–CH$_3$), 136.89 and 135.10 (aromatic quaternary $\underline{C}$–CH(CH$_3$)$_2$), 128.80, 128.09, 125.84, 125,46, 124.66 123.04 and 120.49 (aromatic $\underline{C}$H), 68.33 (quaternary $\underline{C}$=O), 56.92 and 48.46 (2 × backbone $\underline{C}$H$_2$), 29.09, 28.95, 24.28 and 23.60 (4 × –CH($\underline{C}$H$_3$)$_2$), 26.17 and 25.23 (2 × $\underline{C}$H(CH$_3$)$_2$), 21.01 (pyridyl $\underline{C}$H$_3$).

(3.7)   {Bis[1,3-(4-isopropoxyphenyl)imidazolin-2-ylidene}dichloro{N-(4-isopropoxy-phenyl)-N-[2-(N-formyl-4-isopropylphenylamino)ethyl]amido}palladium(II)
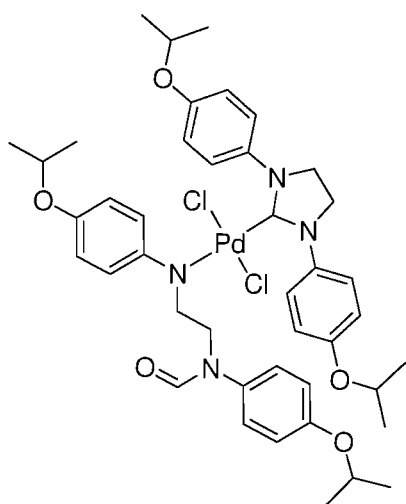
This was prepared in the same way as compound **3.4** using the following: bis[1,3-(4-isopropoxyphenyl) imidazolinium chloride (**2.13c**) (0.33 g, 0.89 mmol), KN(SiMe$_3$)$_2$ (0.20 g, 1.0 mmol) and Pd(AcO)$_2$ (0.20 g, 0.89 mmol). After stirring overnight, the solvent was removed, the solid obtained was dissolved in toluene, filtered through Celite and evaporated under vacuum. The solid was dissolved in the minimum amount of THF and was layered with petroleum to yield dark yellow crystals. Yield 0.03 g (0.34 mmol), 38 %.

^{1}H NMR (300MHz, CD$_2$Cl$_2$), δ: 9.41 (1H, s, $\underline{H}$C=O), 7.61 (4H, d, J = 8.7 Hz, aromatic C$\underline{H}$), 6.69 (8H, m, aromatic C$\underline{H}$), 6.59 (4H, m, aromatic C$\underline{H}$), 4.00 (4H, s, 2 × backbone C$\underline{H}_2$), 2.67 (2H, m, ethylene C$\underline{H}_2$), 2.11 (2H, m, ethylene C$\underline{H}_2$), 2.41 (6H, s, O–C$\underline{H}_3$), 2.00 (3H, s, O–C$\underline{H}_3$), 1.81 (3H, s, O–C$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$), δ: 164.49 (H$\underline{C}$=O) 154.32 (aromatic quaternary $\underline{C}$–N), 153.02 (aromatic quaternary $\underline{C}$–N), 132.31 (aromatic quaternary $\underline{C}$-OCH$_3$), 131.53 (aromatic quaternary $\underline{C}$–OCH$_3$), 130.08, 129.56, 128.13, and 109.10 (aromatic $\underline{C}$H), 58.18 and 56.32 (backbone $\underline{C}$H$_2$), 40.33 and 39.19 (ethylene $\underline{C}$H$_2$), 33.76 (O–$\underline{C}$H$_3$), 28.38 (O–$\underline{C}$H$_3$).

(3.8)   **Di(μ^2-Acetato-$\kappa^2 O,O'$)bis{2-[3-(2-methylphenyl)imidazolin-2-ylidene]-3-methylphenyl-$\kappa^2 C,C'$}dipalladium(II)**
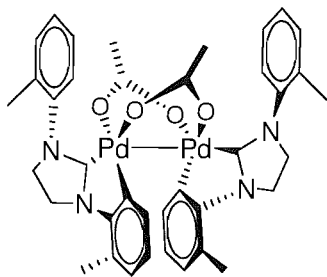
Bis[1,3-(2-methylphenyl)imidazolinium chloride[17] (0.25 g, 0.89 mmol), Pd(AcO)$_2$ (0.20 g, 0.89 mmol) and NaH (0.24 g, 1.0 mmol) were placed in an ampoule. Toluene (15 mL) was added and the ampoule was sealed under partial vacuum. It was then heated at 50 °C for 3 hours and then cooled to rt. The resulting suspension was filtered through Celite and the solution was reduced to the minimum and was then layered with petrol to yield yellow crystals. Yield 0.28 g (0.68 mmol), 76 %.

Anal. Calcd for $C_{97}H_{104}N_8O_8Pd_4$: C, 60.19; H, 5.42; N, 5.79 %. Found: C, 60.3; H, 5.5; N, 5.9%.

^{1}H NMR (300MHz, $C_6D_5CD_3$), δ: 7.52 (2H, d, J = 7.2 Hz, aromatic C$\underline{H}$), 7.13 (2H, d, J = 6.3 Hz, aromatic C$\underline{H}$), 7.00–6.40 (10H, m, 10 × aromatic C$\underline{H}$) 6.21 (2H, d, J = 5.9 Hz, aromatic C$\underline{H}$), 3.40 (4H, t, J = 10.2 Hz, 2 × backbone C$\underline{H}_2$), 2.68 (4H, t, J = 10.2 Hz, 2 × backbone C$\underline{H}_2$), 2.31 (6H, s,C$\underline{H}_3$COO), 1.60 (6H, s, aromatic C$\underline{H}_3$), 1.20 (6H, s, aromatic C$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, $C_6D_5CD_3$), δ: 198.25 (carbene $\underline{C}$-Pd), 136.12 (aromatic $\underline{C}$–Pd), 130.33 (quaternary aromatic $\underline{C}$–N), 130.16 (quaternary aromatic $\underline{C}$–N), 129.84, 129.06, 124.07, 123.75, 123.43, 120.67, 118.27, 115.82 and 107.73 (aromatic carbons), 52.58 (acetate $\underline{C}$CH$_3$), 44.04 (backbone $\underline{C}$H$_2$), 41.72 (backbone $\underline{C}$H$_2$), 22.32(acetate $\underline{C}$H$_3$), 16.28(aromatic $\underline{C}$H$_3$), 15.94 (aromatic $\underline{C}$H$_3$).

(3.9)   **[1,3-Bis(2-isopropylphenyl)imidazolin-2-ylidene]chloro{2-[3-(2-isopropylphenyl)imidazolin-2-ylidene]-3-isopropylphenyl-$\kappa^2 C,C'$}palladium(II)**
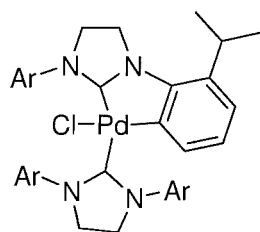
Bis[1,3-(2-isopropylphenyl)imidazolinium chloride (**2.16c**) (0.62 g, 1.80 mmol), Pd(AcO)$_2$ (0.20 g, 0.89 mmol) and KO^{t}Bu (0.22 g, 2.0 mmol) were placed in an ampoule. Toluene (15 mL) was added and the ampoule was sealed under partial vacuum. It was then heated at 50 °C for 3 hours and then cooled to rt. The resulting suspension was filtered through Celite and the solution was reduced to the minimum and was then layered with petrol to yield colourless crystals. Yield 0.49 g (0.65 mmol), 73 %.

Anal. Calcd for $C_{42}H_{51}ClN_4Pd$: C, 66.92; H, 6.82; N, 7.43 %. Found: C, 66.9; H, 6.8; N, 7.4%.

^{1}H NMR (300MHz, C_6D_6), δ:7.41 (3H, d, J = 8.7 Hz, aromatic C$\underline{H}$), 6.49 (3H, dd, J = 8.7, 2.7 Hz, aromatic C$\underline{H}$), 6.42 (3H, d, J = 2.7 Hz, aromatic C$\underline{H}$), 6.31 (6H, m, aromatic C$\underline{H}$) 3.63 (4H, s, 2 × backbone C$\underline{H}_2$), 3.41 (4H, s, 2 × backbone C$\underline{H}_2$), 3.37 and 3.26 (2 × 2H, septet, J = 6.9 Hz, 4 × C$\underline{H}$(CH$_3$)$_2$), 1.59, 1.56, 1.48 and 1.42 (4 × 6H, d, J = 6.9 Hz, 4 × CH(C$\underline{H}_3$)$_2$).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6), δ:202.23 (carbene $\underline{C}$–Pd), 198.40 (carbene $\underline{C}$–Pd),161.99 (activated aromatic $\underline{C}$–Pd), 155.32 (aromatic quaternary $\underline{C}$–N), 149.25 (aromatic quaternary $\underline{C}$–N), 142.61 (aromatic quaternary $\underline{C}$–CH(CH$_3$)$_2$), 129.69 (aromatic quaternary $\underline{C}$–CH(CH$_3$)$_2$), 139.86, 137.45, 132.44, 129.56, 128.27, 126.92, 126.54, 126.02, 123.50 and 121.37 (16 × aromatic $\underline{C}$H), 56.26 and 54.01 (backbone $\underline{C}$H$_2$), 52.89 and 49.16 (backbone $\underline{C}$H$_2$), 29.01 and 27.99 ($\underline{C}$H(CH$_3$)$_2$), 27.31 and 26.40 ($\underline{C}$H(CH$_3$)$_2$), 25.89 and 24.91 (CH($\underline{C}$H$_3$)$_2$), 24.51 and 23.85 (CH($\underline{C}$H$_3$)$_2$).

(3.10) Bis[1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene] palladium(0)
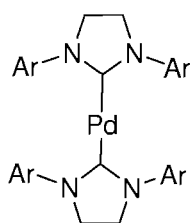
Ar = Mes

1,3-Bis(2,4,6-trimethylphenyl)imidazolinium chloride[17] (0.57 g, 1.66 mmol) was dissolved in THF (20 mL) at –78 °C, to this a solution of KO^{t}Bu (0.22 g, 1.99 mmol) in THF (15 mL) at –78 °C was added. The mixture was allowed to warm up to –10 °C and stirred for 2 h. It was then cooled to –78 °C and added to a cold (–78 °C) solution of Pd(TMEDA)Me$_2$ (0.20 g, 0.79 mmol) in THF (10 mL). The reaction mixture was allowed to warm up to r.t. and stirred over night. The solvent was removed from the resulting solution and the solid obtained was dissolved in petrol. It was then filtered through Celite, the volume was reduced to the minimum and the resulting saturated solution was placed in the freezer to give bright yellow crystals. Yield: 0.46 g (0.64 mmol), 81 %.

Anal. Calculated for $C_{42}H_{52}N_4Pd$: C, 70.13; H, 7.29; N, 7.79 % Found: C, 69.7; H, 7.2; N, 7.9%

^{1}H NMR (300MHz, C_6D_6), δ: 7.03 (4H, s, 4 × aromatic C$\underline{H}$), 3.32(4H, s, 2 × backbone C$\underline{H}_2$), 2.63 (6H, s, 2 × aromatic p-C$\underline{H}_3$), 2.41(12H, s, 4 × aromatic o-C$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6), δ: 218.61 (carbene $\underline{C}$–Pd), 139.10 (aromatic quaternary $\underline{C}$-N), 136.59 (aromatic quaternary o-$\underline{C}$-CH$_3$), 135.25 (aromatic quaternary p-$\underline{C}$–CH$_3$), 127.68 (aromatic m-$\underline{C}$H), 49.00 (backbone $\underline{C}$H$_2$), 21.32 (aromatic p-$\underline{C}$H$_3$), 18.71 (aromatic o-$\underline{C}$H$_3$).

(3.11)   Bis[1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene] η^2-dioxygen palladium(II)
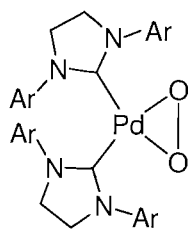
This was prepared by exposing a solution of **3.10** (0.23 g, 0.32 mmol) in petroleum (20 mL) to atmospheric air. The precipitating cream white solid was collected by filtration and was then dried under vacuum. Diffraction quality crystals were obtained by layering a thf solution of the complex with petroleum. Yield: 0.22 g (0.29 mmol), 92 %.

Ar = Mes

Anal. Calculated for $C_{49}H_{60}N_4O_2Pd$: C, 69.78; H, 7.17; N, 6.64% Found: C, 69.7; H, 7.2; N, 6.6%

^{1}H NMR (300MHz, C_6D_6), δ: 7.55 (4H, s, 4 × aromatic C$\underline{H}$), 3.39 (4H, s, 2 × backbone C$\underline{H}_2$), 2.63 (6H, s, 2 × aromatic p-C$\underline{H}_3$), 2.51(12H, s, 4 × aromatic o-C$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6), δ: 217.23 (carbene $\underline{C}$–Pd), 137.59 (aromatic quaternary $\underline{C}$–N), 136.40 (aromatic quaternary o-$\underline{C}$–CH₃), 135.93 (aromatic quaternary p-$\underline{C}$–CH₃), 129.55 (aromatic m-$\underline{C}$H), 51.16 (backbone $\underline{C}$H₂), 21.33 (aromatic p-$\underline{C}$H₃), 18.62 (aromatic o-$\underline{C}$H₃).

(3.12) Bis[1,3-bis(2-isopropylphenyl)imidazolin-2-ylidene] dimethyl palladium(II)
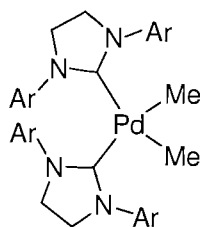
1,3-Bis(2-isopropylphenyl)imidazolinium chloride (**2.16c**) (0.57 g, 1.66 mmol) was dissolved in THF (20 mL) at –78 °C, to this a solution of KO^{t}Bu (0.22 g, 1.99 mmol) in THF (15 mL) at –78 °C was added. The mixture was allowed to warm up to –10 °C and stirred for 2 h. It was then cooled to –78 °C and added to a cold (–78 °C) solution of Pd(TMEDA)Me₂ (0.20 g, 0.79 mmol) in THF (10 mL). The reaction

Ar = 2-ipp

mixture was allowed to warm up to 0 °C and stirred over night at this temperature. The solvent was removed from the resulting white solution and the solid obtained was dissolved in toluene. It was then filtered through Celite, the volume was reduced to the minimum and was layered with petroleum to give white crystals Yield: 0.49 g (0.65 mmol), 83 %.

Anal. Calculated for $C_{44}H_{58}N_4Pd$: C, 70.33; H, 8.05; N, 7.46% Found: C, 70.5; H, 8.1; N, 7.5%

^{1}H NMR (300MHz, C_6D_6), δ: 7.53 (2H, d, J = 9.0 Hz, aromatic C$\underline{H}$), 7.40 (4H, m, aromatic C$\underline{H}$), 7.18 (2H, m, aromatic C$\underline{H}$), 4.45 (4H, s, 2 × backbone C$\underline{H}_2$), 3.40 (2H, septet, J = 6.9 Hz, 2 × C$\underline{H}$(CH₃)₂), 1.58 (12H, d, J = 6.9 Hz, 2 × CH(C$\underline{H}_3$)₂), 0.42 (3H, s, Pd-C$\underline{H}_3$).

$^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6), δ: 211.33 (carbene $\underline{C}$–Pd), 143.58 (aromatic quaternary $\underline{C}$–N), 132.38 (aromatic quaternary $\underline{C}$–CH(CH$_3$)$_2$), 128.56, 128.01, 127.51 and 126.90 (4 × aromatic $\underline{C}$H), 52.98 (backbone $\underline{C}$H$_2$), 27.35 ($\underline{C}$H(CH$_3$)$_2$), 23.28 (CH($\underline{C}$H$_3$)$_2$), 18.55 (Pd–$\underline{C}$H$_3$).

(3.13) Bis[1,3-bis(2-isopropylphenyl)imidazolin-2-ylidene] palladium(0)
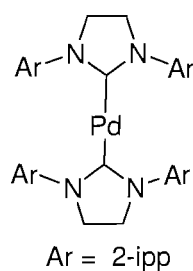
Ar = 2-ipp

1,3-Bis(2-isopropylphenyl)imidazolinium chloride (**2.16c**) (0.57 g, 1.66 mmol) was dissolved in THF (20 mL) at –78 °C, to this a solution of KO^{t}Bu (0.22 g, 1.99 mmol) in THF (15 mL) at –78 °C was added. The mixture was let to warm up to –10 °C and stirred for 2 h. It was then cooled to –78 °C and added to a cold (–78 °C) solution of Pd(TMEDA)Me$_2$ (0.20 g, 0.79 mmol) in THF (10 mL). The reaction mixture was allowed to warm up to 25 °C and stirred over night at this temperature. The solvent was removed from the resulting deep red solution and the solid obtained was dissolved in petroleum. It was then filtered through Celite, the volume was reduced to the minimum and the resulting saturated solution was placed in the freezer to give dark red crystals. Yield: 0.42 g (0.58 mmol), 74 %.

Anal. Calculated for $C_{42}H_{52}N_4Pd$: C, 69.93; H, 7.55; N, 7.77% Found: C, 69.9; H, 7.6; N, 7.8%

^1H NMR (300MHz, C_6D_6), δ: 7.45 (2H, d, J = 9.0 Hz, aromatic C$\underline{H}$), 7.31 (4H, m, aromatic C$\underline{H}$), 7.12 (2H, m, aromatic C$\underline{H}$), 3.43 (2H, septet, J = 6.9 Hz, 2 × C$\underline{H}$(CH$_3$)$_2$), 3.30 (4H, s, 2 × backbone C$\underline{H}_2$), 1.31 (12H, d, J = 6.9 Hz, 2 × CH(C$\underline{H}_3$)$_2$).

$^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6), δ: 142.56 (aromatic quaternary $\underline{C}$–N), 131.29 (aromatic quaternary $\underline{C}$–CH(CH$_3$)$_2$), 129.97, 128.29, 126.98 and 125.95 (4 × aromatic $\underline{C}$H), 53.54 (backbone $\underline{C}$H$_2$), 28.29 ($\underline{C}$H(CH$_3$)$_2$), 24.23 (CH($\underline{C}$H$_3$)$_2$).

(3.14) [1,3-Bis(2-isopropylphenyl)imidazolin-2-ylidene]{1,3-bis(6-isopropylphenyl-2-yl)imidazolin-2-ylidene-κ^3C,C',C''}palladium(II)
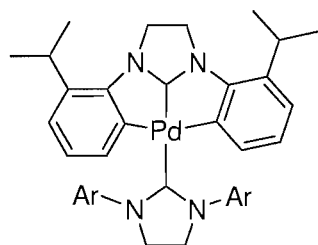
Ar = 2-ipp

1,3-Bis(2-isopropylphenyl)imidazolinium chloride (**2.16c**) (0.57 g, 1.66 mmol) was dissolved in THF (20 mL) at –78 °C, to this a solution of KO^{t}Bu (0.22 g, 1.99 mmol) in THF (15 mL) at –78 °C was added. The mixture was let to warm up to –10 °C and stirred for 2 h. It was then cooled to –78 °C and added to a cold (–78 °C) solution of Pd(TMEDA)Me$_2$ (0.20 g, 0.79 mmol) in THF (10 mL). The reaction mixture was allowed to warm up to 50 °C and

stirred over night at this temperature. The solvent was removed from the resulting yellow solution and the solid obtained was dissolved in benzene. It was then filtered through celite, the volume was reduced and the resulting solution was layered with petroleum to give yellow crystals. Yield: 0.39 g (0.54 mmol), 68 %.

Anal. Calculated for $C_{42}H_{50}N_4Pd$: C, 70.13; H, 7.29; N, 7.79% Found: C, 70.4; H, 7.4; N, 7.9%

^{1}H NMR (300MHz, CD_2Cl_2), δ: 8.09 (2H, m, aromatic C$\underline{H}$), 7.61 (6H, m, aromatic C$\underline{H}$), 7.32 (2H, m, aromatic C$\underline{H}$), 7.10 (2H, m, aromatic C$\underline{H}$), 6.95 (2H, m, aromatic C$\underline{H}$), 4.50 (4H, s, 2 × backbone C$\underline{H_2}$), 4.36 (4H, s, 2 × backbone C$\underline{H_2}$), 3.82 (2H, septet, J = 6.9 Hz, 2 × C$\underline{H}$(CH$_3$)$_2$), 3.43 (2H, septet, J = 6.9 Hz, 2 × C$\underline{H}$(CH$_3$)$_2$), 1.62 (12H, d, J = 6.9 Hz, 2 × CH(C$\underline{H_3}$)$_2$), 1.53 (12H, d, J = 6.9 Hz, 2 × CH(C$\underline{H_3}$)$_2$).

^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2), δ: 214.21 (carbene $\underline{C}$–Pd), 157.91 (activated aromatic $\underline{C}$–Pd), 152.27 (aromatic quaternary $\underline{C}$–N), 145.72 (aromatic quaternary $\underline{C}$–N), 140.60 (aromatic quaternary $\underline{C}$–CH(CH$_3$)$_2$), 130.29 (aromatic quaternary $\underline{C}$–CH(CH$_3$)$_2$), 138.38, 129.56, 128.27, 126.92, 126.54, 126.02, 123.50 and 121.37 (7 × aromatic $\underline{C}$H), 55.25 (backbone $\underline{C}$H$_2$), 51.99 (backbone $\underline{C}$H$_2$), 28.17 ($\underline{C}$H(CH$_3$)$_2$), 27.23 ($\underline{C}$H(CH$_3$)$_2$), 24.79 (CH($\underline{C}$H$_3$)$_2$), 24.50 (CH($\underline{C}$H$_3$)$_2$).

(3.15)   [1,3-Bis(4-methoxyphenyl)imidazolin-2-ylidene]{2-[3-(4-methoxyphenyl)-imidazolin-2-ylidene]-5-methoxyphenyl-$\kappa^2 C,C'$}methylpalladium(II)
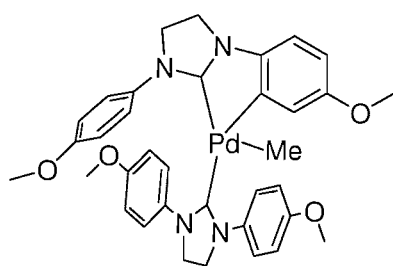
1,3-Bis(4-methoxyphenyl)imidazolinium chloride (**2.10c**) (0.53 g, 1.66 mmol) was dissolved in THF (20 mL) at –78 °C, to this a solution of KO^{t}Bu (0.22 g, 1.99 mmol) in THF (15 mL) at –78 °C was added. The mixture was allowed to warm up to –10 °C and stirred for 2 h. It was then cooled to –78 °C and added to a cold (–78 °C) solution of Pd(TMEDA)Me$_2$ (0.20 g, 0.79 mmol) in THF (10 mL). The reaction mixture was allowed to warm up to r.t. and stirred over night. The solvent was removed from the resulting dark yellow solution and the solid obtained was dissolved in benzene. It was then filtered through Celite, the volume was reduced and the resulting solution was layered with petroleum to give brown crystals. Yield: 0.35 g (0.51 mmol), 64 %.

Anal. Calculated for $C_{35}H_{38}N_4O_4Pd$: C, 61.36; H, 5.59; N, 8. 18% Found: C, 61.3; H, 5.6; N, 8.1%

^{1}H NMR (300MHz, C_6D_6), δ: 7.52 (4H, d, J = 8.7 Hz, aromatic C$\underline{H}$), 6.83 (8H, m, aromatic C$\underline{H}$), 6.51 (3H, m, aromatic C$\underline{H}$), 4.10 (4H, s, 2 × backbone C$\underline{H_2}$), 3.97 (4H, s, 2

× backbone C$\underline{H}_2$), 2.34 (6H, s, O–C$\underline{H}_3$), 2.01 (3H, s, O–C$\underline{H}_3$), 1.85 (3H, s, O–C$\underline{H}_3$), 0.41 (3H, s, Pd–C$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$), δ: 154.32 (aromatic quaternary $\underline{C}$-N), 153.02 (aromatic quaternary $\underline{C}$-N), 132.31 (aromatic quaternary $\underline{C}$-OCH$_3$), 131.53 (aromatic quaternary $\underline{C}$-OCH$_3$), 130.08, 129.56, 128.13, and 109.10 (aromatic $\underline{C}$H), 112.35 (aromatic quaternary $\underline{C}$-Pd), 58.18 and 56.32 (backbone $\underline{C}$H$_2$), 43.76 (O-$\underline{C}$H$_3$), 18.38 (O-$\underline{C}$H$_3$).

(3.16)   [1,3-Bis(2,4-dimethoxyphenyl)imidazolin-2-ylidene]]{2-[3-(2,4-dimethoxy phenyl)imidazolin-2-ylidene]-3,5-dimethoxyphenyl-κ^2C,C'} methylpalladium(II)
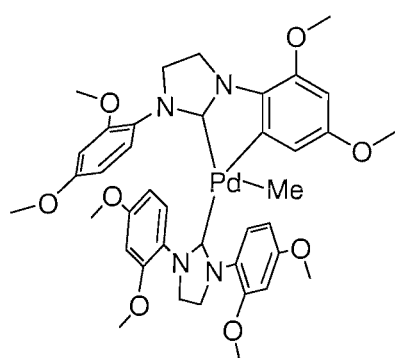
This was prepared in the same way as complex **3.15** using the following: 1,3-bis(2,4-dimethoxyphenyl) imidazolinium chloride (**2.11c**) (0.63 g, 1.66 mmol), KO^{t}Bu (0.22 g, 1.99 mmol) and Pd(TMEDA)Me$_2$ (0.20 g, 0.79 mmol) to yield colourless crystals. Yield: 0.45 g (0.56 mmol), 71 %.

Anal. Calculated for C$_{39}$H$_{46}$N$_4$O$_8$Pd: C, 58.17; H, 5.76; N, 6. 96% Found: C, 58.1; H, 5.9; N, 6.9%

^{1}H NMR (300MHz, C$_6$D$_6$), δ: 7.38 (4H, d, J = 8.7 Hz, aromatic C$\underline{H}$), 6.47 (4H, dd, J = 8.7, 2.7 Hz, aromatic C$\underline{H}$), 6.39 (3H, d, J = 2.7 Hz, aromatic C$\underline{H}$), 3.64 (6H, s, 2 × O–C$\underline{H}_3$), 3.58 (10H, s, 2 × backbone C$\underline{H}_2$ and 2 × O–C$\underline{H}_3$), 3.41 (10H, s, 2 × backbone C$\underline{H}_2$ and 2 × O–C$\underline{H}_3$), 2.10 (3H, s, O–C$\underline{H}_3$), 1.76 (3H, s, O–C$\underline{H}_3$), 0.60 (3H, s, Pd–C$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$), δ: 155.89 (aromatic quaternary $\underline{C}$–N), 153.68 (aromatic quaternary $\underline{C}$–N), 129.93 (aromatic quaternary $\underline{C}$–OCH$_3$), 129.28, 124.16, 103.38, and 99.54 (aromatic $\underline{C}$H), 117.59 (aromatic quaternary $\underline{C}$–Pd), 59.12 and 52.51 (backbone $\underline{C}$H$_2$), 55.06 (O–$\underline{C}$H$_3$), 47.76 (O–$\underline{C}$H$_3$).

X-ray Crystallography

All data sets were collected on an Enraf-Nonius Kappa CCD area detector diffractometer with an FR591 rotating anode (Mo/Kα radiation) and an Oxford Cryosystems low temperature device operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. The programs used for control and integration were Collect, Scalepack, and Denzo.[28] The crystals were mounted on a glass fibre with silicon grease, from Fomblin vacuum oil. All solutions and refinements were performed using the WinGX package[29] and all software packages within. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogens were added using a riding model. Crystallographic data collected are presented in Tables 3.2 and 3.3.

