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# Hybrid Phosphine-Carbene Ligands and their use in Homogeneous Catalysis

by

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The work described in this thesis was carried out in the Department of Chemistry at The University of Wales Cardiff under the supervision of Prof. Kingsley J. Cavell and Prof. Peter G. Edwards

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# Abstract

Several chelating phosphine-imidazolium salts have been synthesised and their activity tested in a number of palladium catalysed cross-coupling reactions. The *in-situ* catalyst testing was carried out using parallel screening techniques and moderate catalytic activity was shown by phosphine-imidazolium salts **2**, **6** and **16**.

A number of synthetic routes have been successfully established which have provided viable paths into three main types of phosphine functionalised imidazolium salts. These methodologies have increased the scope for the potential number of interesting chelating phosphine-imidazolium salts.

Several group 10 complexes of these new ligands have been prepared and characterised by the reaction of functionalised nucleophilic heterocyclic carbene's (NHC's), which were generated *in-situ* and reacted with suitable metal precursors. The solid state structure of complex **1** has been obtained, giving an insight into the properties of these chelating ligands. The relative *trans* influence of the phosphine and carbene functions have been measured for this bidentate ligand. Following the results of the *in-situ* catalyst testing, two pre-formed palladium(II) complexes, **1** and **2**, were tested in the Heck and Suzuki cross-coupling with the reaction performed under stricter anaerobic conditions with more favourable results. The synthesis of several silver(I) complexes was also achieved by the reaction of phosphine-imidazolium salts with $Ag_2O$. The preparation of a Rh(I) phosphine-NHC complex was achieved via transmetallation.

# Contents

# Acknowledgements

Many thanks have to go to my supervisors Professor Kingley Cavell and Professor Peter Edwards for excellent supervision and advice throughout the course of this work. I am very grateful for the patience and understanding they showed me after my unscheduled break in my final year. Thanks also to Woody for help and ideas in more practical aspects of my work.

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# Glossary

| | |
|---|---|
| $BARF^-$ | $B[3,5\text{-}(CF_3)C_6H_3]_4^-$ |
| br | Broad (NMR) |
| BQ | 1,4-benzoquinone |
| COD | 1, 5-cyclooctadiene |
| dba | Dibenzylidineacetone |
| DCM | Dichloromethane |
| DMAc | N,N-dimethylacetamide |
| DMF | N,N-dimethylformamide |
| DMSO | Dimethylsulfoxide |
| dipp | 2,6-bis(diisopropyl)phenyl |
| $Et_2O$ | Diethyl ether |
| GC | Gas chromatography |
| JM | Johnson-Matthey |
| L | Neutral, 2 electron donor ligand, e.g. phosphine or carbene |
| M | Metal |
| Me | Methyl |
| Mes | Mesityl or 2,4,6-trimethylphenyl |
| NHC | N-heterocyclic carbene |
| OAc | Acetate anion |
| Ph | Phenyl |
| r.t. | Room temperature |
| THF | Tetrahydrofuran |
| TCT | 2,4,6-trichlorol[1,3,5]triazine |
| X | Anionic Ligand e.g. Halogen |

# CHAPTER ONE

# Introduction

## 1.1: Phosphorus ligands

### 1.1.1: General properties of phosphines

Tertiary phosphines ($PR_3$) have many properties which make them desirable as ligands. They readily coordinate to a large range of transition metals in a variety of oxidation states. One of their most useful characteristics is the ability to act as both π-acids as well as σ-bases therefore assisting the stabilisation of metals in low oxidation states. A phosphine-metal bond can be considered to consist of two components, σ and π. The σ-bond character (P→M) of the phosphine bond comes from σ donation of the lone pair of electrons on the phosphorus to an empty orbital of the metal, and the π-bond character (M→P) is derived from back-donation to the empty orbitals on the phosphine from the filled metal d-orbitals. This back donation is postulated to be either to the empty d-orbitals on the phosphorus atom[1] or to a σ* antibonding molecular orbital on the phosphine (figure 1.1).[2-5]

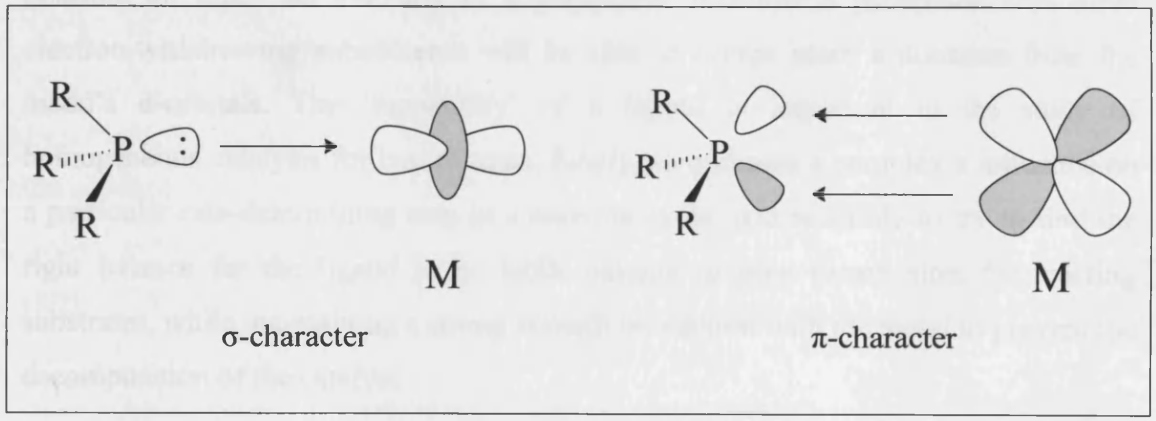



Figure 1.1

The electronic influence on the 'strength of σ-bond' depends mainly on the Lewis acidity of the metal; the more electropositive metals form stronger σ-bonds. However, for each individual phosphine the σ-bonding ability is governed by the electron affinity of its substituents. The σ basicity of a phosphine, which is formally a measure of Brønsted basicity or proton affinity, is usually measured as the $pK_a$ of the conjugate acid (the phosphonium salt). The $pK_a$ values of a few common phosphines are quoted in table 1.2.[6]

| Phosphine | $pK_a$ |
|---|---|
| $P(4\text{-}F\text{-}C_6H_4)_3$ | 1.97 |
| $PPh_3$ | 2.73 |
| $PMeEt_2$ | 8.61 |
| $PCy_3$ | 9.70 |
| $P^tBu_3$ | 11.40 |

Table 1.2: $pK_a$ values of selected phosphonium salts

This is not actually a true reflection of their net donor characteristics as the π acceptor nature of the phosphine is not taken into account. The π-acidity of a phosphine can be increased by replacing the R groups on the phosphine with more electron withdrawing groups. The opposite is true for donating groups which makes it possible to 'tune' the π-acidity of a phosphine, therefore a phosphine with more electron-withdrawing substituents will be able to accept more π-donation from the metal's d-orbitals. The 'tuneability' of a ligand is important in the study of homogeneous catalysis for two reasons. Firstly, to optimise a complex's influence on a particular rate-determining step in a reaction cycle, and secondly to try to find the right balance for the ligand to be labile enough to give vacant sites for reacting substrates, while maintaining a strong enough interaction with the metal to prevent the decomposition of the catalyst.

The relative π-acidity of a phosphine can also be measured by the influence it has on other (particularly π accepting) coligands. Phosphines which accept more electron density from the metal d-orbitals thereby lessen the amount of back donation that is possible to the other ligands bonded to the same metal (figure 1.3).[2-5]

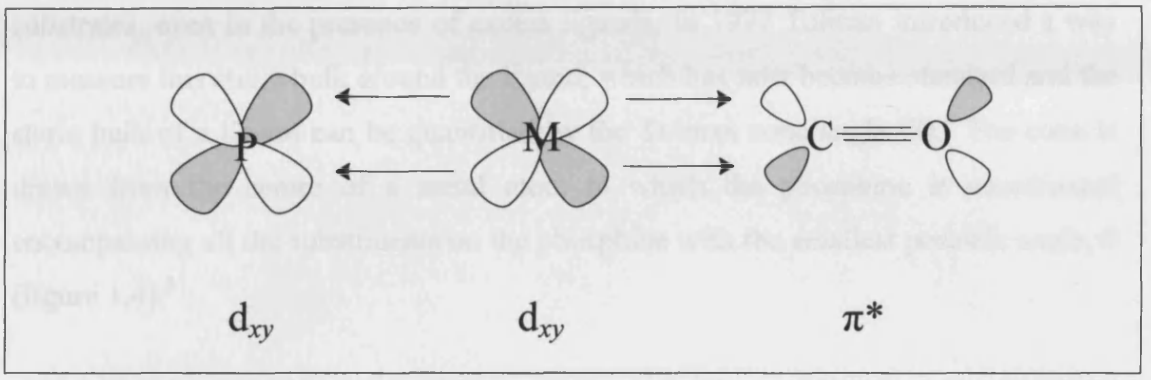



Figure 1.3

This effect has been quantified where carbon monoxide is the ligand trans to the phosphine; since accepting electron density from the metal acts to weaken the C-O bond, due to fact that the π-accepter character of CO is an antibonding orbital (C-O π*).[7] The strength of the C-O bond can be measured directly by infra-red spectroscopy, thus the greater the back-bonding to the phosphine, the less the back-bonding to the CO and the stronger the C-O bond, hence the higher the value of $\nu_{max}$ $cm^{-1}$. It was Tolman who first suggested a way of measuring this by making complexes with different phosphines and CO.[7] He achieved this by preparing a range of $Ni(CO)_3(PR)_3$ and measuring the $\nu_{max}$ $cm^{-1}$ of the *trans* CO. Given these measurements he set $Ni(CO)_3P(^tBu)_3$ complexes as the standard, and calculated $\chi$ – the incremental increase in $cm^{-1}$ that each individual R group contributes to the overall measured increase in $\nu_{max}$ $cm^{-1}$ from the standard. Thus, from this empirical series it is possible to calculate the electronic effect $\nu_{max}$ in $cm^{-1}$ of $PR_1R_2R_3$ in an additive manner using the $\chi$ for each individual R group.

Although the electronic influences in these systems are significant, steric properties of these ligands may have a greater effect on the activity and properties of

the resultant metal complexes. Some tertiary phosphines are bulky and can therefore stabilise coordinatively unsaturated complexes simply because of their size. The bulky phosphines do not allow enough space around the metal for it to achieve its electronically desired coordination number by coordinating additional phosphine ligands. During catalysis this leaves a free coordination sites for the reacting substrates, even in the presence of excess ligands. In 1977 Tolman introduced a way to measure this steric bulk around the ligand, which has now become standard and the steric bulk of a ligand can be quantified by the Tolman cone angle (θ).[8] The cone is drawn from the centre of a metal atom to which the phosphine is coordinated encompassing all the substituents on the phosphine with the smallest possible angle, θ (figure 1.4).[8]

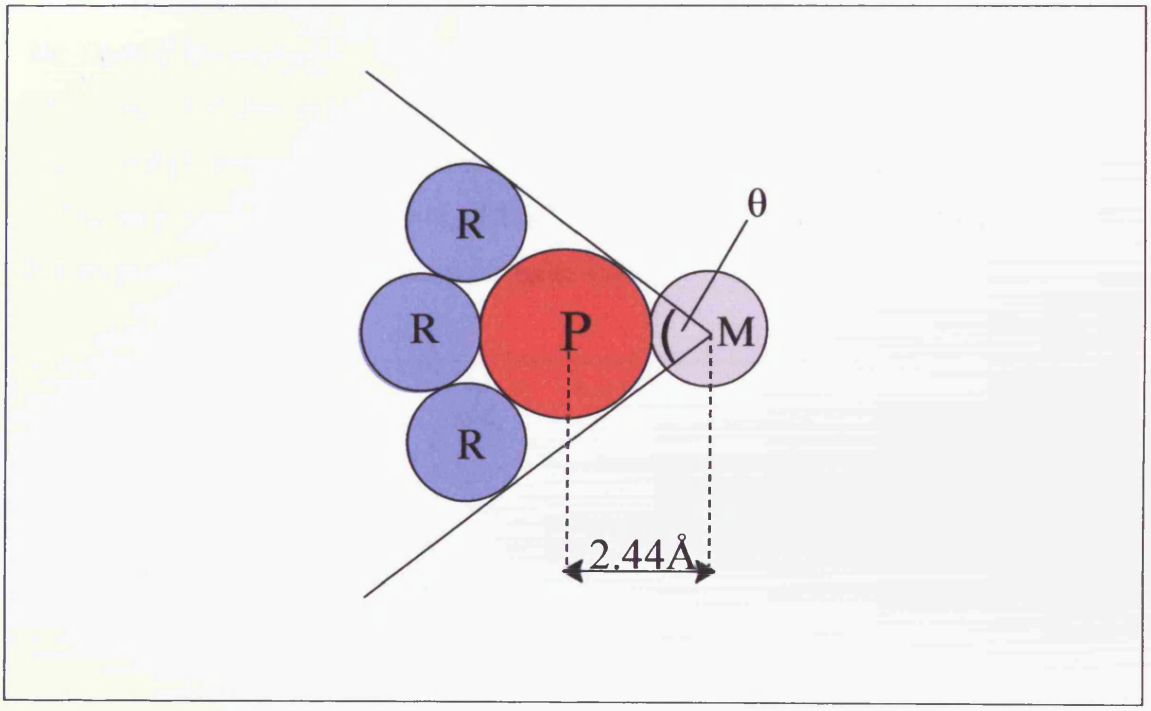



Figure 1.4: Tolman cone angle, θ.

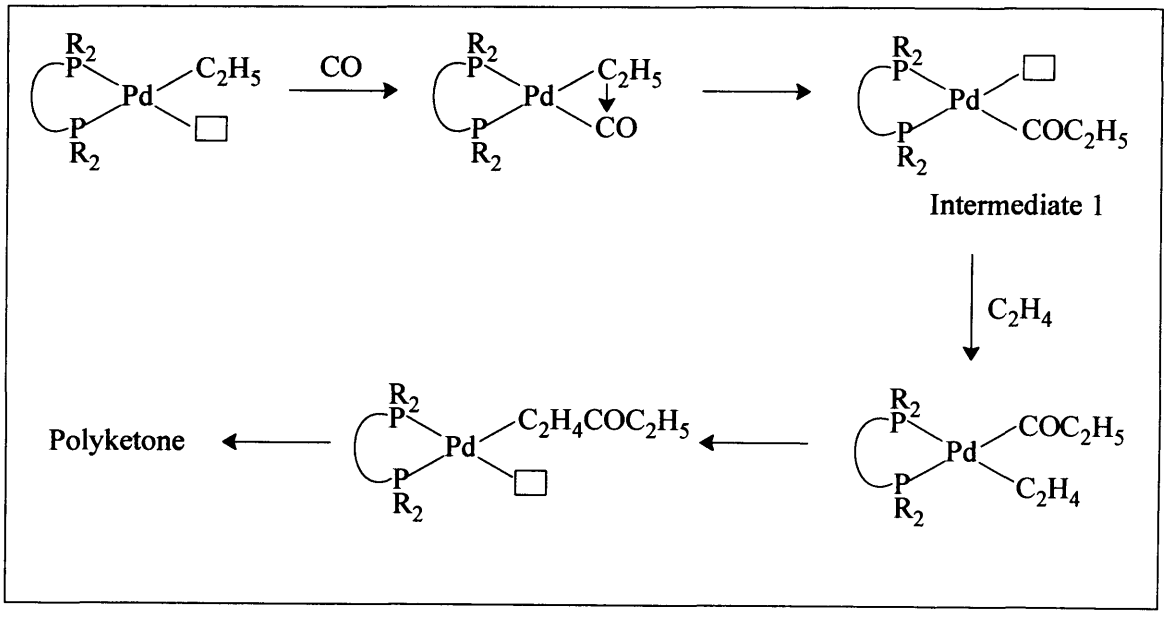
## 1.1.2: Monodentate versus bidentate phosphines

Replacing a monodentate phosphine with a chelating phosphine can alter the range of products and their distribution in some catalytic cycles. In general terms the chelate effect refers to the increased stability of a complex system containing a chelate ring, in comparison to the stability of the same system that has no chelate ring.[9] This is shown in the following examples of equilibrium constants:

$Ni^{2+}$ (aq) + $6NH_3$ (aq) = $[Ni(NH_3)_6]^{2+}$ (aq) $\quad\quad$ log β = 8.61

$Ni^{2+}$ (aq) + 3en (aq) = $[Ni\ en_3]^{2+}$ (aq) $\quad\quad$ log β = 18.28

The complex $[Ni\ en_3]^{2+}$ (en = ethylenediamine) in which three chelate rings are formed is nearly $10^{10}$ times as stable as that in which there is no chelate ring.[9] Drent reported that in the palladium catalysed co-polymerisation of ethene and CO only methyl propionate is formed with monodentate phosphines, whilst with a bidentate phosphine co-polymer, $(CH_2CH_2CO)_n$, is formed.[10,11] He explained this by his proposed catalytic mechanism (scheme 1.5).




Scheme 1.5: Drent's proposed mechanism of co-polymerisation.

Drent proposed that the key intermediate in this mechanism is the palladium acyl species (intermediate 1), which can either chain terminate via methanolysis to give methyl propionate or insert further ethene and CO to form a chain growth co-polymer. When the ligands are mono-phosphines the organic acyl fragment and the vacant coordination site can be *trans* to each other and therefore insertion of ethene is not favoured and methyl propionate was the major product observed. Drent postulated that the sterically bulky monodentate phosphine is the reason that *trans* complexes are formed. When the ligand is a bidentate phosphine, however, the organic acyl fragment and the vacant coordination site are forced to occupy *cis* positions in the square planar palladium(II) complex, making insertion and chain growth more viable.

### 1.1.3: The effect of bridge length of bidentate phosphines on selectivity

Drent also showed how changing the phosphine bridge length of the chelate made a significant difference to the reaction rate and the polymer chain length in the catalytic co-polymerisation of ethene and CO (table 1.6).[10,11]

| Phosphine | N | Reaction rate |
|---|---|---|
| $Ph_2PCH_2PPh_2$ | 2 | 1 |
| $Ph_2P(CH_2)_2PPh_2$ | 100 | 1000 |
| $Ph_2P(CH_2)_3PPh_2$ | 180 | 6000 |
| $Ph_2P(CH_2)_4PPh_2$ | 45 | 2300 |
| $Ph_2P(CH_2)_5PPh_2$ | 6 | 1800 |
| $Ph_2P(CH_2)_6PPh_2$ | 2 | 5 |

Table 1.6: Effects of chelate length.

(N is the number of ethene/CO monomers in a polymer of the general formula $CH_2CH_2CO_n$. The reaction rate is measured in $g_{product}/g_{Pd}/hr$).

The length of the chelate chain has a clear effect on both the rate of reaction and molecular weight of the polymer formed, with 1,3-bis(diphenylphosphine) propane being the optimum. The bridge length in this ligand seems to make the most of the stabilizing chelate effect; ligands with short bridges are too strained to be effective chelates and ligands with long bridges are too floppy and dissociate too easily.

## 1.1.4: The effect of bite angle

The geometry around the metal centre can be affected by the bite angle of the bidentate ligands at the metal centre. Van Leeuwen *et al.* discovered that a chelating phosphine with a bite angle of around $110^{o}$ increased the yield of the desired product in the nickel catalysed hydrocyanation of alkenes. The bidentate phosphine enforced a shape change from the square planar nickel(II) complex to the tetrahedral nickel(0) during the rate determining step of the reaction.[12]

## 1.1.5: General properties of phosphites

Tertiary phosphite ligands $P(OR)_3$, like phosphines, have many properties which make them desirable as ligands. One of the more important properties is the ability to act as both π-acids as well as σ-bases, thereby assisting the stabilisation of metals in low oxidation states. Phosphites are better π-acids than phosphines and therefore are more able to accept electron density from the metal centre, which can be very important in catalytic cycles. Phosphite ligands are extremely attractive for catalysis because they are easy to prepare from readily available alcohols and they are less sensitive to air and other oxidising agents than phosphines. Additionally, in contrast to traditional phosphines, the steric coordination environment around the phosphorus atom in phosphites is widely variable, providing further opportunities for the fine-tuning of ligand structure.[13-17]

# 1.2: The coordination chemistry of group 10 metals

The oxidation states of group 10 metals can lie between –I to VI. The lower oxidation states are more stable for nickel and the higher oxidation states are usually more viable for platinum. Although palladium can form both high and low oxidation state complexes, the more stable complexes lie between the two extremes.