	3.2	3.3	3.4	3.5	3.6	3.8	3.9
Chemical formula	$C_{18}H_{22}BrN_3Pd$	$C_{17}H_{19}Br_{0.65}Cl_{1.35}N_3Pd$	$C_{22}H_{30}BrN_3Pd$	$C_{23}H_{33}N_3Pd$	$C_{46}H_{57}N_3O_3Pd$	$C_{97}H_{104}N_8O_8Pd_4$	$C_{42}H_{51}ClN_4Pd$
Formula weight	466.70	471.44	522.80	457.92	1019.31	1935.48	753.72
Crystal system	Triclinic	Orthorhombic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	P-1	$Pbn2_1$	$P2_1/n$	P-1	P-1	$P2/c$	P-1
a / Å	7.0784(3)	6.7056(5)	18.9866(12)	8.480(5)	10.011(5)	16.7336(18)	12.309(2)
b / Å	14.2516(15)	13.8007(12)	8.8545(6)	9.156(4)	11.407(5)	11.2402(12)	12.969(2)
c / Å	18.844(3)	18.9015(14)	25.977(2)	15.777(8)	19.898(5)	22.3834(16)	13.570(2)
α / °	98.576(10)	90	90	89.36(4)	75.432(5)	90	115.906(4)
β / °	100.368(7)	90	99.987(7)	78.48(5)	76.550(5)	100.888(7)	97.093(4)
γ / °	91.312(8)	90	90	62.85(5)	71.712(5)	90	95.803(5)
V / Å^3	1846.6(3)	1749.2(2)	4301.0(5)	1063.5(11)	2058.7(15)	4134.3(7)	1904.3(5)
Z	4	4	8	2	2	4	2
T/ K	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
μ / mm^{-1}	3.171	2.748	2.732	0.885	1.337	0.921	0.591
No. data collected	33340	27733	41063	19792	23712	65825	15723
No. unique data	8510	4025	9947	4879	7477	9583	5080
R_{int}	0.0486	0.1132	0.0700	0.0293	0.0656	0.1604	0.0524
Final R(|F|) for $F_o > 2\sigma(F_o)$	0.0832	0.0396	0.0451	0.0208	0.0707	0.0617	0.0772
Final $wR(F^2)$ for all data	0.2418	0.0704	0.0946	0.0500	0.1756	0.1224	0.2097

Table 3.2: Crystallographic data for compounds **3.2, 3.3, 3.4, 3.5, 3.6, 3.8** and **3.9**

	3.10	3.11	3.12	3.13	3.14	3.15	3.16
Chemical formula	$C_{21}H_{26}N_2Pd_{0.50}$	$C_{49}H_{60}N_4O_2Pd$	$C_{22}H_{29}N_2Pd_{0.5}$	$C_{168}H_{208}N_{16}Pd_4$	$C_{42}H_{50}N_4Pd$	$C_{35}H_{38}N_4O_4Pd$	$C_{78}H_{92}N_8O_{16}Pd_2$
Formula weight	359.64	843.41	374.68	2875.52	717.26	685.09	805.24
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2/c$	$C2/c$	P-1	$P2_1/c$	P-1
a / Å	17.0760(13)	10.3708(2)	22.4014(7)	23.344(2)	10.063(2)	10.4722(5)	11.5140(2)
b / Å	10.4039(7)	29.0870(6)	8.0114(3)	8.0765(4)	12.528(2)	16.0850(9)	17.8268(4)
c / Å	21.6208(17)	15.6449(2)	24.4471(8)	19.6151(18)	14.840(3)	18.4923(9)	18.5840(5)
α / °	90	90	90	90	71.63(3)	90	87.6150(10)
β / °	98.707(4)	101.8300(10)	114.925(2)	100.456(3)	86.25(3)	92.636(2)	86.8100(10)
γ / °	90	90	90	90	89.04(3)	90	85.3690(10)
V / Å^3	3796.8(5)	4619.13(14)	3978.8(2)	3636.8(5)	1771.7(6)	3111.6(3)	3793.52(15)
Z	4	4	4	4	2	4	2
T / K	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
μ / mm^{-1}	0.522	0.442	0.282	0.545	0.559	0.642	0.546
No. data collected	52918	47341	39959	9163	52811	17972	80693
No. unique data	5874	10576	9055	2219	8200	7094	17373
R_{int}	0.1649	0.0598	0.0608	0.0718	0.0755	0.0410	0.0722
Final R(|F|) for $F_o > 2\sigma(F_o)$	0.0879	0.0691	0.0421	0.0560	0.0392	0.0393	0.0492
Final R(F^2) for all data	0.1530	0.2120	0.0927	0.1212	0.0858	0.0780	0.1046

Table 3.3: Crystallographic data for compounds **3.10, 3.11, 3.12, 3.13, 3.14, 3.15** and **3.16**

3.6 References

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Chapter 4:

Pd NHC complexes as catalysts

in Heck coupling reactions

4.1 Introduction

As briefly described in Chapter 1, the Heck (or Mizoroki-Heck[1,2]) reaction is the coupling of an aryl/vinyl halide (or triflate) with an olefin in the presence of a base and a transition metal (most commonly palladium) catalyst, to form a substituted olefin (Scheme 4.1).[3]

$$R^1\text{-}X \ + \ =\!\!\diagup^{R^2} \ + \ \text{Base} \ \xrightarrow{\text{Pd catalyst}} \ R^1\!\diagup\!\!\diagup^{R^2} \ + \ \text{Base·HX}$$
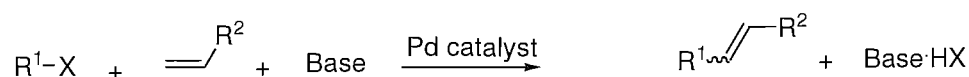
Scheme 4.1: The Heck coupling reaction X = halide, R^1 and R^2 = alkyl, aryl

The cheapest substrates for Heck couplings are the aryl chlorides which unfortunately are the most difficult to couple. The coupling difficulty has been related to the strength of the C–Cl bond (bond dissociation energy 96 kcal mol^{-1}) while the weaker bonded, but more expensive, bromides (81 kcal mol^{-1}) and iodides (65 kcal mol^{-1}) are more easily coupled.[4]

As with other catalytic reactions, Heck coupling catalysis can be performed heterogeneously[5] (polymer supported palladium complexes or nanoparticles) or in a homogeneous solution (using palladium complexes). However there is still debate on the exact nature of the catalytic site in homogeneous catalysis.[6] Homogeneous catalysis of Heck reactions began to be of great interest only after realising that triphenylphosphine (**4.1**, Figure 4.1), when used as a ligand, stabilises the resting state of the catalyst[7] and therefore help in overcoming earlier problems faced, such as the short lifetime of the catalysts that lead to rapid precipitation of palladium (0).

        (4.1)   **(4.2)**   **(4.3)**
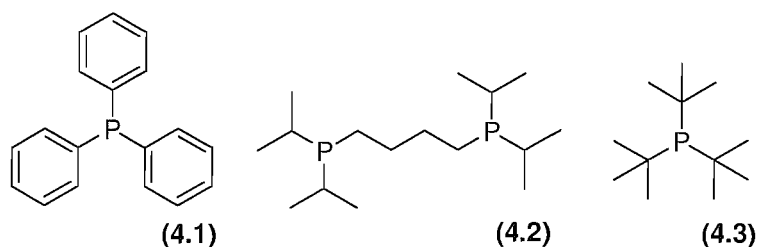
Figure 4.1: Phosphines used as ligands in palladium catalysed Heck couplings

Triphenylphosphine has continued to be the most commonly-employed ligand in the Heck reaction as it provides good performance over a wide range of substrates. A variety of different phosphine ligands were screened over the years in an effort to find catalysts that would activate aryl chlorides (the final frontier). Milstein and co-workers studied bidentate phosphines such as **4.2** in the coupling of aryl-chlorides with a selection of olefins[8] and later on they have published an extensive study on the role of the various bidentate vs. monodentate ligands in Heck reactions.[9] In 1999 Fu[10] had shown that when the bulky trialkylphosphine P(^{t}Bu)$_3$ (**4.3**) was used as a ligand, coupling of the less reactive aryl chlorides was possible. Unfortunately P(^{t}Bu)$_3$ could not be used as a ligand in the industry, since an inert atmosphere was necessary, making the whole process unattractive.

In recent years, economical and environmental concerns have led to a desire to move away from phosphines, despite the good results these ligands provide. In order for phosphine based catalysts to perform well, an excess of the phosphine, which is unrecoverable, must be used. In addition phosphines are toxic and special treatment of the wastes is required, increasing the expenses for the user. Furthermore, in order to avoid the over-ligation (formation of Pd(L)$_3$ or Pd(L)$_4$ species) of the palladium centre that causes reduction in the activity, high catalyst loadings have to be applied.

Tol = o-Me-C$_6$H$_4$ (**4.4**)   (**4.5**)   (**4.6**)   (**4.7**)
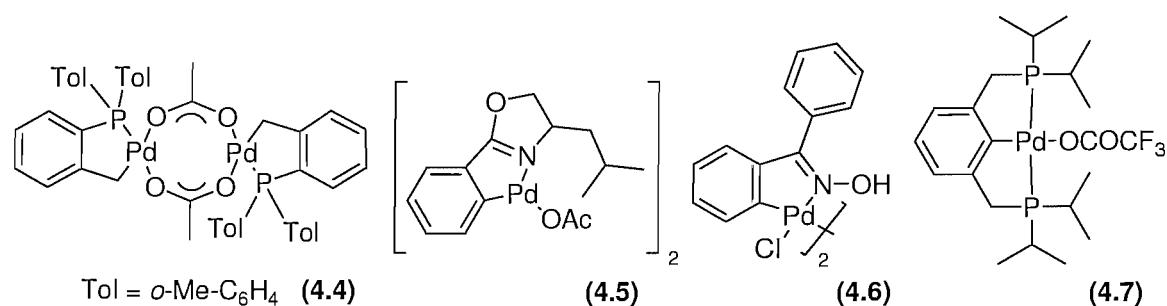
Figure 4.2: Palladacycle complexes used as precatalysts for Heck couplings

A 'new principle' in palladium catalysis was announced by Herrmann and co-workers in 1995 when they reported the palladacycle complex **4.4** (Figure 4.2) that showed very good TONs (2 × 10^5) for couplings of p-formylbromobenzene with acrylates.[11] Many researchers focused on palladacycle chemistry after that and reported even higher TONs for simple couplings.[12] Milstein, for example reported imino-palladacycle complexes (like **4.5**) that were active in couplings of bromobenzene with a selection of olefins,[13]

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while Nájera[14] presented oxime palladacycles (e.g. **4.6**) that were active pre-catalysts for Heck couplings. As with other bidentate palladacycles, the metal complex was a precursor to free Pd(0) and this was evident from the fact that in the first use of the complex, an inductive period was observed [reduction to Pd(0)], while in subsequent uses no such observation was made. Pincer palladacycles, like complex **4.7** reported by Milstein, have been also found to catalyse the couplings of aryl iodides and aryl bromides,[15] although the nature of the true catalytic species of pincer palladacycles has been debated.[16]

R= mesityl **(4.12)**
R= ᵗBu   **(4.13)**
R= CI **(4.10)**   R= ⁱPr   **(4.14)**
R= Me **(4.11)**   R=Cy   **(4.15)**

(4.8)   **(4.9)**

n=2, X= I **(4.16)**
n=3, X=Br **(4.17)**

(4.18)

(4.19)

n=0 **(4.20)**
n=1 **(4.21)**

(4.22)
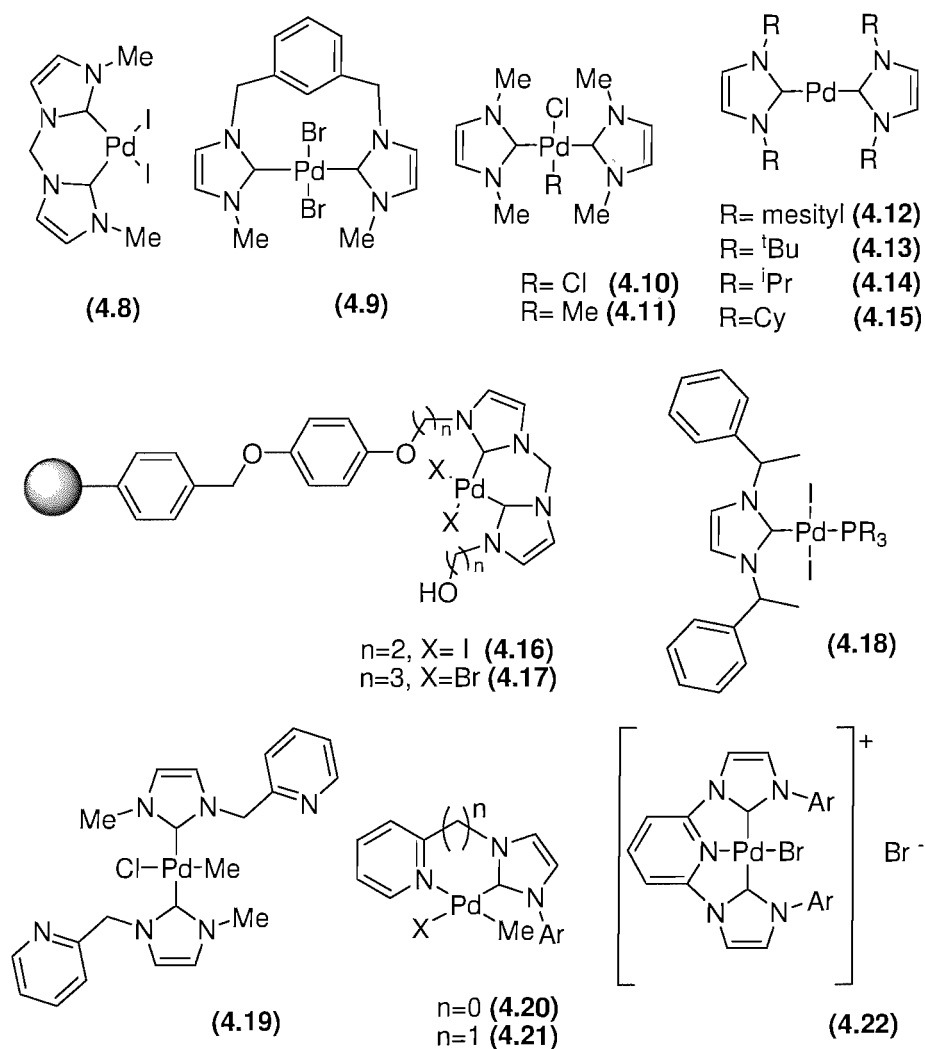
Figure 4.3: Palladium NHC complexes used as precatalysts for Heck couplings

Although palladium NHC complexes as catalysts are relatively new in the area of Heck couplings, they have already displayed very good TONs.[17] Palladium NHC complexes are effective catalysts because they are air- and moisture-stable, and possess high thermal stability. Preparation of such complexes is convenient, cost effective and provides the

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possibilities of polymer-supported[18] (**4.16** and **4.17**) or mixed carbene-phosphine complexes (**4.18**).[19]

Chelating Pd(II) NHC complexes **4.8**[20] and **4.9**[21] were reported as good precatalysts for couplings of bromoarenes and chloroarenes. Interestingly, these chelated bis-carbene complexes have displayed similar TONs as the non-chelated bis-carbene complexes **4.10** and **4.11**.[21] Apart from Pd(II) NHC complexes, Pd(0) precatalysts (**4.12** – **4.15**) were also prepared and successfully used in coupling reactions.[22] Some other examples of good pre-catalyst systems include palladium NHC complexes with dangling pyridine substituents (**4.19**),[23] pyridine-functionalised NHC palladium complexes[24] (**4.20** and **4.21**) and pyridine-functionalised NHC pincer Pd(II) complex (**4.22**).[25]

4.2 Mechanism of the Heck Coupling Reaction

Usually a Pd(II) precatalyst is used and it is believed that this is reduced to Pd(0) *in situ*, allowing the oxidative addition of the aryl halide to form a Pd(II) intermediate (Scheme **4.2**). The Pd(II) intermediate can then bind to the olefin (loss of ligand) that will then insert into the palladium-aryl bond (ligand gained back) and create a new carbon-carbon bond. The organic product is then ejected from the complex by a β-hydride elimination. Finally a base removes the bound HX from the complex, thus regenerating the catalyst.[16]
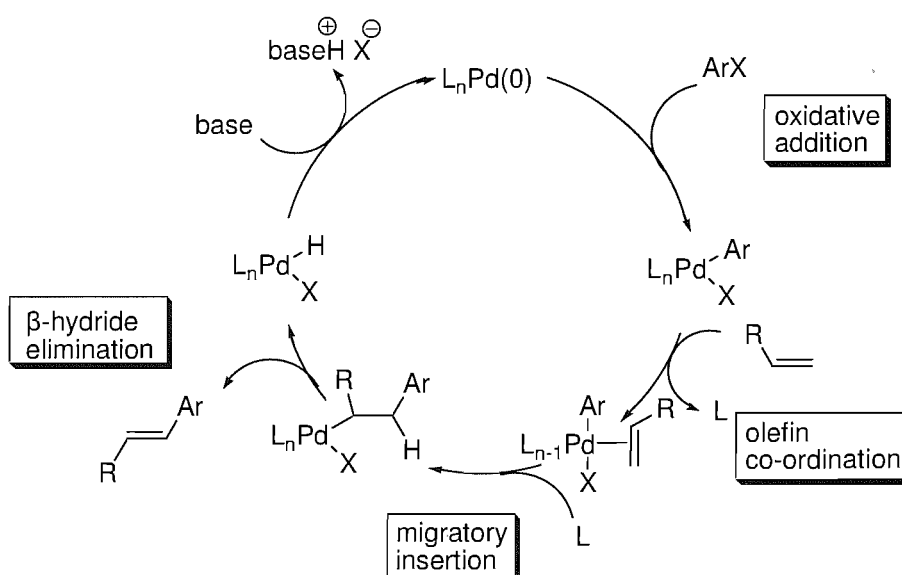
Scheme 4.2: Traditional mechanism of the Heck reaction[16]

The proposed Heck reaction mechanism for Pd NHC complexes (seen in Scheme **4.3**) is again a Pd(0)/Pd(II) pathway.[26] Experimental evidence[27] and theoretical calculations[28] agree and support this proposed pathway. Again in the NHC case, the active catalyst is a Pd(0) complex that undergoes an oxidative addition of R^1X to form a *trans* (carbene)$_2$PdR^{1}X intermediate.

Loss of halide X^- create a free coordination site for the insertion of the olefin and then, *cis-trans* isomerism provides the route for the insertion of the olefin into the Pd–R^1 bond and co-ordination of the halide anion, leading to the formation of the new carbon-carbon bond. β-hydride elimination produces the product olefin and a base removes HX from the system and the catalyst is therefore regenerated.
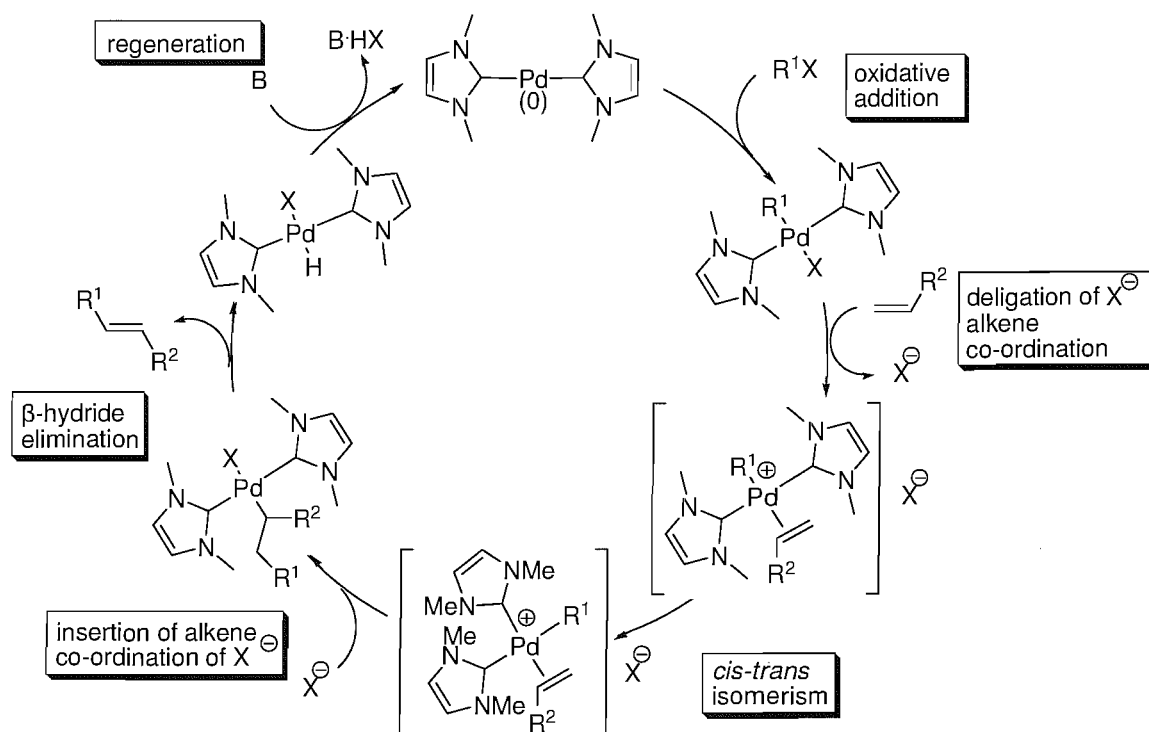
Scheme 4.3: Postulated mechanism of the Heck reaction for NHC complexes[26]

Palladium NHC complexes have not been studied mechanistically in as much depth as other systems, but it is known that they bind to the Pd(II) centre much stronger than phosphines and therefore ligand dissociation is unlikely. [23] It has been therefore also suggested that the olefin insertion occurs through penta-co-ordinated intermediates. [29]

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4.3 Results and Discussion

The Pd NHC complexes that have been tested as catalysts for the Heck coupling reaction are shown in Figure 4.4 below. The catalytic details and performances of these are summarised in Tables 4.1, 4.2, 4.3 and 4.4.
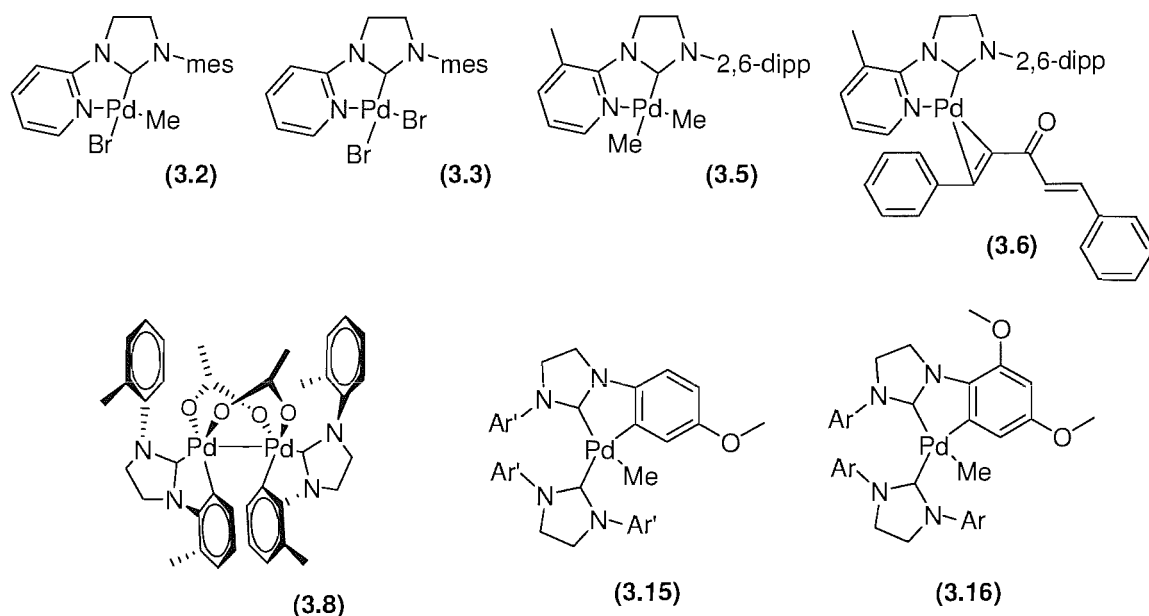
Figure 4.4: Pd NHC complexes tested as catalysts for Heck coupling reactions

Ar = 2,4-dimethoxyphenyl, Ar' = 4-methoxyphenyl

The Pd NHC catalysts were compared against a standard Heck reaction catalyst, the *in situ* formed PPh₃ palladium complex[7] denoted **4.1***; against the most active catalyst to be reported up to date, the *in situ* formed P(*t*Bu)₃ palladium complex[10] denoted **4.3***; and against a Pd(II) source, Pd(CH₃COO)₂ denoted **4.23**. A wide selection of solvents and bases were used in order to achieve the highest possible conversions. The catalyst loading for all catalytic reactions was 1.5 mol% leading to a catalyst:substrate ratio of 1:66, unless otherwise stated. Butyl acrylate was the selected olefin used in all reactions as shown in Scheme 4.4.
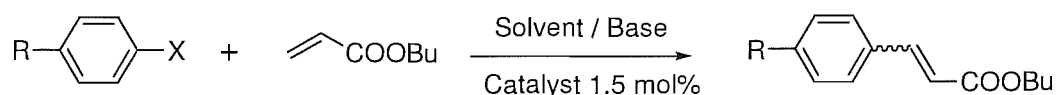
Scheme 4.4: General outline of the Heck coupling catalytic reaction

Entry	Catalyst	Solvent	Temp. /°C	Base	X	R	Time / h	Conversion / %
1	**4.1***	dioxane	110	NEt₃	Br	H	18	>99
2	**4.3***	dioxane	110	NEt₃	Br	H	18	>99
3	**3.2**	dioxane	110	NEt₃	Br	H	18	60
4	**3.3**	dioxane	110	NEt₃	Br	H	18	18
5	**3.5**	dioxane	110	NEt₃	Br	H	18	20
6	**3.6**	dioxane	110	NEt₃	Br	H	18	10
7	**3.8**	dioxane	110	NEt₃	Br	H	18	90
8	**3.15**	dioxane	110	NEt₃	Br	H	18	>99
9	**4.1***	NMP	140	NEt₃	Br	H	18	>99
10	**4.3***	NMP	140	NEt₃	Br	H	18	>99
11	**3.2**	NMP	140	NEt₃	Br	H	18	75
12	**3.3**	NMP	140	NEt₃	Br	H	18	67
13	**3.5**	NMP	140	NEt₃	Br	H	18	75
14	**3.6**	NMP	140	NEt₃	Br	H	18	50
15	**3.8**	NMP	140	NEt₃	Br	H	18	>96
16	**3.15**	NMP	140	NEt₃	Br	H	18	>99

Table 4.1: Catalytic Heck reactions using bromobenzene as the substrate

As shown in Table 4.1, from the Pd NHC complexes, only **3.8** and **3.15** performed well at low temperatures (110 °C) and gave comparable conversions to the standard Heck reaction catalyst (**4.1***). However, the increase of the reaction temperature resulted in the increase of the conversions but unfortunately complexes **3.2**, **3.3**, **3.5** and **3.6** still did not perform as well as the phosphine based catalysts **4.1*** and **4.3***.

For allowing the easy comparison of the catalytic results summarised in Table 4.1, a schematic representation of the maximum percentage conversions achieved by each catalyst at the various temperatures is given in Scheme 4.5. As displayed in Scheme 4.5 complex **3.15** along with **4.1*** and **4.3*** perform extremely well, giving virtually full conversions. Complex **3.8** performs very well too giving conversions of up to 96%.
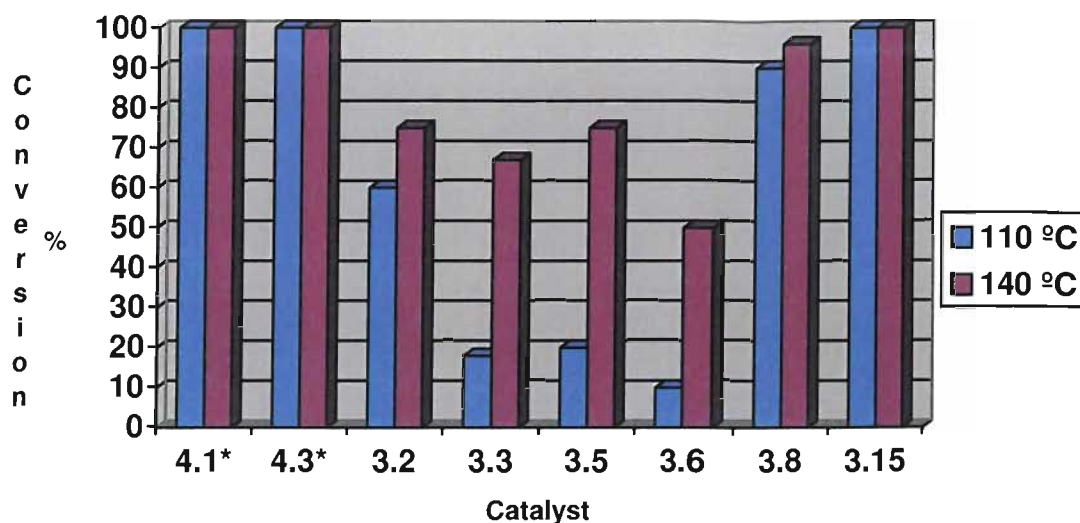
Scheme 4.5: Catalyst performance in Heck reactions of bromobenzene

Compared with bromobenzene, 4-bromotoluene is a deactivated substrate in the Heck reaction, due to the electron-donation of the methyl group. As outlined in Table 4.2, complexes **3.15** and **3.16** performed better compared to the standard Heck reaction catalyst (**4.1***) giving complete conversions even at reaction temperatures of 140 °C. The use of an ionic liquid (Bu$_4$NBr), as a solvent, seems to have increased the activity of all catalysts; however, the increase of the reaction temperature might have had some beneficial effects too.

Entry	Catalyst	Solvent	Temp. /°C	Base	X	R	Time / h	Conversion / %
1	**4.1***	NMP	140	NEt$_3$	Br	CH$_3$	18	95
2	**4.3***	NMP	140	NEt$_3$	Br	CH$_3$	18	>99
3	**3.8**	NMP	140	NEt$_3$	Br	CH$_3$	18	90
4	**3.15**	NMP	140	NEt$_3$	Br	CH$_3$	18	>99
5	**3.16**	NMP	140	NEt$_3$	Br	CH$_3$	18	>99
6	**4.1***	Bu$_4$NBr	160	NaOAc	Br	CH$_3$	18	>99
7	**4.3***	Bu$_4$NBr	160	NaOAc	Br	CH$_3$	18	>99
8	**3.8**	Bu$_4$NBr	160	NaOAc	Br	CH$_3$	18	93
9	**3.15**	Bu$_4$NBr	160	NaOAc	Br	CH$_3$	18	>99
10	**3.16**	Bu$_4$NBr	160	NaOAc	Br	CH$_3$	18	>99

Table 4.2: Catalytic Heck reactions using 4-bromotoluene as the substrate

Interestingly, the use of the ionic liquid (Bu$_4$NBr) delays and sometimes prevents the formation of palladium(0), compared to reactions involving liquid solvents (*e.g.* NMP, DMF *etc*). Scheme 4.6 gives a visual comparison of the complexes tested in the Heck reaction of 4-bromotoluene, while Scheme 4.7 gives a graphical representation of the catalytic performance of selected complexes.
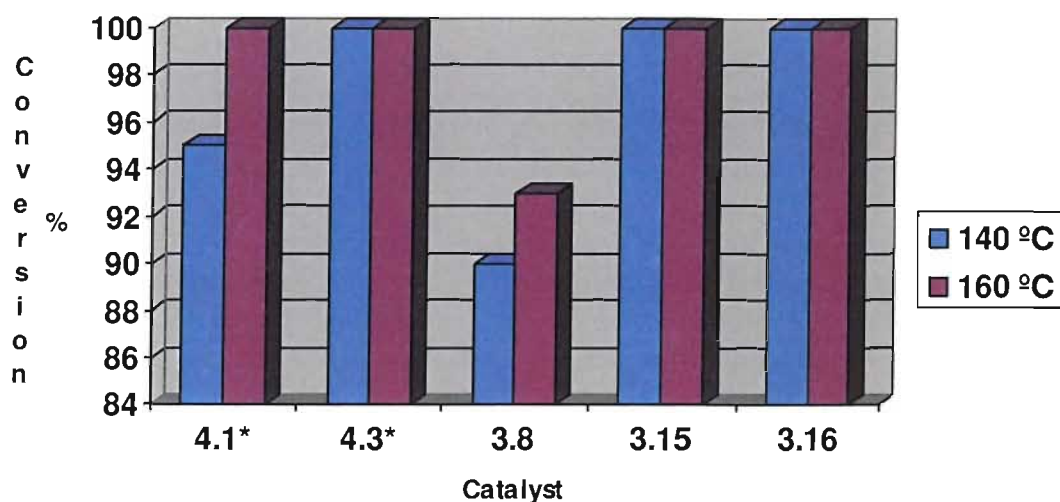
Scheme 4.6: Catalyst performance in Heck reactions of 4-bromotoluene
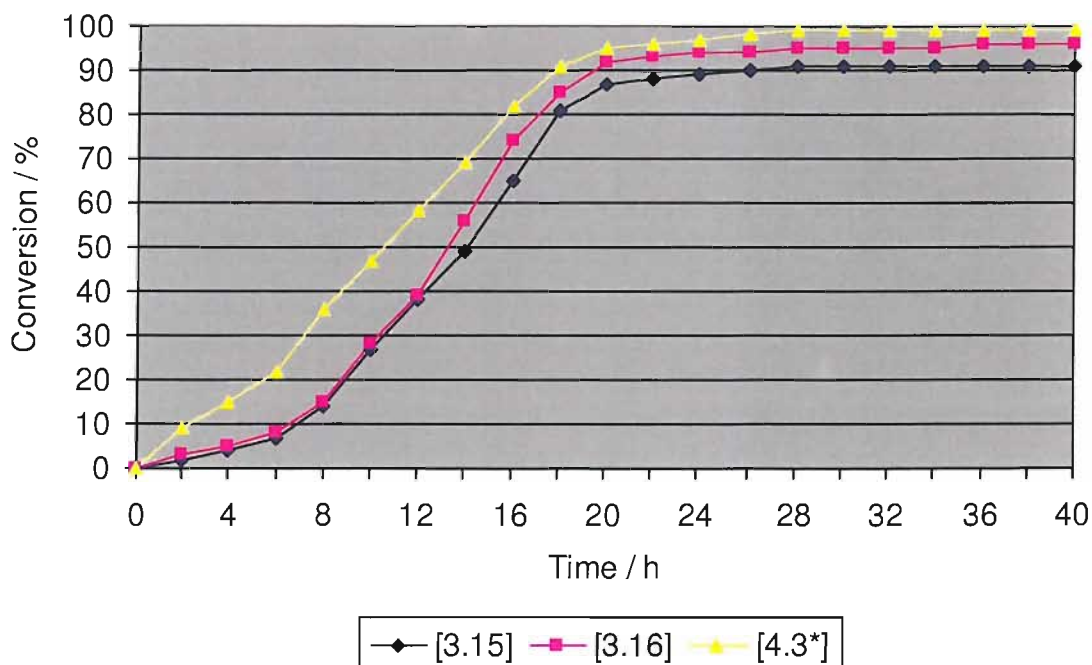
Scheme 4.7: Graphical representation of the catalytic performance of complexes **3.15**, **3.16** and **4.3*** in the Heck coupling of 4-bromotoluene (Table 4.2 entries 9, 10 and 2 respectively)

Complex **3.8** lacks the activity of the other Pd NHC complexes but still performs well and it can be considered comparable to the palladium triphenylphosphine complex catalyst.

4-Chloroacetophenone is an activated aryl chloride substrate and therefore is one of the easiest (chloroarene) substrates to activate towards a Heck coupling reaction. The Pd NHC complexes were tested against the Pd phosphine complexes **4.1*** and **4.3*** and also against a source of Pd(II), $Pd(CH_3COO)_2$. The catalytic results of the Heck coupling reactions using 4-chloroacetophenone as the substrate are summarised in Table 4.3.

Entry	Catalyst	Solvent	Temp. /°C	Base	X	R	Time / h	Conversion / %
1	4.1*	NMP	140	NEt$_3$	Cl	COCH$_3$	18	26
2	4.3*	NMP	140	NEt$_3$	Cl	COCH$_3$	18	83
3	3.8	NMP	140	NEt$_3$	Cl	COCH$_3$	18	15
4	3.8	NMP	140	NaOAc	Cl	COCH$_3$	18	15
5	3.8	NMP	140	NaO^{i}Pr	Cl	COCH$_3$	18	0 [a]
6	3.8	DMF	140	NEt$_3$	Cl	COCH$_3$	18	50
7	3.8	DMAC	140	NEt$_3$	Cl	COCH$_3$	18	5
8	3.15	DMF	160	NEt$_3$	Cl	COCH$_3$	18	28
9	3.16	DMF	140	NBu$_3$	Cl	COCH$_3$	18	38
10	4.23	Bu$_4$NBr	140	NEt$_3$	Cl	COCH$_3$	18	0
11	4.23	Bu$_4$NBr	140	NaOAc	Cl	COCH$_3$	18	15
12	4.23	Bu$_4$NBr	160	NaOAc	Cl	COCH$_3$	18	19
13	4.1*	Bu$_4$NBr	160	NaOAc	Cl	COCH$_3$	18	58
14	4.3*	Bu$_4$NBr	160	NaOAc	Cl	COCH$_3$	18	94
15	3.8	Bu$_4$NBr	140	NEt$_3$	Cl	COCH$_3$	18	5
16	3.8	Bu$_4$NBr	140	NaOAc	Cl	COCH$_3$	18	70
17	3.8	Bu$_4$NBr	160	NaOAc	Cl	COCH$_3$	18	78
18	3.15	Bu$_4$NBr	160	NaOAc	Cl	COCH$_3$	18	79
19	3.16	Bu$_4$NBr	160	NaOAc	Cl	COCH$_3$	18	84

Table 4.3: Catalytic Heck coupling reactions using 4-chloroacetophenone as the substrate

Notes: [a] A side reaction involving 4-chloroacetophenone takes place

Complex **3.8** performed better when DMF was used as a solvent instead of NMP (15 and 50 % conversions respectively), while when an ionic liquid was employed, as the solvent, the performance was even better (70 % conversion). An increase of the temperature (160 °C instead of 140 °C, entries 17 and 16 respectively) also increases the performance of the catalyst. All three Pd NHC complexes tested (**3.8**, **3.15** and **3.16**), performed better than the standard palladium triphenylphosphine complex **4.1***, while $Pd(CH_3COO)_2$ performs rather poorly.

The performance of complexes **3.15** (79 % conversion) and especially **3.16** (84 % conversion) are comparable to the performance of the Pd phosphine complex **4.3*** (94 % conversion) and that makes them potential candidate catalysts for industrial applications.
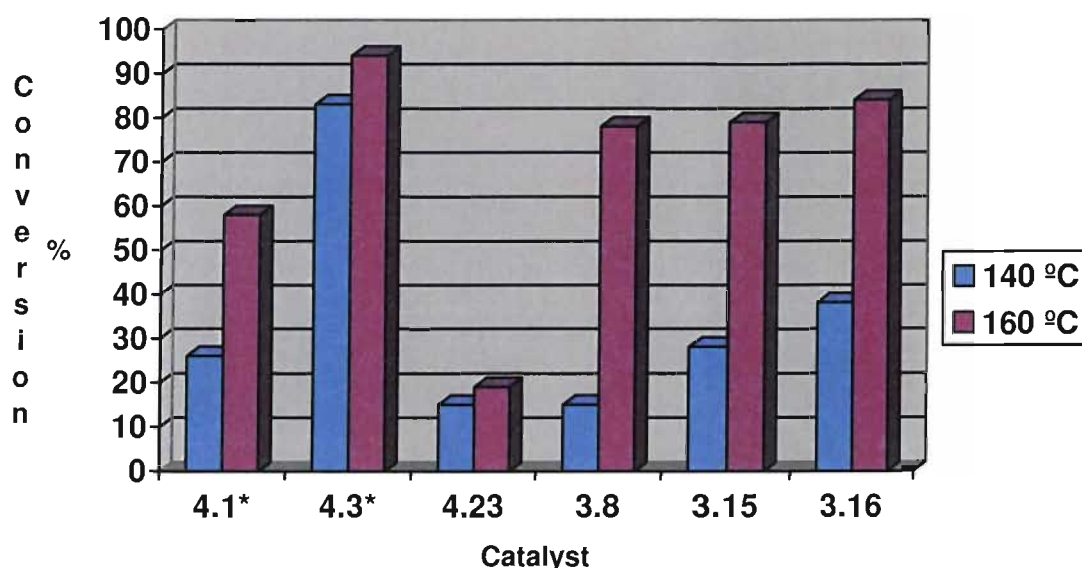
Scheme 4.8: Catalyst performance in Heck reactions of 4-chloroacetophenone

Interestingly, there was a reproducible difference between the conversions of complexes **3.15** and **3.16** at both temperatures employed (always complex **3.15** seemed to be slightly less reactive). This was probably due to the electronic difference between the two complexes. Complex **3.16** has two electron donating methoxy groups on each phenyl ring, at *ortho* and *para* positions, while complex **3.15** has only one methoxy group at the *para* position. The increased electron density may therefore promotes the electrophilicity of the Pd centre, therefore enhancing the catalytic performance.
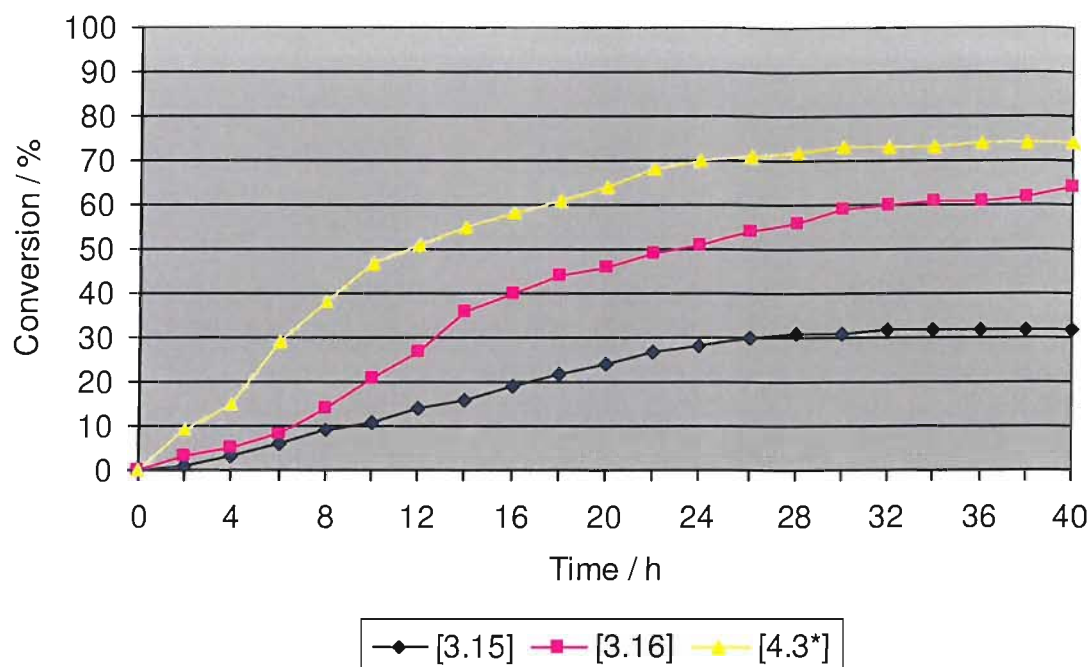
Scheme 4.9: Graphical representation of the catalytic performance of complexes **3.15**, **3.16** and **4.3*** in the Heck coupling of 4-chloroacetophenone (Table 4.3 entries 18, 19 and 14 respectively)

The same trend was observed, in the activity of the complexes, in the Heck coupling of chlorobenzene. As seen in Table 4.4, complex **3.16** performs better when compared to complex **3.15** (35 % conversion and 22 % conversion at 160 °C respectively). Pd phosphine complex **4.3*** still performed slightly better (46 % conversion) compared to complex **3.16** which is one of the most active Pd NHC complexes in the Heck coupling of chlorobenzene reported to date.[12, 16, 30, 31]

Entry	Catalyst	Solvent	Temp. /°C	Base	X	R	Time / h	Conversion / %
1	4.1*	NMP	140	NEt$_3$	Cl	H	18	6
2	4.3*	NMP	140	NEt$_3$	Cl	H	18	41
3	4.23	NMP	140	NEt$_3$	Cl	H	18	0
4	3.8	NMP	140	NEt$_3$	Cl	H	18	0
5	3.8	DMF	140	NEt$_3$	Cl	H	18	0
6	3.8	DMF	140	NO^{i}Pr	Cl	H	18	4
7	3.16	DMF	140	NEt$_3$	Cl	H	18	15
8	3.16	DMF	160	NBu$_3$	Cl	H	18	25
9	3.16	DMF	160	NBu$_3$	Cl	H	18	35 ^{a}
10	3.15	DMF	160	NBu$_3$	Cl	H	18	13
11	3.16	NMP	160	NBu$_3$	Cl	H	18	23
12	4.1*	Bu$_4$NBr	160	NaOAc	Cl	H	18	16
13	4.3*	Bu$_4$NBr	160	NaOAc	Cl	H	18	46
14	4.23	Bu$_4$NBr	160	NaOAc	Cl	H	18	0
15	3.8	Bu$_4$NBr	160	NaOAc	Cl	H	18	6
16	3.15	Bu$_4$NBr	160	NaOAc	Cl	H	18	22
17	3.16	Bu$_4$NBr	160	NaOAc	Cl	H	18	35

Table 4.4: Catalytic Heck reactions using chlorobenzene as the substrate

^{a} Catalyst loading 3.0 mol%

Palladium acetate (complex **4.23**) was unable to activate chlorobenzene in order to undergo a Heck coupling, while complex **3.8** performed rather poorly (6 % conversion at 160 °C). Once more, both complexes **3.15** and **3.16** were proved superior catalysts to the palladium triphenylphosphine complex **4.1*** (16 % conversion at 160 °C). Doubling of the catalyst loading for complex **3.15** (Entries 8 and 9, Table 4.4), results in higher conversions, while maintaining a relatively low catalyst : substrate ratio. Scheme 4.10 gives a schematic comparison of the results summarised in Table 4.4, while Scheme 4.11 gives a graphical representation of the catalytic performance of selected complexes.
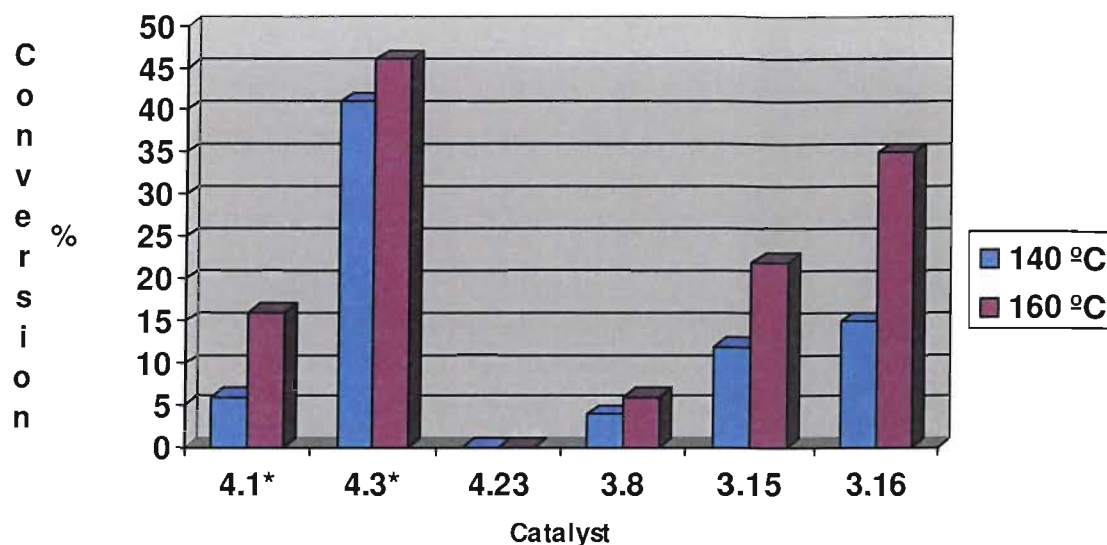
Scheme 4.10: Catalyst performance in Heck reactions of chlorobenzene
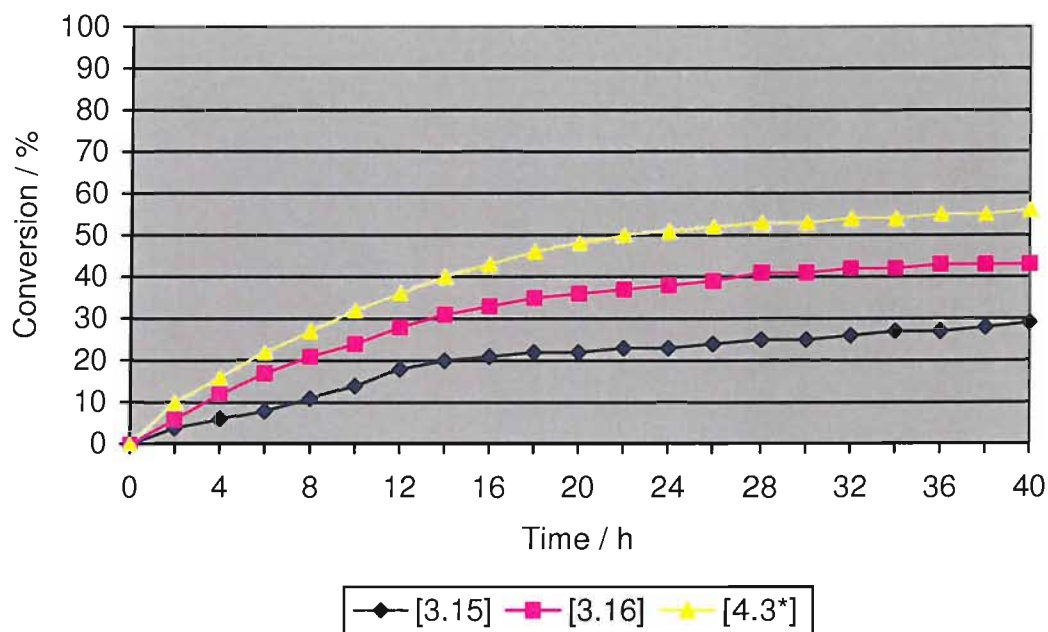
Scheme 4.11: Graphical representation of the catalytic performance of complexes **3.15**, **3.16** and **4.3*** in the Heck coupling of chlorobenzene (Table 4.4 entries 16, 17 and 13 respectively)

4.4 Conclusions

A series of Pd NHC complexes have been tested as catalysts for Heck coupling reactions. Two of them have been found to be excellent for the Heck couplings of aryl bromides, deactivated aryl bromides and activated aryl chlorides. Furthermore, moderate results for the Heck coupling of chlorobenzene have been achieved. These complexes surpass the activity of palladium triphenylphosphine complexes and are amongst the most active Pd NHC complexes reported to date.

4.5 Experimental Details

General Materials and Methods

All manipulations were performed under nitrogen in a M. Braun glove-box or using standard Schlenk techniques, unless otherwise stated. Solvents were dried using standard methods and distilled under nitrogen prior use (see Appendix 2). The synthesis of all Pd NHC complexes can be found in Chapter 3. Complexes **4.1***[7] and **4.3***[10] were prepared according to literature procedures. All other materials used were purchased from Aldrich or Lancaster and used without further purification.

Instrumentation

Gas chromatographs were obtained from a Varian 3400GC fitted with a Varian 8100 auto-sampler, equipped with a flame ionisation detector, fitted with a J&W Scientific column (Phase: DBWAX) and linked to a Hewlett-Packard 3396 Series 2 integrator.

GC Programming

Initial column temperature: 50 °C, initial column temperature hold time: 4 min., final column temperature: 200 °C, temperature increase: 20 °C/min, final column temperature hold time: 2 min, injector temperature: 220 °C, detector temperature 220 °C, program total run time: 13.50 min.

Catalytic reactions using liquid solvents

The aryl halide (1.0 mmol), butyl acrylate (25.6 mg, 2.0 mmol), the base (1.2 mmol), diglyme (internal standard) (1.0 mmol) and the catalyst (15.0 μmol) were placed in an ampoule. The solvent (dioxane, NMP, DMF or DMAC) (2.0 mL) was added and the ampoule was then sealed under partial vacuum. It was then placed in a pre-heated oil bath at 140 °C for 18 h. After cooling, the solution was filtered through a short patch of silica, the products were identified by comparison to original samples and the conversion was calculated by gas chromatography.

Catalytic reactions using an ionic liquid as the solvent

The aryl halide (1.0 mmol), butyl acrylate (25.6 mg, 2.0 mmol), sodium acetate (12.6 mg, 1.2 mmol), the catalyst (15.0 μmol) and tetrabutylammonium bromide (2.0 g) were placed in an ampoule that was then sealed under partial vacuum. It was then placed in a pre-heated oil bath at 160 °C for 18 h. After cooling, diglyme (1.0 mmol) was added as the internal standard. The mixture was then diluted with water (5 mL) and extracted with ether (3 × 5 mL). The combined organic layers were dried over sodium sulphate and filtered through a short patch of silica. The solvents were reduced to the minimum, the products were identified by comparison to original samples and the conversion was calculated by gas chromatography.

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Chapter 5:

Rhodium and iridium

NHC complexes

5.1 Introduction

In recent years, functionalised *N*-heterocyclic carbenes have been used as ligands for the tuning of the co-ordination sphere of catalytic platinum group metals.[1] They can give rise to unusual bidentate or polydentate complexes with potential hemilability, electronic discrimination of coordination sites and chirality. In this area, our research group studied various bidentate pyridyl- and phosphine-functionalised NHC complexes of Pd, and 'pincer' tridentate pyridyl di-carbenes of metals from across the periodic table.[2] The electronic similarity between the trialkylphosphines and the NHCs points to a potential resemblance of the pyridyl-NHC donor system to the pyridyl-PR$_3$, which are found in numerous catalysts, such as Crabtree's hydrogenation catalyst, palladium polymerisation and carbonylation catalysts.[3]
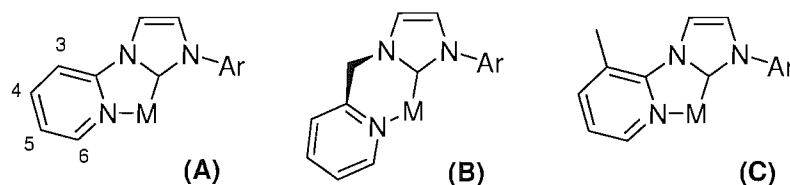
Figure 5.1: Schematic representation of the pyridyl-functionalised NHC ligands

Pyridyl-NHC metal complexes (Figure 5.2) prepared by former members of the group featured unexpected metal-pyridine binding. In one case C–H activation took place and the pyridyl ring was co-ordinated to the metal not *via* the nitrogen but *via* C3 (structure **A**, Figure 1), giving rise to an Ir(III) complex. In the other case, the pyridyl-subsituent remained uncoordinated, but there was a persistent Rh–H3 agostic interaction present in solution and the solid state.[4]
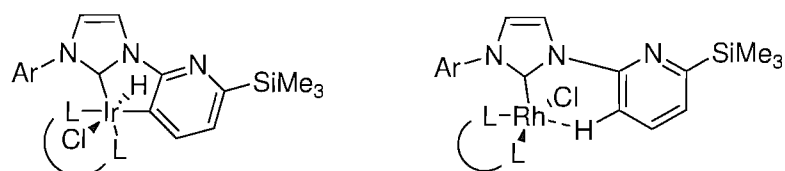
Figure 5.2: Reported NHC complexes featuring unexpected binding

(Ar = 2,6-diisopropylphenyl, L-L = η^4-cycloocta-1,5-diene) [4]

This interaction was absent in analogous picolyl-functionalised rhodium complexes (structure **B**, Figure 5.1), while it was not possible to prepare well-defined iridium complexes with the latter ligand. The C–H activation of other aliphatic and aromatic substituents of NHC ligands has recently been reviewed.[5] It was therefore postulated that reactivity of this type may cause problems in catalysis where M(I)/M(III) cycles are operating, especially in view of the stability of Ir–C(aryl) bonds. In this chapter, it is shown that methyl substitution at the C3 of the pyridyl ring in ligand systems of type **A** (Figure 5.1) allowed the isolation of stable low oxidation state rhodium and iridium complexes (type **C**, Figure 5.1) in various coordination geometries.

5.2 Results and Discussion

5.2.1 Picolyl functionalised imidazol-2-ylidene complexes

The novel Rh/Ir picolyl-functionalised imidazol-2-ylidene complexes prepared are summarised in Scheme 5.1 below.[6] These were prepared by the reaction of [M(COD)Cl]$_2$ (M = Rh, Ir) with the free carbene ligand **2.1b** in THF.