## 1.2.1: High oxidation state complexes

The only oxidation states above (IV) in group 10 are the platinum fluoro and oxofluoro complexes. Platinum(V) pentafluoride and platinum(VI) hexafluoride are formed in the presence of fluorine gas with hot Pt metal. $PtF_6$ is one of the strongest oxidising agents.[9] Platinum(IV) complexes are well known[9] and include organometallic complexes such as $[Me_3PtCl]_4$, amine complexes $Pt(NH_3)_6^{4+}$ and halides $PtCl_6^{2-}$. Palladium(IV) complexes however were less common until the 1980s, limited to mono- and bis(pentafluorophenyl) derivatives.[18,19] But over the last twenty-five years Canty and others have synthesised and studied a large range of Pd(IV) complexes.[20-23] Nickel forms $K_2NiF_6$ which is a strong enough oxidising agent to liberate $O_2$ from water.

## 1.2.2: Phosphine complexes in the +II oxidation state

The +II oxidation state is by far the most common for all three Pt group metals. There is an abundance of such complexes in the literature. The electronic configuration of these (Pt(II), Pd(II), and Ni(II)) complexes is $d^8$ and they are typically square planar. Unlike platinum and palladium, square planar nickel has a tendency to add a further ligand to give 5-coordinate complexes.[9] Thus, ligand exchange processes in platinum and palladium often follow a dissociative mechanism whereas nickel tends to follow associative mechanisms, and nickel is capable of forming complexes with a wide range of geometries and coordination numbers. The

crystal field stabilisation energies for the various possible geometries of the $d^8$ complexes are shown in figure 1.7.

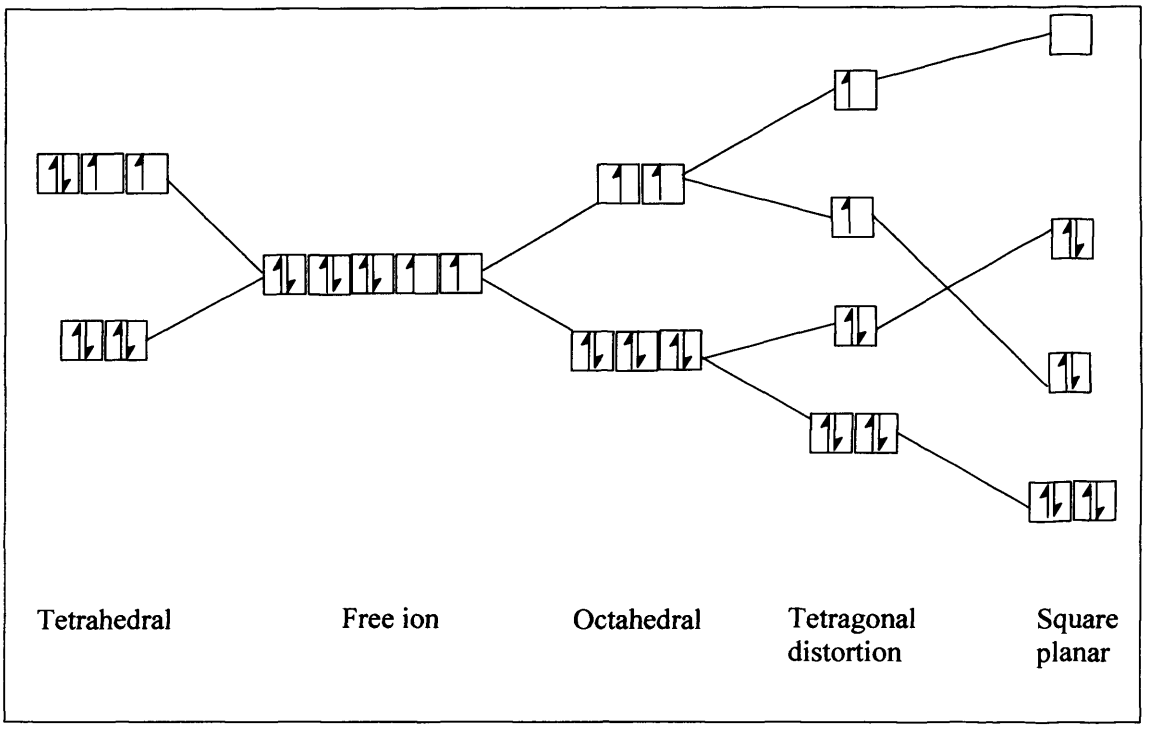



Figure 1.7

There are general trends as to which geometry a particular nickel(II) complex adopts and there is a fine balance between electronic and steric effects. Hard ligands such as O- or N-donors often form paramagnetic octahedral complexes whereas soft ligands such as P, or S form diamagnetic square planar complexes.[6] These geometries can be rationalised by the comparison of the crystal field stabilisation energies, which show that the octahedral structure is more favourable than tetrahedral, but in the presence of a strong enough ligand field square planar geometry is lower again in energy. Many complexes of both palladium(II) and platinum(II) have the general formula $ML_2X_2$ where L is a neutral donor ligand (e.g. phosphine or carbene) and X is an anionic coordinated ligand (e.g. Cl, Br, $NO_2$).

## 1.2.3: Zerovalent phosphine complexes

There are numerous examples of zerovalent group 10 complexes and these tend to be tetrahedral or square planar. Nickel can form simple zerovalent carbonyl complexes like $Ni(CO)_4$, whereas palladium and platinum can only form mixed carbonyl phosphine compounds such as $Pd(CO)(PPh_3)_3$ and $Pt(CO)_2(PPh_3)_2$.[9] All three metals can form compounds with only phosphine ligands, for example $Ni(PMe_3)_4$, $Pd(PPh_3)_4$ and $Pt(PEt_3)_4$. These complexes also have a tendency to dissociate in solution to give 16-electron $M(PR_3)_3$ and some even $M(PR_3)_2$ complexes.[24-26] The extent of the dissociation is governed by the basicity and size of the phosphine and although both are unsaturated complexes Pt complexes with the smaller phosphine $PMe_3$ gives $Pt(PMe_3)_3$, whereas the larger $PCy_3$ ligand will only form $Pt(PCy_3)_2$. $M(PR_3)_4$ complexes have widely different properties depending on the nature of the ligands; for example $NiL_4$ is air stable when L is the phosphite ligand $P(OPh)_3$, but is pyrophoric if L is $PMe_3$.

The $M(PR_3)_4$ complexes readily undergo substitution reactions with CO, $C_2H_4$, dienes and alkynes, however, one of the most important aspects is their ability to oxidatively add to give +II complexes, which is the key to many catalytic cycles. This oxidative addition is reversible in many cases, and is vital in catalytic reactions such as Heck, Suzuki, amination and telomerization etc.

# 1.3: Nucleophilic heterocyclic carbene-NHC's

## 1.3.1: The electronic state of carbenes and related properties

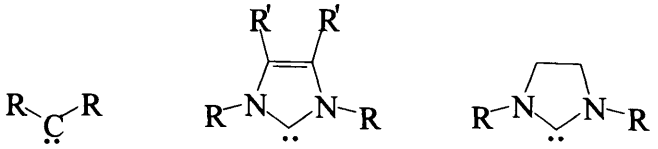
The term 'carbene' was first used in 1956 by Doering to describe divalent carbon compounds having two singly covalently bonded substituents and two unshared electrons.[27] Since then the term carbene has been extended to include other carbon atoms with six valence shell electrons, two pairs of bonding electrons and two nonbonding electrons. Carbenes can be divided into two types; Type 1; triplet carbenes and Type 2; singlet carbenes[28] (table 1.8).

| Type 1: Triplet Carbene, bond angle 130-150°, observable by ESR | Type 2: Singlet Carbene bond angle 100-110° all electrons paired. No ESR |
|---|---|
| :$CH_2$ | :$CCl_2$ |
| :CHPh | :CHCl |
| :CHR | :$C(OMe)_2$ |
| :$CPh_2$ | Heterocyclic carbenes (NHC) |

Table 1.8

The two observed classes of carbenes originate from the two possible arrangements of electrons (spin states) and are termed singlet and triplet. The orbitals are the same in both cases, but triplet carbenes have one electron in each of the two molecular orbitals, while in singlet carbenes both electrons are paired in the $sp^2$ orbital. All carbenes have the potential to exist in either the singlet or triplet state, but most types of carbenes are more stable as triplets because the energy to be gained by bringing the electron in the p orbital down into the $sp^2$ orbital is insufficient to overcome the repulsion that exists between two electrons in a single orbital. For most triplet carbenes, the singlet spin states that would arise by pairing up the two electrons lie about 40 kJ/mol above the ground (triplet) state.[28]

The simplest example of a carbene is methylene, $R_2C$, **1.1,** R = H (figure 1.9). Methylene is highly reactive and therefore a short lived reaction intermediate, electrophilic in nature when substituents R are not electron donating groups.[29] Carbenes that have a singlet ground state have electron-rich substituents carrying lone pairs adjacent to the carbene centre. These lone pairs can interact with the p orbital of the carbene to produce a new, lower energy, orbital which the two carbene electrons occupy. This stabilisation of the lone pair provides the energetic incentive that the electron in the p orbital needs to pair up in the $sp^2$ orbital.



**1.1** **1.2** **1.3**

Figure 1.9

Traditionally carbene complexes were thought to contain an M=C double bond, formed by σ-donation by the carbene and π-back bonding from the metal. Two contrasting types of bonding were suggested for the earliest carbene complexes, depending upon the nature of the carbene and the metal. In 'Fischer' type (singlet) carbenes[30] the metal is electronegative, usually middle to late transition metals, which causes the π electron density to be concentrated on the metal and the carbene carbon becomes electrophilic. Carbenes of this type also require a heteroatom bonded to the carbene carbon for stabilisation by electron donation to relieve some of the electrophilicity. The other extreme is the 'Schrock' type carbene[31] (alkylidenes), which have a triplet configuration with one electron in each of the carbon σ- and pπ-orbitals and form covalent bonds to metals in high oxidation states.[32,33] NHC's have a singlet configuration with two electrons in the carbon σ-orbital and coordinate to the metal by a predominantly σ-bond (figure 1.10).[33]

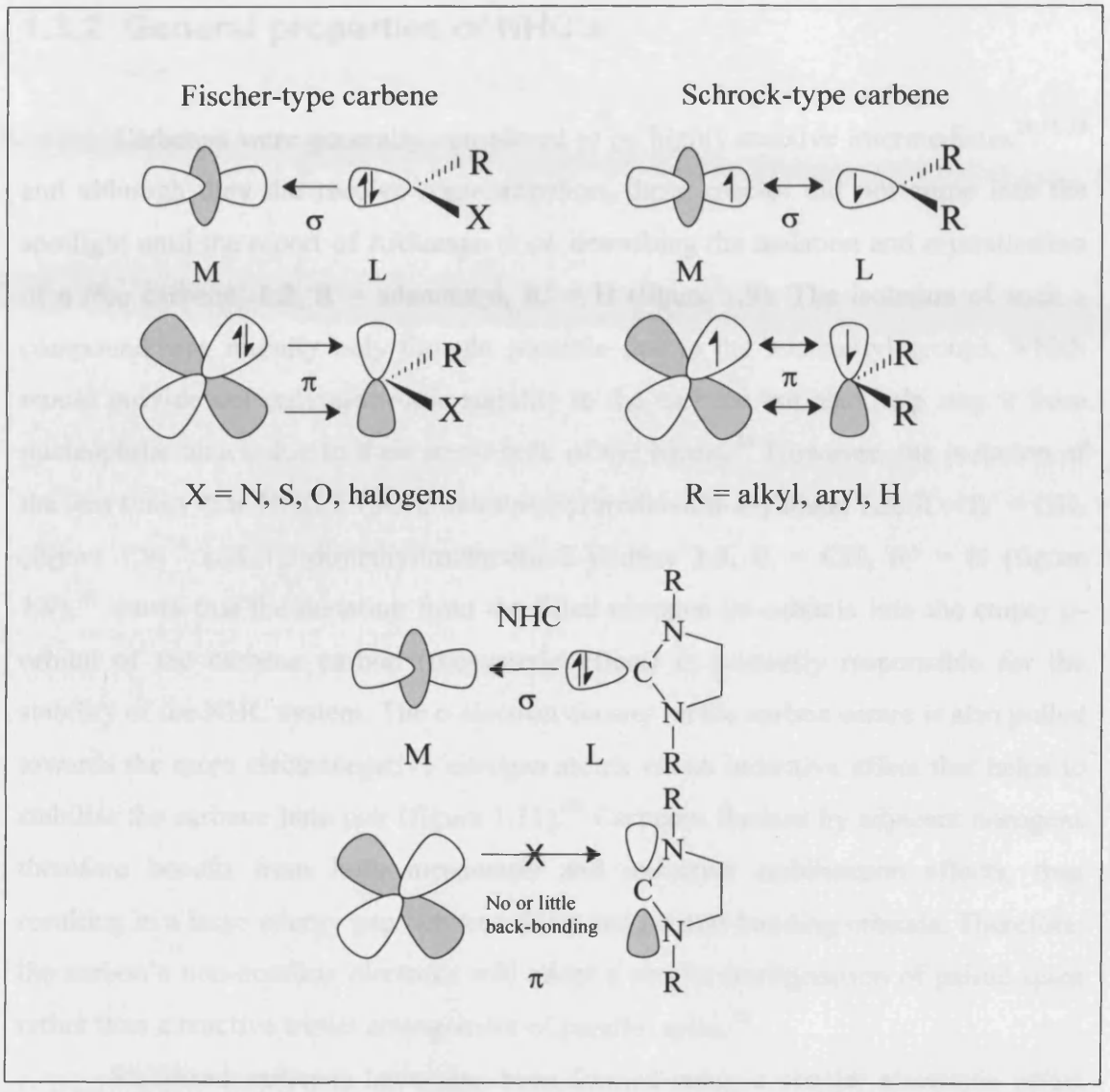



Figure 1.10: Bonding in metal complexes of: (a) Fischer carbene; (b) Schrock carbenes; and (c) Heterocyclic carbene. Adapted from Boehme and Frenking.[33]

When bound to a metal, NHC's are significantly less reactive than the Fischer and Schrock carbenes, and can be thought of as spectator ligands.[34] Although there is no doubt that NHC's are less reactive, recent reports have indicated that they are certainly not inert, e.g. NHC ligands have been shown to undergo reductive elimination, *vide infra*.

## 1.3.2: General properties of NHC's

Carbenes were generally considered to be highly reactive intermediates[29,35-38] and although they did receive some attention, these species did not come into the spotlight until the report of Arduengo *et al.* describing the isolation and crystalisation of a free carbene, **1.2**, R = adamantyl, R' = H (figure 1.9). The isolation of such a compound was initially only thought possible due to the adamantyl groups, which would provide not only electronic stability to the carbene but also help stop it from nucleophilic attack due to their steric bulk of the ligand.[36] However, the isolation of the less bulky free NHC's 1,3,4,5-tetramethylimidazolin-2-ylidene **1.3**, R = R' = $CH_3$ (figure 1.9)[39] and 1,3-dimethylimidazolin-2-ylidene **1.3**, R = $CH_3$ R' = H (figure 1.9),[39] shows that the donation from the filled nitrogen p$\pi$-orbitals into the empty p-orbital of the carbene carbon (mesomeric effect) is primarily responsible for the stability of the NHC system. The $\sigma$ electron density on the carbon centre is also pulled towards the more electronegative nitrogen atoms via an inductive effect that helps to stabilise the carbene lone pair (figure 1.11).[40] Carbenes flanked by adjacent nitrogens therefore benefit from both mesomeric and inductive stabilisation effects, thus resulting in a large energy gap between the $\sigma$ and p$\pi$ non-bonding orbitals. Therefore, the carbon's non-bonding electrons will adopt a singlet configuration of paired spins rather than a reactive triplet arrangement of parallel spins.[41]

Stabilised carbenes have also been formed using a similar electronic effect with other electronegative $\pi$-donor atoms such as sulphur or oxygen replacing one of the nitrogen atoms, for example benzothiazole carbene, **1.4**,[42] acyclic aminoxo, **1.5**,[34] and aminothiocarbene, **1.6**,[43] are known (figure 1.12).

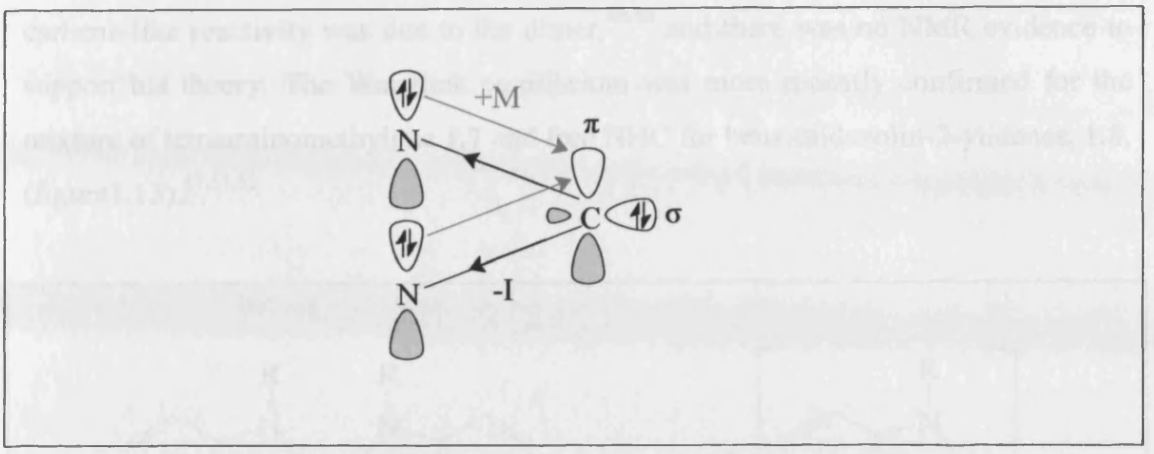
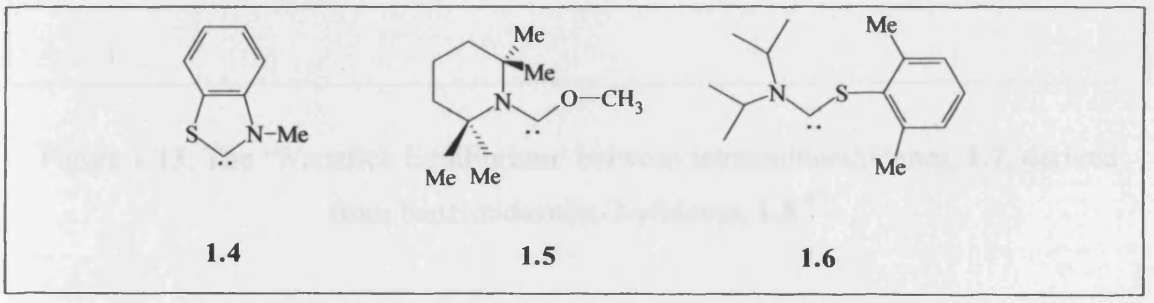



Figure 1.11: Stabilisation of free carbene through mesomeric and inductive effects. Adapted from Herrmann, *et al.*[40]



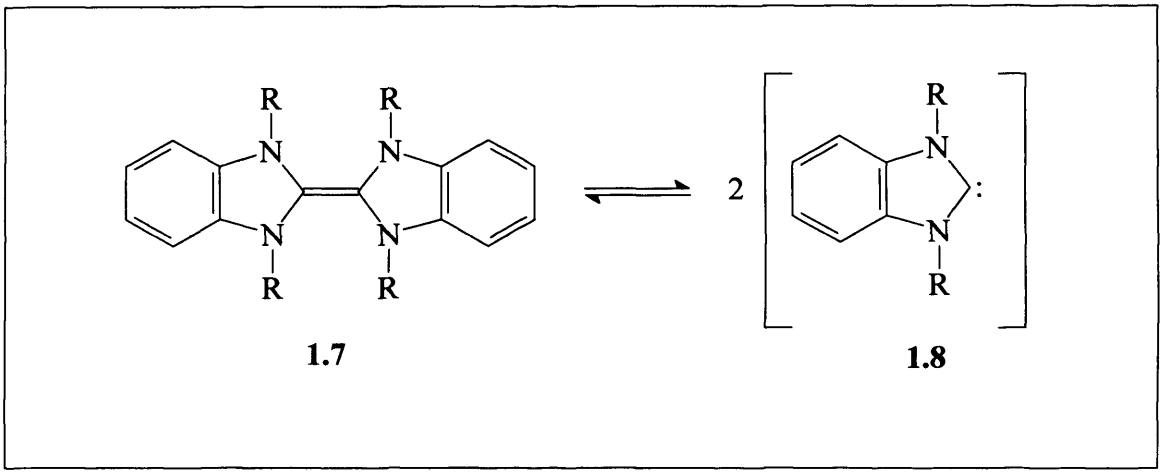

**1.4** **1.5** **1.6**

Figure 1.12

## 1.3.3: Early attempts to isolate free NHC's

The isolation of the first stable nucleophillic heterocyclic carbene (NHC) 1,3,bis(1-adamantyl)imidazolin-2-ylidene was a ground-breaking step.[36] However, carbenes derived from the imidazole ring were first studied by Wanzlick's group as early as the 1960's. Their work focussed on saturated systems and the resulting imidazolidin-2-ylidenes, **1.8** (figure 1.13). Wanzlick and coworkers formed electron rich dimeric tetraaminoethylenes, analogous to **1.7,** which were proposed to be in equilibrium with free the carbene, labelled the 'Wanzlick Equilibrium' (figure 1.13).[44-47] However, his work was disregarded by his peers because they believed the

carbene-like reactivity was due to the dimer,[48-50] and there was no NMR evidence to support his theory. The Wanzlick equilibrium was more recently confirmed for the mixture of tetraaminomethylene **1.7** and free NHC for benzimidazolin-2-ylidenes, **1.8**, (figure1.13).[47,51,52]




**1.7** **1.8**

Figure 1.13: The 'Wanzlick Equilibrium' between tetraaminoethylenes, **1.7**, derived from benzimidazolin-2-ylidenes, **1.8**.[67]

## 1.3.4: Preparation of free NHC's

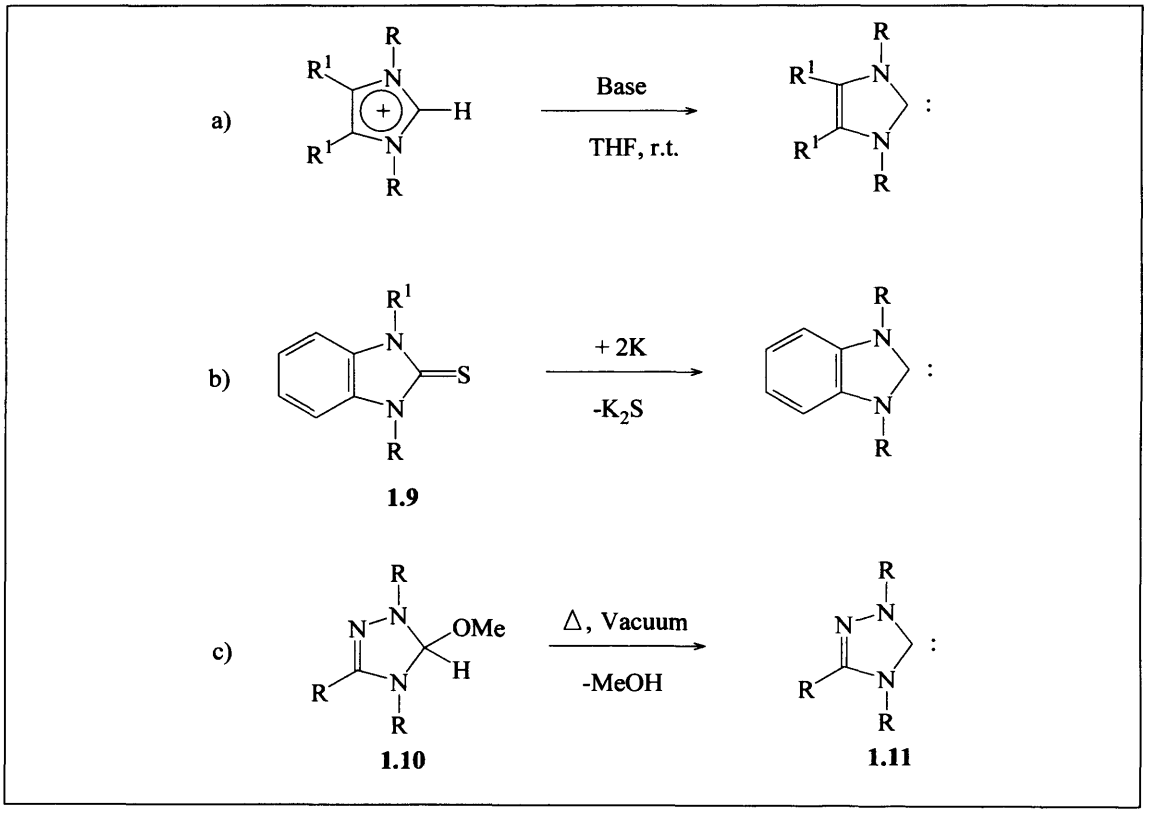
The most frequently used method for the generation of a free carbene is based on the deprotonation of an imidazolium salt at the 2-position by a strong base. However, a number of approaches have been developed (scheme 1.14):

(a) Arduengo's group used bases such as $KOBu^t$ and NaH in THF at room temperature, with a catalytic amount of DMSO.[36] These reactions require stringent Schlenk-line techniques, and some functionalised groups on imidazolium salts cannot be reacted with such strong bases. Lithium alkyls, e.g. BuLi,[53,54] are also effective reagents in the deprotonation of imidazolium salts, while milder reagents such as amides,[55-58] e.g. $K[N(SiMe_3)_2]$ and $Li(N^iPr_2)$, have proven to be valuable, high yielding bases and are often more compatible with functional NHC's with acidic methylene bridging protons.[59] $Ag_2O$ is also a very useful reagent in the preparation of

functionalised palladium complexes and will be discussed later in this chapter.

(b) Desulfurisation of imidazolin-2-thiones requires relatively forcing conditions (potassium metal in refluxing THF) but is effective in some cases, for example benzimidazolin-2-ylidenes, **1.9** (scheme 1.14).[60] The reaction is high yielding but this method is limited to thermally stable NHC's.

(c) The thermal elimination of stable small molecules,[61] e.g. ROH. This approach is rarely used to prepare imidazolin-2-ylidenes of type **1.2** (figure 1.9), and is also limited to thermally stable NHC's. However, this method was used for the isolation of the first free 1,2,4 triazolin-2-ylidene, **1.11** (scheme 1.14).[61] A variety of 2-substituents can be used, with the elimination of $NHMe_2$,[62] $CH_3Cl$[44] and ROH (R = Me, $Bu^t$) reported.[62-66]




Scheme 1.14: Methods for the preparation of free NHC's: (a) Deprotonation of imidazolium salts in the presence of base; (b) reduction of imidazolin-2-thiones; and (c) thermal elimination of small molecules from imidazoline precursors.

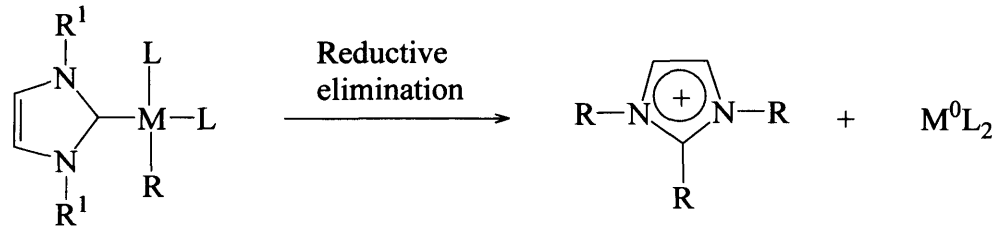
# 1.4: General characteristics of N-Heterocyclic carbenes as ligands

The coordination chemistry of NHC ligands is often compared to that of phosphines[67] and at first glance it is understandable why these comparisons are made. Both ligands are neutral, two-electron strong σ-donors and both can be sterically demanding. However, taking a closer look will reveal significant differences between the two ligand classes. The metal-NHC bond is characterised by stronger σ-donor properties[40,68,69] and negligible π-back bonding, hence carbenes form stable complexes with $Be^{2+}$ which has no electrons for back bonding.[70,71] Therefore, in $PdCl_2(NHC)(PR_3)$ complexes the dissociation of the phosphine ligand is considerably more favourable than the dissociation of the NHC. Heterocyclic carbenes with bulky substituents (e.g. mesityl, diisopropylphenyl) can also be more sterically demanding than even bulky phosphines such as $PCy_3$ or $P\textit{i}Pr_3$.

A number of theoretical and experimental studies have confirmed the essentially pure σ-donor nature of NHC ligands when bound to a metal.[72-75] Carbonyl stretching frequency studies on mixed NHC-carbonyl complexes have also confirmed that NHC's are, in general, even stronger σ-donors than trialkylphosphines.[41,67] It has already been noted that NHC's form stable complexes with metals which have no capacity for π-back bonding,[76,77] but even in the electron-rich transition metals the contribution from back-bonding is very small, although measurable. This is because the NHC carbon pπ-orbital is already largely occupied by the donation of electron density by the neighbouring nitrogen atoms.[40] X-ray diffraction data has also shown that M-NHC bond lengths are typically those of M-C single bonds.[40,41,76,78]

Although NHC's have been used as supporting ligands in a variety of catalytic reactions, a number of reports have highlighted that NHC ligands can be prone to a facile reductive elimination process to give 2-hydrocarbylimidazolium salts (scheme 1.15).[70,79-84] This low energy decomposition pathway can potentially affect the catalytic capabilities of NHC-based systems when intermediate complexes bearing hydrocarbyl ligands are formed during a catalytic reaction. However, bidentate

ligands are believed to decrease the rate of reductive elimination by restricting the reduction of the bite angle between reacting species.[79]



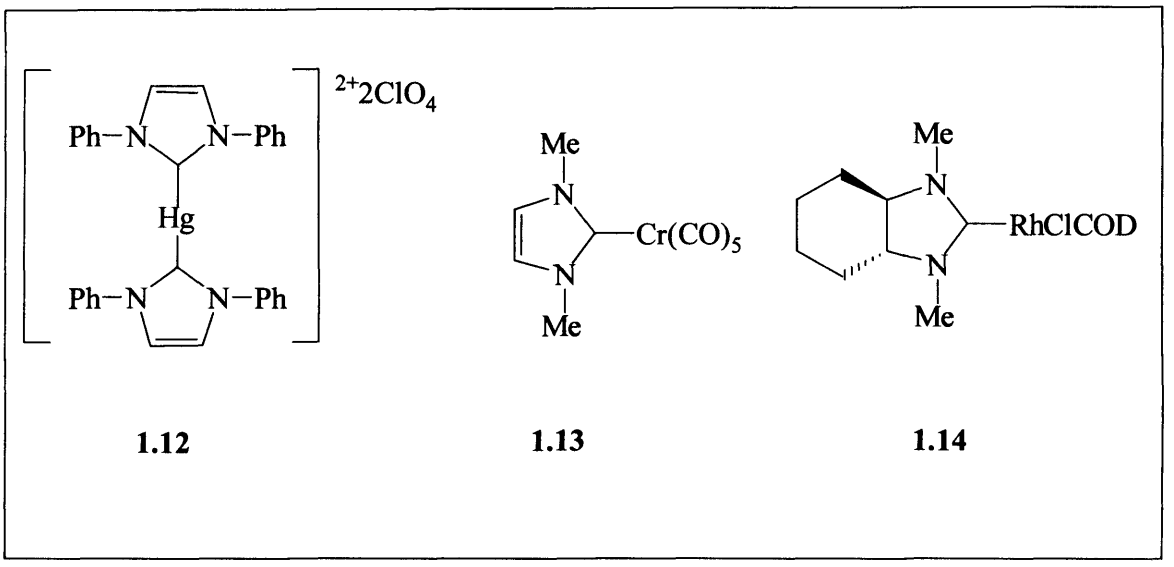

Scheme 1.15: Reductive elimination of NHC's from Pd and Ni to give 2-hydrocarbyl imidazolium salts

## 1.4.1: Early metal carbene complexes

The use of NHC's as ligands for transition metal complexes was described independently in 1968 by Wanzlick and Schönherr,[85] and Öfele[86]. The free NHC was never isolated but Wanzlick and Schönherr recognised that the two nitrogen atoms played a key role in helping to stabilise the carbene carbon.[45,87] The carbenes were prepared *in-situ* from the corresponding imidazolium salts, which were deprotonated and trapped by a basic metal precursor. Wanzlick and Schönherr prepared the first mercury-carbene complex, **1.12** (figure 1.16), by the reaction of 1,3-diphenylimidazolium perchlorate with $Hg(OAc)_2$. This reaction of metal acetate with an imidazolium salt provides a simple route to metal-carbene bonds and is used by many groups to form other metal-carbene complexes with a variety of metals.[88,89]

The Öfele group also formed a metal complex by the reaction of an imidazolium salt with a chromium carbonyl complex to give the corresponding $Cr(0)(CO)_5$NHC complex, **1.13** (figure 1.16).[86] In the 1970's Lappert and coworkers formed a range of metal-NHC complexes, e.g. **1.14** (figure 1.16), by the thermal

cleavage of electron rich tetraaminethylenes with the appropriate metal precursors, to form a range of NHC-metal complexes.[90-95]




**1.12** **1.13** **1.14**

Figure 1.16: The first reported NHC-metal complexes.[96]

## 1.4.2: Metal complexes via the free carbene route

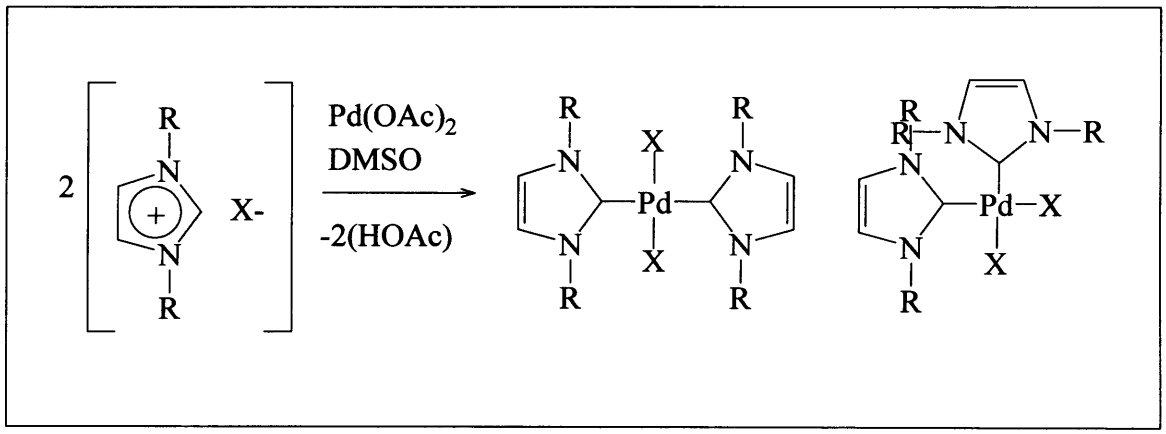
As previously described, free NHC's can be prepared in a number of different ways and allow the synthesis of a wide variety of NHC-complexes by simple combination of the free ligand with a metal precursor complex. Therefore this process is arguably the most effective route to forming metal-carbene complexes. NHC's are strong σ-donors and when added stiochiometricaly will typically displace other donor ligands, including phosphines, from both Pd(0)[40,53,70,97,98] and Pd(II)[78,99-104] precursor complexes. Chelating ligands such as 1,5-cyclooctadiene can also be displaced from metal precursor complexes with the general formula $MCl_2COD$ to give palladium Group 10 M(II), $[M^{II}L(NHC)(\mu\text{-}X)]_2$.[56,57,78]

The only disadvantages of the 'free carbene route' are those involved in the generating and handling of the free carbenes, as these are highly air and moisture sensitive; there can also be problems with stability if the NHC functional groups have

acidic protons. These problems can sometimes be avoided by forming the free NHC at low temperature with bases such as $KN(SiMe_3)_2$, followed by *in-situ* reaction with the metal precursor, *vide infra*.[54,99,105]

## 1.4.3: Reaction of imidazolium salts to form Pd(II) complexes

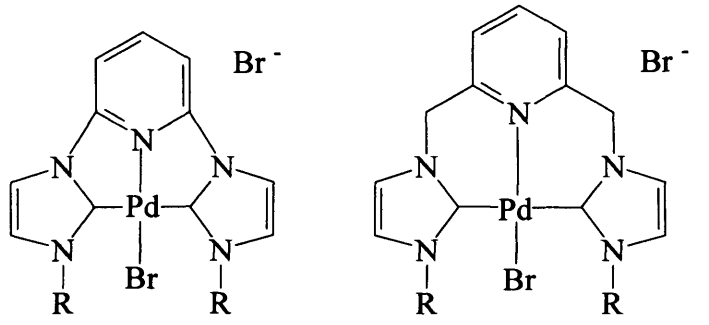
Palladium diacetate is the most widely used precursor to form Pd(II) complexes with imidazolium salts because of the simplicity of the procedure. Each basic ligand on the metal precursor complex deprotonates one equivalent of imidazolium salt, to give a palladium-NHC complex and one molecule of acetic acid.[41] The product of such a reaction would have the general formula $Pd(NHC)_2X_2$, where X was formerly the imidazolium salt anion (scheme 1.17). DMSO is the solvent preferred in the reaction with $Pd(OAc)_2$[41] due to its high boiling point and the good solubility of the reactants and products. The primary advantage of the 'palladium acetate route' is its ease of execution and robustness towards the presence of oxygen and moisture.




Scheme 1.17: Formation of $Pd^{II}(NHC)_2X_2$ complexes via the reaction of $Pd(OAc)_2$ with imidazolium salts.

The reports of Pd(II) complexes such as **1.15**,[106] **1.16**,[102] and **1.17** (figure 1.18),[107] bearing examples of the pyridine-functionalised bis-NHC ligands, shows that

with careful control of the reaction temperature it is possible to react some functionalised imidazolium salts with $Pd(OAc)_2$ in DMSO. The main draw-back of this method is that only Pd(II) halide complexes may be prepared.



**1.15** R = Me
**1.16** R = $^{n}$Bu



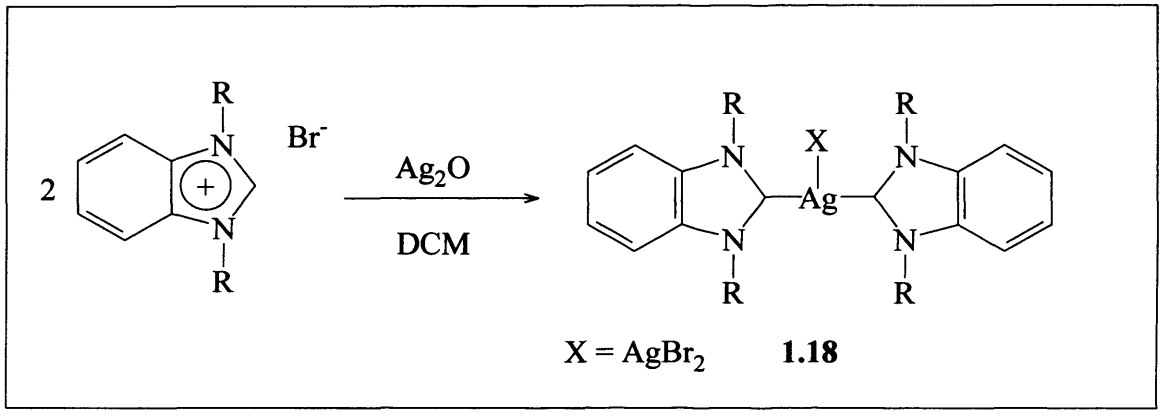
**1.17** R = Me

Figure 1.18: Formation of $Pd^{II}$(pincer NHC)X complexes via the reaction of $Pd(OAc)_2$ with imidazolium salts.