(5.4) 90%   **(5.5)** 72%   **(5.1a)**

Na[B(Ar^F)$_4$]   i) [Rh(COD)Cl]$_2$ +
Et$_2$O   ii) CH$_2$Cl$_2$ [Rh(COD)Cl]$_2$
                                          THF

                                                          (5.1b)

[Ir(COD)Cl]$_2$
—————————   Ar = 2,6-dipp **(2.1b)**   Na[B(Ar^F)$_4$]
THF   Et$_2$O

(5.3) 83%

(5.2) 83%
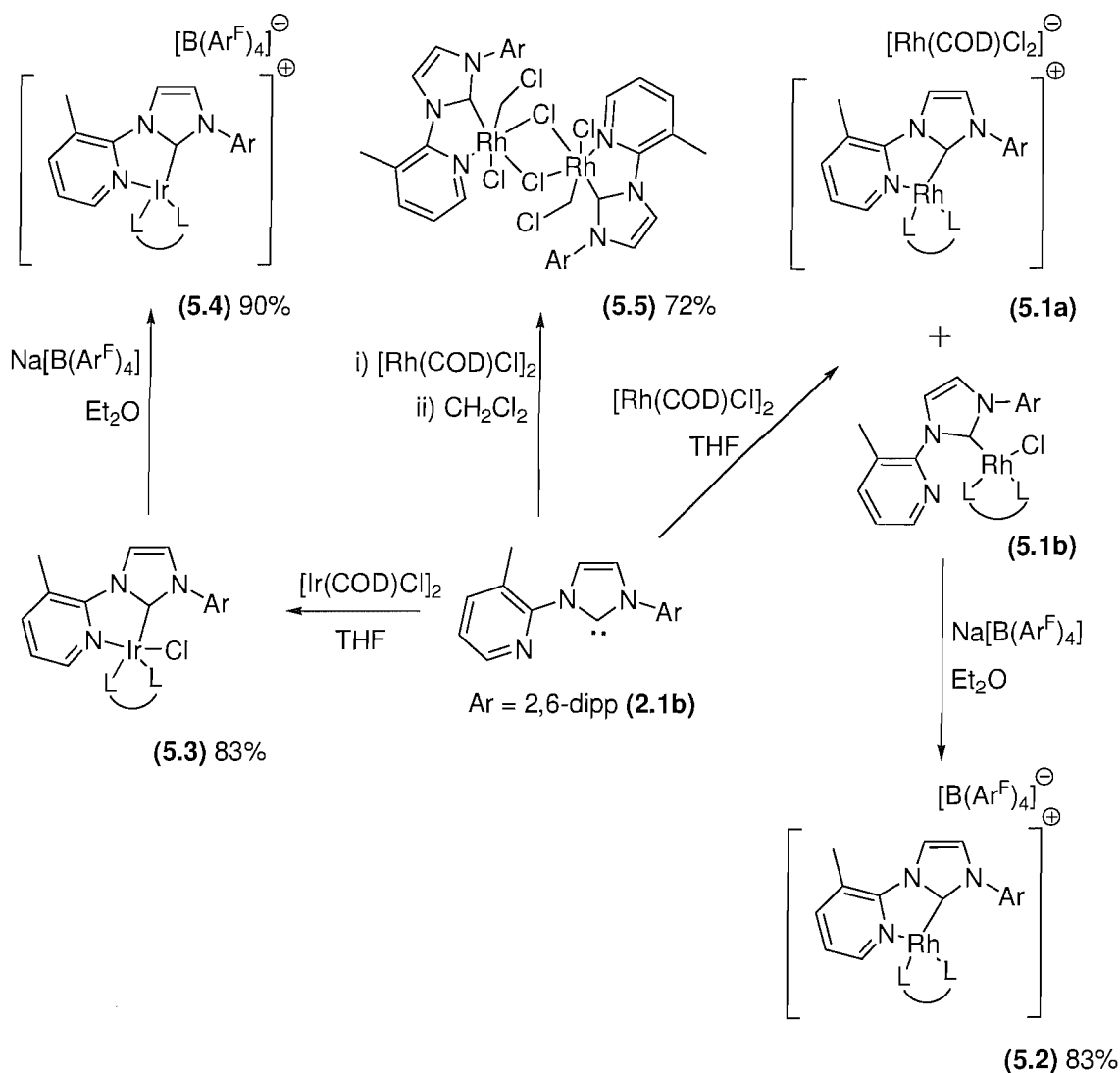
Scheme 5.1: Preparation of Rh and Ir NHC complexes **5.1 – 5.5**

L-L = η^4cycloocta-1,5-diene, Ar^F = 3,5-bis(trifluoromethyl)phenyl

When M = Rh the nature of the products is dependent on the reactant ratio; pure salt **5.1a** was only obtained by using a deficiency of the carbene ligand. With higher ligand to metal ratios the materials isolated after crystallisation were mixtures of **5.1a** and **5.1b**.

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Unfortunately, we were unable to isolate compound **5.1b** free from **5.1a**. The salt **5.2** can be conveniently prepared in good yields in one pot by reacting **5.1a** or mixtures of **5.1a** and **5.1b** with sodium tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate, denoted: $Na^+[B(Ar^F)_4]^-$.

When M = Ir the five co-ordinate complex **5.3** was isolated which was reacted further with $Na^+[B(Ar^F)_4]^-$ to give salt **5.4**. Interestingly, reactions of $[M(COD)Cl]_2$, M = Rh, Ir with silver carbene complexes in various solvents were found to be very slow (as judged by the rate of AgCl precipitation) and usually gave intractable mixtures.[7] However, this behaviour is to be contrasted to the facile formation of $[Rh(COD)(N^\wedge C^{mes})]Cl$ and $[Rh(COD)(N^\wedge C^{mes})]^+[B(Ar^F)_4]^-$ {where $(N^\wedge C^{mes})$ = 3-(2,4,6-Me$_3$C$_6$H$_2$)-1-[2-(α-picolyl)]imidazol-2-ylidene (structure **B** in Figure 1, M = Rh)} by transmetallation from the corresponding silver carbene followed by salt metathesis, respectively.[8] Transmetallation was also used in the synthesis of (COD)M(carbene)Cl, where carbene is monodentate unsaturated NHC.[9]

All complexes **5.1 – 5.4** were isolated as air-stable crystalline materials, soluble in THF and aromatic hydrocarbons. They react after prolonged exposure (>2 h) with dichloromethane giving rise to the products of the oxidative addition of ClCH$_2$–Cl bond as described later (complex **5.5**). The structures of **5.1a**, **5.1b**, **5.2**, **5.3** and **5.4** have been determined by single crystal X-ray diffraction and the ORTEP diagrams are given in Figures 5.3 – 5.7.
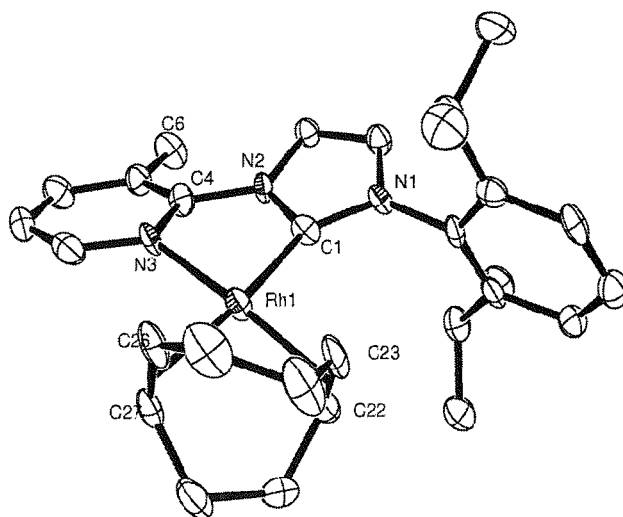
Figure 5.3: ORTEP representation of the cation in **5.1a** showing 50% probability ellipsoids. H atoms, one C_6H_6 molecule (solvent) and the $Rh(COD)Cl_2$ anion are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Rh1–C1: 2.011(7), Rh1–N3: 2.102(6), Rh1–C22: 2.114(7), Rh1–C23: 2.133(7), Rh1–C26: 2.186(7), Rh1–C27: 2.195(7), C1–Rh1–N3: 77.8(2), C22–Rh1–C23: 38.5(3).
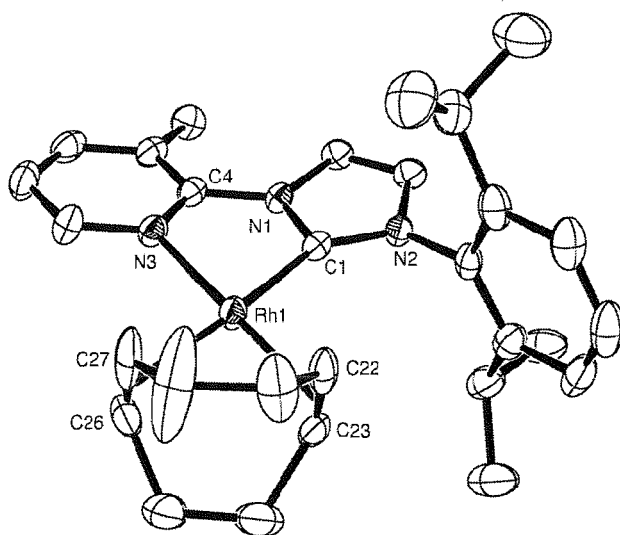
Figure 5.4: ORTEP representation of cation in **5.2** showing 50% probability ellipsoids. H atoms and one $[B(Ar^F)_4]$ anion are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Rh1–C2: 2.012(3), Rh1–N1: 2.107(2), Rh1–C22: 2.214(3), Rh1–C23: 2.207(3), Rh1–C26: 2.141(3), C22–C23: 1.357(4), C26–C27: 1.389(4), Rh1–C27: 2.142(3), C2–Rh1–N1: 77.66(9).
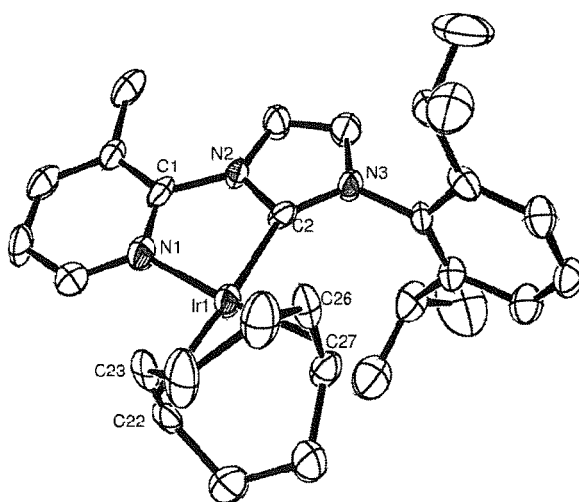
Figure 5.5: ORTEP representation of complex **5.4** showing 50% probability ellipsoids. H atoms and C_6H_6 molecules (solvent) are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: C2–Ir1: 2.015(9), C22–Ir1: 2.182(9), C23–Ir1: 2.227(10), C26–Ir1: 2.143(9), C27–Ir1: 2.153(9), C22–C23: 1.362(15), C26–C27: 1.417(14), C2–Ir1–N1: 78.0(4), C2–Ir1–C26: 97.9(4), C2–Ir1–C27: 100.6(4), N1–Ir1–C22: 95.9(4), N1–Ir1– C23: 96.2(4).

The cations in **5.1a**, **5.2** and **5.4** (Figures 5.3, 5.4 and 5.5 respectively) feature square-planar metal centres with chelating carbene and COD ligands. The bite angle of the carbene is within 77 – 78 ° range, while the aromatic carbene and pyridyl rings of the backbone and the chelate ring are virtually coplanar. The angle between the diisopropylphenyl ring and the carbene rings is in the range 87 – 102 °. The metal–carbene bond lengths are comparable with those reported in the literature (for Rh complexes) or shorter (in the case of the Ir complex).[9,10,11] The distance between the metal and the mid-point (centroid) of the COD double bond *trans* to the NHC is longer than the distance the one *trans* to the pyridyl (for **5.2**: 2.104 and 2.026 Å, respectively, for **5.4**: 2.096 and 2.027 Å, respectively), however, the C–C bond length *trans* to the carbene is shorter than the one *trans* to the pyridine.
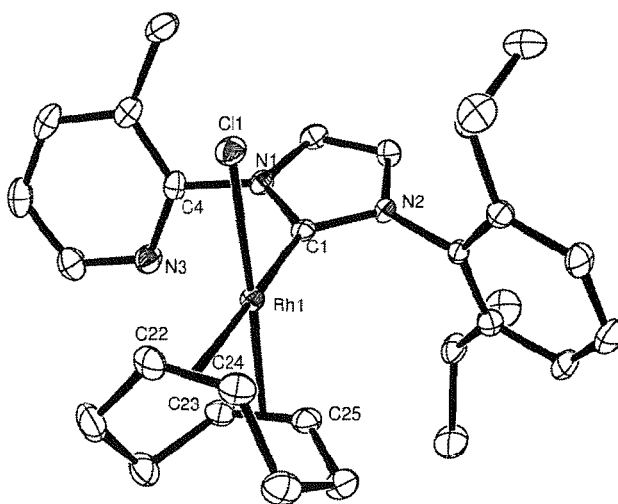
Figure 5.6: ORTEP representation of complex **5.1b** showing 50% probability ellipsoids. H atoms and one C_6H_6 molecule (solvent) are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: C1–Rh1: 2.0347(17), Cl1–Rh1: 2.3769(5), C(22)-Rh(1): 2.1796(18), C(23)-Rh(1): 2.1125(17), C(24)-Rh(1): 2.2092(18), C(25)-Rh(1): 2.1095(18), C1–Rh1–Cl1: 87.43(5), C1–Rh1–C25: 91.94(7), C1–Rh1–C23: 95.58(7), C25– Rh1–C24: 81.07(7), C23–Rh1–C24: 89.35(7).

The metal geometry in **5.1b** is square planar with chelating COD, monodentate carbene and dangling pyridyl groups. Here, the angle between the coordination plane and the NHC plane is 79.6 °. The Rh–C carbene bond is slightly longer than in **5.1a** and **5.2**.
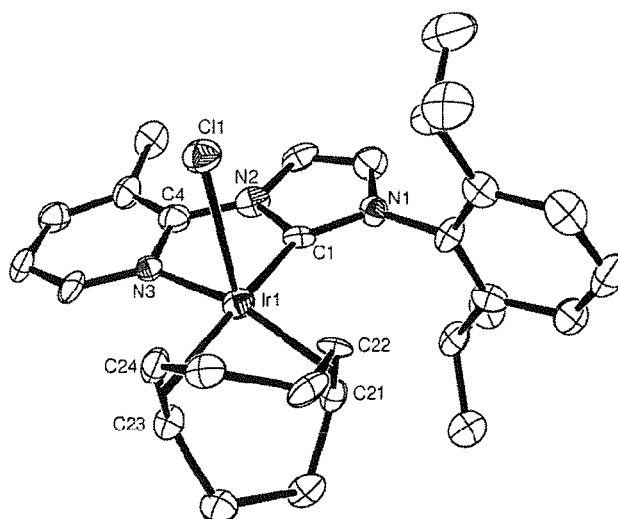
Figure 5.7: ORTEP representation of complex **5.3** showing 50% probability ellipsoids. H atoms and three C_6H_6 molecules (solvent) are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: C1–Ir1: 1.994(10), C21–Ir1: 2.102(9), C22–Ir1: 2.061(10), C23–Ir1: 2.164(10), C24–Ir1: 2.188(10), N3–Ir1: 2.104(8), Cl1–Ir1: 2.546(3), C21–C22: 1.423(14), C23–C24: 1.404(14), C1–Ir1– N3: 77.7(4), N3–Ir1–Cl1: 83.4(2), C1–Ir1–Cl1: 87.1(3).

The geometry around the metal in complex **5.3** is best described as distorted square pyramidal with apical chloride; the COD and the bidentate carbene occupy the basal sites. The Ir–C carbene bond is one of the shortest reported, even shorter than the corresponding bond in **5.4**. The Ir–C bond length of the double bond of the COD ligand (as defined above) which is *trans* to the carbene is longer (2.188 Å) than the one trans to the pyridine (2.061 Å), and the C–C bond length trans to the carbene and the one *trans* to the pyridine are equal within the observed estimated standard deviations.

The structural data described above support strong metal–carbene bonds and higher *trans*-influence of the NHC relative to the pyridine. The observation of the dangling pyridine points to a kinetic barrier for the formation of the metal–pyridine bond in the Rh complex **5.1b**. Abstraction of the Cl leads to facile pyridine co-ordination and

concomitant formation of the square planar complexes **5.1a** and **5.2**. The higher co-ordination numbers that are possible for iridium, account for the formation of the five coordinate species **5.3**. On the other hand, it has been observed that when a C–H bond is present in the C-3 position of the pyridyl ring of the carbene ligand (for numbering see Figure 5.3), it is situated in close proximity to the metal and interacts with it to form either an agostic bond (Rh) or oxidative addition products (Ir).[4]

Attempts to crystallise **5.1a** or **5.1b** from CH_2Cl_2 resulted in the isolation of product **5.5**, which originates from the oxidative addition of $Cl–CH_2Cl$ to the metal centre. The complex is very insoluble in organic solvents, which hampered the collection of any NMR data. However, X-ray quality crystals were obtained by the slow diffusion of petroleum into the dichloromethane solution, allowing structural characterisation of the complex (**5.5**). The diagram of the molecule is shown in Figure 5.8.
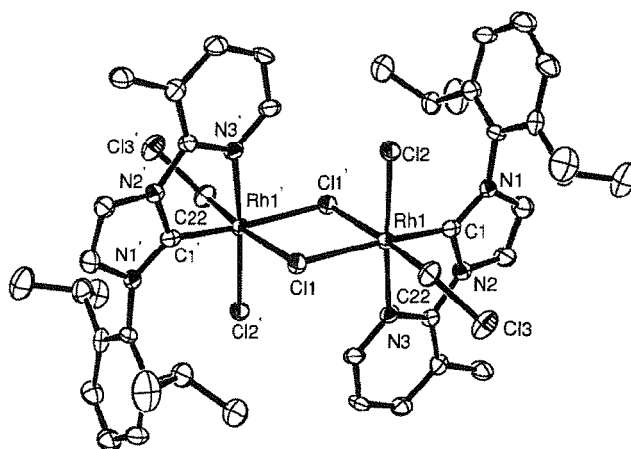
Figure 5.8: ORTEP representation of complex **5.5** showing 50% probability ellipsoids. H atoms and CH_2Cl_2 molecules (solvent) are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Rh1–C1: 1.949(5), Rh1–Cl2: 2.3379(11), Rh1–C22: 2.031(5), Rh1–N3: 2.051(3), Rh1–Cl1: 2.4712(12), C22–Rh1–N3: 91.71(17), C1–Rh1–N3: 79.48(16), C1–Rh1–C22: 93.05(19).

Complex **5.5** is a centrosymmetric dimer with two octahedral rhodium centres bridged by two chloride ligands. The co-ordination sphere of each rhodium comprises of, two chlorides, one bidentate carbene ligand, one terminal chloride and one CH_2Cl moiety. The metrical data for **5.5** are not unusual and does not warrant any further comments. The ease of the observed oxidative addition reaction may be due to the increased nucleophilicity of the Rh(I) centre after the coordination of the carbene ligand. However,

it was not possible to distinguish whether there is higher reactivity towards the oxidative addition in a complex of type **5.1a** or **5.1b**.

5.2.2 Picolyl-functionalised imidazolin-2-ylidene complexes

Saturated NHCs are considered to be better σ-donors compared to the more widely used unsaturated NHCs,[12] and therefore, when co-ordinated to a metal, make the metal centre of the complex more nucleophilic. This in turn might affect the catalytic properties of the complex, making it a better catalyst.

In order to be able to directly compare the imidazolin-2-ylidene (saturated NHC) metal complexes to the unsaturated counterparts, imidazol-2-ylidenes, the imidazolin-2-ylidene precursor **2.6c** was selected because of the striking similarities to **2.1b**. Both compounds have 3-picolyl as one of the substituents and 2,6-diisopropylphenyl as the other. This way the metal complexes bearing the carbene derived from **2.6c** can be directly compared to the complexes prepared earlier in this chapter.

i) KN(SiMe₃)₂ / THF

ii) [Ir(COD)Cl]₂ / THF

Ar = 2,6-dipp **(2.6c)**   **(5.6)** 79%
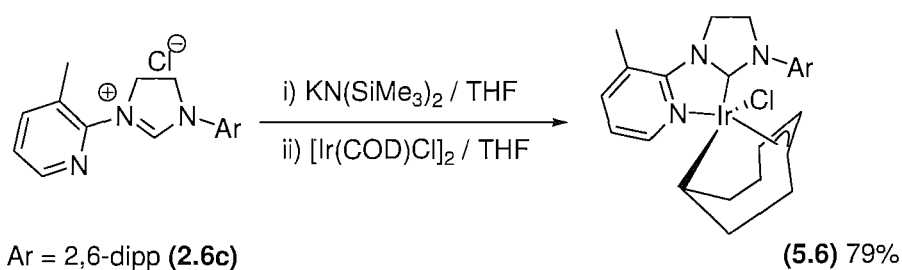
Scheme 5.2: Synthesis of Ir(I) carbene complex **5.6**

As shown in Scheme 5.2, the imidazolinium salt **2.6c** was reacted with KN(SiMe₃)₂ in order to prepare the free carbene *in situ*. The metal complex precursor, [Ir(COD)Cl]₂, was then added to the carbene, to yield the Ir(III) complex **5.6** that was then crystallised by layering a toluene solution of the complex with petrol. The molecular structure of complex **5.6** is displayed in Figure 5.9. Such types of activations of the COD ligand, have been reported in the past[13] and were investigated thoroughly by others.[13a,13b]
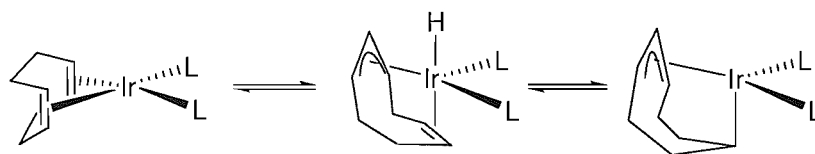
Scheme 5.3: Proposed mechanism for $1,2,5,6\text{-}\eta\text{-}C_8H_{12}$ to $1\text{-}\kappa\text{-}4,5,6\text{-}\eta\text{-}C_8H_{12}$ rearrangement.[13a]

It is believed that the process of the transformation involves a reversible sequence of an allylic C–H activation,[13a] leading to the formation of a reactive hydride intermediate, followed by an intramolecular insertion to give the $L_2Ir(1\text{-}\kappa\text{-}4,5,6\text{-}\eta\text{-}C_8H_{12})$ complex as shown in Scheme 5.3. However, in the case of complex **5.6** (Scheme 5.4), it is plausible that the co-ordination of the pyridyl ring inhibits the reverse sequence of the intramolecular insertion, since there is no free co-ordination site for the hydride elimination to take place and therefore the isolation of the final structure as a single product is achieved.
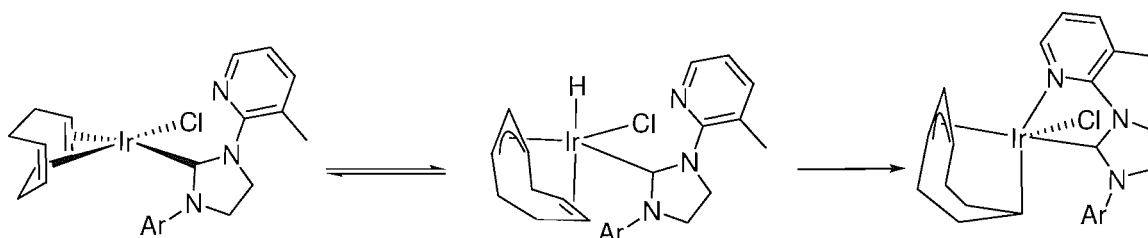
Scheme 5.4: Postulated mechanism for $1,2,5,6\text{-}\eta\text{-}C_8H_{12}$ to $1\text{-}\kappa\text{-}4,5,6\text{-}\eta\text{-}C_8H_{12}$ rearrangement in complex **5.6**.

Complex **5.6** that can be compared to complex **5.3**, adopts a distorted octahedral geometry around the metal centre with the chloride and coordinated carbon of the COD moiety (C26) as the top and the bottom apical positions of the octahedron respectively. The ligand bite angle is 76.4(3) ° which is slightly smaller compared to the ligand bite angle of complex **5.3** (77.7(4) °). The metal carbene bond distance is equal to that of **5.3** within the observed estimated standard deviations.
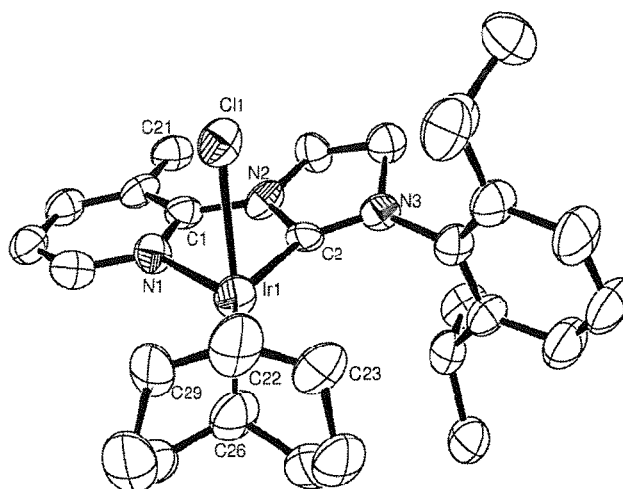
Figure 5.9: ORTEP representation of the structure of **5.6** showing 50% probability ellipsoids. H atoms and one $C_6H_5CH_3$ molecule (solvent) are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Ir1–C2: 1.990(9), Ir1–N1: 2.099(7), Ir1–C23: 2.167(10), Ir1–C22: 2.120(11), Ir1–C29: 2.206(10), Ir1–C26: 2.092(12), C2–Ir1–C29: 179.5(4), C2–Ir1–C23: 108.9(4), N1–Ir1–C29: 104.1(4), N1–Ir1–C2: 76.4(3).

Complexes **5.2** and **5.4** have been extensively tested as catalysts in olefin hydroformylations, olefin molecular hydrogenations and transfer hydrogenations of carbonyl compounds. All details and catalytic results are thoroughly described in Chapter 6.

5.3 NMR Spectroscopy

All prepared carbene complexes (except complex **5.5**) were characterised by ^1H and ^{13}C NMR spectroscopy. A common feature of the ^1H NMR spectra of **5.1a**, **5.2** and **5.4** is the presence of two doublets in the range 1.30–1.70 ppm assignable to two groups of diastereotopic methyls on the o-isopropyl groups of the aromatic rings. This is in agreement with the presence of a plane of symmetry which coincides with the coordination plane. The two ends of the COD ligand are also non-equivalent, being trans to electronically different donor atoms. Interestingly, the complexes **5.1b** and **5.3**, which have lower molecular symmetry, exhibit the same pattern in the methyl region of their ^1H NMR spectra possibly due to accidental coincidence while **5.6** exhibits four doublets assignable to the four methyls of the o-isopropyl groups. The carbene C was observed by ^{13}C NMR spectroscopy only in complexes **5.3** and **5.6**. The limited stability of all

complexes in chlorinated solvents precluded acquisition with long pulse delays which may have facilitated the observation of the slow relaxing carbene C.

5.4 Conclusions

Five novel picolyl-functionalised imidazol-2-ylidene complexes of Rh(I) and Ir(I) have been synthesised and characterised. The catalytic activity for some of these complexes is described in Chapter 6. Furthermore, one novel picolyl functionalised imidazolin-2-ylidene Ir(III) complex featuring a $1\text{-}\kappa\text{-}4,5,6\text{-}\eta\text{-}C_8H_{12}$ moiety has been synthesised and characterised.

5.5 Experimental Details

General Materials and methods

All manipulations were performed under nitrogen in a M. Braun glove-box or using standard Schlenk techniques, unless otherwise stated. Solvents were dried using standard methods and distilled under nitrogen prior to use (see Appendix 2). [Rh(COD)(μ-Cl)]$_2$ was prepared according to the literature procedure,[14] [Ir(COD)(μ-Cl)]$_2$ was purchased from Johnson Matthey. All other materials used were purchased from Aldrich or Lancaster and used without further purification.

(5.1a) (Cycloocta-1,5-diene)-κ^2-{1-[2-(3-picolyl)]-3-(2,6-diisopropylphenyl)imidazol-2 –ylidene}rhodium dichloro (cycloocta-1,5-diene) rhodium
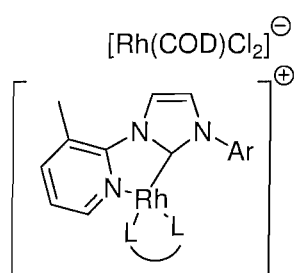
Ar = 2,6-dipp, L-L = COD

[Rh(COD)Cl]$_2$ (0.05 g, 0.10 mmol) was suspended in THF at – 78 °C. To this a solution of 1-[2-(3-methyl)pyridyl]-3-[(2,6-diisopropyl)phenyl]imidazol-2-ylidene **(2.1b)** (0.03 g, 0.10 mmol) in THF (10 mL) was added at –78 °C. The mixture was allowed to warm to r.t. and was stirred for 2 h. After evaporation of the solvent under reduced pressure, the resulting red solid was crystallised by layering a benzene solution with petroleum.

Anal. Calcd for $C_{37}H_{49}Cl_2N_3Rh_2$: C, 54.69; H, 6.07; N, 5.15 %. Found: C, 54.3; H, 5.5; N, 5.0 %.