## 1.4.4: Formation of Pd(II) NHC complexes via transmetallation

$Ag^{I}$(NHC) complexes are valuable intermediates in the preparation of functionalised $Pd^{II}$(NHC) complexes, especially for NHC ligands bearing base-sensitive functional groups or acidic protons.[59] Preparation of $Ag^{I}$(NHC) complexes in general is usually straightforward and was first reported by Arduengo in 1993,[29] where free 1,3-dimesitylimidazolin-2-ylidene displaced the weakly coordinated triflate ligand from the silver to give the homoleptic silver-NHC complex. However, the major breakthrough in utilising Ag as a transfer agent came in 1998 when Wang and Lin reported that 1,2-diethylbenzimidazolium bromide reacts with

$Ag_2O$ in DCM to give the corresponding $Ag^I$(NHC) complexes, **1.18** (scheme 1.19),[108] in high yield. The principal advantages of this reaction were its tolerance to oxygen and moisture and, more importantly, Wang and Lin also found that $Ag^I$(NHC) complexes were efficient NHC transmetallation agents for Pd(II) (scheme 1.19). Although Ag is by far the most useful transfer agent of NHC ligands to Pd(II), other transition metals have been used.[109,110]

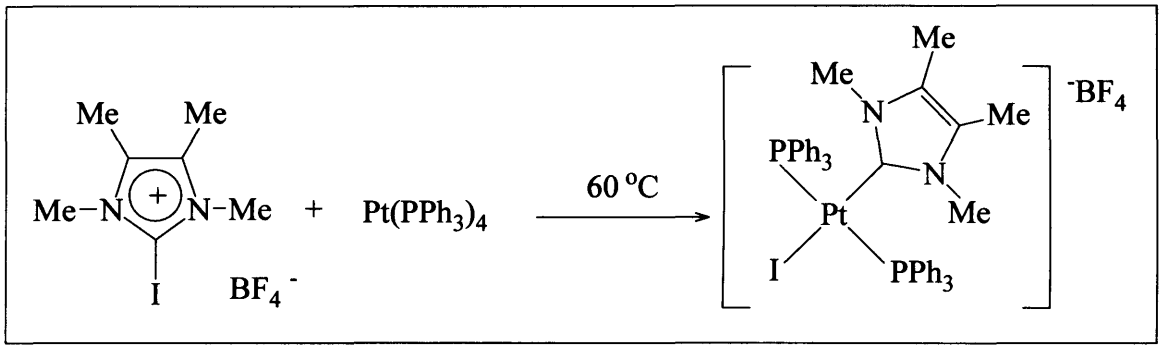



Scheme 1.19: Reaction of two imidazoliums with $Ag_2O$ in DCM to give the corresponding $Ag^I(NHC)_2$ complex.

## 1.4.5: Oxidative addition of imidazolium salts to M(0)

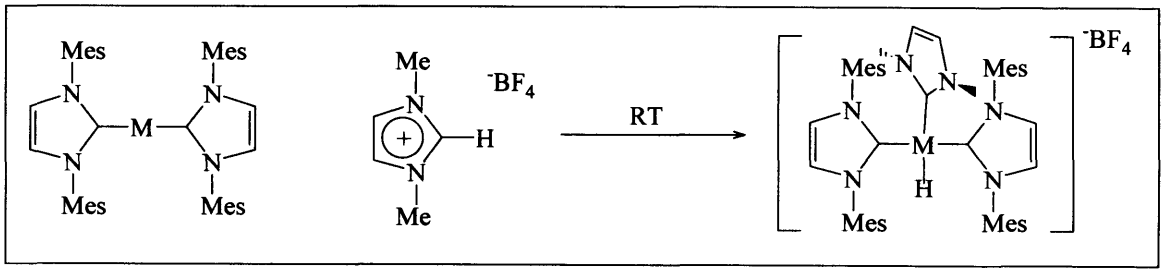
The oxidation of thiazolium salts to group 10 metals was first described as early as 1974 by Stone *et al.*, in which M(II)-thiozlin-2-ylidene complexes were synthesised by the oxidative addition of 2-chlorothiazolium salt to precursor complexes such as $Pd^0(PPh_3)_4$ and $Pt(PMePh_2)_4$.[111,112] Subsequently, in 2001 Cavell and coworkers showed that the oxidative addition of 2-haloimidazolium salts to M(0) substrates was a facile reaction[113] (scheme 1.20) by the addition of 2-iodo tetramethyl imidazolium tetrafluoroborate with $Pd^0$ and $Pt^0$ precusors.[113] The same group also published density functional calculations suggesting that $M^{II}$(hydrido)(NHC) complexes could be generated by oxidation addition of 2-H-imidazolium salts to zerovalent group 10 metal precursors.[113] These theoretical calculations were

supported by the reaction of 1,3-dimethylimidazolium tetrafluoraborate with the coordinatively unsaturated 14-electron $Pt^0$ species.[113] They showed that using $Pt(PPh_3)_2$ as the starting material instead of $Pt(PPh_3)_4$ led to a significantly more successful reaction (15% to 63% yield), since the reaction was an equilibrium, and the dissociation of two phosphines was unfavourable.[113]




Scheme 1.20: Preparation of a $Pt^{II}$(NHC) complex by oxidation addition of a 2-haloimidazolium salt to a Pd(0) precursor.[113]

In 2004 Cavell reported that the reaction of imidazolium salts, typically used as ionic liquid with low-valent $M^0$ (M = Pd, Ni) complexes bearing strong σ-donor ligands, could be a facile process for the generation of surprisingly stable carbene-M-hydrido complexes[114,115] (scheme 1.21). The ease of formation of these complexes together with their remarkable stability is an example of how NHC ligands may allow the isolation of new, normally highly reactive species.[114,115]

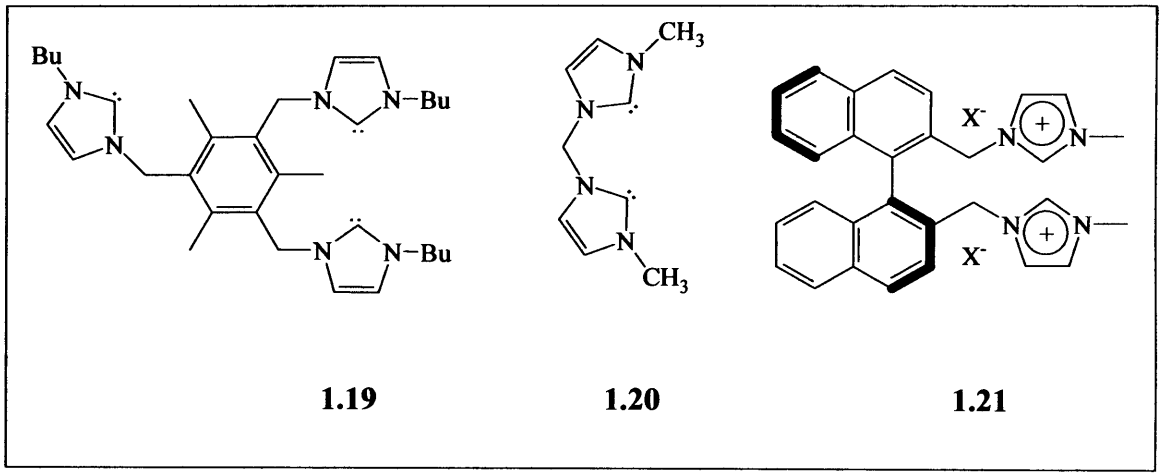



Scheme 1.21: The reaction of imidazolium salts with low-valent $M^0$ (M = Pd, Ni) to form carbene-M-hydrido complexes.

# 1.5: Chelating ligands

## 1.5.1: Bidentate carbene systems

Bidentate phosphine and phosphite ligands have played a major role in homogeneous catalysis for a number of years. Monodentate NHC's have been found to stabilise catalytic cycles and have a number of advantages over the conventional monodentate phosphorus ligand systems. Hence, it was only a matter of time before bidentate carbene systems came into of focus.




**1.19** **1.20** **1.21**

Figure 1.22: Examples of chelating ligands.

A wide range of ligands are known with two or more NHC groups. Some examples include **1.19** (figure 1.22), isolated by Dias and Jin in 1994;[116] **1.20** (figure 1.22), isolated by Herrmann in 1996;[66] and **1.21** (figure 1.22), the first chiral bidenatate bis-imidazolium salt reported by Rajan Babu in 2000.[117]

## 1.5.2: Mixed carbene-donor ligands

Another emerging area of research in carbene chemistry is mixed donor ligands; NHC's bearing functionalised side chains. Herrmann and coworkers reported imidazolium salts with heteroatom substituted (O, N, and P) functional groups.[40] They expected that NHC's with such functional groups would have a broad range of applications in organometallic catalysis, due to the fact that NHC's normally form particularly strong bonds with transition metals and the pendant arm could turn the ligand into a possible hemi-labile chelating ligand (figure 1.23).

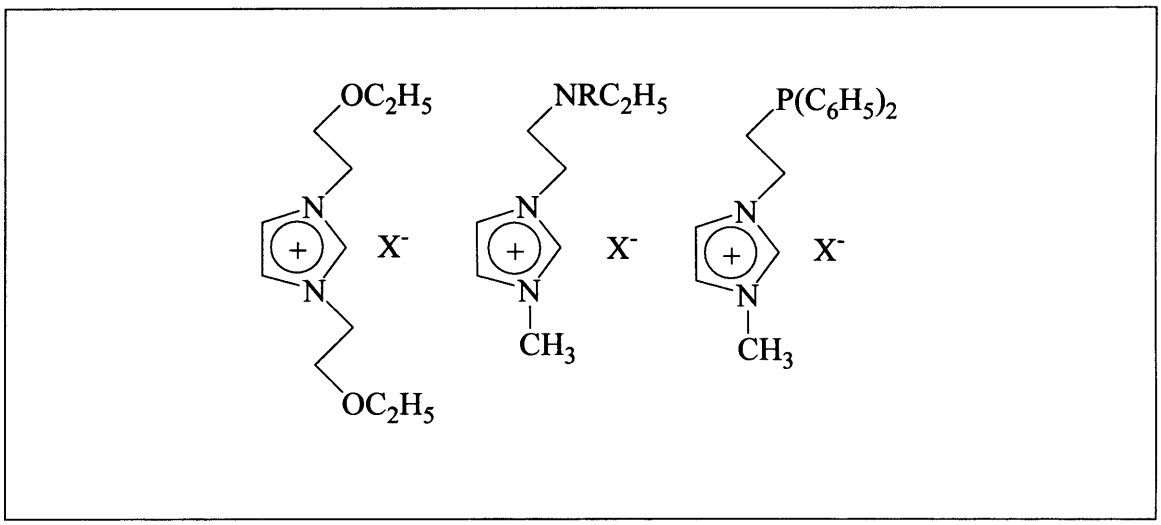
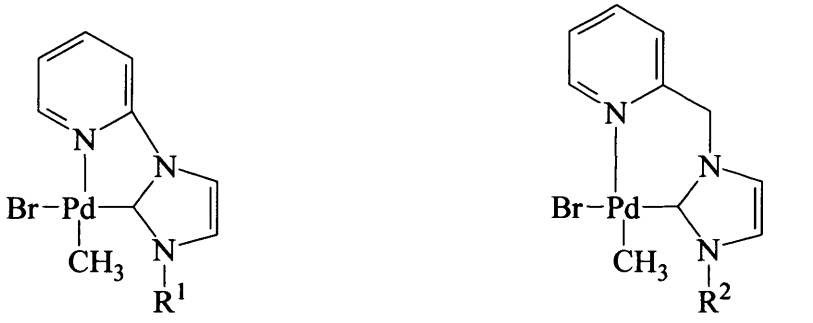



Figure 1.23: NHC's with functionalised side chains.

A paper by Cavell *et al.* in 2000 reported fully characterised mixed donor N-picolyl-functionalised imidazolium salts and their corresponding silver(I), and methyl Pd(II) carbene complexes.[118] Cavell *et al.* understood that the hemi-labile carbene ligands could prove useful in stabilising catalytic centres while creating a degree of coordinative and electronic unsaturation.[89] This will be described fully in further chapters. The group of Danopoulos later published the synthesis and substitution chemistry of palladium complexes with pyridyl-, picolyl-, methoxymethyl- and diethycarbomoxymethyl-functionalised imidazolin-2-ylidenes.[56]

The σ-donating pyridine ring tethered to the NHC's would add versatility to the ligand design for the following reasons:[56,89,118] (i) The pyridine function is expected to bind weakly to lower oxidation state metals.[56] (ii) The variable linker lengths would adjust the size of the chelating ring and promote ligand hemi-lability, with possible implications on the catalytic activity.[56] (iii) The electronic asymmetry of the chelating N-functionalised NHC ligand renders the corresponding *trans* sites electronically inequivalent, due to larger differences in the *trans* effect of the two chelating groups.[56] (iv) The donor and steric characteristics of the pyridine and NHC functional groups are easily modified by addition of a variety of substituents.[56] These are the sorts of parameters that need to be explored to gain an understanding of the working of a catalyst cycle and the effects of ligand design (scheme 1.24).




$R^1 = 2,6\text{-}Pr^i_2C_6H_3$ $R^2 = 2,4,6\text{-}Me_3C_6H_2$

Scheme 1.24: Functionalised NHC complexes of palladium.[56,89,118]

## 1.5.3: Phosphine-carbene ligands

Phosphines and carbenes are both recognised as strong *trans* effect/influence ligands and hence they are able to activate/labialise groups coordinated in a position

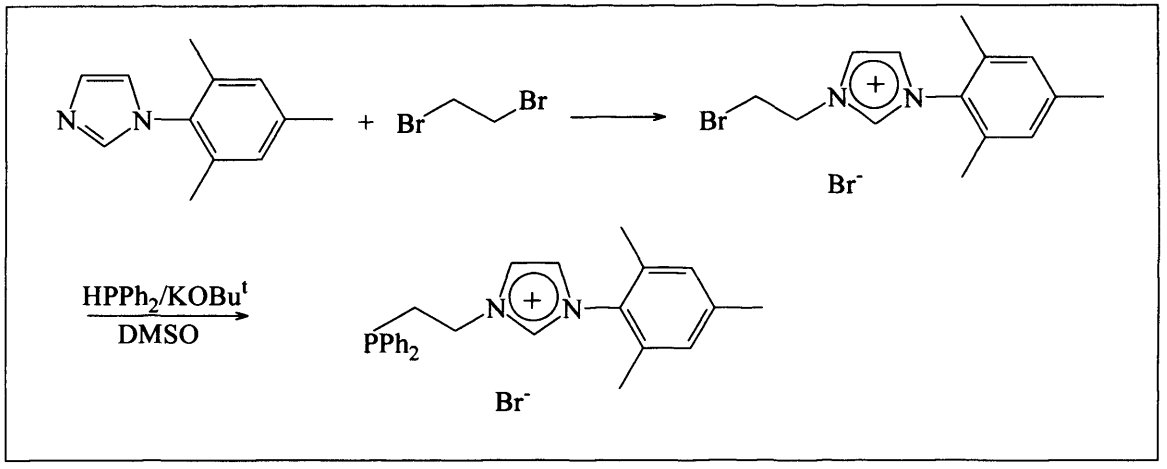
*trans* to themselves. This property is particularly important if the *trans* group is the migrating hydrocarbyl species in a catalytic process such as carbonylation, hydroformylation or other C-C bond forming reactions where the migration process will be promoted. In square planar complexes, if the phosphine and carbene donor systems are linked to form a chelating ligand which is coordinated to the metal centre, then the migrating hydrocarbyl group cannot avoid a strong *trans* influence ligand.

The first phosphine-carbene ligand was reported by Lappert in 1993, where phosphine-carbene molybdenum(0) carbonyls were synthesised.[119] Herrmann published novel functionalised NHC's in which one of the functionalised side chains was a phosphine,[40] and in 1998 the first palladium complex containing a novel and stable carbene-phosphine bidentate chelate was synthesised, *vide infra*.[120] Then, in 2001, Nolan published a new phosphine-imidazolium salt which proved to be highly efficient in the Pd-catalysed Heck coupling reaction of aryl bromide with n-butyl acrylate.[121]

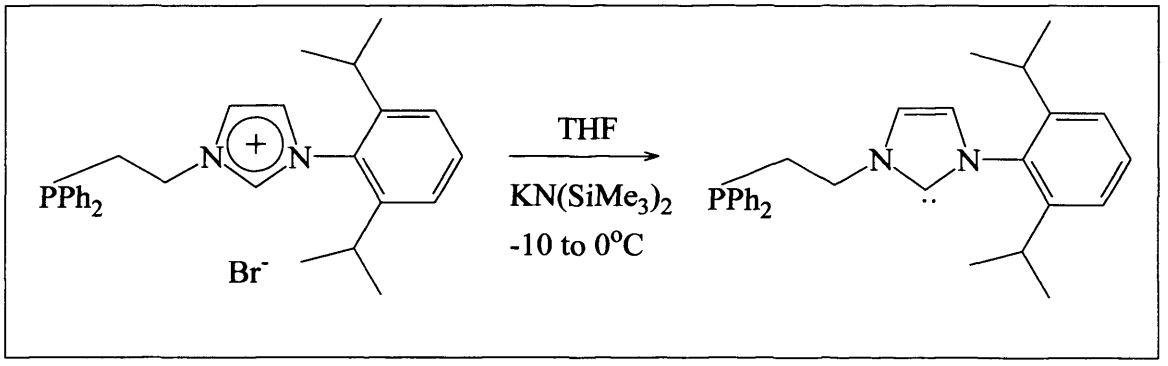
The phosphine-imidazolium salt 1-ethylenediphenylphosphino-3-(mesityl) imidazolium bromide was prepared in a two-step procedure (scheme 1.25).[121] The free carbene or metal complexes were not reported at this time, but the ligand precursor was tested *in-situ* in Heck coupling of both electron-deficient and electron-rich aryl bromides with positive results. Investigations into optimising reaction conditions showed that solvent, and more importantly the nature and amount of base, can play a major role in the reaction rates and overall yields. The formation of carbenes can be very base sensitive and in some cases the *in-situ* testing of imidazolium salts may not be the best way of assessing the ligand's capabilities (this issue will be discussed in later chapters).

Subsequently, Danopoulos published papers on the synthesis of similar ligands to those reported by Nolan, which included the formation of the free carbene-phosphine[55] and its complexation with Pd(II) metal (see section 1.5.4 for Pd(II) complexes).[57] Danopoulos *et al.* described the formation of the diphenylphosphine-functionalised NHC from a deprotonation of the imidazolium salt by $KN(SiMe_3)_2$ in THF[55](scheme 1.26). The crystal structure of the phosphine-NHC ligand determined that the lone pairs on the phosphorus and the carbene carbon were mutually '*anti*', an

arrangement that would minimise the electronic repulsions between the electron lone pairs; a similar conformation has been observed in the solid state structure of 1,2-bis-(diphenylphosphino)ethane.[55] The isolation of this ligand also shows that, in contrast to the known reactivity of phosphines with classical carbenes, which give rise to phosphoranes, free NHC's are inert towards phosphines.[55]



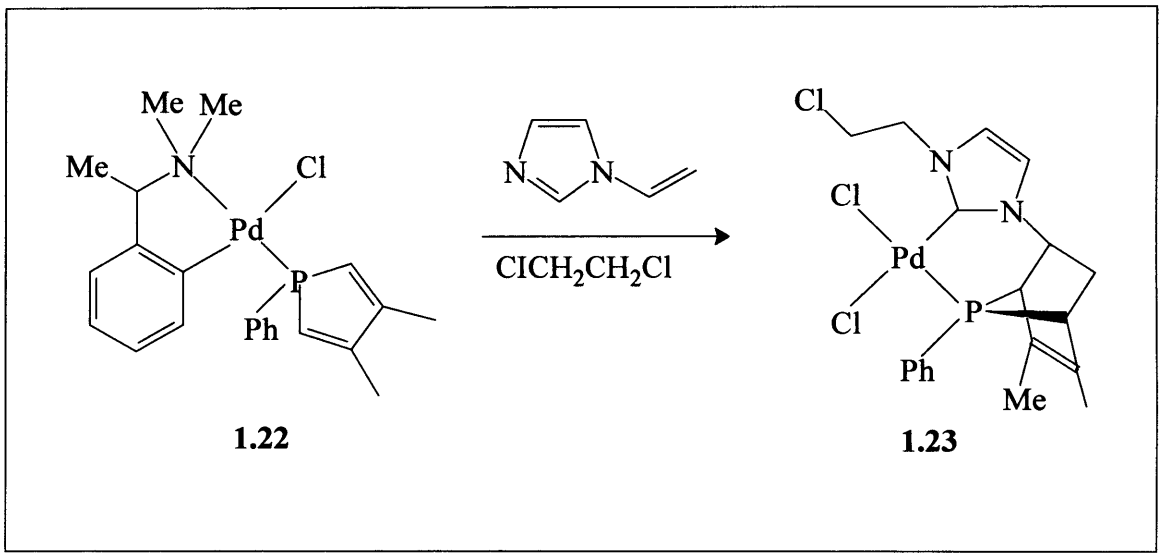

Scheme 1.25: Synthesis of imidazolium salt (1-Ethylenediphosphino-3-(mesityl)imidazolium bromide.[121]




Scheme 1.26: Synthesis of phosphine-carbene ligands.[55]

## 1.5.4: Reported phosphine-NHC complexes

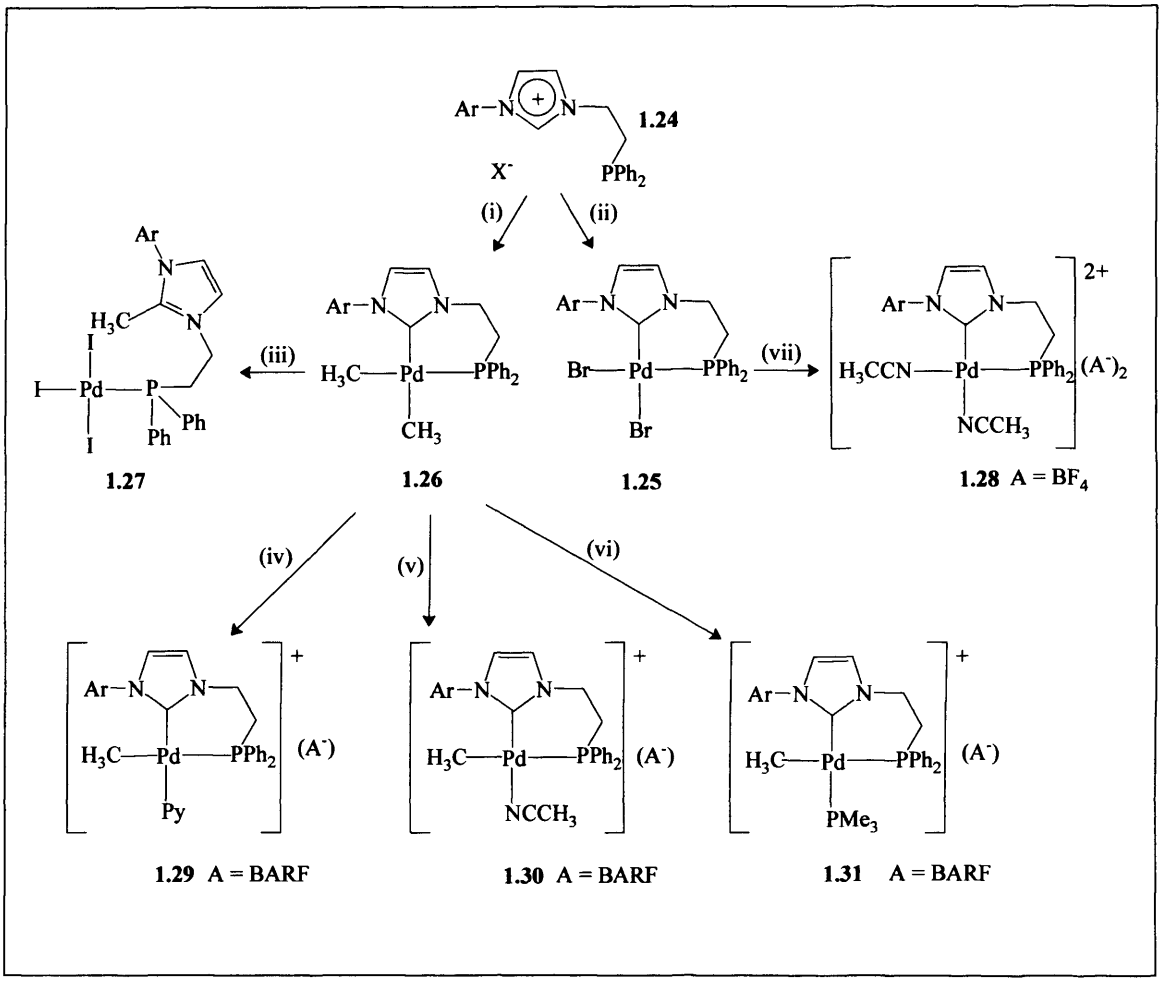
Upon starting this project only one palladium phosphine-carbene complex had been reported in the literature.[120] The palladium complex was produced via a metal-template synthesis, in which complexes **1.22** was first treated with silver perchlorate and then reacted with 1-vinylimidazole in 1,2-dichloroethane for 30 days at 84 °C, (scheme 1.27). The resulting mixture bidentate phosphine-carbene complex, **1.23**, was isolated in 40% yield and a crystal structure showed that the palladium atom was in a slightly distorted square-planar geometry.[120]




**1.22** **1.23**

Scheme 1.27: Palladium complexes containing a novel P-NHC bidentate chelate.

Subsequently while this project was undertaken, a series of functional NHC-phosphine complexes of palladium were synthesised by the group of Danopoulos in 2003.[122] Their work focussed on the formation of palladium(II) complexes with two main ligands which were both (diphenylphino)alkyl-functional NHC's. The phosphine-imidazolium salts were deprontonated with $KN(SiMe_3)_2$ in THF at -78 °C, then reacted *in-situ* with the Pd precursor to give the desired metal complex, (scheme 1.28).[122]




Scheme 1.28: Palladium phosphine-NHC complexes.[122]

Ar = dipp **1.24-1.31**, Mes **1.24-1.26**. (i) 1.1 equiv. of $KN(SiMe_3)_2$ in THF at -78 °C and 1 equiv. of $tmedPd(CH_3)_2$; (ii) 1.1 equiv. of $KN(SiMe_3)_2$ in THF at -78 °C and 1 equiv. $PdCODCl_2$; (iii) excess $CH_3I$ in THF; (iv) 1 equiv. of $H(Et_2O)$[BARF] at -78 to -30 °C and then 1 equiv of Py; (v) 1 equiv. of $H(Et_2O)$[BARF] at -78 to -30 °C and then 1 equiv of $PMe_3$; (vi) 1 equiv. of $H(Et_2O)$[BARF] at -78 to -30 °C and then 1 equiv of $CH_3CN$; (vii) 2 equiv. of $Ag_2O$ in $CH_3CN$.

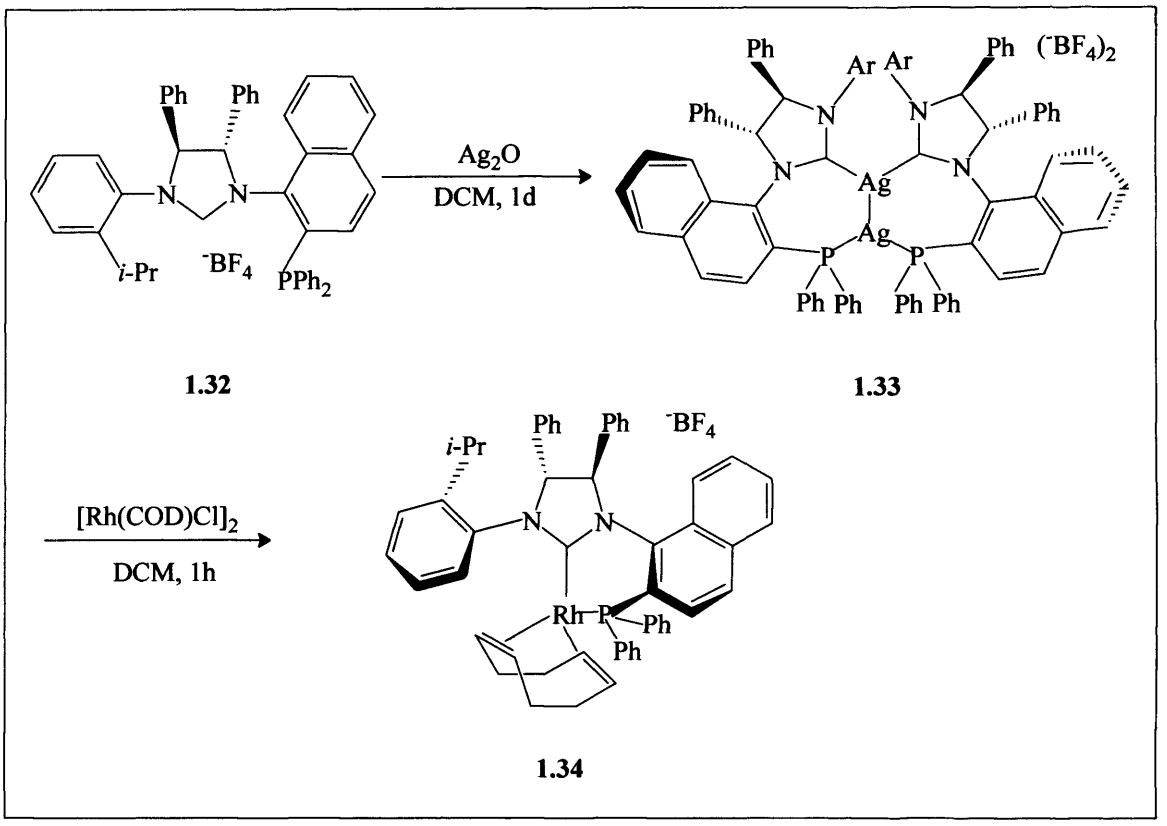
Complexes **1.25** and **1.26** were both isolated in good yield as air stable solids, however, complex **1.26** developed a dark colour after a few hours. The crystal structure of these two chelating complexes revealed some interesting facts; in complex **1.26** the two Pd-$CH_3$ bond lengths were roughly equal and in complex **1.25** the Pd-Br bond length *trans* to the phosphine was longer than that *trans* to the NHC.[122] These observations contrast with what was expected because NHC ligands

are better σ-donors than the trialkyphosphine and thus should have a greater *trans* influence.

Several more complexes, **1.27-1.31**, were synthesised by reacting the dimethyl and dibromide complexes with a variety of different reagents. The reaction of complexes **1.26** with excess $CH_3I$ afforded complex **1.27**. The square planar Pd complex contains one imidazolium functional phosphine, two iodides and one chloride atom; Danopoulos *et al.* proposed a Pd(II)-Pd(IV) mechanism and chloride was accounted for by the solvent which was DCM.

Recently Helmchen synthesised complexes of a novel chiral diphenylphosphino-functional NHC.[123] The thoughtful design of ligand **1.32** was based on the excellent results that Grubbs and coworkers had with Ru-complexes formed from dihydroimidazolium salts.[124] The Rh P-NHC chelating complex, **1.34**, was formed via the transmetallation from the corresponding silver(I) complex. The dihdroimidazolium salt, **1.32**, was reacted with one equivalent of $Ag_2O$, which is needed for the full conversion, to give the resulting silver(I) complex following the method of Wang and Lin.[125] The transmetallation was achieved by the reaction of complex **1.33** with one equivalent of $[Rh(COD)Cl]_2$ in DCM after one hour.[123] Both the $^{31}$P-NMR of complexes **1.33** and **1.34** showed two isomers, characterised by doublets with an intensity ratio of 2:1.[123] The barrier of rotation of the complexes was higher than that of the corresponding salt and no interconvertion occurred at r.t.,[123] Helmchen *et al.* also deduced that the atropisomers of **1.33** were translated onto the corresponding Rh-complex.[123] Highly enantioselective asymmetric hydrogenation was achieved with the Rh-complex.[123]

In 2005 the group of Zhou reported the *in-situ* catalyst testing of four different triaryl phosphine-functionalised NHC ligands in the Heck coupling reaction.[126] Three of the ligands were chelating ligands, the other a tridentate pincer ligand. Although all the testing was done *in-situ,* the ligand, base, and palladium source were first stirred in N,N-dimethylacetamide (DMAc) for half an hour before the coupling reagents were added.[126] The paper gives only one example of spectroscopic data of these complexes, where R = dipp **1.36**, which was characterised by $^1$H and $^{31}$P-NMR, (scheme 1.30).

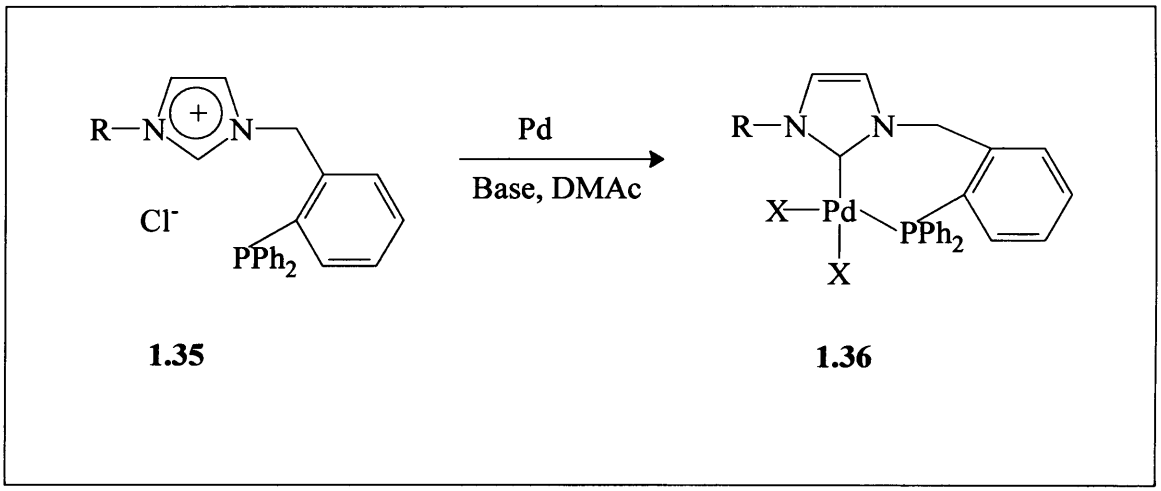



Scheme 1.29: Complexes of a novel chiral diphenylphosphine-functionalised NHC.[123]

Another report of a new tridentate pincer phosphine-N-heterocyclic carbene ligand and the corresponding palladium complexes came from Lee *et al.* in 2004[127] and a subsequent paper in 2005, in which the same ligand was complexed with silver and ruthenium.[128] The formation of the palladium complex **1.39** was achieved by two different routes, (scheme 1.31); one route was by the reaction of the pincer imidazolium salt, **1.37**, with half an equivalent of silver oxide, followed by the transmetallation with $PdCl_2$.[127]

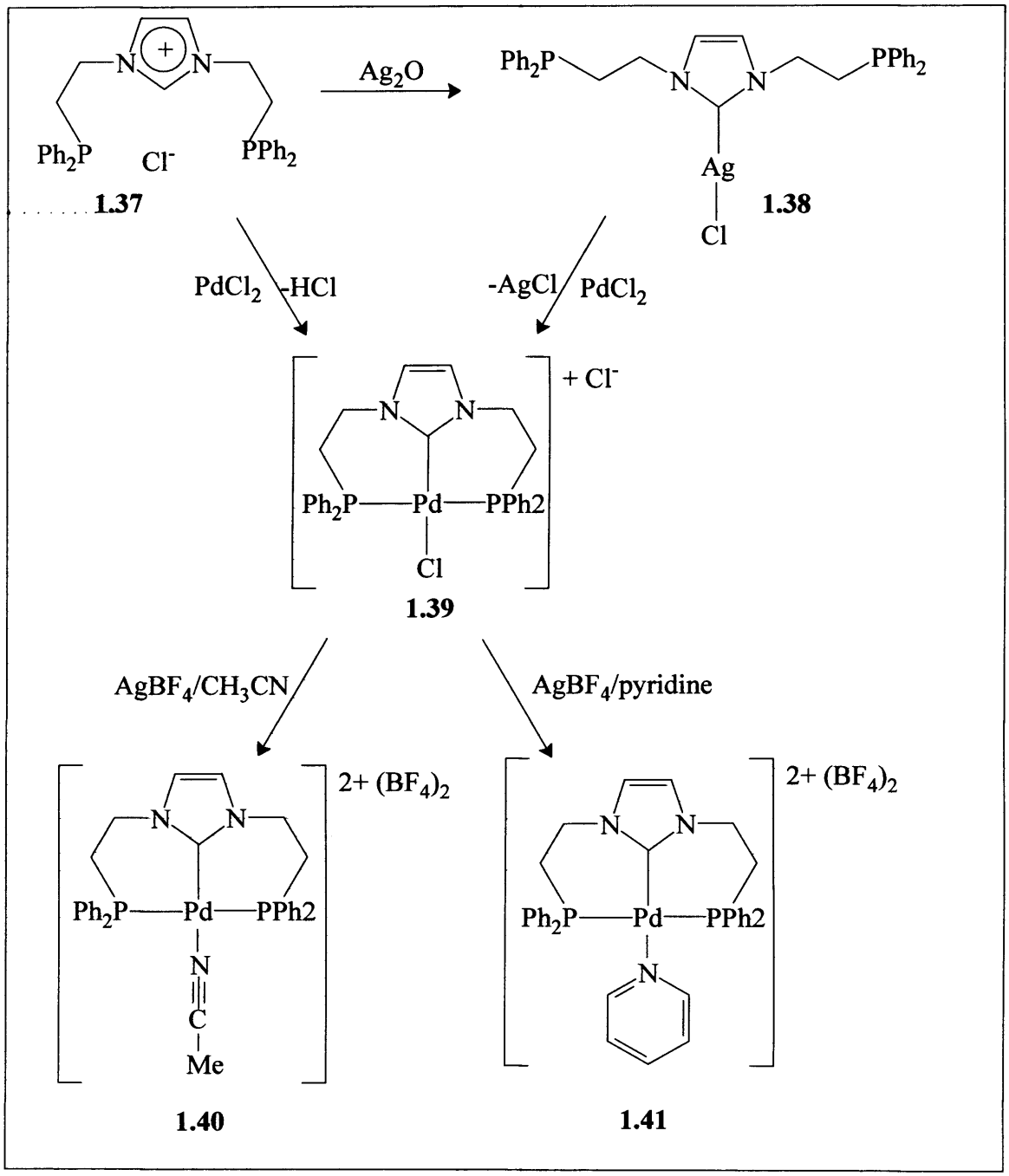
The second method achieved the formation of complex **1.39** by the reaction of the imidazolium salt, **1.37**, with $PdCl_2$. Remarkably the reaction was done without the need of a base. The reaction is the first example of the formation of a palladium(II) NHC complex from the direct reaction of an imidazolium salt with $PdCl_2$ and justified by the inherent high acidity of imidazolium salt **1.37**.[127] The reaction of Pd complex **1.39** with $AgBF_4$ in acetonitrile and then pyridine afforded the ionic complexes **1.40**

and **1.41** respectively, (scheme 1.31). In the following paper the solid state structure of the silver complex was investigated and it was found to contain three silver atoms, three chlorides and two pincer ligands, where the extra chloride presented in the compound is believed to have come from the dichloromethane during the reaction.[128] Several ruthenium complexes were also formed.[128]




**1.35** **1.36**

Scheme 1.30: Synthesis of triaryl phosphine-fuctionalised NHC complex.[126]




Scheme 1.31: Synthesis of tridentate pincer phosphine-NHC complex.[127]

## 1.6: Aims of this thesis

The main aim of this thesis was the design and synthesis of hybrid phosphine-carbene ligands. Ligand design is an important aspect in the development of efficient homogenous catalysts, as ligands may influence reaction behaviour in a number of ways including electronic and steric effects, chelation, bite angle, ligand rigidity and hemi-lability. Phosphines, phosphites and more recently carbenes, have been utilised to control and modify catalyst behaviour. By the synthesis of a wide range of phosphine-carbene ligands the crucial parameters mentioned above may be tested.