ES$^+$MS: m/z (%):530 [M+H]$^+$

^{1}H NMR (300MHz, CD$_2$Cl$_2$), δ: 8.35 (1H, d, J = 5.4 Hz, o-C$\underline{H}$ picolyl), 8.20 (1H, d, J = 4.2 Hz, p-C$\underline{H}$ picolyl), 7.90 and 7.15 (2 × 1H, d, J = 2.1 Hz, imidazolium backbone C$\underline{H}$), 7.60 (2H, m, m-H picolyl and p-C$\underline{H}$ aromatic), 7.35 (2H, m, m-C$\underline{H}$ aromatic), 5.10, 4.15 and 3.90 (2 × 2H and 1 × 4H, m, olefinic C$\underline{H}$ of two COD ligands), 2.85 (3H, s, picolyl C$\underline{H}_3$), 2.60 (2H, septet, J = 6.9 Hz, 2 × C$\underline{H}$(CH$_3$)$_2$), 2.10 (16H, m, aliphatic C$\underline{H}_2$ of COD ligands), 1.35 (6H, d, J = 6.9 Hz, CH(C$\underline{H}_3$)$_2$), 1.10 (6H, d, J = 6.9 Hz, CH(C$\underline{H}_3$)$_2$).

^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$), δ: 145.90, 144.36, 130.54, 125.37, 123.73, 123.16 and 118.88 (aromatic carbons), 98.80 (olefinic $\underline{C}$H of COD), 77.50 (olefinic $\underline{C}$H of COD), 30.37 (aliphatic $\underline{C}$H$_2$ of COD), 27.78 (aliphatic $\underline{C}$H$_2$ of COD), 27.42 ($\underline{C}$H(CH$_3$)$_2$), 24.85 (CH($\underline{C}$H$_3$)$_2$), 21.59 (CH($\underline{C}$H$_3$)$_2$), 20.65 (picolyl $\underline{C}$H$_3$).

(5.1b)(Cycloocta-1,5-diene)-κ^1-{1-[2-(3-picolyl)]-3-(2,6-diisopropylphenyl)imidazol-2-ylidene}rhodium chloride
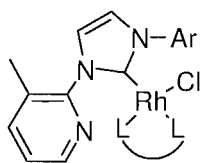
Ar = 2,6-dipp, L-L = COD

[Rh(COD)Cl]$_2$ (0.10 g, 0.20 mmol) was suspended in THF at – 78 °C. To this a solution of 1-[2-(3-methyl)pyridyl]-3-[(2,6-diisopropyl)phenyl]imidazol-2-ylidene **(2.1b)** (0.13 g, 0.40 mmol) in THF at –78 °C was added. The mixture was allowed to warm to r.t. and stirred for 2 h. After evaporation of the solvent under reduced pressure the resulting orange solid was dissolved in benzene and crystallised by layering with petroleum. The products that crystallised were **5.1b** (major component, yellow) and **5.1a** (minor component, red). Further attempts to isolate **5.1b** by repeated re-crystallisations or by performing the reactions under various conditions were not successful. (The characterisation data outlined below were obtained from a sample containing *ca.* 20% of **5.1a**).

^{1}H NMR (300MHz, C$_6$D$_6$), δ: 8.40 (1H, d, J = 5.4 Hz, o-C$\underline{H}$ picolyl), 7.25 (1H, m, m-C$\underline{H}$ picolyl), 7.15 (3H, m, imidazolium backbone C$\underline{H}$ and p-C$\underline{H}$ picolyl), 6.80 (1H, m, p-C$\underline{H}$ dipp), 6.45 (2H, d, J = 7.8 Hz, m-C$\underline{H}$ dipp), 5.00, 3.85 and 3.20 (4H, m, olefinic C$\underline{H}$ of COD), 2.53 (2H, septet, J = 6.9 Hz, 2 × C$\underline{H}$(CH$_3$)$_2$), 2.40 (3H, s, picolyl C$\underline{H}_3$), 2.00 and 1.70 (2 × 4H, m, aliphatic C$\underline{H}_2$ COD), 1.45 (6H, d, J = 6.9 Hz, CH(C$\underline{H}_3$)$_2$), 1.05 (6H, d, J = 6.9 Hz, CH(C$\underline{H}_3$)$_2$).

^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$), δ: 145.90, 144.36, 130.54, 125.37, 123.73, 123.16 and 118.88 (aromatic carbons), 98.80 (olefinic $\underline{C}$H of COD), 77.50 (olefinic $\underline{C}$H of COD), 30.37 (aliphatic $\underline{C}$H$_2$ of COD), 27.78 (aliphatic $\underline{C}$H$_2$ of COD), 27.42 ($\underline{C}$H(CH$_3$)$_2$), 24.85 (CH($\underline{C}$H$_3$)$_2$), 21.59 (CH($\underline{C}$H$_3$)$_2$), 20.65 (picolyl $\underline{C}$H$_3$).

(5.2) **(Cycloocta-1,5-diene)-κ^2-{1-[2-(3-picolyl)]-3-(2,6-diisopropylphenyl)imidazol-2-ylidene}rhodium tetrakis-[3,5-bis(trifluoromethylphenyl)]borate**

Ar = 2,6-dipp, L-L = COD

[Rh(COD)Cl]$_2$ (0.12 g, 0.24 mmol) was suspended in THF at $-$78 °C. To this a solution of 1-[2-(3-methyl)pyridyl]-3-[(2,6-diisopropyl)phenyl]imidazol-2-ylidene **(2.1b)** (0.154 g, 0.48 mmol) in THF at $-$78 °C was added. The mixture was allowed to warm to room temperature and was stirred for 2 h. After evaporation of the solvent under reduced pressure, the resulting solid, was suspended in ether and to this a solution of Na[B{3,5-(CF$_3$)$_2$C$_6$H$_2$}$_4$] (0.42 g, 0.48 mmol) in ether was added. The resulting dark red suspension was filtered and evaporated to dryness giving a red solid residue which was crystallised by dissolving in benzene and layering the solution with petroleum. Yield: 0.28 g (0.20 mmol), 83%.

Anal. Calcd for C$_{61}$H$_{49}$BF$_{24}$N$_3$Rh: C, 52.56; H, 3.55; N, 3.01 %. Found: C, 52.3; H, 3.4; N, 2.8 %.

ES$^+$MS: m/z (%):530 [M+H]$^+$

^{1}H NMR (300MHz, CD$_2$Cl$_2$), δ: 8.10 (1H, d, J = 5.4 Hz, o-C$\underline{H}$ picolyl), 8.00 (1H, m, p-C$\underline{H}$ picolyl), 7.80 (8H, s, o-C$\underline{H}$ of [Ar$^F_4$B]), 7.75 (2H, m, m-C$\underline{H}$ picolyl and aromatic p-C$\underline{H}$), 7.70 (4H, s, p-C$\underline{H}$ of [(Ar^F)$_4$B]), 7.50 (2H, d, J = 2.1 Hz, imidazolium backbone C$\underline{H}$), 7.40 (2H, m, m-C$\underline{H}$ aromatic), 5.15 and 4.15 (2 × 2H, m, olefinic C$\underline{H}$ of COD), 2.80 (3H, s, picolyl C$\underline{H}_3$) 2.70 (2H, septet, J = 6.9 Hz, 2 × C$\underline{H}$(CH$_3$)$_2$), 2.45, 2.40 and 2.20 (8H, m, aliphatic C$\underline{H}_2$ of COD), 1.60 (6H, d, J = 6.9 Hz, CH(C$\underline{H}_3$)$_2$), 1.30 (6H, d, J = 6.9 Hz, CH(C$\underline{H}_3$)$_2$).

^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$), δ: 161.41, 160.42, 145.40, 145.14, 143.82, 132.01, 130.78, 124.85, 123.68, 122.15, 117.00, 116.44 (aromatic carbons), 133.76 and 122.50 ([(Ar^F)$_4$B] $\underline{C}$H), 98.92 (olefinic $\underline{C}$H of COD), 78.30 (olefinic $\underline{C}$H of COD), 30.87 (aliphatic $\underline{C}$H$_2$ of COD), 27.55 (aliphatic $\underline{C}$H$_2$ of COD), 27.02 ($\underline{C}$H(CH$_3$)$_2$), 24.63 (CH($\underline{C}$H$_3$)$_2$), 21.37 (CH($\underline{C}$H$_3$)$_2$), 19.75 (picolyl $\underline{C}$H$_3$).

(5.3) **(Cycloocta-1,5-diene)-κ^2-{1-[2-(3-picolyl)]-3-(2,6-diisopropylphenyl)imidazol-2-ylidene}iridium chloride**
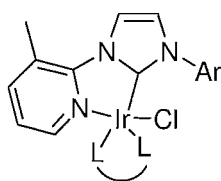
Ar = 2,6-dipp, L-L = COD

[Ir(COD)Cl]$_2$ (0.10 g, 0.15 mmol) was suspended in THF at $-$78 °C. To this a solution of 1-[2-(3-methyl)pyridyl]-3-[(2,6-diisopropyl)phenyl]imidazol-2-ylidene **(2.1b)** (0.096 g, 0.30 mmol) in THF at $-$78 °C was added. The mixture was

allowed to warm to r.t. and was stirred for 2 h. Evaporation of the solvent under reduced pressure gave a dark orange solid which was crystallised by layering a benzene solution with petroleum. Yield: 0.165 g (0.25 mmol), 83%.

Anal. Calcd for $C_{47}H_{55}ClIrN_3$: C, 63.45; H, 6.23; N, 4.72 %. Found: C, 62.8; H, 6.0; N, 4.6%.

ES^+MS: m/z (%):618 $[M+H]^+$

^1H NMR (300MHz, C_6D_6), δ: 8.10 (1H, d, J = 5.4 Hz, o-C$\underline{H}$ picolyl), 7.20 (3H, m, aromatic C$\underline{H}$), 6.90 and 6.30 (2 × 1H, d, J = 2.1 Hz, imidazolium backbone C$\underline{H}$), 6.80 (1H, d, J = 4.2 Hz, p-C$\underline{H}$ picolyl), 6.45 (1H, m, m-C$\underline{H}$ picolyl), 4.00 and 3.40 (2 × 2H, m, olefinic C$\underline{H}$ of COD), 2.35 (4H, m, 4 × aliphatic C$\underline{H}_2$ of COD), 1.90 (3H, s, picolyl C$\underline{H}_3$), 1.80 (2H, septet, J = 6.9 Hz, 2 × C$\underline{H}$(CH_3)_2), 1.50 (6H, d, J = 6.9 Hz, CH(C$\underline{H}_3$)_2), 1.05 (6H, d, J = 6.9 Hz, CH–(C$\underline{H}_3$)_2).

$^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6), δ: 175.70 (carbene $\underline{C}$–Ir), 145.46 (quaternary picolyl $\underline{C}$CH_3), 133.89 (picolyl $\underline{C}$H), 129.62, 127.53, 125.04, 122.98, 121.95, 121.25 and 116.38 (aromatic and picolyl carbons), 87.65 (olefinic $\underline{C}$H of COD),31.01 (aliphatic $\underline{C}$H of COD), 27.50 ($\underline{C}$H(CH_3)_2), 24.98 (CH($\underline{C}$H_3)_2), 21.58 (CH($\underline{C}$H_3)_2), 20.63 (picolyl $\underline{C}$H_3).

(5.4) (Cycloocta-1,5-diene)-κ^2-{1-[2-(3-picolyl)]-3-(2,6-diisopropylphenyl)imidazol-2-}iridium tetrakis-[3,5-bis(trifluoromethylphenyl)]borate
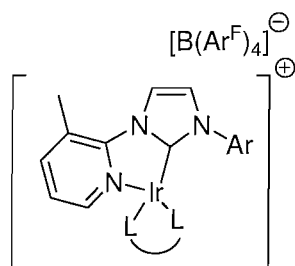
Ar = 2,6-dipp, L-L = COD

Complex 3 (0.10 g, 0.15 mmol) was suspended in ether and to this was added a solution of Na[B{3,5-$(CF_3)_2C_6H_2$}_4] (0.13 g, 0.15 mmol) in ether. The solution turned dark green and was filtered in order to remove inorganic salts. The green solid that was collected after evaporation, was crystallised by layering a benzene solution with petroleum. Yield: 0.09 g (0.13 mmol), 90%.

Anal. Calcd for $C_{143}H_{119}B_2F_{48}Ir_2N_6$: C, 53.02; H, 3.70; N, 2.59 %. Found: C, 52.8; H, 3.5; N, 2.4%.

ES^+MS: m/z (%):618 $[M+H]^+$

^1H NMR (300MHz, CD_2Cl_2), δ: 8.05 (3H, d, J = 5.4 Hz, C$\underline{H}$ picolyl), 7.75 (8H, s, o-C$\underline{H}$ of [$(Ar^F)_4B$]), 7.55 (4H, s, p-C$\underline{H}$ of [$(Ar^F)_4B$]), 7.40 (3H, m, aromatic C$\underline{H}$), 7.05 (2H, d, J = 2.2 Hz, imidazolium backbone C$\underline{H}$), 4.90 and 3.70 (2 × 2H, m, olefinic C$\underline{H}$ of COD), 2.85 (3H, s, picolyl C$\underline{H}_3$), 2.64 (2H, septet, J = 6.9 Hz, C$\underline{H}$(CH_3)_2), 2.10 (8H, m, aliphatic C$\underline{H}_2$ of COD), 1.40 (6H, d, J = 6.9 Hz, CH(C$\underline{H}_3$)_2), 1.13 (6H, d, J = 6.9 Hz, CH(C$\underline{H}_3$)_2).

$^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2), δ: 147.55, 145.25,135.20, 127.12, 125.10, 119.00 and 117.84 (picolyl and aromatic carbons), 132.10 and 124.50 ([(Ar^F)$_4$B] $\underline{C}$H) 88.95 (olefinic $\underline{C}$H of COD), 66.77 (olefinic $\underline{C}$H of COD), 33.58 (aliphatic $\underline{C}$H$_2$ of COD), 29.20 (aliphatic $\underline{C}$H$_2$ of COD), 28.98 ($\underline{C}$H(CH$_3$)$_2$), 25.82 (CH($\underline{C}$H$_3$)$_2$), 22.53 (CH($\underline{C}$H$_3$)$_2$), 21.12 (picolyl $\underline{C}$H$_3$).

(5.5) Bis{κ^2-1-[2-(3-picolyl)]-3-[(2,6-diisopropylphenyl)-imidazol-2-ylidene]}chloro methyl(di-μ-chloro)dirhodium
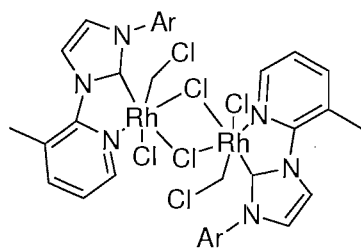
Ar = 2,6-dipp

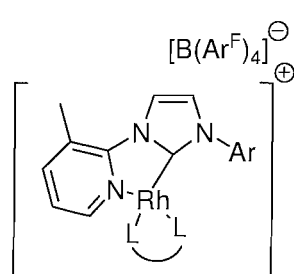[Rh(COD)Cl]$_2$ (0.10 g, 0.20 mmol) was suspended in THF at −78 °C. To this a solution of 1-[2-(3-methyl)-pyridyl]-3-[(2,6-diisopropyl)phenyl]imidazol-2-ylidene (2.1b) (0.128 g, 0.40 mmol) in THF at −78 °C was added. The mixture was allowed to warm to r.t. and was stirred for 2 h. After evaporation of the solvent the resulting orange solid was dissolved in dichloromethane and layered with petroleum to yield light orange crystals. Yield: 0.15 g (0.14 mmol), 72%.

Anal. Calcd for $C_{46}H_{58}Cl_{10}N_6Rh_2$: C, 48.51, H, 5.37, N, 7.71 %. Found: C, 48.5, H, 5.3, N, 7.7%.

No NMR data could be collected, since the complex was insoluble in all common deuterated solvents.

(5.6) [(κ^4-Cyclooct-7-en-1,4-diyl)-κ^2-{1-[2-(3-picolyl)]-3-(2,6-diisopropylphenyl) imidazolin-2-ylidene}iridium chloride
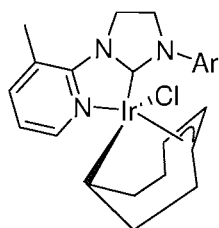
Ar = 2,6-dipp

A THF solution of KN(SiMe$_3$)$_2$ (0.06 g, 0.30 mmol) at −78 °C was added to a THF suspension of imidazolinium salt 2.6c (0.09 g, 0.25 mmol) at −78 °C. The reaction was let to warm up to −10 °C and was let stirring for 1 h. The mixture was then cooled to −78 °C and was added to a suspension of [Ir(COD)Cl]$_2$ (0.08 g, 0.12 mmol) at −78 °C. The reaction was let to warm up to r.t. and was let stirring overnight. The solvents were then removed from the resulting deep brown solution; the obtained solid was dissolved in toluene and then filtered. The solution was concentrated, by removing excess solvents under vacuum, and it was layered with petrol. Yield: 0.12 g (0.19 mmol), 79%

Anal. Calcd for $C_{65}H_{86}Cl_2Ir_2N_6$: C, 55.50, H, 6.16, N, 5.97 %. Found: C, 55.4, H, 6.1, N, 5.9%.

ES$^+$MS: m/z (%):620 [M+H]$^+$

^{1}H NMR (300MHz, C_6D_6), δ: 8.10 (1H, d, J = 5.4 Hz, o-C$\underline{H}$ picolyl), 7.20 (3H, m, aromatic C$\underline{H}$), 6.80 (1H, d, J = 5.1 Hz, p-C$\underline{H}$ picolyl), 6.45 (1H, m, m-C$\underline{H}$ picolyl), 5.92, 5.34 and 4.69 (3 × 1H, m, allylic C$\underline{H}$ of COD), 4.28 and 4.19 (2 × 2H, m, imidazolium backbone C$\underline{H}$), 2.14 and 2.06 (2 × 1H aliphatic C$\underline{H}_2$ of COD), 1.90 (3H, s, picolyl C$\underline{H}_3$), 1.88 and 1.79 (2 × 1H, septet, J = 6.9 Hz, 2 × C$\underline{H}$(CH$_3$)$_2$), 1.75, 1.63, 1.58 and 1.55 (4 × 1H aliphatic C$\underline{H}_2$ of COD), 1.52 and 1.48 (2 × 3H, d, J = 6.9 Hz, CH(C$\underline{H}_3$)$_2$), 1.23 and 1.11 (2 × 1H aliphatic C$\underline{H}_2$ of COD), 1.09 and 1.02 (2 ×3H, d, J = 6.9 Hz, CH(C$\underline{H}_3$)$_2$), 0.85 (1H, m, Ir-C$\underline{H}$ of COD).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6), δ: 178.63 (carbene $\underline{C}$–Ir), 145.46 (quaternary picolyl $\underline{C}$CH$_3$), 133.89, 131.66, 129.62, 127.53, 125.04, 123.56, 122.98, 121.95, 121.25 and 116.38 (aromatic and picolyl carbons), 98.71, 94.33 and 74.29, (3 × allylic $\underline{C}$H of COD), 52.10 and 48.35 (backbone $\underline{C}$H$_2$), 50.01 and 48.47 (aliphatic C$\underline{H}_2$ of COD), 27.95 and 26.12 (2 × $\underline{C}$H(CH$_3$)$_2$), 25.42 and 25.01 (aliphatic C$\underline{H}_2$ of COD), 24.98, 24.12, 21.87 and 21.08 (4 × CH($\underline{C}$H$_3$)$_2$), 20.63 (picolyl $\underline{C}$H$_3$), 19.13 (Ir-$\underline{C}$H of COD).

X-ray Crystallography

All data sets were collected on an Enraf-Nonius Kappa CCD area detector diffractometer with an FR591 rotating anode (Mo/Kα radiation) and an Oxford Cryosystems low temperature device operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. The programs used for control and integration were Collect, Scalepack, and Denzo.[15] The crystals were mounted on a glass fibre with silicon grease, from Fomblin vacuum oil. All solutions and refinements were performed using the WinGX package[16] and all software packages within. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogens were added using a riding model. Crystallographic data collected are presented in Table 5.1

Table 5.1: Crystallographic data for compounds **5.1a, 5.1b, 5.2, 5.3, 5.4, 5.5** and **5.6**

	5.1a	5.1b	5.2	5.3	5.4	5.5	5.6
Chemical formula	$C_{37}H_{49}Cl_2N_3Rh_2$	$C_{32}H_{40}ClN_3Rh$	$C_{61}H_{49}BF_{24}N_3Rh$	$C_{47}H_{55}ClIrN_3$	$C_{143}H_{119}B_2F_{48}Ir_2N_6$	$C_{46}H_{58}Cl_{10}N_6Rh_2$	$C_{65}H_{86}Cl_2Ir_2N_6$
Formula weight	812.51	605.03	1393.75	889.59	3239.46	1255.30	1406.70
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	$C2/c$	P-1	$P2_1/c$	P-1	P-1	$P2_1/n$
a / Å	10.4157(3)	26.1907(12)	14.5133(10)	20.4441(17)	13.5427(9)	14.5761(6)	17.074(3)
b / Å	12.1013(4)	17.6313(8)	15.1913(11)	9.9961(8)	22.4946(13)	14.5909(7)	17.853(5)
c / Å	14.5159(5)	15.2056(6)	16.4013(12)	22.0442(17)	23.7447(15)	16.0317(7)	20.381(6)
α / °	100.9250(10)	90	109.726(2)	90	109.195(2)	65.572(2)	90
β / °	94.963(2)	123.0630(10)	111.909(2)	115.409(3)	97.935(2)	82.870(2)	106.99(2)
γ / °	106.202(2)	90	100.915(2)	90	92.466(2)	63.152(2)	90
V / Å^3	1706.17(10)	5884.6(4)	2945.1(4)	4069.2(6)	6735.7(7)	2761.5(2)	5941(3)
Z	2	8	2	4	2	2	4
T / K	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
μ / mm^{-1}	1.155	0.696	0.409	3.383	2.094	1.118	4.610
No. data collected	26728	29454	38618	26296	96527	46957	40117
No. unique data	7792	6738	11763	7326	24998	12653	10524
R_{int}	0.0585	0.0470	0.0493	0.1326	0.1646	0.1165	0.0888
Final $R(|F|)$ for $F_o > 2\sigma(F_o)$	0.0338	0.0263	0.0422	0.0769	0.0861	0.0569	0.0582
Final $wR(F^2)$ for all data	0.0578	0.0397	0.0649	0.1413	0.1306	0.0978	0.1330

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Chapter 6:

Catalytic properties of

Rh and Ir NHC complexes

N-Heterocyclic carbene complexes of late transition metals have been the focus of increasing research interest due to many factors that have been discussed earlier (Chapters 1 and 2). Many NHC metal complexes show enhanced air- and moisture-stability compared to phosphine-containing analogues; this has suggested the use of NHC complexes in a wide range of catalytic processes. A variety of metal complexes have been prepared in which one or more of the phosphine ligands have been replaced with NHCs; in many reported cases, this change results in an improvement of the catalytic properties and stability of the compounds under the reaction conditions.[1]

As briefly mentioned earlier (Chapter 1), metal NHC complexes are very good catalysts for an array of synthetic organic reactions. This is because NHC ligands both stabilise and activate metal centres in different catalytic steps of the synthetic reactions, due to their unique co-ordination chemistry.[2] In this chapter the catalytic activity of the novel Rh and Ir NHC complexes reported in Chapter 5, in olefin hydroformylations, olefin molecular hydrogenations and transfer hydrogenations of carbonyl compounds, is reported.

6.1 Hydroformylations of olefins

6.1.1 Introduction

Hydroformylation, one of the major achievements of 20th century industrial chemistry, is a powerful synthetic reaction and an important industrial process. It is the reaction of alkenes or alkynes with CO and H_2 in the presence of a transition metal catalyst resulting in the formal addition of H–CHO across the multiple bond (Scheme 6.1). The resulting aldehyde has one more carbon atom than the precursor alkene.[3]
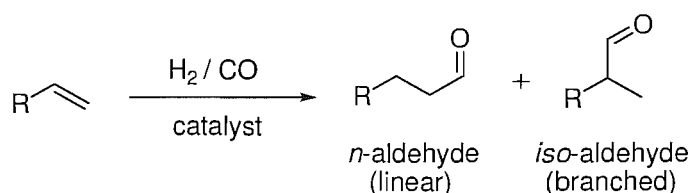
Scheme 6.1: The olefin hydroformylation reaction

Because of the commercial interest in linear plasticiser alcohols, the linear products of the reaction (n–aldehydes) are the most desired and therefore regioselectivity is one of the most important issues addressed when investigating hydroformylation reactions.[4] Regio-selectivity tends to be strongly influenced by added ligands, the temperature of the reaction,[5] and the partial pressure of CO. The $n{:}i$ ratio is found to decrease when temperature is increased for almost all olefins;[6] therefore production plants operate at temperatures lower than 125 °C to maintain a high $n{:}i$ ratio and in order to prevent degradation of the ligand. Furthermore, high CO pressures favour the increase of $n{:}i$ ratios in the hydroformylation of terminal olefins.

Complexes of transition metals such as Rh, Pt, Co and Ru may be used as catalysts for hydroformylation reactions, however, Rh based catalysts work at lower temperatures and are therefore the preferred systems.[7] As far as the ligands are concerned normally phosphine ligands are used, since they offer high activity and regio-selectivity. Furthermore, the mechanisms of the reaction when employing phosphine ligands are well understood.[8] Therefore, it is possible to optimize both activity and selectivity by adjusting the structure of the phosphine ligands.

The catalytic cycle of the hydroformylation reaction is outlined in Scheme 6.2. The regio-selectivity of the aldehyde formation is mainly determined by the step that converts the five co-ordinate [RhH(alkene)L$_2$CO] complex into either a linear or branched four co-ordinate [Rh(alkyl)L$_2$CO] complex.[4]
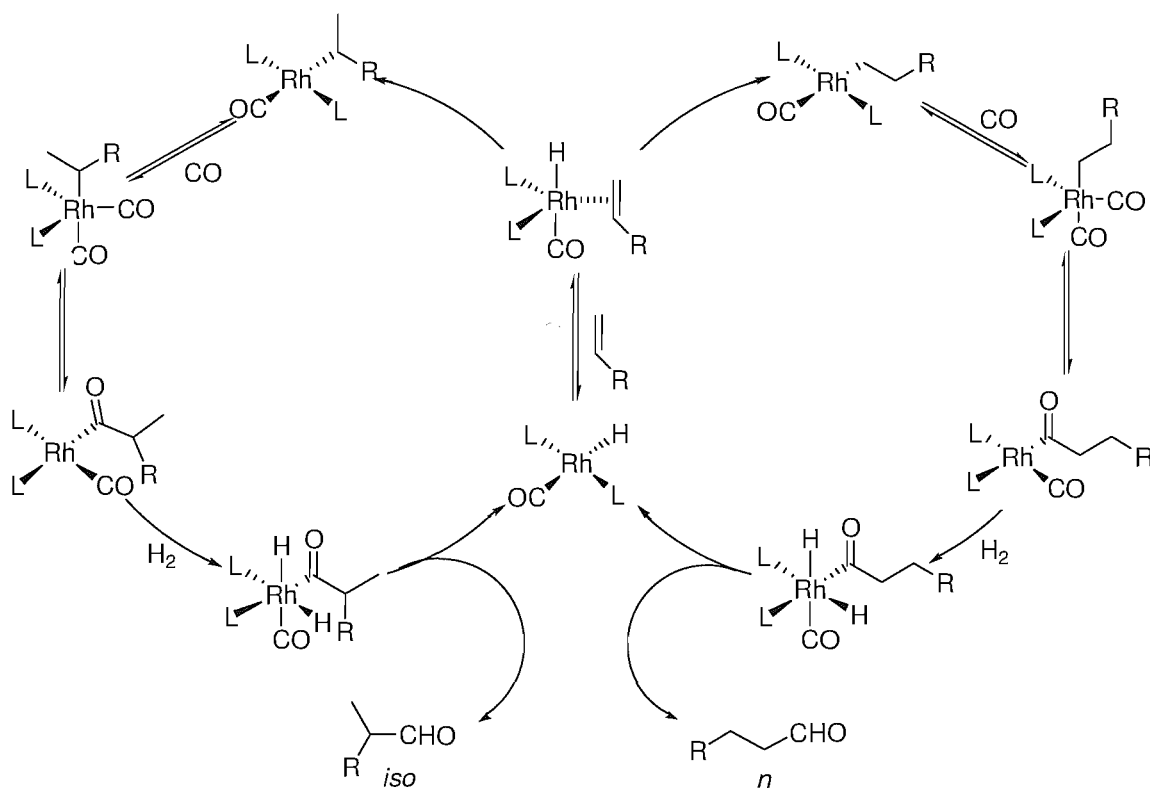
Scheme 6.2: Simplified catalytic cycle for hydroformylation of olefins

Although phosphine ligands are very versatile and offer great reactivity in hydroformylation they have some serious drawbacks. Phosphines and CO have similar binding constants to rhodium and since high CO pressures are applied for hydroformylation reactions, it is therefore necessary to have an excess of phosphine giving rise to a sterically demanding environment around the metal centre, a prerequisite for high $n{:}i$ ratio. Phosphines are also expensive, toxic and when in solution they are easily oxidised by molecular oxygen.