Once this ligand synthesis is achieved the coordination chemistry of some the ligands, the catalytic potential of the ligands and the resultant complexes will be investigated.

# 1.7: References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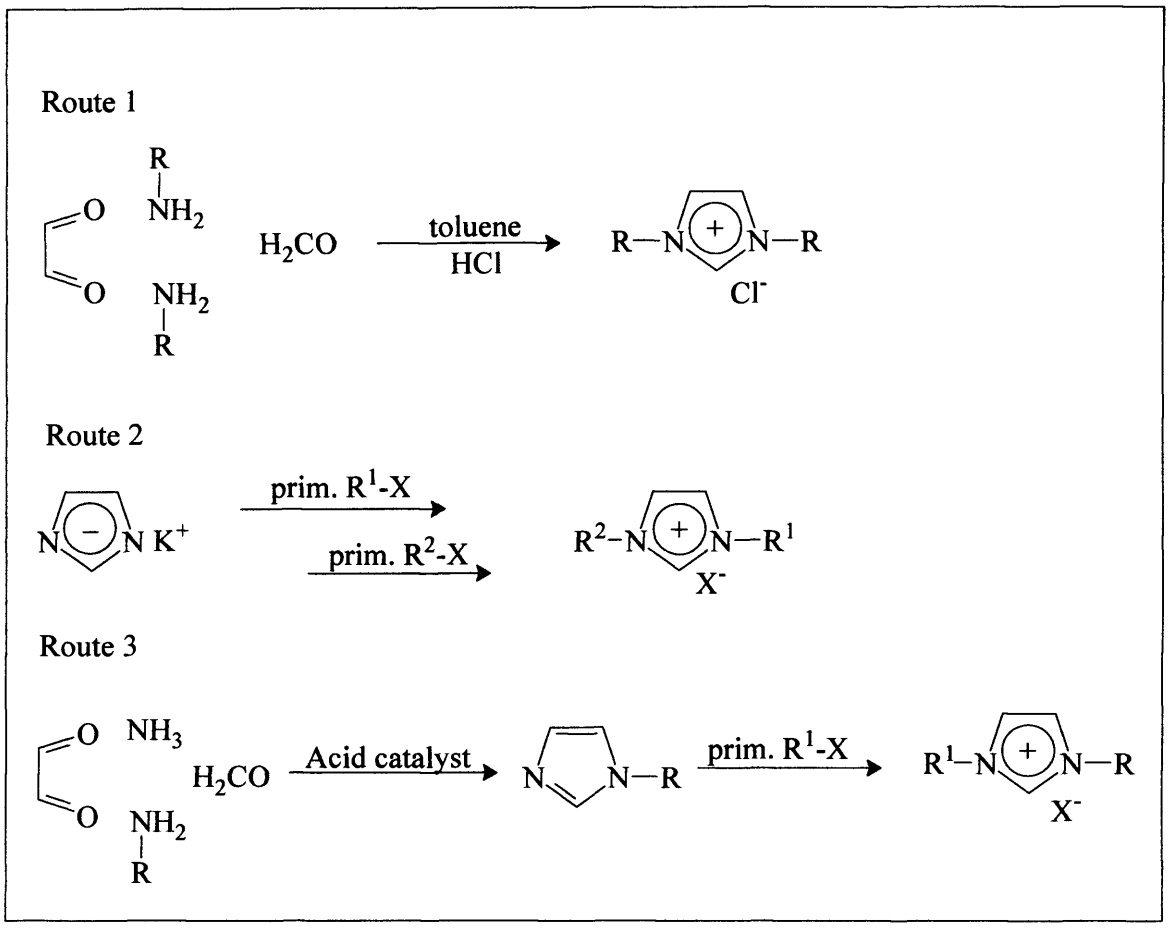
# CHAPTER TWO
# Phosphine-Imidazolium Salts

## 2.1: Introduction

### 2.1.1: Imidazolium salt synthesis

Imidazolium salts can be prepared in a number of different ways, scheme 2.1. **Route 1** is the synthetic procedure applicable to symmetrical 1,3-disubstituted imidazolium salts,[1-3] in which two equivalents of a primary amine are condensed with aqueous glyoxal and paraformaldehyde at ca. pH 3. **Route 2** involves the reaction of the potassium salt of imidazole with one equivalent of primary alkyl halide in a nonpolar solvent, to avoid elimination.[4] The resulting N-alkylated imidazole is reacted with another equivalent of a different alkyl halide in a polar solvent. **Route 2** only works satisfactorily for primary alkyl halides, in the case of secondary or tertiary alkyl halides elimination was found to be a serious side reaction.[2] **Route 3** can also be used in the synthesis of unsymmetrical precursor imidazolium salts. The acid catalysed formation of a wide variety of bulky N-substituted imidazoles is well known.[5,6] The substituted imidazole is then reacted with a primary alkyl halide group, which may or may not contain a functional group. This method has been used with success to synthesise a wide range of chelating imidazolium salts with functionalised alkyl substituents.[7-12] N-alkylation of an imidazole ring follows typical $S_N2$ behaviour and is difficult to achieve with any nucleophile less reactive than a secondary alkyl bromide.[13,14] Thus the nucleophilic attack on an aryl ring by an imidazole is difficult or impossible, and therefore the development of ligands with functionalised aryl groups is limited through this method.

However, a recent paper by Grubbs *et al.* reported the synthesis of N,N'-diaryl imidazolium salts which gave [C,O] chelating ligands.[11] This methodology will be discussed later, but notably its generality has not yet been proven.




Scheme 2.1: Synthetic routes to the formation of imidazolium salts.

## 2.1.2: Chelating phosphine-imidazolium ligands

As discussed in Chapter One, both tertiary phosphines ($PR_3$) and nucleophilic heterocylic carbenes (NHC) have many properties which make them desirable as ligands, and a number of chelating phosphine-carbene ligands have been synthesised. However, this field is still relatively new and the ligand design aspect has not yet reached its full potential. Mixed phosphine-NHC ligands were selected for study in this thesis, because both functionalities have large *trans* influences (but different donor/coordination properties). Hence, both functionalities should be effective in promoting migratory reactions of substrate molecules coordinated in *trans* positions. Of the ligands reported when this work commenced, only one phosphine-imidazolium

salt had been tested in any coupling reaction, yielding positive but not groundbreaking results.[9] However, this salt was tested *in-situ* and metal complexes were not reported. The work described in this thesis sought to establish the synthetic methodology and the structure/activity relationships of a number of novel mixed donor phosphine-NHC ligands. In particular, this work will focus on chelating phosphine-NHC ligands bearing various substituents in order to control the steric and electronic properties of the resulting metal complexes.

The chelating ligand synthesised by Nolan and coworkers was a phosphine-imidazolium salt in which the phosphine was attached to the imidazolium salt by an ethane bridged linker (figure 2.2).[9] This ethane linker does not provide ideal geometry to form a strong chelating ligand and it may be prone to reductive elimination over a period of time during catalysis, thus affecting the catalyst longevity. It was believed that replacing the ethane bridge with a more planar, ridged linker could help to form a 'stronger' bidentate system. Therefore, a number of different types of ligands have been synthesised, based on three main structures. Throughout this work the three main types of ligands will be referred to as **Type I**, **Type II**, and **Type III** respectively, (figure 2.3).

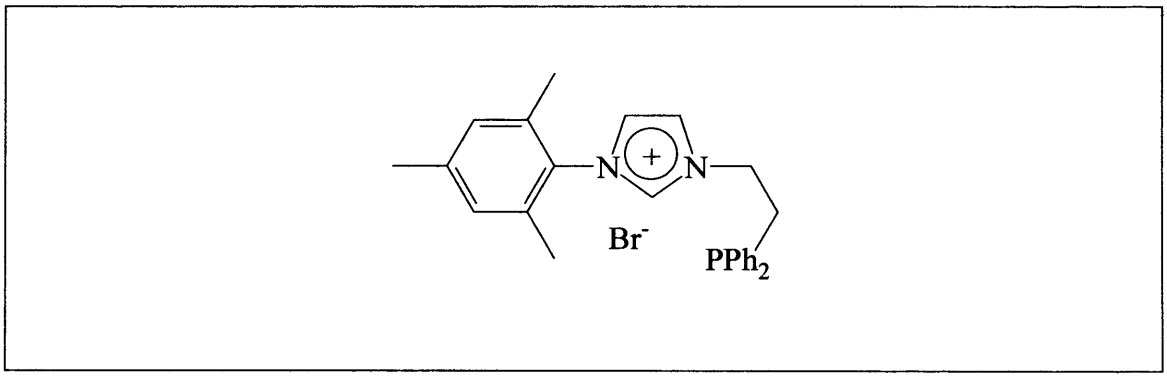



Figure 2.2: Phosphine-imidazolium salt of Nolan *et al.*[9]

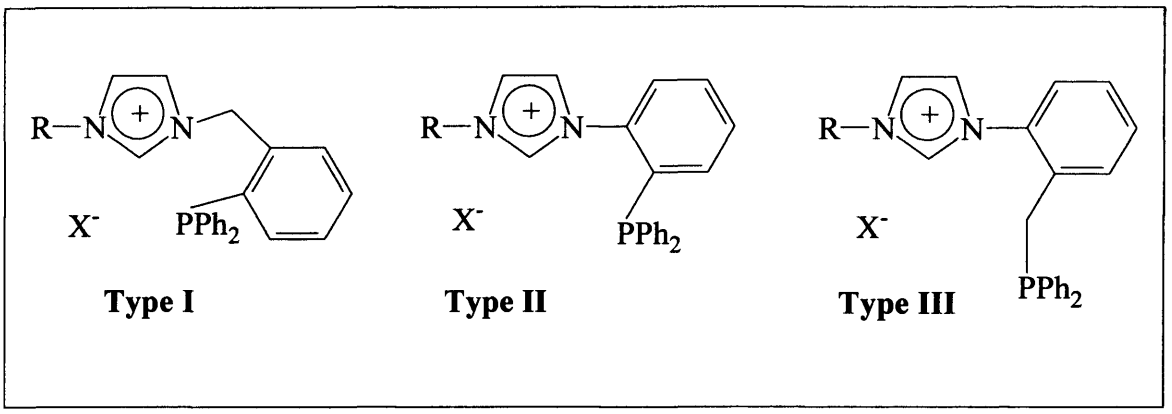



Figure 2.3: Phosphine-imidazolium salts.

| | |
|---|---|
| **Type I** | Phosphine-imidazolium salt with a methyl linker between the imidazolium ring and the phenyl ring. |
| **Type II** | Phosphine-imidazolium salt with no methyl linker. |
| **Type III** | Phosphine-imidazolium salt with a methyl linker between the phosphine and the phenyl ring. |

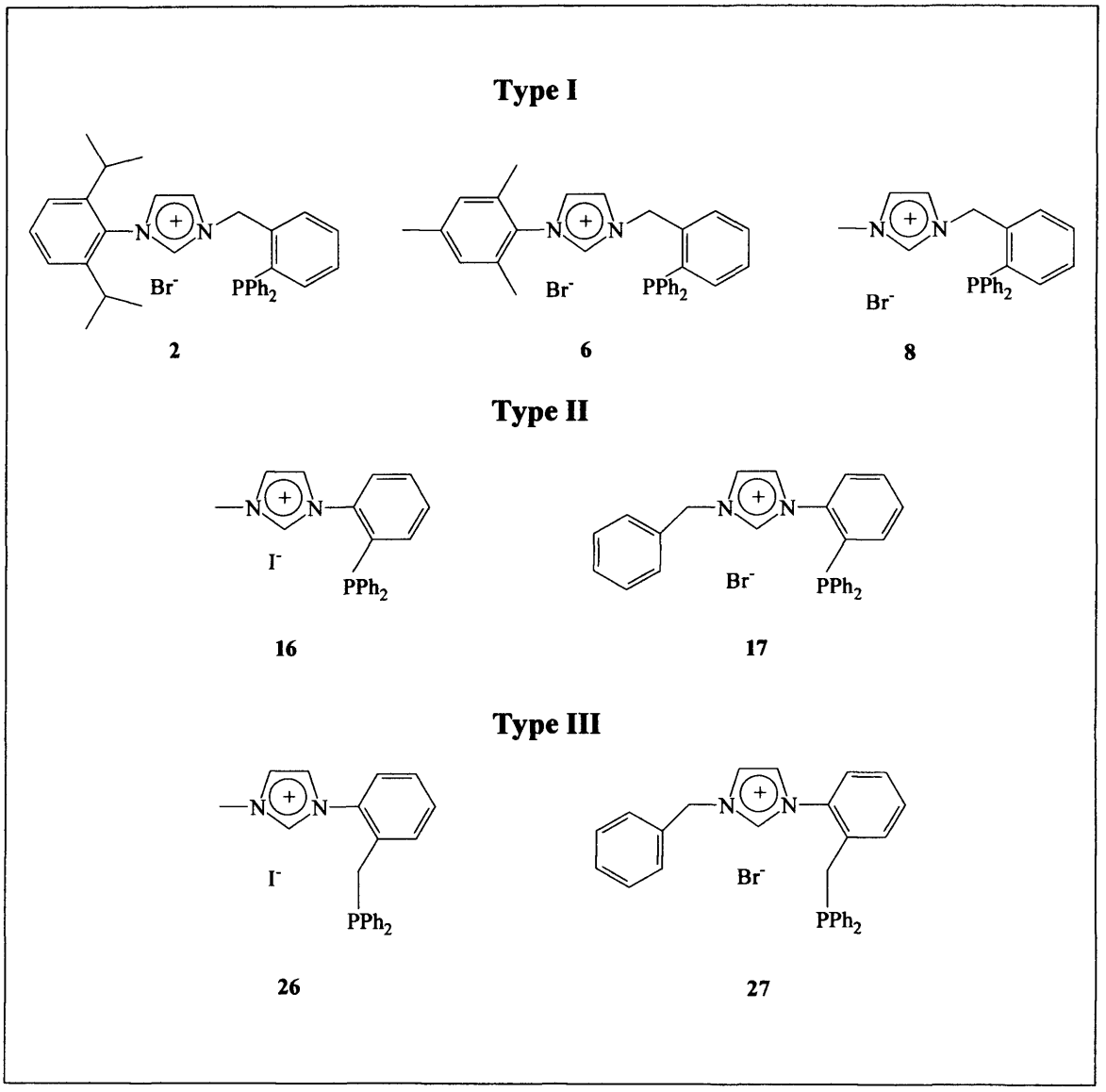
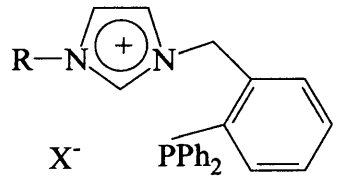



Figure 2.4: Summary of phosphine-imidazolium salts synthesised in this thesis.

# 2.2: Results and discussion

## 2.2.1: Preparation and characterisation of functionalised phosphine-imidazolium salts of Type I

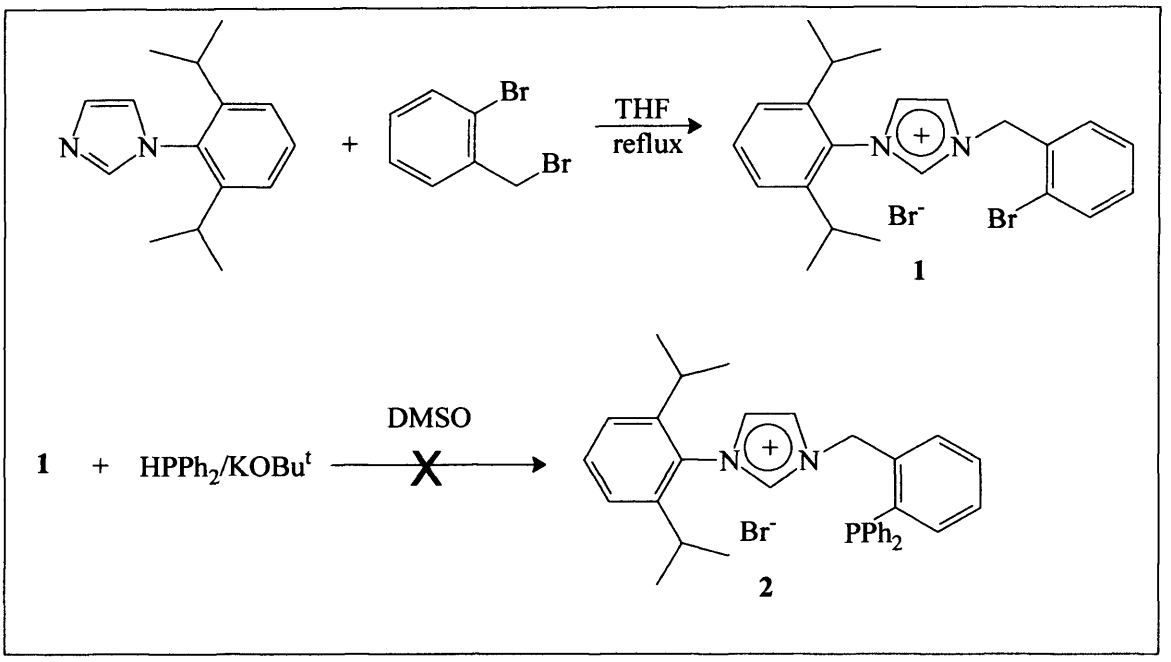
Several methods for the synthesis of the novel ligands of **Type I** were attempted with varying degrees of success.




**Type I**

**Route 1**

The first approach for the synthesis of the phosphine-imidazolium salt was adapted from the work of Nolan *et al.*[9] and initially involved the reaction of a bulky N-substituted imidazole with three equivalents of 2-bromobenzyl bromide in refluxing THF to give the imidazolium salt, **1**, in high yield, 96.2%. The intermediate aryl bromine-imidazolium salt precipitated as a pale tan solid during the reaction. Both the reaction time and the excess of the alkyl bromide was reduced compared to the reported method due to the increased reactivity of 2-bromobenzyl bromide over 1,2-dibromoethane. The second step of the reaction involved the addition of potassium diphenylphosphide, which was freshly prepared *in-situ* from $HPPh_2$ and $KOBu^t$ to imidazolium salt, **1**, (scheme 2.5) in DMSO. Note: Imidazolium salts can be deprotonated by $KOBu^t$ so the potassium diphenylphosphide should be formed and then added to the imidazolium salt. The reaction was worked up following the previous methodology,[9] but from the $^1H$ and $^{31}P$-NMR it was apparent that there was a mixture of the two imidazolium salts as well as unknown side products.




Scheme 2.5: Synthesis of **1** and attempted synthesis of **2**.