On the other hand, NHCs are potent substitutes for phosphines since they usually possess higher binding constants for metals and metal ions than phosphines (phosphine ligands are easily replaced by most NHCs).[1a] They are strong σ-donors and very poor π-acceptors but at the same time form much more stable metal–NHC bonds.[9] NHC complexes are often stable towards air and moisture, and quite recently it was shown that rhodium–NHC bonds are stable under hydroformylation conditions (CO/H_2 pressure: up to 50 bar and temperature up to 100 °C) [8, 10] meaning that CO is not able to substitute NHC ligands in rhodium–NHC complexes.

6.1.2 Results and Discussion

Styrene and oct-1-ene were selected as substrates for catalytic testing because of the significance of these systems in industry. The hydroformylation of styrene derivatives followed by oxidation of the aldehydes provides a useful method for the synthesis of 2-arylpropanoic acids such as ibuprofen.[11] Oct-1-ene is used for the production of n-nonanal used for the production of the short-chain fatty acid nonanoic acid, used in the preparation of plasticisers and lacquers.
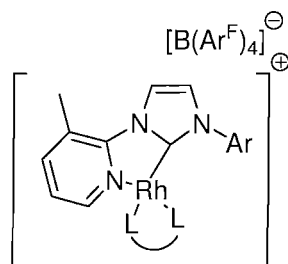
Figure 6.1: Rh–NHC complex **5.2** used in olefin hydroformylation reactions

Ar = 2,6-diisopropylphenyl, L-L = η^4-cycloocta-1,5-diene

Rh–NHC complex **5.2** (Chapter 5) shown in Figure 6.1, was tested as a catalyst for olefin hydroformylation reactions. While complex **5.2** had a bright orange-red colour in toluene solution, when pressurised with synthesis gas the solution became light yellow. This was not investigated in depth, but it is believed that the colour change was the result of the loss of the COD ligand and co-ordination of C≡O and H moieties to the free co-ordination sites. This can be supported by reports of similar cases[9] showing that the catalytically active species is supposed to be a Rh(NHC)H(CO)$_2$ complex which is formed *in situ* under hydroformylation conditions analogous to the Wilkinson catalyst (Scheme 6.3).[12]
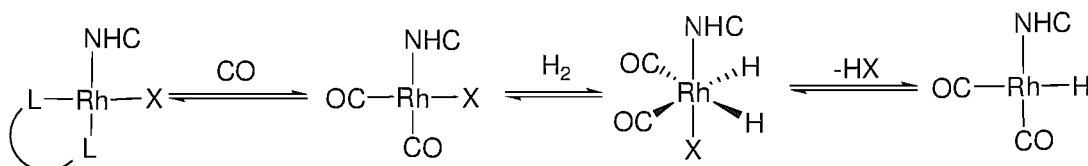
Scheme 6.3: Proposed mechanism for the formation of the active Rh(NHC)H(CO)$_2$ species[9]

As shown in the proposed mechanism (Scheme 6.3), the COD ligand is substituted by C≡O followed by an oxidative addition of hydrogen and a consecutive reductive elimination of HX leading to the formation of the active species.[9] During the whole process, the Rh–NHC bond remains intact.[8,10,13]

Furthermore, in the case of complex **5.2**, the pyridine functionality of the NHC may provide hemilability to the ligand and therefore have an active role in the catalytic cycle. However, we were unable to determine if the pyridine of the ligand remained coordinated throughout the catalytic cycle or was involved as a hemilabile ligand.

The catalytic results of the hydroformylations of oct-1-ene and styrene with complex **5.2** as a catalyst are summarised in Table 6.1. Aldehyde (product) isomerisation occurred in all cases and therefore selectivity was measured as a ratio between the formed n and iso-aldehydes.

	Olefin	Catalyst loading	Temp. / °C	Time / h	Conv.^{a} / %	TOF^b / h^{-1}	Selectivity $n{:}i^c$ ratio
1	styrene	0.04 mol%	90	15	>99	165	20:80
2	styrene	0.04 mol%	90	5	>99	495	20:80
3	styrene	0.04 mol%	50	15	>99	165	10:90
4	oct-1-ene	0.04 mol%	90	15	18	30	66:33
5	oct-1-ene	0.10 mol%	90	15	85	57	66:33
6	oct-1-ene	1.00 mol%	50	15	68	4.5	85:15

Table 6.1: Hydroformylation of olefins catalysed by rhodium NHC complex **5.2**. Notes: ^{a}Conv. = conversion determined by GC; ^{b} TOF = turnover frequency measured in moles of converted olefin per mole of catalyst per hour ^{c} $n{:}i$ = linear:branched aldehyde product, determined by GC

As shown in Table 6.1, complex **5.2** proves to be very reactive as a catalyst for styrene hydroformylations even at short reaction times (5 h). High selectivity is also achieved when relatively low temperatures (50 °C) are employed. This was not a surprise since the $n{:}i$ ratio is generally found to decrease when temperature is increased for almost all olefins.[6] When compared to other Rh–NHC systems,[14] complex **5.2** can be considered

a relatively good system since it gives higher activity (but unfortunately lower selectivity).

Oct-1-ene appears to be a more difficult substrate to hydroformylate. Higher catalyst loadings (0.1 mol%) compared to styrene are required in order to achieve a relatively high conversion (85%). However, the high temperatures employed (90 °C) favour the formation of the branched aldehyde (unfavourable) product and therefore the selectivity drops. It is worth mentioning that, as it has been shown recently, neither the COD moiety nor the $[B(Ar^F)_4]$ anion has any influence on the results of the hydroformylation of oct-1-ene.[8]

Other Rh–NHC systems have been reported[9] to perform faster (1 hour of reaction time, excluding induction period) with lower catalyst loadings (0.02 mol%) in the case of oct-1-ene hydroformylations compared to complex **5.2**. However, the reported turn over frequencies are based on one hour reactions, rather than fifteen hour reactions, as in our case and therefore can not be directly compared.

6.2 Molecular hydrogenations of olefins

6.2.1 Introduction

Olefin hydrogenation using molecular hydrogen is widely applied in the processing and conversion of vegetable oils to solid or semi-solid fats, such as those present in margarine.[15] Hydrogenation (Scheme 6.4) is formally the direct addition of diatomic hydrogen under pressure to unsaturated organic compounds such as alkenes to give alkanes and aldehydes to give alcohols. A metal catalyst, used for activating the hydrogen, is always required in hydrogenation reactions.
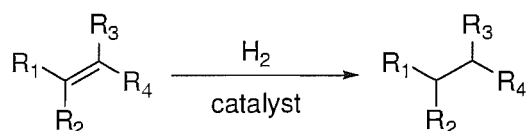
Scheme 6.4: The olefin hydrogenation reaction

159

Although heterogeneous catalytic systems such as Raney nickel[16] are favoured in the hydrogenation industry, homogeneous systems like rhodium and iridium NHC complexes, have been reported to be suitable catalysts for the hydrogenation of olefins.[1a,17]

6.2.2 Results and Discussion

A series of olefins and olefins containing other functional groups were selected as substrates for the catalytic testing. The presence of functional groups such as a carbonyl or an ester group within the molecule of the substrate will enable to determine the selectivity of the catalyst. Reduction of the functional group prior the hydrogenation of the double bond is highly undesirable. However, it was expected that the functional group would remain unaltered under the hydrogenation conditions employed. Typically the catalytic reactions were performed with 0.1 or 1.0 mol% of catalyst loading in 5 mL of DCM and 5.0 bar of hydrogen at room temperature or heated at 50 °C.
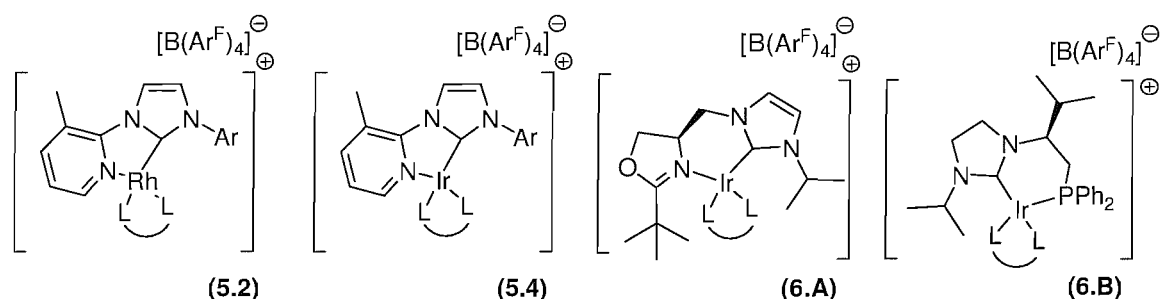
Figure 6.2: Rh–NHC complex **5.2** and Ir–NHC complex **5.4** used in olefin hydrogenation reactions Ar = 2,6-diisopropylphenyl, L-L = η^4-cycloocta-1,5-diene

Rh–NHC complex **5.2** and Ir–NHC complex **5.4** (Chapter 5) shown in Figure 6.2, were tested as catalysts for olefin hydrogenation reactions. The catalytic details and performances of **5.2** and **5.4** are summarised in Table 6.2 and 6.3 respectively. Complex **5.4** can be compared to the reported complexes **6.A** and **6.B** (Figure 6.2) by Pfaltz and co-workers.[18]

	Olefin	Catalyst loading	Temp. $/ ^\circ C$	Time $/ h$	Conv.^{a} $/ \%$	TOF^b $/ h^{-1}$
1	styrene	0.1 mol%	50	15	>99	67
2	styrene	0.1 mol%	25	15	>99	67
3	styrene	0.1 mol%	25	5	>99	200
4	β-citronellol	1.0 mol%	50	15	>99	6.7
5	β-citronellol	1.0 mol%	25	15	>99	6.7
6	β-citronellol	1.0 mol%	25	5	>99	20
7	β-citronellal	1.0 mol%	50	15	>99	6.7
8	β-citronellal	1.0 mol%	50	5	82	16
9	β-citronellal	1.0 mol%	25	15	53	3.5
10	trans-stilbene	1.0 mol%	50	15	>99	6.7
11	trans-stilbene	1.0 mol%	50	5	97	19
12	trans-stilbene	1.0 mol%	25	15	73	4.9
13	methyl-trans-cinnamate	1.0 mol%	50	15	>99	6.7
14	methyl-trans-cinnamate	1.0 mol%	50	5	>99	20
15	methyl-trans-cinnamate	1.0 mol%	25	15	85	5.7

Table 6.2: Hydrogenation of olefins catalysed by rhodium NHC complex **5.2**. Notes: ^{a}Conv. = conversion determined by GC; ^{b} TOF = turnover frequency measured in moles of converted olefin per mole of catalyst per hour

Both complex **5.2** and complex **5.4** performed well as hydrogenation catalysts even with relatively low catalyst loadings (0.1 mol%). The highest achieved activity (calculated as TOF) was 200 moles of converted olefin per mole of catalyst per hour. The maximum activity was recorded in the case of styrene and is comparable to other Rh–NHC complexes that only perform better when additives are employed.[19] It is worth noting that the activity was not calculated for shorter reaction times and therefore it is representing an average, rather than a high-end activity.

	Olefin	Catalyst loading	Temp. / °C	Time / h	Conv.[a] / %	TOF[b] / h^{-1}
1	styrene	0.1 mol%	50	15	>99	67
2	styrene	0.1 mol%	25	15	>99	67
3	styrene	0.1 mol%	25	5	>99	200
4	β-citronellol	1.0 mol%	50	15	>99	6.7
5	β-citronellol	1.0 mol%	50	5	>99	20
6	β-citronellol	1.0 mol%	25	5	60	12
7	β-citronellal	1.0 mol%	50	15	>99	6.7
8	β-citronellal	1.0 mol%	50	5	>99	20
9	β-citronellal	1.0 mol%	25	15	81	5.4
10	trans-stilbene	1.0 mol%	50	15	>99	6.7
11	trans-stilbene	1.0 mol%	50	5	>99	20
12	trans-stilbene	1.0 mol%	25	15	14	0.9
13	methyl-trans-cinnamate	1.0 mol%	50	15	>99	6.7
14	methyl-trans-cinnamate	1.0 mol%	50	5	93	19
15	methyl-trans-cinnamate	1.0 mol%	25	15	45	3

Table 6.3: Hydrogenation of olefins catalysed by iridium NHC complex 5.4. Notes: [a]Conv. = conversion determined by GC; [b] TOF = turnover frequency measured in moles of converted olefin per mole of catalyst per hour

Notably, both 5.2 and 5.4 can catalyse the hydrogenation of styrene at room temperature relatively quickly (within 5 hours), using low catalyst loadings (0.1 mol%). Furthermore complex 5.2 gives very good results with β-citronellol, although a higher catalyst loading (1.0 mol%) is required in order to achieve full conversion at room temperature within a relatively small time frame (5 hours). As was expected, the carbonyl group of β-citronellol and β-citronellal and the ester group of methyl-trans-cinnamate remained unaltered even after 15 hours under hydrogenation conditions.

Although our results could not be directly compared to those reported by Pfaltz et al.[18], since slightly different reaction conditions (25 °C, 50 bar H₂) were employed, it can be derived that complex 5.4 is a fast and efficient hydrogenation catalyst giving full conversion (>99%) for styrene, trans-stilbene, β-citronellal and β-citronellol within 5 hours.

Unfortunately, we were unable to determine if the pyridine functionality of the NHC ligand was involved in the catalytic reaction either as a hemilabile ligand or remained coordinated throughout the catalytic cycle.

6.3 Transfer hydrogenations of carbonyl compounds

6.3.1 Introduction

Transfer hydrogenation is probably the simplest and safest catalytic method available for reduction.[20] As displayed in Scheme 6.5, it is the addition of hydrogen to a molecule from a source other than gaseous H_2. The process is mainly employed for the reduction of aldehydes/ketones and imines to alcohols and amines, respectively.
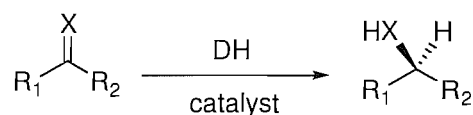
Scheme 6.5: The transfer hydrogenation of carbonyl compounds

DH = hydrogen donor

The hydrogen donor (transfer agent) is typically isopropanol, which coverts to acetone upon donation of hydrogen.[21] Furthermore, isopropanol is easy to handle (b.p. 82 °C), relatively non-toxic, environmentally benign, and inexpensive. Finally, the volatile acetone product can be easily removed to shift an unfavourable equilibrium.[22]
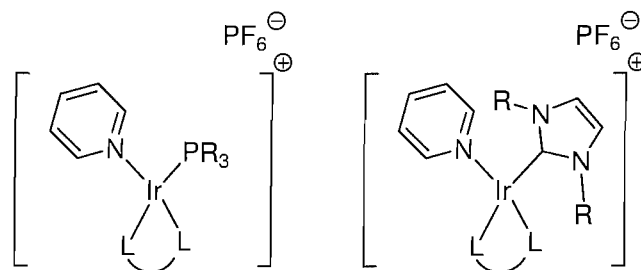
Figure 6.3: Crabtree's catalyst (left)[23] and Ir–NHC complex synthesised by Nolan *et al.* (right)[21] R = cyclohexyl, L-L = η^4-cycloocta-1,5-diene

The use of metal NHC complexes as catalysts in transfer hydrogenation reactions has been limited; only a few examples of such catalysts have been reported.[24] An Ir–NHC catalyst synthesised by Nolan *et al.* that is based on Crabtree's catalyst[23] (Figure 6.3), is probably the most active up to date.[21] However, the ligand modification possibilities of NHCs can be used for tuning the activity and selectivity of transfer hydrogenation reactions. Furthermore many NHC metal complexes show enhanced air- and moisture-stability compared to phosphine-containing analogues and therefore are much easier to handle.[25]

6.3.2 Results and Discussion

A wide range of aldehydes and ketones were selected as substrates for the catalytic testing. Typically, the catalytic reactions were performed with 0.2 mol% of catalyst loading and potassium hydroxide was added as the base, in 2 mL of isopropanol and were heated at 82 °C.

$$[B(Ar^F)_4]^\ominus \qquad\qquad [B(Ar^F)_4]^\ominus$$

(5.2)   (5.4)
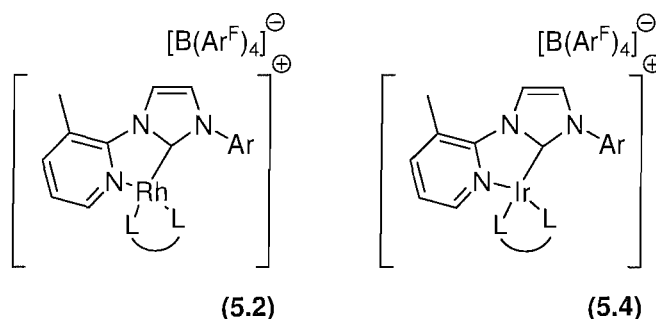
Figure 6.4: Rh–NHC complex **5.2** and Ir–NHC complex **5.4** used in transfer hydrogenation reactions of carbonyl compounds Ar = 2,6-diisopropylphenyl, L-L = η^4-cycloocta-1,5-diene

Rh–NHC complex **5.2** and Ir–NHC complex **5.4** (Chapter 5) shown in Figure 6.4, were tested as catalysts for transfer hydrogenation reactions of carbonyl compounds. The catalytic details and performances of **5.2** and **5.4** are summarised in Table 6.4 and 6.5 respectively.

Once again, the role of the pyridine functionality of the NHC ligand, in the catalytic cycle, could not be successfully determined.

	Substrate	Catalyst loading	Temp. /°C	Time / h	Conv.[a] / %	TOF[b] / h^{-1}
1	cyclohexanone	0.2 mol%	82	20	83	20.8
2	cyclohexanone	1.0 mol%	82	12	>99	8.3
3	2,4-dimethylpentan-3-one	0.2 mol%	82	20	14	3.5
4	2,4-dimethylpentan-3-one	1.0 mol%	82	12	85	7.1
5	4-bromoacetophenone	0.2 mol%	82	20	18	4.5
6	4-bromoacetophenone	1.0 mol%	82	12	87	7.3
7	acetophenone	0.2 mol%	82	20	44	11
8	acetophenone	1.0 mol%	82	12	>99	8.3
9	4-methoxyacetophenone	0.2 mol%	82	18	43	11.9
10	4-methoxyacetophenone	1.0 mol%	82	12	>99	8.3
11	4-chloroacetophenone	0.2 mol%	82	18	17	4.7
12	4-chloroacetophenone	1.0 mol%	82	12	82	6.8
13	benzaldehyde	0.2 mol%	82	22	19	4.3
14	benzaldehyde	1.0 mol%	82	12	89	7.4
15	2,4,6-trimethylbenzaldehyde	0.2 mol%	82	22	23	5.2
16	2,4,6-trimethylbenzaldehyde	1.0 mol%	82	12	94	7.8
17	butanal	0.2 mol%	82	14	>99	35.7
18	butanal	1.0 mol%	82	12	>99	8.3

Table 6.4: Transfer hydrogenation of carbonyls catalysed by rhodium NHC complex **5.2**.

Notes: [a]Conv. = conversion determined by GC; [b] TOF = turnover frequency

Rh-NHC complex **5.2** performed only moderately as a catalyst for transfer hydrogenation reactions. When using a relatively low catalyst loading (0.2 mol%) only butanal has been completely converted (>99%) after 14 hours of reaction, giving an activity of 35.7 moles of converted butanal per mole of catalyst per hour.

	Substrate	Catalyst loading	Temp. /°C	Time /h	Conv.[a] / %	TOF[b] /h^{-1}
1	acetophenone	1.0 mol %	82	0.25	>99	400
2	acetophenone	0.2 mol %	82	4	81	101
3	cyclohexanone	0.2 mol %	82	5	>99	100
4	heptan-4-one	0.2 mol %	82	12	62	25.8
5	4-bromoacetophenone	0.2 mol %	82	12	93	38.8
6	4-methoxyacetophenone	0.2 mol %	82	15	86	28.7
7	4-chloroacetophenone	0.2 mol %	82	15	89	29.7
8	2-bromoacetophenone	0.2 mol %	82	15	38	12.7
9	2-nitroacetophenone	0.2 mol %	82	15	12	4
10	4-methoxybenzaldehyde	0.2 mol %	82	0.5	>99	1000
11	2,4,6-trimethylbenzaldehyde	0.2 mol %	82	15	61	20.3
12	benzaldehyde	0.5 mol %	82	1	>99	250
13	benzaldehyde	0.2 mol %	82	15	63	21
14	β-citronellal	1.0 mol %	82	0.08	>99	1250
15	β-citronellal	0.1 mol %	82	0.33	>99	3000
16	butanal	0.2 mol %	82	3	>99	166.7

Table 6.5: Transfer hydrogenation of carbonyls catalysed by iridium NHC complex **5.4**

Notes: [a]Conv. = conversion, determined by GC; [b] TOF = turnover frequency

Complex **5.4** appears to perform better in the catalytic reactions involving aldehydes rather than the reactions of ketones. It is an excellent catalyst for the transfer hydrogenation of β-citronellal and 4-methoxy-benzaldehyde giving activities of 3000 and 1000 moles of converted substrate per mole of catalyst per hour respectively. Other Ir-NHC catalytic systems used in the transfer hydrogenation of β-citronellal require longer reaction times (up to 1.5 hours) and give activities of 670 moles of converted substrate per mole of catalyst per hour. This is also true in the case of 4-methoxy-benzaldehyde that requires up to 6 hours of reaction time for partial conversion (83 %) giving activities of 240 moles of converted substrate per mole of catalyst per hour.[17d]

Furthermore complex **5.4** performs better as a catalyst for the transfer hydrogenation of acetophenone (TOF = 400 h^{-1}) compared to other systems (TOF = 100 h^{-1}) using the same conditions.[25]

On the other hand, these other Ir-NHC catalytic systems perform better (compared to complex **5.4**) when 4-bromoacetophenone, 4-methoxyacetophenone or benzaldehyde are used as substrates, giving activities of 1000, 800 and 1000 moles of converted substrate per mole of catalyst per hour respectively.[17d,25]

6.4 Conclusions

Rh-NHC complex **5.2** and Ir-NHC complex **5.4** have been extensively tested as catalysts in olefin hydroformylations, olefin molecular hydrogenations and transfer hydrogenation reactions of carbonyl compounds. However, we were unable to determine if the pyridine functionality of the NHC ligand remained coordinated throughout the catalytic cycle or acted as a hemilabile ligand.

Complex **5.2** was found to be a good catalyst in the hydroformylation of styrene, giving high activities and relatively good selectivities even at low catalyst loadings. Complex **5.4** performed as an excellent catalyst for the hydrogenation (by transfer) of β-citronellal and 4-methoxybenzaldehyde giving activities of up to 3000 moles of converted substrate per mole of catalyst per hour.

6.5 Experimental Section

General materials and methods

All manipulations were performed under nitrogen in a M. Braun glove-box or using standard Schlenk techniques, unless otherwise stated. Solvents were dried using standard methods and distilled under nitrogen prior to use (see Appendix 2). The preparation details of complexes **5.2** and **5.4** can be found in Chapter 5. All other materials used were purchased from Aldrich or Lancaster and used without further purification.

6.5.1 Hydroformylations of olefins

Based on a published method,[9] all experiments were carried out in a Berghof high pressure reactor, fitted with a Teflon liner. The reactor was flushed with nitrogen and filled with a standard solution (2.0 mL) of **5.2** [14 mg of **5.2** in 20.0 mL toluene], toluene (5.0 mL) and the olefin substrate (2.5×10^{-3} mol) leading to a substrate:catalyst ratio of 2500:1 (0.04 mol%). Mesitylene (0.3 g) was added as internal standard. The mixture was flushed with synthesis gas ($CO:H_2 = 1:1$) and the pressure was adjusted to 50 bar while heated at 90 °C and was then kept at this temperature for the required amount of time. Samples were quantified *via* gas chromatography. Products were identified by comparison of GC retention times with those of authentic samples.

6.5.2 Molecular hydrogenations of olefins

Based on a reported method,[26] all experiments were carried out in a Büchi high pressure glass reactor. The container was flushed with nitrogen and filled with a standard catalyst solution (5.0 mL) [15 mg of **5.4** (or 14 mg of **5.2**) in 20.0 mL DCM], and the substrate (2.5×10^{-3} mol) leading to a substrate: catalyst ratio of 1000:1 (0.1 mol%). Mesitylene (0.30 g) was added as internal standard. The mixture was flushed with hydrogen gas to clean all supplies before the pressure was adjusted to 5 bar while heated at the required temperature and was then kept at this temperature for the required amount of time. Samples were quantified *via* gas chromatography. Products were identified by comparison of GC retention times with those of authentic samples.

6.5.3 Transfer hydrogenations of carbonyl compounds

Based on a published method,[21] all experiments were carried out in an ampoule fitted with a Young's tap. The ampoule was flushed with nitrogen and filled with a standard catalyst solution (2.0 mL) [28 mg of **5.2** (or 30 mg of **5.4**) and 0.011 g of potassium hydroxide in 20.0 mL isopropanol], and the substrate (2.0 × 10^{-3} mol) leading to a substrate: catalyst ratio of 500:1 (0.2 mol%). Mesitylene (0.240 g) was added as internal standard. The ampoules were partially evacuated and sealed. They were heated at 82 °C and were sampled at regular intervals. Samples were quantified *via* gas chromatography. Products were identified by comparison of GC retention times with those of authentic samples.

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Chapter 7:

Nickel NHC and

nickel diimine complexes

7.1 Introduction

Many well-established N-heterocyclic carbene complexes of late transition metals have been reported to date.[1] In particular, complexes with catalytically-active metals are being intensively investigated. The unique donor and spatial characteristics of NHC ligands are responsible for some unusual reactivity of the isolated complexes.[2] In recent developments, NHCs functionalised with 'classical heteroatom' donors have been used as versatile multidentate spectators on a range of transition metal complexes. In this area former members of the group[3] and other research groups[4] have reported pyridine-, picoline- and lutidine-functionalised NHC complexes of Ru, Rh, Ir and Pd. The notable absence of any functionalised NHC complexes of Ni is to be contrasted with the numerous Ni(0) and Ni(II) complexes with simple monodentate or chelating bidentate NHCs that have appeared in the literature.[5] The extensive applications of Ni complexes in catalysis, for example in polymerisation, telomerisation, C–C formation and C–F activation reactions, prompted our attempts to explore the synthesis and characterisation of pyridyl and picolyl functionalised NHC complexes of Ni.[6]

7.2 Results and Discussion

7.2.1 Pyridyl-functionalised *N*-heterocyclic carbene complexes of nickel

Traditionally, monodentate or bidentate NHC complexes of nickel are synthesised by the interaction of a Ni(II) or Ni(0) precursor with isolated NHCs, prepared by deprotonation of the imidazolium pre-ligands, or by direct metallation of imidazolium salts with Ni(OAc)$_2$. Since the free carbene **2.1b** (shown in Scheme 7.1) has been isolated and fully characterised (see Chapter 2), the former method was the one employed for the nickel NHC complexes described in this chapter.
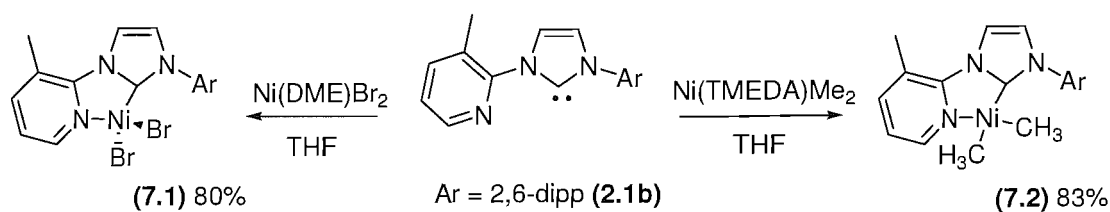
Scheme 7.1: Synthesis of nickel NHC complexes **7.1** and **7.2**

As shown in Scheme 7.1, reaction of Ni(DME)Br$_2$ with free carbene **2.1b** in THF gave high yields of the tetrahedral nickel carbene complex **7.1**. In the same way, reaction of Ni(TMEDA)Me$_2$ with the free carbene **2.1b** gave the square planar nickel carbene dimethyl complex **7.2** in high yields. Both complexes were isolated as solids that were recrystallised from THF solutions layered with petroleum. The molecular structures of **7.1** and **7.2** are displayed in Figures 7.1 and 7.2 respectively.
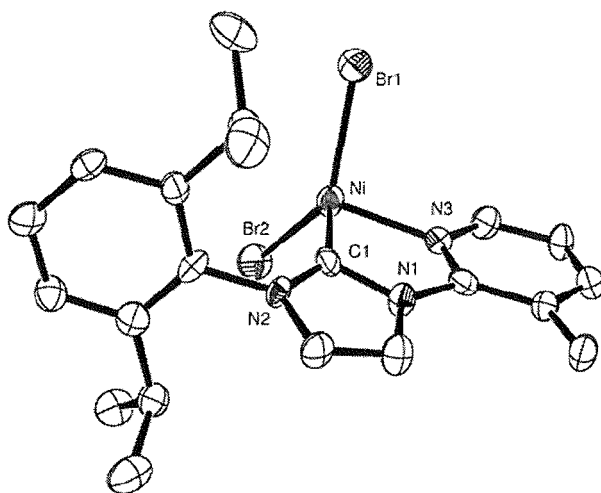
Figure 7.1: ORTEP representation of the structure of **7.1** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: C1–Ni: 1.937(7), N3–Ni: 2.032(5), Br1–Ni: 2.3561(13), Br2–Ni: 2.3445(12), Br2–Ni–Br1: 130.35(4), C1–Ni1–N3: 81.4(3).

Complex **7.1** adopts a distorted tetrahedral geometry [ligand bite angle 81.4(3) ° and Br1–Ni–Br2: 130.35(4) °]. The chelating ligand bite angle does not have a significant effect on the Br1–Ni–Br2 angle, the magnitude of which is possibly controlled by the bromide lone pair repulsions. The aromatic ring of the 2,6-dipp moiety is almost perpendicular to the plane formed by the picolyl and the heterocycle rings [average dihedral angle between the planes is 81 °]. Four co-ordinate complexes of the type [Ni(L–L)(halide)$_2$] are square planar or tetrahedral.[7] The recently reported bidentate bis-NHC complexes[8] invariably adopt square planar geometry. This geometry is also favoured by phosphine complexes of the type Ni(L–L)Br$_2$ [(L–L) = R$_2$P(CH$_2$)$_n$PR$_2$ n = 1–3, R = aryl, alkyl].[9] However, Ni[Me$_2$P(CH$_2$)$_2$PMe$_2$]Cl$_2$ and complexes with large bite angle diphosphines adopt tetrahedral geometry.[10]
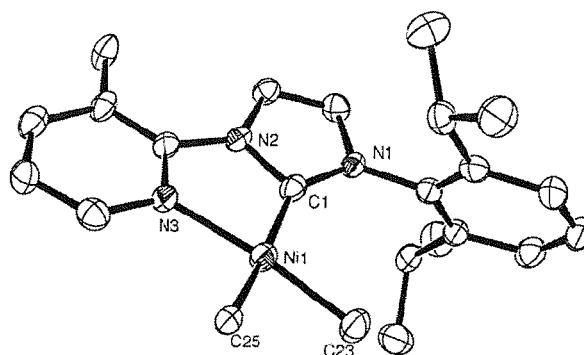
Figure 7.2: ORTEP representation of the structure of **7.2** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Ni1–C1: 1.874(3), Ni1–C23: 1.924(3), Ni1–C25: 1.973(3), Ni1–N3: 1.975(3), C1–Ni1–C23: 97.71(14), C1–Ni1–C25: 170.37(13), C23–Ni1–C25: 86.88(13), C1–Ni1–N3: 80.64(13), C23–Ni1–N3: 170.20(14), C25–Ni1–N3: 96.23(12).

Complex **7.2** adopts a slightly distorted square planar geometry with a ligand bite angle of 80.64(13) ° which is only slightly smaller compared to the ligand bite angle of complex **7.1** [81.4(3) °]. The angle formed between the two methyl groups is 86.88(13) °, C1–Ni1–C23 is 97.71(14) ° and C25–Ni1–N3 is 96.23(12) °. The aromatic ring of the 2,6-dipp moiety is almost perpendicular [average dihedral angle between the planes is 72 ° compared to 81 ° for complex **7.1**] to the plane formed by the picolyl and the heterocycle rings.

7.2.2 Catalytic properties of nickel NHC complexes

Ethylene polymerisation is the fastest-growing segment of the polymer industry since poly(alkenes) have multi-billion kilograms production a year.[11] Unfortunately only a few metal NHC complex (Ti–NHC,[12] V–'pincer NHC' and Ti–'pincer NHC' complexes[13]) have been used successfully to catalyse the polymerisation of ethylene and therefore the successful designing and synthesis of a metal NHC complex able to perform well as an ethylene polymerisation catalyst is still a great challenge.

Complexes **7.1** and **7.2** were tested as ethylene polymerisation catalysts under standard conditions,[14] using MAO as a co-catalyst and found to perform rather poorly; only minute amounts of polyethylene were collected that were considered insignificant.

However, both **7.1** and **7.2** were found to be very good catalysts in the vinyl-type polymerisation of norbornene (Scheme 7.2). Such a polymerisation, which is akin to the classical olefin polymerisation, leaves the bicyclic structural unit intact (*i.e.* opens only the double bond of the 6-member ring), and the product does not contain any double bonds.[15] The vinyl polymerization of cyclic olefins is occasionally also known as 'addition polymerisation'.[16]
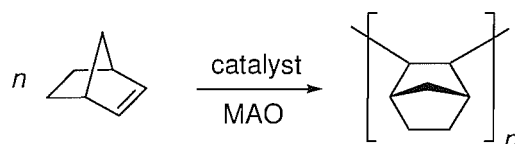
Scheme 7.2: Schematic representation of the vinyl-type polymerisation of bicyclo[2.2.1]hept-2-ene (norbornene)

Usually, the vinyl polymerisation of norbornene with nickel catalysts is carried out in combination with MAO as a co-catalyst;[15] absence of MAO results in non active catalysts.[14,17]

In addition to complexes **7.1** and **7.2**, one nickel picolyl NHC complex (shown in Figure 7.3 and denoted **7.1***) that was prepared by former members of the group[6] was also tested as a catalyst, for comparison purposes. Complex **7.1*** can be directly compared to complex **7.1** since both are of the type $Ni(C–N)Br_2$ [where C–N is a picolyl functionalised *N*-heterocyclic carbene], feature the same aromatic moiety (Ar = 2,6-diisopropylphenyl) and both adopt a tetrahedral geometry.[6] The norbornene polymerisation results for all three nickel complexes are summarised in Table 7.1.
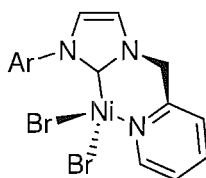
Ar = 2,6-dipp **(7.1*)**

Figure 7.3: Nickel picolyl NHC complex **7.1***[6]

	Complex	MAO / mL	T / °C	Time / min	Conversion / %	Activity^a
1	**7.1**	1.0	25	60	>99	9.4
2	**7.1**	1.0	25	30	89	16.7
3	**7.1**	1.0	50	30	>99	18.6
4	**7.1**	none	25	60	0	0
5	**7.1***	1.0	25	60	91	8.6
6	**7.1***	1.0	25	30	84	15.8
7	**7.1***	1.0	50	30	>99	18.6
8	**7.1***	none	25	60	0	0
9	**7.2**	1.0	25	60	95	8.9
10	**7.2**	1.0	25	30	87	16.4
11	**7.2**	1.0	50	30	>99	18.6
12	**7.2**	none	25	60	0	0
13	none	1.0	25	60	0	0
14	none	1.0	25	30	0	0
15	none	1.0	50	30	0	0

Table 7.1: Polymerisation of norbornene with nickel NHC complexes **7.1**, **7.1*** and **7.2** activated by methylaluminoxane (MAO). Polymerisation conditions: solvent: chlorobenzene (total volume: 10 mL); nickel complex catalyst: 0.2 μmol; MAO concentration: 10% in toluene (MAO/catalyst: 7500); norbornene: 1.88 g (norbornene/catalyst: 100 000). ^{a} In units of 10^6 g of PNB (mol of nickel complex)$^{-1}$ h^{-1}

Complex **7.1** showed the highest activity at both 25 and 50 °C (1.67 × 10^{-7} and 1.86 × 10^{-7} respectively) although the other two complexes (**7.1*** and **7.2**) also gave very good results. All three complexes gave slightly better conversions and activities when compared to other NHC ligated complexes (at 30 °C: 14.6 % conversion and 4.0 10^6 g of polymer (mol of Ni)$^{-1}$ h^{-1} activity; at 60 °C: 59.0 % conversion and 16.5 10^6 g of polymer (mol of Ni)$^{-1}$ h^{-1} activity)[14], while non-NHC ligated complexes show significantly inferior performance (at 30 °C: 54.0 % conversion and 3.02 10^6 g of polymer (mol of Ni)$^{-1}$ h^{-1} activity; at 60 °C: 50.0 % conversion and 2.84 10^6 g of polymer (mol of Ni)$^{-1}$ h^{-1} activity).[17,18,19,20]

The activity of all complexes increased significantly when the temperature of the reaction was increased from 25 to 50 °C. This is probably because the concentration of active centres activated by MAO increases as the temperature is increased.[14] Increase of the reaction time leads to an increase in the conversion, but a decrease in the catalytic activity. The activity decrease is due to the elimination of the monomer concentration during the reaction leading to a decrease to the reaction rate too.

The polynorbornenes obtained were characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. There were no bands at 1680–1620 cm^{-1} in the IR spectra indicating that no double bonds were present, confirming that all polymerisations were vinyl-type rather than ring-opening metathesis polymerisations.[15] The NMR spectra for all polymers obtained are very similar with ^{1}H NMR resonances appearing at around 1.3, 1.8, 2.1 and 2.6 ppm as multiplets while the ^{13}C{^{1}H} NMR spectra featured multiplets at 28.3, 33.7, 41.5 and 50.8 ppm, which are believed to belong to the polynorbornene chain structure (C-1 in Figure 7.4), the bridge carbon (C-2), the bridgehead carbon (C-4), and the backbone carbon (C-3), respectively.[14,21]
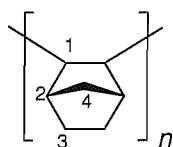
Figure 7.4: Polynorbornene product with indicative numbering

7.2.3 Nickel diimine complexes

Metal diimine complexes are very good catalysts for many polymerisation reactions.[11] For example, Brookhart's Pd-diimine catalyst,[22] was the first successful complex to give good results in the copolymerisation of ethylene with acrylates.[23]

Traditional diimine complexes used as polymerisation catalysts display three key characteristics:[11] a) the highly electrophilic, cationic nickel (or palladium) metal centres; b) the use of sterically bulky α-diimine ligands; and c) the use of non-coordinating counter-ions or the use of reagents thought to produce non-coordinating counter-ions.[24] The electrophilic nickel (or palladium) metal centre offers rapid rates for olefin insertions, while bulky ligands favour the insertion over chain transfers and finally the

178

use of non-coordinating counter-ions provides an accessible coordination site for the incoming olefins.

The steric and electronic properties of α-diimine ligands are easily varied and therefore are considered to be an important feature of the nickel α-diimine catalyst systems. Currently there are several synthetic routes for preparing α-diimine ligands available, enabling modifications on the backbone and the aryl substituents, offering the opportunity for the preparation of arrays of ligands with independent control over the steric and electronic effects at the metal centre. It is also worth mentioning that α-diimine ligands are well-known to stabilize organometallic complexes.[25]

An easy and efficient way for preparing α-diimine ligands is the reaction of the desired aniline with glyoxal in a propanol-water 1:1 solvent mixture.[26] As shown in Scheme 7.3 2,4,6-trimethoxyaniline was reacted with an aqueous solution of glyoxal to give good yields of N,N'-bis(2,4,6-trimethoxyphenyl)ethylenediamine (7.3). When the prepared diimine is complexed to a metal, the electron donating methoxy groups on the phenyl rings might provide the metal centre with more electron density compared to non-substituted phenyl analogues. This extra electron density might have beneficial effects in various catalytic applications.
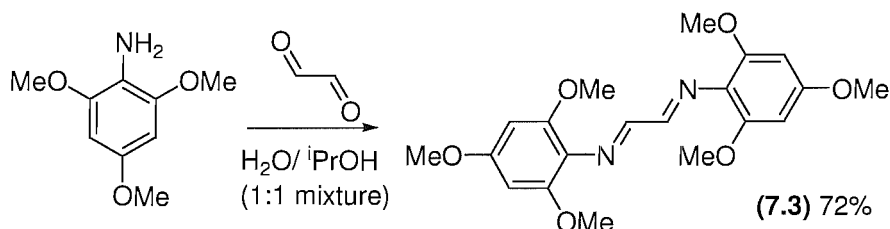
Scheme 7.3: Synthesis of N,N'-bis(2,4,6-trimethoxyphenyl)ethylenediamine

The displacement of dimethoxyethane from Ni(DME)Br$_2$ or tetramethylethylenediamine from Ni(TMEDA)Me$_2$ (simple displacements of labile ligands from the precursor complexes) is probably one of the easiest methods for preparing nickel-diimine complexes.[11] Therefore, as shown in Scheme 7.4, diimine 7.3 displaced the DME ligand from Ni(DME)Br$_2$ to yield complex 7.4. However when the diimine was reacted with Ni(TMEDA)Me$_2$ not only TMEDA was displaced but also the two methyl groups were displaced (as ethane gas) and substituted by another diimine ligand, yielding complex 7.5. The yield of 7.5 appears to be low (42%) but since diimine 7.3 was reacted in

quantitative (1:1) amounts with the nickel precursor complex, while complex **7.5** requires a 2:1 ratio of ligand to precursor, the yield can be considered high (84% in analogy).

Scheme 7.4: Synthesis of nickel diimine complexes **7.4** and **7.5**

Complex **7.4** was crystallised from a hot methanol solution, while **7.5** was crystallised by layering a THF solution with petroleum. The molecular structures of complexes **7.4** and **7.5** are displayed in Figures 7.5 and 7.6 respectively.

Figure 7.5: ORTEP representation of the structure of **7.4** showing 50% probability ellipsoids. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Br1–Ni1: 2.468(2), Ni1–N1: 2.030(3), Ni1–O3: 2.292(3), N1–Ni1–N1': 81.52(19), N1–Ni1–O3: 152.44(12), N1'–Ni1–O3: 73.65(12), O3–Ni1–O3': 132.92(15), N1–Ni1–Br1': 93.03(10), O3–Ni1–Br1': 83.54(10), N1-Ni1–Br1: 107.82(11), O3–Ni1–Br1: 85.61(10), Br1'-Ni1-Br1: 152.60(5).

As seen in Figure 7.5, complex **7.4** is a symmetric molecule that adopts a heavily distorted tetrahedral geometry with a ligand bite angle of 81.52(19) ° and Br1'–Ni1–Br1 angle of 152.60(5) °. As mentioned earlier, four co-ordinate complexes of the type [(L–L)Ni(halide)$_2$] are either square planar or tetrahedral.[7] The square planar geometry is normally favoured by phosphine complexes of the type NiBr$_2$(L–L) [(L–L) =

$R_2P(CH_2)_nPR_2$ n = 1–3, R = aryl, alkyl].[9] Although not shown in Figure 7.5, there is a close contact [Ni1–O3: 2.292(3)] between the nickel metal centre and O3.
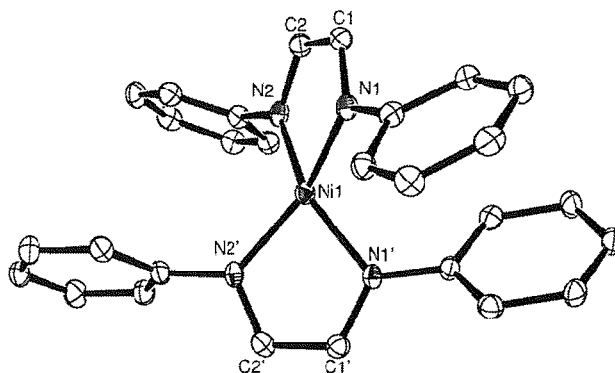
Figure 7.6: ORTEP representation of the structure of **7.5** showing 50% probability ellipsoids. H atoms and all –OMe groups are omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Ni1–N2: 1.9117(15), Ni1–N1: 1.9265(14), N1–C1: 1.338(2), N1–C3: 1.410(2), N2–C2: 1.336(2), N2–C12: 1.424(2), N2–Ni1–N2': 110.17(9), N2–Ni1–N1': 147.00(6), N2–Ni1–N1: 82.86(6).

Complex **7.5** again exhibits distorted tetrahedral geometry (Figure 7.6). The ligand bite angle is 82.86(6) °, N2–Ni1–N2' is 110.17(9) ° and N2–Ni1–N1' is 147.00(6) ° while the phenyl rings of each ligand have an average dihedral angle of 58 °.

Ethylene polymerisations can be catalyzed by α-diimine-derived catalysts and especially by Ni and Pd centres bearing α-diimine ligands. Such catalysts are amongst the most active, and are the most thoroughly described in the literature at present.[11] Preliminary catalytic results indicated that complexes **7.5** and especially **7.4** might be good catalysts for several reactions including ethylene polymerisation or other polymerisation reactions. Unfortunately, time constraint prevented examination of the diimine complexes in alkene polymerisation. This is a potential topic for further work.

7.3 NMR Spectroscopy

As complexes **7.1** and **7.4** were found to be paramagnetic (μ_{eff} 3.3 and 3.2 BM respectively), NMR data have been only collected for complexes **7.2** and **7.5** and for ligand **7.3**.

The ^{1}H and ^{13}C NMR spectra of complex **7.2** can be compared to the spectra of the free carbene ligand **2.1b**. It appears that all signals of the ligand appear in the spectra of complex **7.2** and have very similar chemical shifts. Furthermore, complex 7.2 has two additional signals at –0.50 and –0.75 ppm (in the ^{1}H NMR spectrum) that belong to the two methyl groups on the nickel metal centre. The signals of these methyl groups appear at 4.12 and 0.06 ppm in the ^{13}C NMR spectrum. The carbene carbon atom of complex **7.2** appears at 191.99 ppm (in the ^{13}C NMR spectrum), which is characteristic for a metal carbene signal.[27]

Complex **7.5** has very similar ^{1}H NMR and ^{13}C NMR spectra to the free ligand **7.3**. The free diimine ligand **7.3** has really simple ^{1}H and ^{13}C{^{1}H} NMR spectra due to its symmetry. In the ^{1}H NMR spectrum, 4 singlet signals appear at 8.79, 6.16, 3.81 and 3.80 ppm that belong to the ethylene CH, aromatic CH and the *ortho* and *para* OCH$_3$ groups respectively. Similarly the ^{1}H NMR spectrum of complex **7.5** has signals at 9.53, 6.07, 3.57 and 3.46 ppm that are assigned in the same way as the signals of the ligand. The same trend is observed in the ^{13}C{^{1}H} NMR spectrum that is reported analytically in the experimental section.

7.4. Conclusions

Two novel picolyl functionalised NHC complexes of nickel have been synthesised. These complexes show high activities for the vinyl-type polymerisation of norbornene with MAO used as co-catalyst. Furthermore, one new diimine ligand has been synthesised that has successfully displaced labile ligands from nickel precursor complexes to yield two novel nickel diimine complexes.

7.5 Experimental Details

General Materials and Methods

All manipulations were performed under nitrogen in a M. Braun glove-box or using standard Schlenk techniques, unless otherwise stated. Solvents were dried using standard methods and distilled under nitrogen prior use (see Appendix 2). The synthetic method for the preparation of 2,4,6-trimethoxyaniline can be found in Appendix 1. Ni(TMEDA)Me$_2$[28] was prepared according to literature procedures. All other materials used were purchased from Aldrich or Lancaster and used without further purification. Magnetic susceptibilities in the solid state were measured at room temperature using a Johnson-Matthey balance. Diamagnetic corrections were ignored.

(7.1) (1-(2,6-Diisopropylphenyl)-3-[2-(3-picolyl)]imidazol-2-ylidene)nickel dibromide

Ar = 2,6-dipp
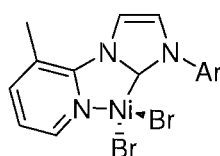
To a suspension of Ni(DME)Br$_2$ (0.15 g, 0.49 mmol) in THF (30 mL) at −78 °C, a solution of 1-(2,6-diisopropylphenyl)-3-[2-(3-picolyl)] imidazol- 2- ylidene (2.1b) (0.16 g, 0.49 mmol) in THF, pre-cooled to −78 °C, was added. The mixture was allowed to warm to r.t. and was stirred for 2 h. The resulting green solution was filtered and the solvent was then removed under vacuum. The green solid was crystallised from a THF solution layered with petroleum. Yield: 0.21 g (0.39 mmol), 80%.

Anal. Calcd for C$_{21}$H$_{25}$Br$_2$N$_3$Ni: C, 46.88, H, 4.68, N, 7.82% Found C, 46.6, H, 4.6, N, 7.5%.

μ_{eff} = 3.3 BM.

(7.2) (1-(2,6-Diisopropylphenyl)-3-[2-(3-picolyl)]imidazol-2-ylidene)dimethylnickel
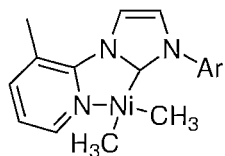
This was prepared in the same way as compound **7.1** using Ni(TMEDA)Me$_2$ (0.10 g, 0.49 mmol) and 1-(2,6-diisopropylphenyl)-3-[2-(3-picolyl)]imidazol-2-ylidene (**2.1b**) (0.16 g, 0.49 mmol). The purple solid was crystallised from a THF solution layered with petroleum. Yield: 0.17 g (0.41 mmol), 83%.

Ar = 2,6-dipp

Anal. Calcd for C$_{23}$H$_{31}$N$_3$Ni: C, 67.67, H, 7.65, N, 10.29% Found: C, 67.6, H, 7.7, N, 10.2%.

^{1}H NMR (300MHz, d_8-THF), δ: 8.85 (1H, d, J = 5.4 Hz, pyridyl C$\underline{H}$), 8.02 (1H, d, J = 2.1 Hz, imidazolium backbone C$\underline{H}$), 7.70 (1H, d, J = 7.5 Hz, aromatic C$\underline{H}$), 7.30 (1H, d, J = 2.1 Hz, imidazolium backbone C$\underline{H}$), 7.10 (4H, m, aromatic and pyridyl C$\underline{H}$), 2.75 (2H, sept., J = 6.9 Hz, 2 × C$\underline{H}$(CH$_3$)$_2$), 2.60 (3H, s, pyridyl C$\underline{H}_3$), 1.20 (6H, d, J = 6.9 Hz, CH(C$\underline{H}_3$)$_2$), 1.00 (6H, d, J = 6.9 Hz, CH(C$\underline{H}_3$)$_2$), –0.50 (3H, s, Ni-C$\underline{H}_3$), –0.75 (3H, s, Ni-C$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, d_8-THF), δ:191.99 (carbene $\underline{C}$–Ni), 149.88 (quaternary $\underline{C}$–N), 136.40 (quaternary aromatic $\underline{C}$–CH(CH$_3$)$_2$), 144.87, 138.42, 128.72, 125.24, and 122.85 (aromatic and pyridyl $\underline{C}$H), 120.61 and 115.60 (imidazolium backbone $\underline{C}$H), 46.05 (2 × $\underline{C}$H(CH$_3$)$_2$) 27.87 and 22.41 (2 × CH($\underline{C}$H$_3$)$_2$), 19.10 (pyridyl CH$_3$), 4.12 and 0.06 (2 × Ni-CH$_3$).

Polymerisation of norbornene

In a typical procedure, the nickel complex **7.1**, **7.1*** or **7.2** (0.20 μmol) and norbornene (1.88 g, 0.02 mol) were dissolved in chlorobenzene (9.0 mL) and were added into a flask (20 mL) with strong stirring under an inert atmosphere. After the mixture was kept at the desired temperature for 10 min, MAO (10% w/w in toluene, 1.0 mL) was charged into the polymerisation system *via* a syringe, and the reaction was started. After the required reaction time passed, acidified ethanol ($V_{methanol}$:$V_{concd\ HCl}$ = 20:1) was added to terminate the reaction. The polymer was isolated, washed with methanol, and dried at 80 °C for 48 h under vacuum. For all the polymerization procedures, the total reaction volume was 10.0 mL, which can be achieved by variation of the added chlorobenzene when necessary. Data for isolated polymers:

IR (KBr): 2943 (vs), 2866 (vs), 1470 (m), 1456 (s), 1378 (m), 1295 (m), 1257 (m), 1221 (m), 1150 (m), 1107 (m), 1040 (w), 941 (w), 898 (m) cm^{-1}.

^{1}H NMR (300MHz, C$_6$D$_5$Cl), δ: 1.3 (2H, m, $\underline{H}$-1), 1.8 (2H, m, $\underline{H}$-2), 2.1 (4H, m, $\underline{H}$-4), 2.6 (4H, m, $\underline{H}$-3).

$^{13}C\{^1H\}$ NMR (75 MHz, C_6D_5Cl), δ: 28.3 (m, $\underline{C}H$-1), 33.7 (m, $\underline{C}H$-2), 41.5 (m, $\underline{C}H_2$-4), 50.8 (m, $\underline{C}H_2$-3). (For numbering used, see Figure 7.4)

(7.3) *N,N'*-Bis(2,4,6-trimethoxyphenyl)ethylenediimine
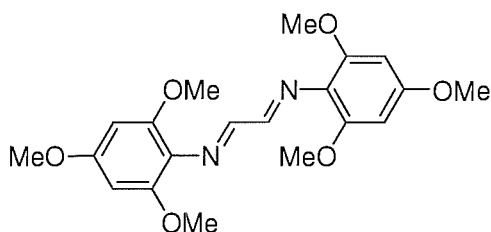
Glyoxal (0.39 g of 40% aq. solution, 2.5 mmol) was dissolved in a mixture of propan-2-ol (30 mL) and water (10 mL) and was slowly added to a solution of 2,4,6-trimethoxyaniline (1.0 g, 5.0 mmol) in propanol (100 mL). The mixture was stirred overnight. The resulting brown-yellow ppt was then filtered, washed with cold water and dried under vacuum. Yield: 0.7g (1.8 mol), 72%.

ES^+MS: m/z (%): 389.0 and 390.0 $[M+H]^+$.

HRMS (ES^+): calcd for $[C_{20}H_{24}N_2O_6]^+$: 388.1634, found: 388.1629.

^1H NMR (300MHz, $CDCl_3$), δ: 8.79 (2H, s, ethylene $C\underline{H}$), 6.16 (4H, s, aromatic $C\underline{H}$), 3.81 (12H, s, *o*-$OC\underline{H}_3$), 3.80 (6H, s, *p*-$OC\underline{H}_3$).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$), δ: 163.86 (ethylene $\underline{C}H$), 159.37 (quaternary $\underline{C}$–N), 154.24 and 121.80 (quaternary aromatic $\underline{C}$–OMe), 90.95 (aromatic $\underline{C}H$), 55.86 (*o*-$O\underline{C}H_3$), 55.28 (*p*-$O\underline{C}H_3$).

(7.4) *N,N'*-Bis(2,4,6-trimethoxyphenyl)ethylenediiminenickel dibromide

Ar = 2,4,6-trimethoxyphenyl
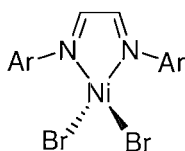
A suspension of $Ni(DME)Br_2$ (0.30 g, 0.96 mmol) in ether was mixed with a suspension of *N,N'*-bis(2,4,6-trimethoxyphenyl)ethylenediimine (**7.3**) (0.37 g, 0.96 mmol) in ether and the mixture was stirred at r.t. for 4 hrs. The solution turned dark orange and then the solvents were removed under vacuum. The dark orange air stable solid was crystallised from hot methanol. Yield: 0.49 g (0.83 mmol), 86%.

Anal. Calcd for $C_{20}H_{24}Br_2N_2NiO_6$: C, 39.58, H, 3.99, N, 4.62% Found C, 39.5, H, 3.9, N, 4.6%.

HRMS (ES^+): calcd for $[C_{20}H_{24}Br_2N_2NiO_6]^+$: 693.9355, found: 693.9366

μ_{eff} = 3.2 BM.

(7.5) Bis[*N,N'*-bis(2,4,6-trimethoxyphenyl)ethylenediimine]nickel
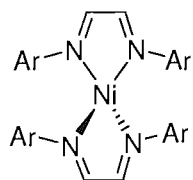
Ar = 2,4,6-trimethoxyphenyl

To an ether (15 mL) solution of Ni(TMEDA)Me$_2$ (0.15 g, 0.73 mmol) cooled to −78 °C, a pre-cooled (−78 °C) ether (15 mL) solution of *N,N'*-bis(2,4,6-trimethoxy-phenyl)ethylenediimine (**7.3**) (0.28 g, 0.73 mmol) was added. The reaction mixture was let to warm up to r.t. and stirred for 2 hrs. The solvents were removed and the solids were dissolved in THF. The mixture was stirred for 3 hrs and the resulting red solution had its volume reduced by evaporation under vacuum and was then layered with petroleum to yield dark red crystals. Yield: 0.26 g (0.31 mmol), 42%.

Anal. Calcd for C$_{40}$H$_{48}$N$_4$NiO$_{12}$: C, 57.50, H, 5.79, N, 6.71% Found C, 57.6, H, 5.8, N, 6.8%.

^{1}H NMR (300MHz, C$_6$D$_6$), δ:9.53 (2H, s, ethylene C$\underline{H}$), 6.07 (4H, s, aromatic C$\underline{H}$), 3.57 (6H, s, *p*-OC$\underline{H}_3$), 3.46 (12H, s, *o*-OC$\underline{H}_3$).