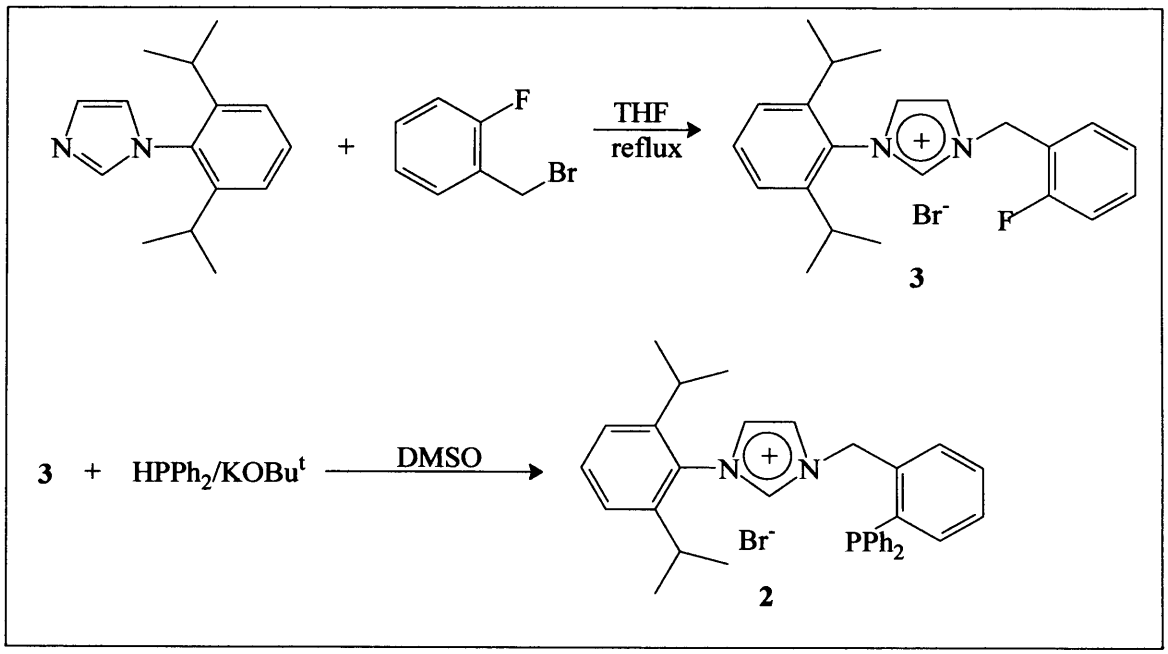
All attempts to purify the product failed. The whole reaction procedure was repeated for the N-substituted mesityl-imidazole, however, the outcome was the same. In an attempt to convert all the imidazolium salt, **1**, into the desired phosphine imidazolium salt, **2**, the reaction was repeated, this time using two equivalents of potassium diphenylphosphide. However, the reaction still did not go to completion and the amount of by-product increased.

**Route 2**

The second approach for the synthesis of the phosphine-imidazolium salt, **2**, (scheme 2.6) was to replace 2-bromobenzyl bromide with 2-fluorobenzyl bromide. The change was prompted by the fact that the fluoride aryl bond is known to react more readily with potassium diphenylphosphide than the bromide aryl bond,[15-17] hopefully giving a greater yield of the desired product and less bi-products. The bulky N-substituted imidazole was again refluxed with three equivalents of 2-fluorobenzyl bromide, giving the desired imidazolium salt, **3**, as an off-white solid which

precipitated from THF over a period of 12h in a yield of 96.6%. The preparation of 1-(*o*-benzyldiphenylphosphino)-3-(2,6-diisopropylphenyl)imidazolium bromide, **2**, was achieved in moderate yield through the reaction of imidazolium salt, **3**, with one equivalent of potassium diphenylphosphide in DMSO at room temperature (r.t.) for 24h (scheme 2.6).

The reaction work-up involved the removal of DMSO under reduced pressure, followed by the addition of MeOH to quench any unreacted $KPPh_2$, the MeOH was then removed. The crude product was washed with copious amounts of diethyl ether and recrystalised from DCM as a white solid by the drop-wise addition of THF. The phosphine imidazolium salt was then recrystalised twice using the same method to give the desired product, **2**, which was then characterised by $^{1}H$, $^{31}P$, and $^{13}C$-NMR and high resolution MS. A singlet was observed in the $^{31}P$-NMR spectra at -15.49 ppm which corresponds to the free phosphine ligand, which is similar to related compounds.[9,16-18] The characteristic peaks in the $^{1}H$-NMR were the $_{im}C_2$-H proton which was observed at 10.73 ppm, the $CH_2$ protons at 6.16 ppm and the 2,6-bis(diisopropyl)phenyl (dipp) protons at 2.17 ppm (sep), and two doublets at 1.14 ppm and 1.03 ppm respectively.

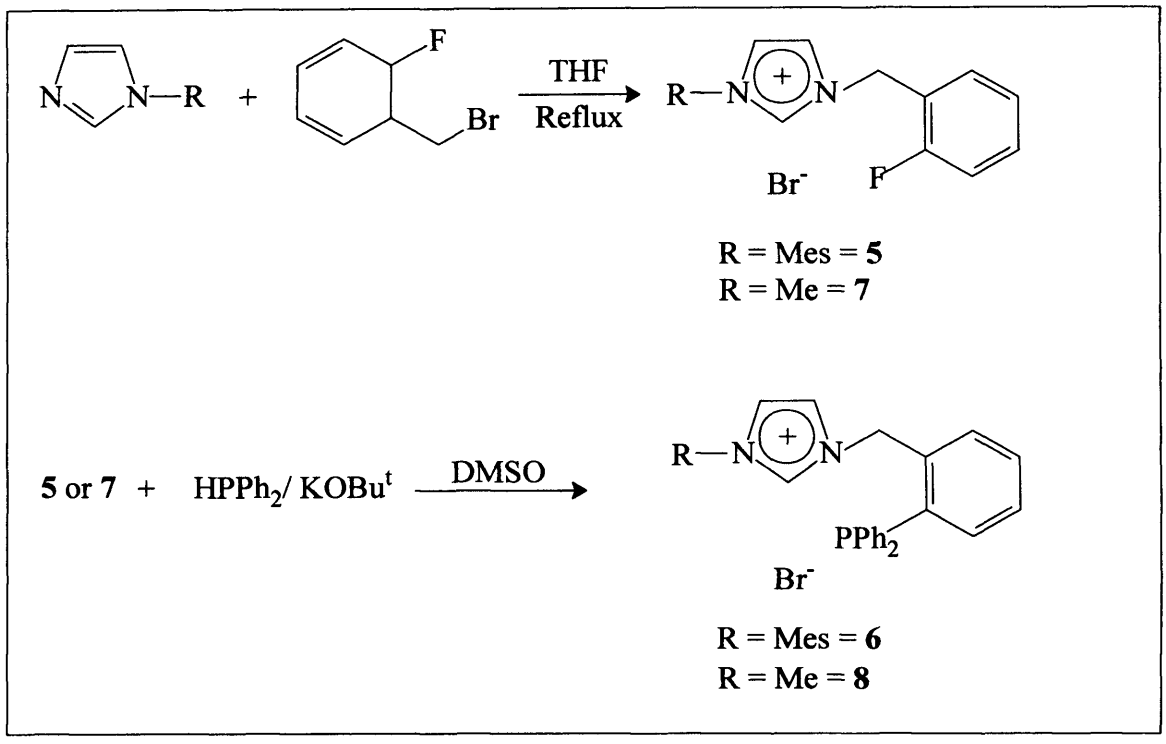



Scheme 2.6: Synthesis of imidazolium salts **2** and **3**.

Attempts were made to change the reaction solvent from DMSO to DMF due to the more favourable characteristics of the latter solvent that make it easier to remove at the end of the reaction; it is also miscible with solvents such as diethyl ether, which simplifies product purification. However, the fluoride imidazolium salts in which there is a methyl bridge between the imidazolium ring and the phenyl ring **(Type I)** are only sparingly soluble in DMF at r.t. The yield of the phosphine-imidazolium salt, **2**, was reduced by the use of DMF at r.t. Increasing the temperature of the reaction so that the imidazolium salt was soluble produced an increased amount of unwanted side-products. The highest yield was achieved when the reaction was stirred for 24h.

The intermediate salts 1-(*o*-fluorobenzyl-3-mesityl)imidazolium bromide, **5**, and 1-(*o*-fluorobenzyl-3-methyl)imidazolium bromide, **7**, were also achieved in almost quantitative yields following the reaction of the corresponding imidazole and 2-fluorobenzyl bromide, (scheme 2.7). The method for the synthesis of phosphine-imidazolium salt, **2**, **(Route 2)**, was successfully applied to give the analogous imidazolium salts, 1-(*o*-benzyldiphenylphosphino-3-mesityl)imidazolium bromide, **6**, and 1-(*o*-benzyldiphenylphosphino-3-methyl)imidazolium bromide, **8**, in moderate yields. All imidazolium salts, **5-8**, were characterised by $^{1}H$ and $^{13}C$-NMR and by high resolution MS and, where appropriate, $^{31}P$-NMR spectroscopy. The $^{31}P$-NMR spectra of salts **6** and **8** both showed a single peak at -15.56 and -16.72 ppm respectively, which corresponds to the free phosphine. Although these chemical shift values are somewhat up-field to that of $PPh_3$ ($\delta$ = -6.0 ppm) the values are similar to related compounds with *ortho*-substituents to the phosphine.[9,16-20]

Figure 2.8 shows the $^{1}H$-NMR spectra of the crude mixture imidazolium salts **7** and **8** following the synthetic methodology described, **(Route 2)**, before the recrystalisation steps. From the $^{1}H$-NMR spectra the yield of the desired phosphine-imidazolium salt, **8**, can be calculated to be around 43%. The isolated yields of all the phosphine-imidazolium salts of **Type 1** structure (**2**, **6** and **8**) are between 41% - 43%. Figure 2.9 shows the $^{1}H$-NMR spectra of compounds **7** and **8** in $CDCl_3$.




Scheme 2.7: Synthesis of imidazolium salts **5-8**.

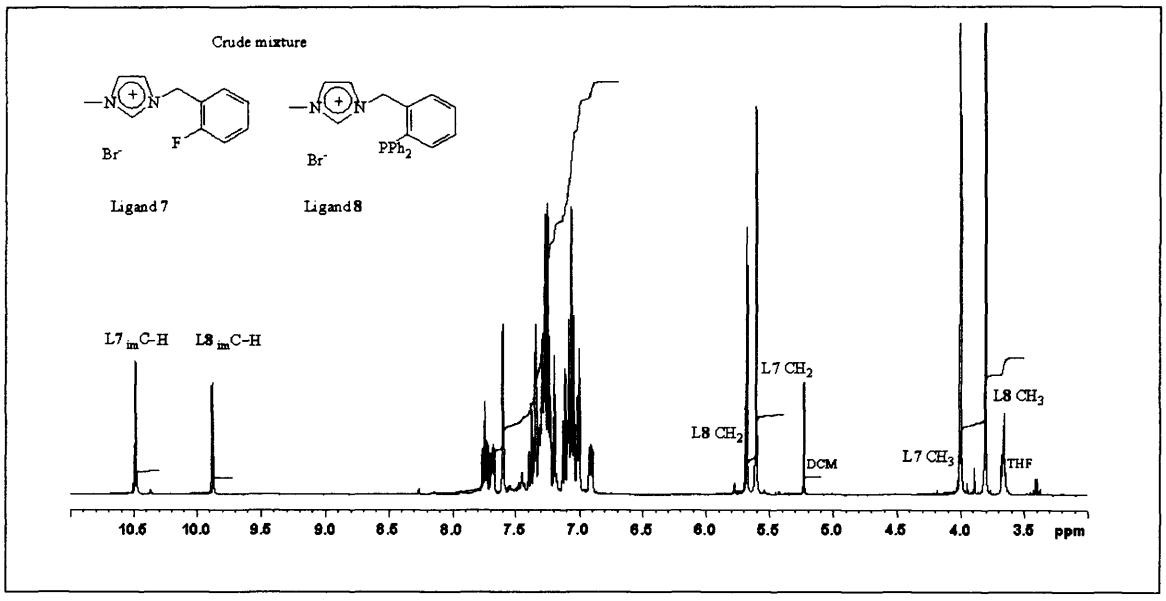



Figure 2.8: $^{1}$H-NMR spectra crude mixture of imidazolium salts **7**:**8** in a 1:0.8 ratio.

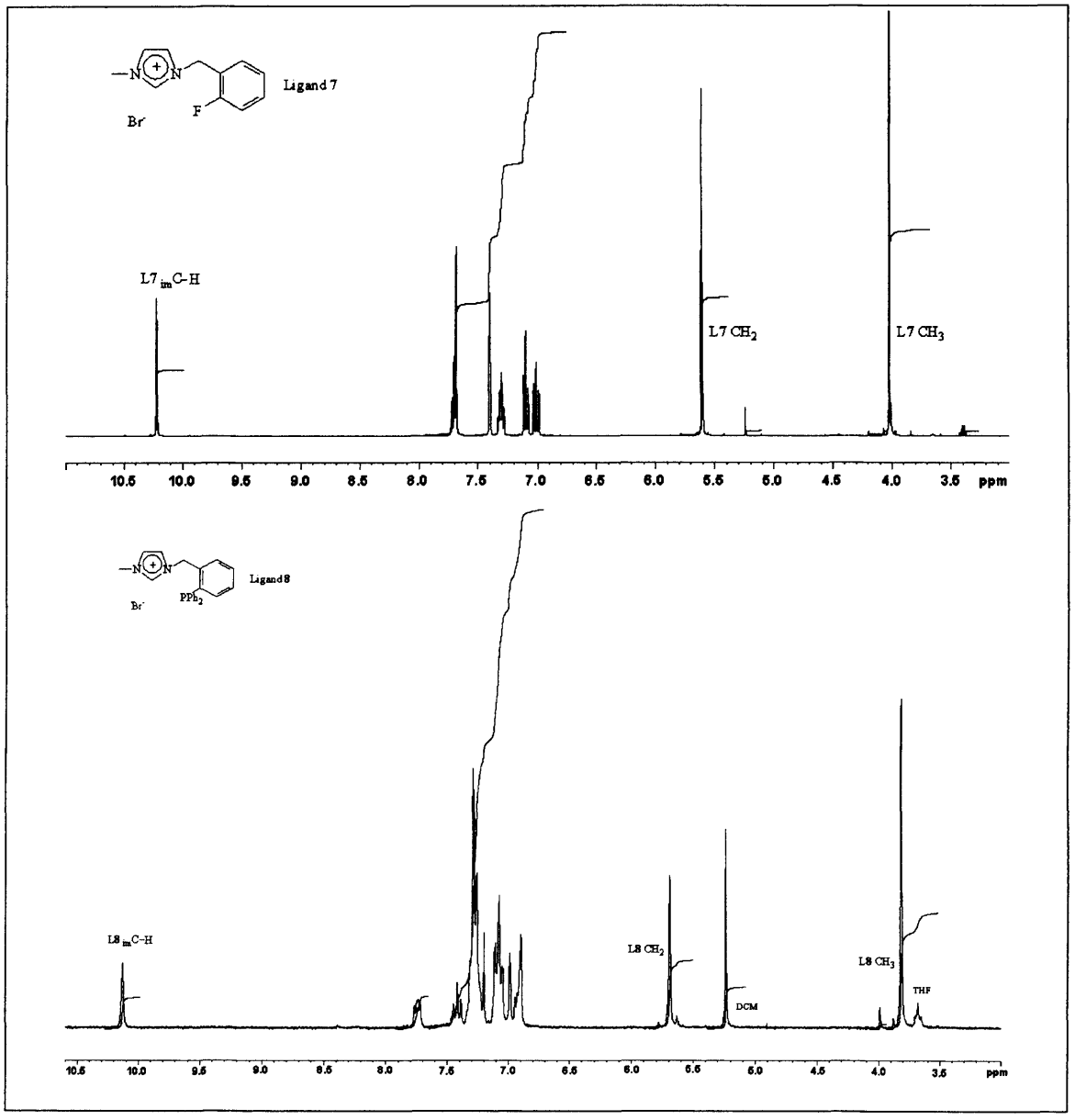
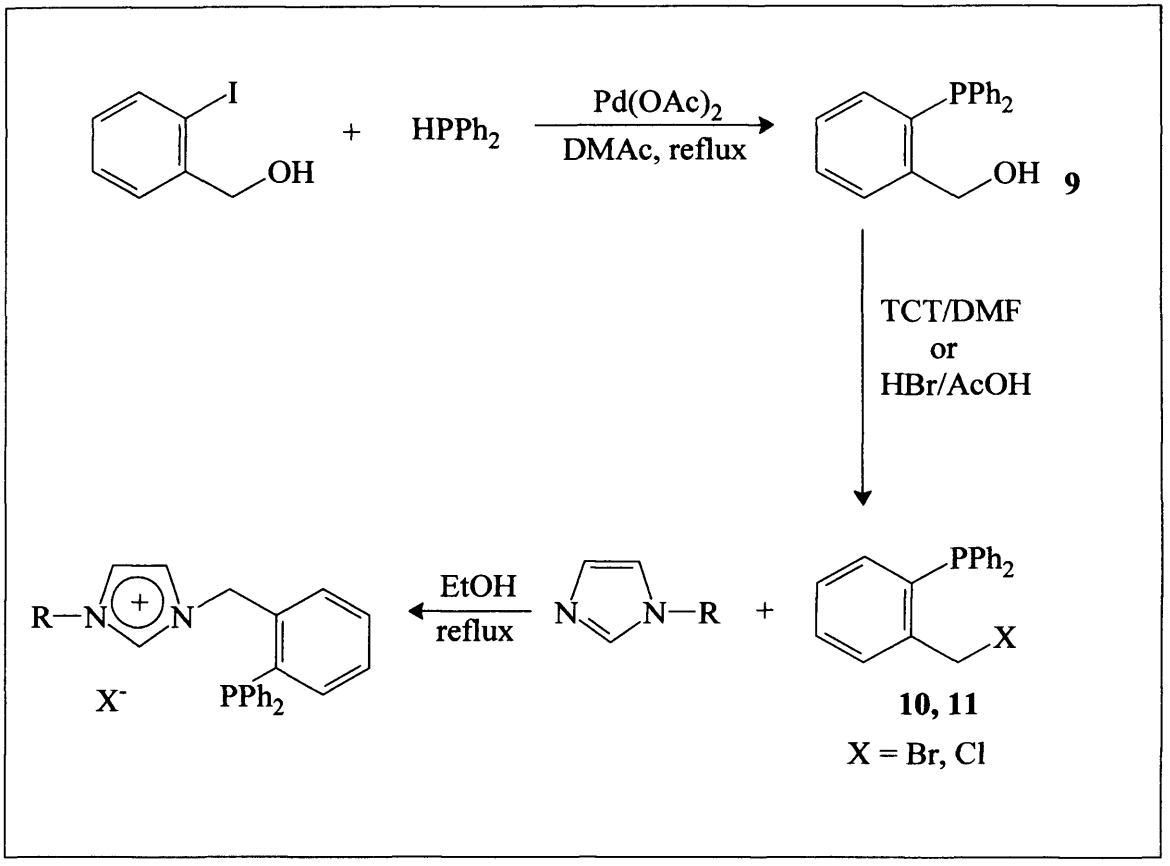



Figure 2.9: $^{1}$H-NMR spectra ($CDCl_3$) of the imidazolium salts **7** and **8**.

**Route 3**

This third approach sought to simplify the synthetic methodology and improve the yield of the phosphine-imidazolium salts.




Scheme 2.10: Synthesis of compounds **9**, **10**, and **11**.

**Route 3** involved the formation of an alkyl halide containing a phosphine functional-group, e.g. $PPh_3$. The advantages of putting the phosphine on the alkyl halide first and then reacting it with an appropriate N-substituted imidazole, includes the wide range of phosphine-imidazolium salts that could be synthesised in one straightforward step from **10** or **11**.