^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$), δ:166.32 (ethylene $\underline{C}$H), 160.71 (quaternary $\underline{C}$–N), 153.42 and 134.66 (quaternary aromatic $\underline{C}$–OMe), 110.53 (aromatic $\underline{C}$H), 53.51 (*p*-O$\underline{C}$H$_3$), 49.12(*o*-O$\underline{C}$H$_3$).

X-ray Crystallography

All data sets were collected on an Enraf-Nonius Kappa CCD area detector diffractometer with an FR591 rotating anode (Mo/Kα radiation) and an Oxford Cryosystems low temperature device operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. The programs used for control and integration were Collect, Scalepack, and Denzo.[29] The crystals were mounted on a glass fibre with silicon grease, from Fomblin vacuum oil. All solutions and refinements were performed using the WinGX package[30] and all software packages within. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogens were added using a riding model. Crystallographic data collected are presented in Table 7.2

	7.1	7.2	7.4	7.5
Chemical formula	$C_{21}H_{25}Br_2N_3Ni$	$C_{23}H_{31}N_3Ni$	$C_{20}H_{24}Br_2N_2NiO$	$C_{40}H_{48}N_4NiO_{12}$
Formula weight	537.97	408.22	606.92	835.53
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\,2/m$	$P\,2_1/c$	$C2/c$	$C2/c$
a / Å	9.0549(10)	10.458(2)	10.622(12)	20.641(4)
b / Å	17.381(3)	11.956(2)	17.793(9)	15.542(3)
c / Å	13.676(2)	16.957(6)	12.526(5)	14.494(3)
α / °	90	90	90	90
β / °	90.884(9)	106.10(2)	97.12(8)	122.91(3)
γ / °	90	90	90	90
V / Å³	2152.1(6)	2037.2(9)	2349(3)	3903.6(13)
Z	4	4	4	4
T / K	120(2)	120(2)	120(2)	120(2)
μ / mm⁻¹	4.625	0.965	4.266	0.566
No. data collected	21291	17771	19393	20620
No. unique data	4672	4700	2698	4462
R_{int}	0.1865	0.1020	0.0752	0.0428
Final $R(F1)$ for $F_o > 2\sigma(F_o)$	0.0590	0.0632	0.0502	0.0351
Final $R(F^2)$ for all data	0.1011	0.1186	0.1082	0.0820

Table 7.2: Crystallographic data for compounds **7.1**, **7.2**, **7.4**, and **7.5**

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Chapter 8:

Conclusions

8.1 Conclusions

Several new synthetic methods for preparing imidazolinium salts have been successfully developed. Using these new methodologies, four novel pyridyl functionalised imidazolinium salts, six novel alkoxyphenyl imidazolinium salts, two novel aryl substituted imidazolinium salts and three fluorinated aryl functionalised imidazolinium salts have been synthesised. In addition, three novel pyridyl functionalised imidazolium salts have been synthesised, using reported methodologies.[1] Deprotonation of two of the imidazolium salts lead to the isolation of their free carbenes.

In situ formed carbenes, derived from a series of the prepared imidazolinium salts, were reacted with palladium precursor complexes; while in other cases, the silver carbene (prepared by the reaction of an imidazolinium salt with silver (I) oxide) was reacted with palladium precursor complexes resulting in a mild transmetallation. As a result, five novel pyridyl functionalised imidazolin-2-ylidene complexes of palladium, three novel imidazolin-2-ylidene palladacycle complexes, four novel aryl substituted imidazolin-2-ylidene palladium complexes and two novel alkoxyphenyl imidazolin-2-ylidene palladacycle complexes have been synthesised and characterised. Interestingly, we have managed to isolate and characterise the first palladium 'C–C–C pincer' type complex (3.14) shown in figure 8.1. Plausible mechanisms for the formation of complex 3.14 and the alkoxyphenyl imidazolin-2-ylidene palladacycle complexes have been suggested.

(3.14)
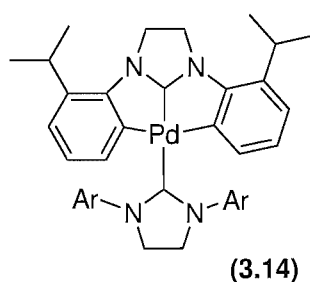
Figure 8.1: Palladium 'C–C–C pincer' type complex **3.14**

Ar = 2-isopropylphenyl

Selected palladium imidazolin-2-ylidene complexes have been tested as catalysts for Heck coupling reactions. [1,3-Bis(4-methoxyphenyl)imidazolin-2-ylidene]{2-[3-(4-methoxyphenyl)imidazolin-2-ylidene]-5-methoxyphenyl-$\kappa^2 C,C'$} methylpalladium(II) and [1,3-bis(2,4-dimethoxyphenyl)imidazolin-2-ylidene]]{2-[3-(2,4-dimethoxy phenyl)-

imidazolin-2-ylidene]-3,5-dimethoxyphenyl-$\kappa^2 C,C'$} methylpalladium(II) have been found to be excellent catalysts for the Heck couplings of aryl bromides, deactivated aryl bromides and activated aryl chlorides. Furthermore, moderate results for the Heck coupling of chlorobenzene have been achieved. These complexes surpass the activity of standard palladium phosphine complexes and are amongst the most active palladium NHC complexes reported to date.[2]

Five novel picolyl-functionalised imidazol-2-ylidene complexes of Rh(I) and Ir(I) have been prepared and characterised by the reaction of [M(COD)Cl]$_2$ (M = Rh, Ir) with 1-[2-(3-methyl)pyridyl]-3-[(2,6-diisopropyl)phenyl]imidazol-2-ylidene. When M = Rh the nature of the products was found to be dependent on the reactant ratio. Furthermore, one novel Ir(III) picolyl functionalised imidazolin-2-ylidene complex featuring a 1-κ-4,5,6-η-C$_8$H$_{12}$ moiety (**5.6**, Figure 8.2) has been synthesised by reacting [Ir(COD)Cl]$_2$ with, *in situ* formed, 1-[2-(3-picolyl)]-3-(2,6-diisopropylphenyl) imidazolin-2-ylidene. Such types of activations of the COD ligand have been reported in the past.[3] A plausible mechanism for the formation of this complex has been suggested.

(5.6)
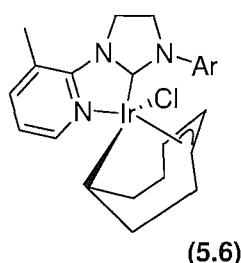
Figure 8.2: Iridium(III) picolyl functionalised imidazolin-2-ylidene complex **5.6**

Ar = 2,6-diisopropylphenyl

(Cycloocta -1,5- diene) -κ^2- {1-[2-(3-picolyl)] -3- (2,6-diisopropylphenyl) imidazol-2-ylidene}rhodium tetrakis-[3,5-bis(trifluoromethylphenyl)]borate and (cycloocta-1,5-diene)-κ^2-{1-[2-(3-picolyl)]-3-(2,6-diisopropylphenyl)imidazol-2-}iridium tetrakis-[3,5-bis(trifluoromethylphenyl)]borate have been extensively tested as catalysts in olefin hydroformylations, olefin molecular hydrogenations and transfer hydrogenation reactions of carbonyl compounds. The rhodium imidazol-2-ylidene complex was found to be a good catalyst in the hydroformylation of styrene, giving high activities and relatively good selectivities even at low catalyst loadings. The iridium imidazol-2-ylidene complex performed as an excellent catalyst for the hydrogenation (by transfer) of β-citronellal and

4-methoxybenzaldehyde giving activities of up to 3000 moles of converted substrate per mole of catalyst per hour. However, we were unable to determine if the pyridine functionality of the NHC ligand remained coordinated throughout the catalytic cycle or acted as a hemilabile ligand.

Finally, two novel picolyl functionalised imidazol-2-ylidene complexes of nickel have been synthesised by the reaction of nickel precursor complexes with 1-[2-(3-methyl)pyridyl]-3-[(2,6-diisopropyl)phenyl]imidazol-2-ylidene. These complexes show high activities for the vinyl-type polymerisation of norbornene with MAO used as co-catalyst. Furthermore, one novel diimine ligand (N,N'-bis(2,4,6-trimethoxyphenyl) ethylenediamine) has been synthesised. The diimine ligand has successfully displaced labile ligands from nickel precursor complexes to yield two novel nickel diimine complexes. Preliminary catalytic results indicated that these diimine complexes might be good catalysts for several reactions including ethylene polymerisation or other polymerisation reactions.

8.2 References

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Appendix 1:

Preparation of anilines

A.1.1 Preparation of alkoxy functionalised anilines
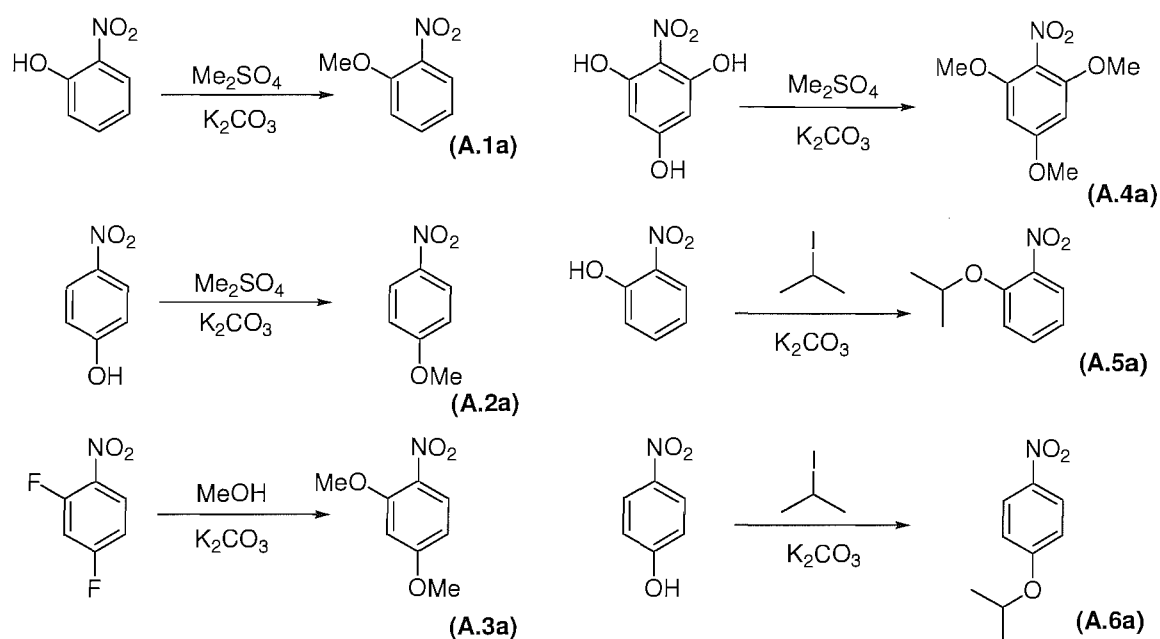
Scheme A.1: Preparation of aniline precursors **A.1a** – **A.6a**

Based on a reported method [1] compounds **A.1a**, **A.2a** and **A.4a** were synthesised by heating the corresponding nitro-phenols with Me_2SO_4 in the presence of K_2CO_3 as a base. Similarly compound **A.3a** was prepared by refluxing 2,4-difluoronitrobenzene and methanol in the presence of a base. Compounds **A.5a** and **A.6a** were synthesised by stirring the nitro-phenols at room temperature with 2-iodopropane and excess of base. No heating was required for this reaction because of the high reactivity of 2-iodopropane.

R_1 = MeO R_2 = H R_3 = H	(A.1a)	R_1 = MeO R_2 = H R_3 = H	(A.1b)
R_1 = H R_2 = MeO R_3 = H	(A.2a)	R_1 = H R_2 = MeO R_3 = H	(A.2b)
R_1 = MeO R_2 = MeO R_3 = H	(A.3a)	R_1 = MeO R_2 = MeO R_3 = H	(A.3b)
R_1 = MeO R_2 = MeO R_3 = MeO	(A.4a)	R_1 = MeO R_2 = MeO R_3 = MeO	(A.4b)
R_1 = ^{i}PrO R_2 = H R_3 = H	(A.5a)	R_1 = ^{i}PrO R_2 = H R_3 = H	(A.5b)
R_1 = H R_2 = ^{i}PrO R_3 = H	(A.6a)	R_1 = H R_2 = ^{i}PrO R_3 = H	(A.6b)
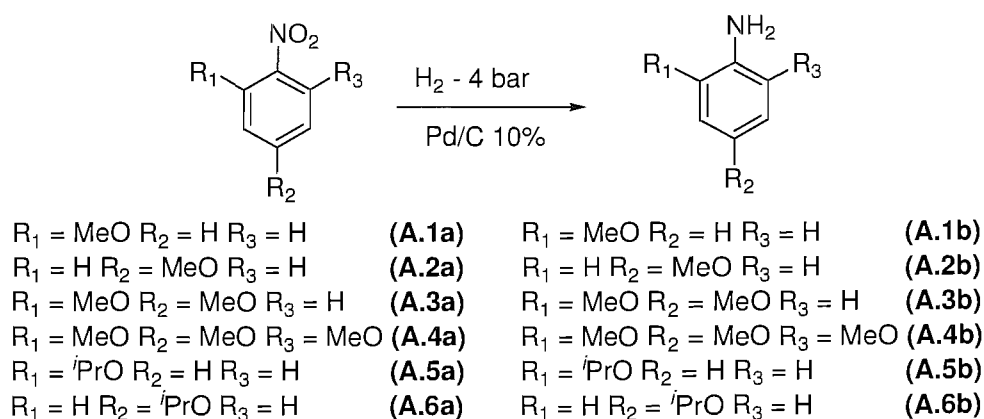
Scheme A.2: Preparation of anilines **A.1b** – **A.6b**

All anilines (**A.1b** – **A.6b**) were prepared by the hydrogenation[2] of the corresponding nitro-compound by using molecular hydrogen at 4 bar pressure in the presence of 10% palladium/carbon as a catalyst. All hydrogenations proceed almost quantitatively.

A.1.2 Experimental Details

(A.1a) 2-methoxynitrobenzene

2-nitrophenol (8.34 g, 60 mmol), Na_2CO_3 (12.5 g) and dimethyl sulphate (150 mL) were heated at 125°C for 45 min. The resulting liquid was poured in cold water and was made alkaline with NaOH (aq.). It was then heated just below its boiling point. After cooling to rt, the mixture was treated with ether (2 x 40 mL) and the ether layers were collected, washed with brine and dried over Na_2SO_4. The solvent was removed under vacuum to get a yellow oil. Yield 8.0g (52.2 mmol), 87%. All data in agreement with published [1] data.

ES^+MS: m/z (%):154.1 and 155.1 $[M+H]^+$

NMR ($CDCl_3$), ^1H, δ 7.81 (1H, d, J= 8.1 Hz, o-C$\underline{H}$), 7.53 (1H, m, m-C$\underline{H}$), 7.03 (2H, m, p-C$\underline{H}$), 3.94 (3H, s, O-C$\underline{H}_3$).

NMR ($CDCl_3$), $^{13}C\{^1H\}$, δ 152.87 (quat. $\underline{C}$-NO_2), 137.49 (quat. $\underline{C}$-OMe), 134.14, 125.54, 120.19 and 113.47 (aromatic $\underline{C}$H), 56.40 (O-$\underline{C}H_3$).

(A.2a) 4-methoxynitrobenzene

This was prepared in exactly the same way as compound **A.1a** using 4-nitrophenol (8.34 g, 60 mmol) to get a light grey solid. Yield 7.6g (49.8 mmol), 83%. All data in agreement with published [1] data.

ES^+MS: m/z (%):154.0 and 155.0 $[M+H]^+$

NMR ($CDCl_3$), ^1H, δ 8.19 (2H, d, J= 9.3 Hz, aromatic C$\underline{H}$), 6.94 (2H, d, J= 9.3 Hz, aromatic C$\underline{H}$), 3.90 (3H, s, O-C$\underline{H}_3$).

NMR ($CDCl_3$), $^{13}C\{^1H\}$, δ 164.56 (quat. $\underline{C}$-NO_2), 141.52 (quat. $\underline{C}$-OMe), 125.84, and 113.97 (aromatic $\underline{C}$H), 55.91 (O-$\underline{C}H_3$).

(A.3a) 2,4-dimethoxynitrobenzene

2,4-difluoronitrobenzene (4.65 g, 30.0 mmol), Na_2CO_3 (12.5 g) and MeOH (150 mL) were refluxed overnight. After cooling to r.t. the solvent was removed under vacuum. The solids were dissolved in water (200 mL) and were treated with ethyl acetate (3 x 50 mL). The organic layers were combined, washed with NaOH (50 mL, 4M solution), $NaHCO_3$ (50 mL, saturated solution) and then brine (50 mL). The organic layer was

collected and dried over Na_2SO_4. Solvents were removed to get a solid that was re-crystallised from ether to get light yellow crystals. Yield 4.23g (23.1 mmol), 77%.

All data in agreement with published [1] data.

ES^+MS: m/z (%):184.2 and 185.2 $[M+H]^+$

NMR (CDCl$_3$), ^{1}H, δ 7.96 (1H, d, J= 9.0 Hz, o-C$\underline{H}$), 6.51 (1H, s, m-C$\underline{H}$), 6.47 (1H, d, J= 2.9 Hz, m-C$\underline{H}$), 3.93 (3H, s, O-C$\underline{H}_3$), 3.87 (3H, s, O-C$\underline{H}_3$).

NMR (CDCl$_3$), ^{13}C{^{1}H}, δ 164.76 (quat. $\underline{C}$-NO$_2$), 155.62 and 132.84 (quat. $\underline{C}$-OMe), 128.35, 104.74, and 99.55 (aromatic $\underline{C}$H), 56.39 and 55.85 (O-$\underline{C}$H$_3$).

(A.4a) 2,4,6-trimethoxynitrobenzene

Nitrophloroglucinol [1] (5 g, 33 mmol), Na$_2$CO$_3$ (12.5 g) and dimethyl sulphate (100 mL) were heated at 125°C for 45 min. The resulting liquid was poured in cold water and was made alkaline with NaOH (aq.). It was then heated just below its boiling point. After cooling to rt, the ppt was filtered and treated with acetone in order to collect the ether. The orange-yellow compound was recrystallised from hot methanol. Yield 3.3g (15.4 mmol), 47%. All data in agreement with reported [3] data.

(A.5a) 2-isopropoxynitrobenzene

This was prepared by following the reported method. [4] Yield 4.5g (24.8 mmol), 82%. All data in agreement with published [4] data.

(A.6a) 4-isopropoxynitrobenzene

Prepared by following the same procedure as with compound **A.5a** but using 4-nitrophenol (16.8 g, 0.12 mol). Yield 18.26g (0.10 mmol), 84%. All data in agreement with published [4] data.

ES^+MS: m/z (%):181.1 and 182.1 $[M+H]^+$

NMR (CDCl$_3$), ^{1}H, δ 8.12 (2H, d, J= 9.3 Hz, C$\underline{H}$ aromatic), 6.88 (2H, d, J= 9.3 Hz, C$\underline{H}$ aromatic), 4.64 (1H, septet, J= 6.0 Hz, C$\underline{H}$(CH$_3$)$_2$), 1.35 (6H, d, J= 6.0 Hz, CH(C$\underline{H}_3$)$_2$).

NMR (CDCl$_3$), ^{13}C{^{1}H}, δ 163.12 (quaternary $\underline{C}$-NO$_2$), 140.89 (quaternary $\underline{C}$-O^{i}Pr), 125.76 and 115.09 (aromatic $\underline{C}$H), 70.87 ($\underline{C}$H(CH$_3$)$_2$), 21.64 (CH($\underline{C}$H$_3$)$_2$).

(A.1b) 2-methoxyaniline

2-methoxynitrobenzene (2.75 g, 18.0 mmol) was dissolved in ethanol (150 mL) in a pressure vessel. To this Pd/C 10% (500mg) was added. The vessel was pressurised at 2 bar with hydrogen gas and was stirred overnight. The resulting mixture was filtered

through celite and the solvent was removed. The resulting light yellow oil was dried under vacuum. Yield 2.05 g (16.7 mmol), 93%. All data in agreement with published [1] data.

ES^+MS: m/z (%):124.2 and 125.2 $[M+H]^+$

NMR ($CDCl_3$), ^1H, δ 6.80(4H, m, aromatic C$\underline{H}$), 3.87 (3H, s, O-C$\underline{H}_3$), 3.79 (2H, br.s, -N$\underline{H}_2$).

NMR ($CDCl_3$), $^{13}C\{^1H\}$, δ 147.06 (quaternary $\underline{C}$-NH$_2$), 136.02 (quaternary $\underline{C}$-OMe), 120.84, 118.10, 114.75 and 110.24 (4 x aromatic $\underline{C}$H), 55.12 (O$\underline{C}$H$_3$).

(A.2b) 4-methoxyaniline

This was prepared in exactly the same way as compound **A.1b** using 4-methoxy-nitrobenzene **A.2a** (2.75 g, 18.0 mmol) to get a light yellow oil. Yield 2.01g (16.4 mmol), 91%. All data in agreement with published [1] data.

ES^+MS: m/z (%):124.1 and 125.1 $[M+H]^+$

NMR ($CDCl_3$), ^1H, δ 6.74 (2H, d, J= 9 Hz, C$\underline{H}$ aromatics), 6.65 (2H, d, J= 9 Hz, C$\underline{H}$ aromatics), 3.74 (3H, s, -OC$\underline{H}_3$), 3.44 (2H, br.s, -N$\underline{H}_2$).

NMR ($CDCl_3$), $^{13}C\{^1H\}$, δ 152.88 (quaternary $\underline{C}$-NH$_2$), 139.78 (quaternary $\underline{C}$-OMe), 116.46 and 114.82 ($\underline{C}$H aromatic), 55.72 (O$\underline{C}$H$_3$).

(A.3b) 2,4-dimethoxyaniline

This was prepared in exactly the same way as compound **A.1b** using 2,4-di-methoxy-nitrobenzene **A.3a** (5 g, 27.3 mmol) to get a light yellow oil. Yield 3.63g (15.4 mmol), 87% All data in agreement with reported data. [2]

ES^+MS: m/z (%):154.2 and 155.2 $[M+H]^+$

NMR ($CDCl_3$), ^1H, δ 6.63 (1H, d, J= 8.4 Hz, *m*-C$\underline{H}$ aromatic), 6.46 (1H, d, J= 2.4 Hz, *o*-C$\underline{H}$ aromatic), 6.35 (1H, dd, J= 2.4, 8.4 Hz, *m*-C$\underline{H}$ aromatic), 3.82 (3H, s, -OC$\underline{H}_3$), 3.75 (3H, s, -OC$\underline{H}_3$), 3.55 (2H, br.s, -N$\underline{H}_2$).

NMR ($CDCl_3$), $^{13}C\{^1H\}$, δ 153.02 (quaternary $\underline{C}$-NH$_2$), 148.24 (quaternary $\underline{C}$-OMe), 129.72 (quaternary $\underline{C}$-OMe), 115.10, 104.17 and 99.30 ($\underline{C}$H aromatic), 55.65 (O$\underline{C}$H$_3$), 55.36 (O$\underline{C}$H$_3$).

(A.4b) 2,4,6-trimethoxyaniline

2,4,6-trimethoxynitrobenzene [1] (**A.4a**) (2.5 g, 11.6 mmol) was dissolved in ethanol (150 mL) in a pressure vessel. To this Pd/C 10% (500mg) was added. The vessel was pressurised at 2 bar with hydrogen gas and was stirred overnight. The resulting mixture

was filtered through celite and the solvent was removed. The resulting brown oil was dried under vacuum. Yield 1.8 g (10 mmol), 86%.

All data in agreement with reported data. [2]

(A.5b) 2-isopropoxyaniline

This was prepared in exactly the same way as compound **A.1b** using 2-isopropoxynitrobenzene **A.5a** (5 g, 27.6 mmol) to get light yellow oil. Yield 3.67 g (24.3 mmol), 88%. All data in agreement with reported data.[4]

(A.6b) 4-isopropoxyaniline

This was prepared in exactly the same way as compound **A.1b** using 4-isopropoxynitrobenzene **A.6a** (5 g, 27.6 mmol) to get a light yellow oil. Yield 3.63g (24.0 mmol), 87%. All data in agreement with reported data.[4]

ES^+MS: m/z (%):152.2 and 153.2 $[M+H]^+$

NMR ($CDCl_3$), ^1H, δ 6.72 (2H, d, J= 9.0 Hz, aromatic C$\underline{H}$), 6.60 (2H, d, J= 9.0 Hz, aromatic C$\underline{H}$), 4.35 (1H, septet, J= 6.0 Hz, C$\underline{H}$(CH_3)$_2$), 3.43 (2H, br.s, -N$\underline{H}_2$), 1.28 (6H, d, J= 6.0 Hz, CH(C$\underline{H}_3$)$_2$).

NMR ($CDCl_3$), $^{13}C\{^1H\}$, δ 150.63 (quaternary $\underline{C}$-NH_2), 140.16 (quaternary $\underline{C}$-O^{i}Pr), 117.76 and 116.17 (aromatic $\underline{C}$H), 70.94 ($\underline{C}$H(CH_3)$_2$), 22.05 (CH(C$\underline{H}_3$)$_2$).

A.1.3 References

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Appendix 2:

General Information

A.2.1 General Information

General Considerations

All manipulations were carried under nitrogen in a Braun glovebox or by using standard Schlenk techniques unless otherwise stated. Solvents used were dried using standard techniques (THF, Et_2O, C_6H_6, dioxane and petroleum ether spirits over sodium-ketyl; toluene over Na; CH_2Cl_2 over CaH_2; C_6H_5Cl and CH_3CN over P_2O_5; pyridine over K; DMF over $MgSO_4$) and distilled under nitrogen prior to use or stored in ampoules fitted with Youngs' taps over molecular sieves ($4\mathring{A}$) under a nitrogen atmosphere. Petroleum ether had a boiling point 40-60 °C throughout unless otherwise stated. $BH_3{\cdot}DMS$, n-BuLi (2.5 M in hexanes) and MeLi (3 M in diethyl ether) were purchased from Aldrich and were stored in an ampoule fitted with Youngs tap at 5 °C under a nitrogen atmosphere. $KN(SiMe_3)_2$ was prepared by reacting KH and $NH(SiMe_3)_2$ in refluxing toluene under nitrogen and was kept in the glovebox.

Deuterated solvents were degassed by three freeze-thaw-pump cycles and were dried as follows: d_8-THF, C_6D_6 and d_8-toluene over Na/K, d_5-py over K, CD_2Cl_2 and CD_3CN over CaH_2, $CDCl_3$ was stirred overnight over molecular sieves ($4\mathring{A}$), d_5-PhCl over P_2O_5. The solvents were separated from the drying agent by vacuum distillation under a static vacuum and were stored in the glovebox in ampoules fitted with Youngs' taps over molecular sieves ($4\mathring{A}$).

Elemental analyses were carried by the University College, London microanalytical laboratory.

Instrumentation

^{1}H-NMR spectra were recorded on Bruker AM-300 or Bruker AV-300 spectrometers.

$^{13}C\{^1H\}$-NMR spectra were recorded on a Bruker AC-300 or Bruker AV-300 or Bruker DPX-400 spectrometers.

$^{19}F\{^1H\}$-NMR spectra were recorded on a Bruker AC-300 or Bruker AV-300 spectrometer.

^{1}H-NMR and $^{13}C\{^1H\}$-NMR spectra were referenced internally from the residual protio solvent (^{1}H) or the signals of the solvent (^{13}C).

$^{19}F\{^1H\}$-NMR spectra were referenced externally relative to either C_6F_6 (positive δ values in this manuscript) or $CFCl_3$ (negative δ values in this manuscript).

Mass spectra were recorded on electrospray mode (positive or negative), unless otherwise stated, on a VG Biotech Platform.

Gas chromatographs were obtained from a Varian 3400GC fitted with a Varian 8100 auto-sampler, equipped with a flame ionisation detector, fitted with a J&W Scientific column (Phase: DBWAX) and linked to a Hewlett-Packard 3396 Series 2 integrator.

Magnetic susceptibilities in the solid state were measured at room temperature using a Johnson-Matthey balance. Diamagnetic corrections were ignored.

X-ray Crystallography

All data sets were collected on an Enraf-Nonius Kappa CCD area detector diffractometer with an FR591 rotating anode (Mo/Kα radiation) and an Oxford Cryosystems low temperature device operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. The programs used for control and integration were Collect, Scalepack, and Denzo.[1] The crystals were mounted on a glass fibre with silicon grease, from Fomblin vacuum oil. All solutions and refinements were performed using the WinGX package[2] and all software packages within. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogens were added using a riding model. Crystallographic data are presented in tables in the experimental part of each chapter.

A.2.2 References

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