The preparation of 2-diphenylphosphinobenzyl alcohol, **9**, was previously reported by Brauer's group in 2002.[17] Compound **9** was synthesised by the palladium catalysed cross-coupling reaction of the secondary phosphine (diphenylphosphine) and iodobenzyl alcohol. The reaction was carried out in refluxing N,N-dimethylacetamide (DMAc) with $Pd(OAc)_2$ and using KOAc as the base, yielding the desired product as a colourless oil in 97.0% yield. Compound **9** was characterised by $^1H$ and $^{31}P$-NMR spectroscopy, which corresponded with the reported values, where

the characteristic peaks were the $CH_2$ bridge at 4.74 ppm, OH at 2.81 ppm in the $^1$H-NMR and -15.54 ppm in the $^{31}$P-NMR ($CDCl_3$).[17]

The conversion of the alcohol, **9**, into the corresponding halide was carried out in two different ways. The first method was adapted from the procedure of Baker *et al.*[21] and involved the bromination of the appropriate hydroxymethylarene, **9**, with 45% w/v HBr in acetic acid. The reaction was carried out at r.t. and compound **10** was produced in high yield as the free phosphine after a base-assisted aqueous work-up. The second method followed the methodology of a paper published in 2002, in which Baker *et al.* described a mild and quantitative conversion of alkyl alcohols into alkyl chlorides using 2,4,6-trichloro[1,3,5]triazine (TCT).[22] The reaction of TCT with DMF afforded a white solid that was reacted with one equivalent of the alcohol in DCM. The reaction was stirred at r.t. for 4h and after an organic work-up, gave the chloride **11** in moderate yield. The functionalised aryl halide was then reacted with an appropriate imidazole in refluxing EtOH for 7 days. The solvent was then removed and the residue washed with a large volume of THF and recrystalised from DCM/THF to give the imidazolium salts **2** and **8** as white solids in moderate yield. Salts **2** and **8** were characterised $^1$H, $^{13}$C, $^{31}$P-NMR spectroscopy and high resolution MS, which were discussed early in **Route 2.**

Towards the end of this work a couple of papers were published on the synthesis of phosphine-imidazolium salts of **Type I** following a similar method to **Route 3**.[19,20] In this work however, Wang *et al.* followed the method Pregosin for the synthesis of compound **11**.[23]

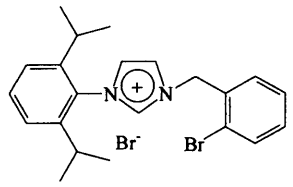
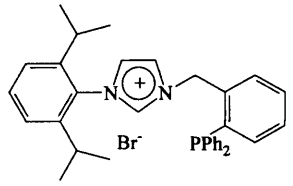
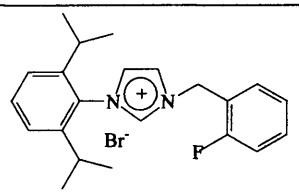
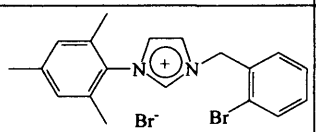
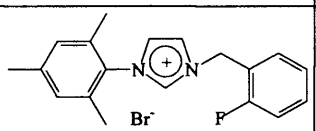
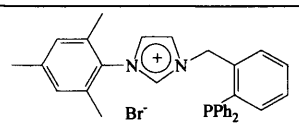
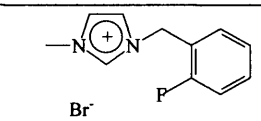
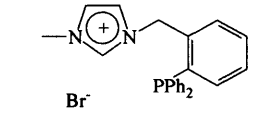
| Imidazolium salts | Number | Characteristic peaks in the $^1$H-NMR (ppm) | $^{31}$P-NMR (ppm) | Yield |
|---|---|---|---|---|
|  | **1** | 10.40, s, $_{im}C_2$-*H*, 5.97, s, C*H*$_2$, 2.23, sep, 2C*H*Me$_2$, 1.12, d, CH*Me*$_2$, 1.12, d,CH*Me*$_2$ | — | 96.2% |
|  | **2** | 10.7, s, $_{im}C_2$-*H*, 6.16, s, C*H*$_2$, 2.17, sep, 2C*H*Me$_2$, 1.14, d, CH*Me*$_2$, 1.03, d,CH*Me*$_2$ | -15.49 | 41.0% (53.3%) |
|  | **3** | 10.6, s, $_{im}C_2$-*H*, 6.10, s, C*H*$_2$, 2.15, sep, 2C*H*Me$_2$, 1.13, d, CH*Me*$_2$, 1.03, d,CH*Me*$_2$ | — | 96.6% |
|  | **4** | 10.35, s, $_{im}C_2$-*H*, 6.06, s, C*H*$_2$, 2.32, s, C*H*$_3$, 2.06, d,CH$_3$ | — | 91.5% |
|  | **5*** | 9.77, s, $_{im}C_2$-*H*, 5.69, s, C*H*$_2$, 2.33, s, C*H*$_3$, 2.02, d,CH$_3$ | — | 93.9% |
|  | **6** | 10.53, s, $_{im}C_2$-*H*, 6.18, s, C*H*$_2$, 2.33, s, C*H*$_3$, 2.01, d,CH$_3$ | -15.56 | 43.1% |
|  | **7** | 10.23, s, $_{im}C_2$-*H*, 5.66, s, C*H*$_2$, 4.02, s, C*H*$_3$ | — | 96.2% |
|  | **8** | 10.13, s, $_{im}C_2$-*H*, 5.70, s, C*H*$_2$, 3.81, s, C*H*$_3$ | -16.71 | 42.0% (54.5%) |

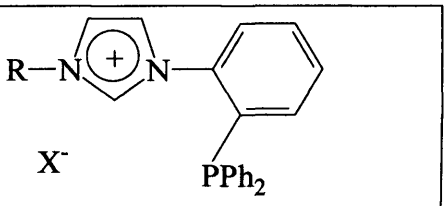
Table 2.11: Summary of imidazolium salts synthesised in Section **2.2.1**

All NMR spectra were recorded in $CDCl_3$ except **5*** which was recorded in $d_6$-DMSO.

(Yield %) corresponds to **Route 3**.

## 2.3: Preparation and characterisation of functionalised phosphine-imidazolium salts of Type II

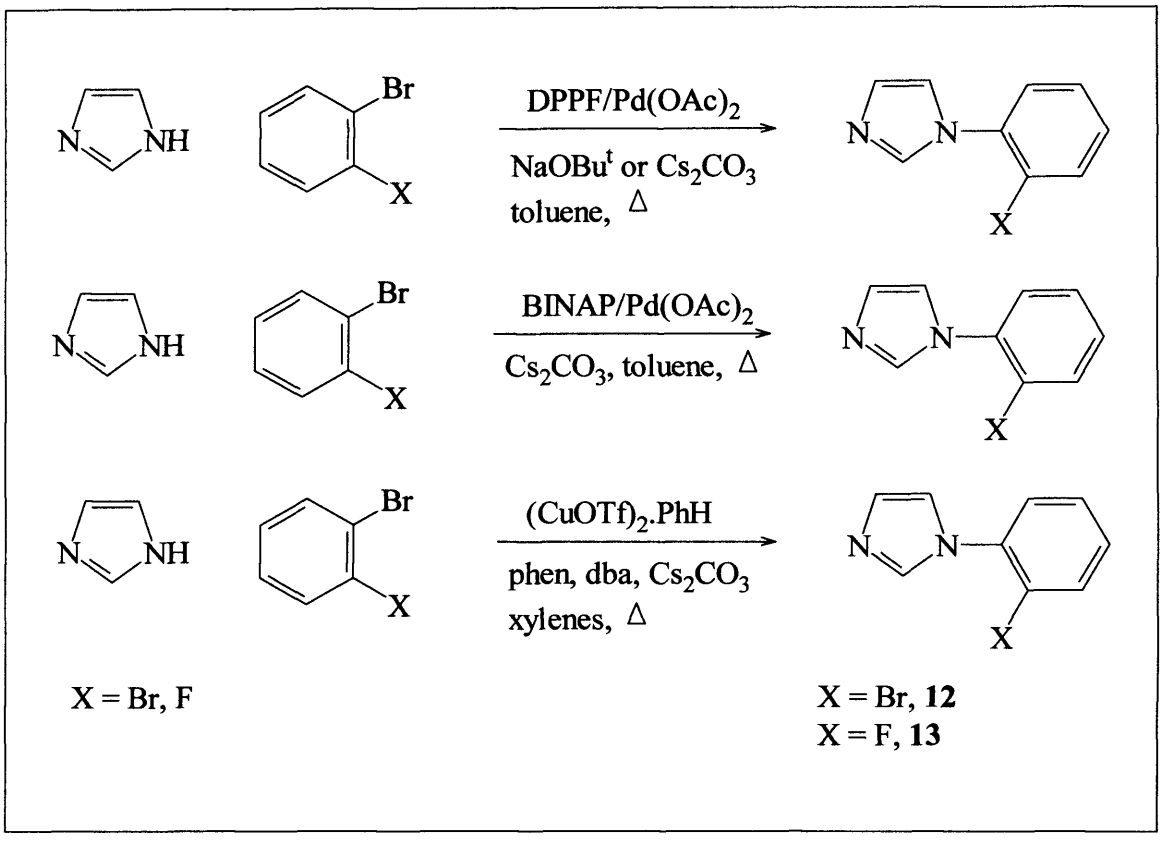
Several methods for the synthesis of the novel ligands of **Type II** structure were attempted with varying degrees of success before an effective method was established.




**Type II**

**Route 1**

The first approach in the synthesis of phosphine-imidazolium salts of **Type II** involved the coupling reaction of aryl halides with imidazole. These catalysed coupling reactions have been reported by the groups of Buchwald[24,25] and Hartwig,[26] all showing catalysed amination reactions of aryl halides or aryl triflates. Two of the three reports employed palladium as the catalyst source and the other was a copper catalysed system. All three methodologies were investigated in an attempt to synthesise compounds **12** and **13**, (scheme 2.12), changing a variety of variables such as temperature, time of reaction, base, ligand, catalyst loading, etc. The copper-catalysed system of Buchwald *et al.*[24] was by far the most successful method of the three for the cross-coupling reactions attempted in this work. The copper-catalysed N-arylation of imidazoles was carried out in the presence of 1,10-phenanthroline (phen) and *trans,trans*-dibenzylideneactone (dba), with $(CuOTf)_2$·benzene as copper source and $Cs_2CO_3$ as the base. The best results were obtained in xylenes, at 125 °C after 48h, and the desired product was isolated after a standard organic work-up, followed by flash chromatography on silica gel. However, yields were still poor with the maximum isolated yield being 34.2%, and so only the highest yielding example is given in the experimental section of this work.

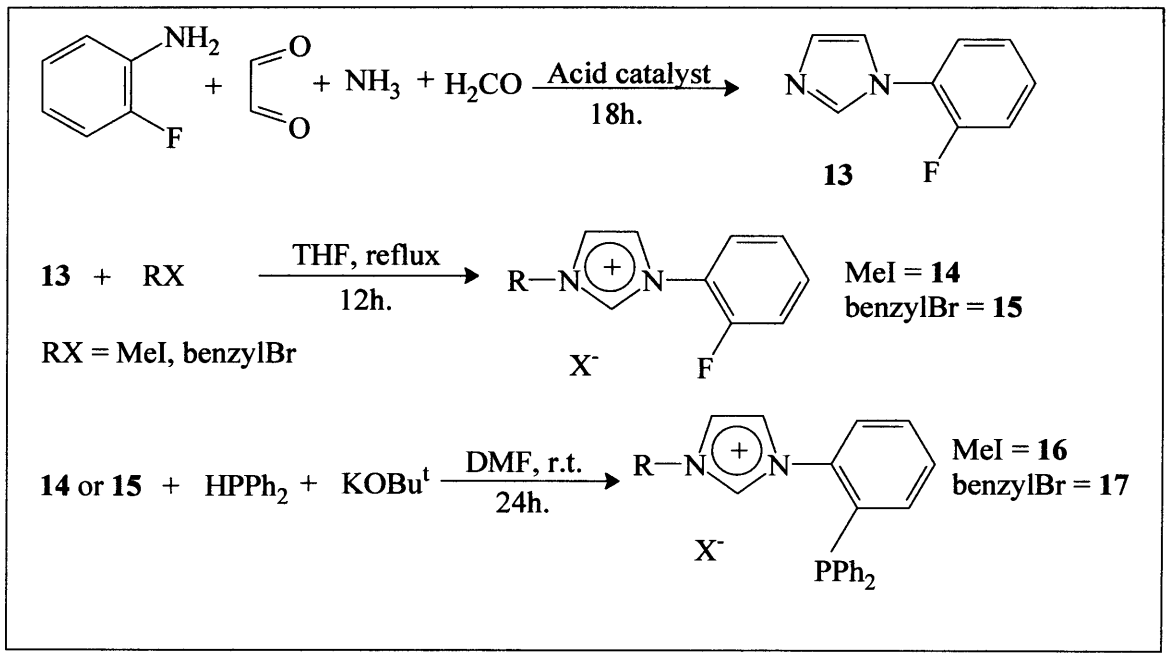



Scheme 2.12: Attempted synthesis of **12** and **13**.

**Route 2**

The second route was adapted from the literature method for the formation for N-substituted imidazoles[5,6] and sought to build the imidazole ring from the corresponding amine, which proved to be a much more effective method. The synthesis of compound **13** was achieved using the acid catalysed reaction of 2-fluoroaniline, ammonium acetate, glyoxal and formaldehyde to give the desired product in moderate yield, 39.3%. The N-substituted 1-(2-fluorobenzene)imidazole can be reacted with alkyl halide to give desired imidazolium salts. In this work, 1-(2-fluorobenzene)imidazole was reacted with methyl iodide and benzyl bromide to give the corresponding imidazolium salts (1-fluorophenyl-3-methyl)imidazolium iodide, **14**, and (1-fluorophenyl-3-benzyl)imidazolium bromide, **15**, in almost quantitative yields. The only limiting factor for the scope of this synthesis for this type of ligands

is that usually only less bulky alkyl halides will react with imidazoles.[14] However, alkylation with bulkier groups such as *iso*-propyl would be expected to be achieved if 1-(2-fluorobenzene)imidazole was reacted with 2-bromopropane under more forcing conditions.[14] The long term aim, which is currently being realised in related projects within our group, is the synthesis of this ligand type with a bulky and perhaps more importantly, an electronically donating group at the $_{im}N_3$ position. An unsymmetrical N,N'-diaryl imidazolium salt has been reported by Grubbs *et al.*,[11] which would indicate that given the right reaction conditions, it would be possible to synthesise this type of ligand containing two different N-substituted aryl groups.




Scheme 2.13: Synthesis of compounds **13-17**.

The fluorophenyl imidazolium salt was then reacted with potassium tertiary butoxide and diphenylphosphine at room temperature (r.t.) for 24h, giving phosphine-imidazolium salts **16** and **17**. The reaction was first carried out in DMSO in the way described for the synthesis of ligand **2**, (scheme 2.6); however imidazolium salts **14** and **15** are freely soluble in DMF at r.t. and it was found that a higher isolated yield was obtained when DMF was used as the solvent. This was due to the fact that

DMF is miscible with diethyl ether ($Et_2O$) used in the work-up and therefore the work-up is cleaner and simpler.

During the course of the reaction between **14** and potassium diphenylphosphine, the reaction changed from deep red to a pale red/orange colour, as the potassium diphenylphosphine was consumed. After 24h the solvent volume was removed under vacuum and MeOH was added to quench any unreacted $KPPh_2$. The MeOH was then removed under vacuum and DCM was added to the crude mixture, which was then filtered and the volume of DCM was reduced under vacuum. $Et_2O$ was added to give a precipitate that was washed with a large volume of $Et_2O$ to give the desired imidazolium salt **16** as a pale red solid. The product was fully characterised by $^{1}H$, $^{31}P$, and $^{13}C$-NMR, by high resolution MS and elemental analysis. In the $^{1}H$-NMR the $_{im}C_2$-H proton was observed at 9.16 ppm, the $CH_3$ protons at 3.99 ppm and a singlet was observed in the $^{31}P$-NMR spectra at -16.86 ppm in $CD_3Cl$. Diffusion of hexane into a DCM solution of **16** yielded crystals suitable of a single crystal X-ray crystallographic determination.

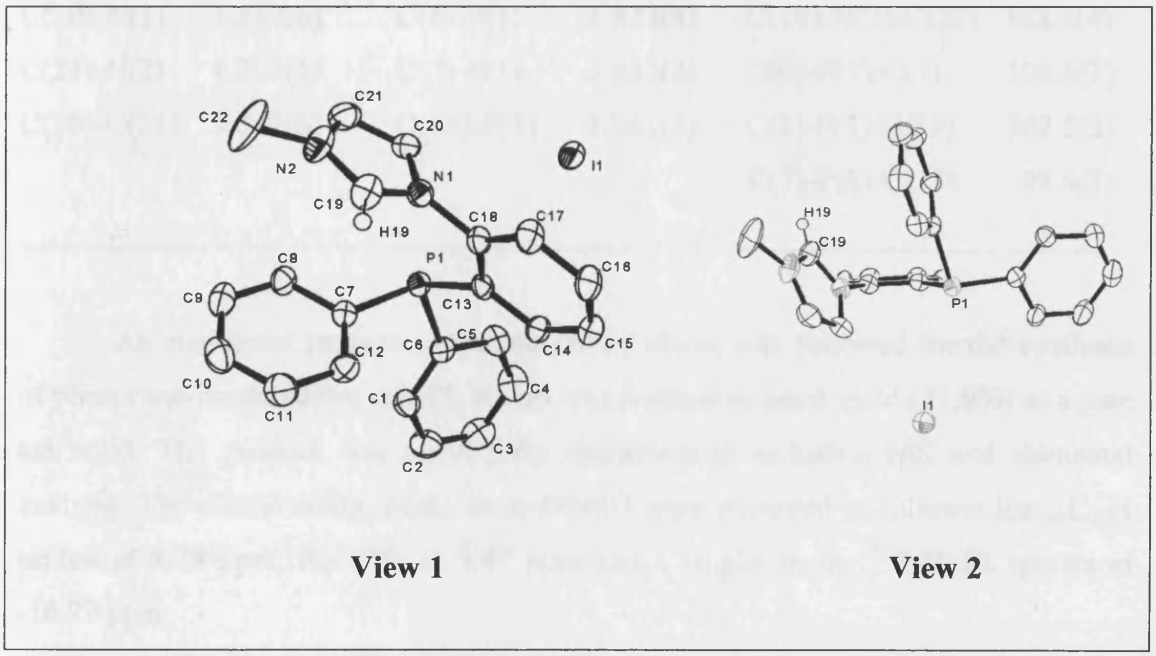



Figure 2.14: ORTEP projection of phosphine-imidazolium salt **16**. Hydrogen atoms (except H 19) and two dichloromethane molecules are omitted for clarity.

The structure and labelling scheme for **16** is shown in figure 2.14 and selected bond lengths and angles are collected in table 2.15. **View 2** of figure 2.14 shows the view through the plane of the central benzene ring, in which both the phosphine and the imidazolium ring are attached, and it shows that the imidazolium proton is orientated in the opposite direction to the phosphine lone pair, probably because of the electrostatic repulsion in that region. The dihedral angle between the plane of the imidazolium ring and the plane of the central benzene ring is approximately 63.2°. The $_{im}C_2$-H proton does not interact with the iodine ion H(19)·····I = 8.60(0)Å (approx.), or with any other atom. The average P-C bond length (1.833(3)Å) and C-P-C bond angle (102.1(9)°) are not changed significantly from the corresponding value in $PPh_3$, P-C (1.831(1)Å) and C-P-C (102.8(2)°).[16]

Table 2.15: Selected bond lengths (Å) and angles (degrees) for imidazolium salt **16**.

| | | | | | |
|---|---|---|---|---|---|
| C(19)-N(1) | 1.333(5) | C(18)-N(1) | 1.441(5) | N(1)-C(19)-N(2) | 108.4(3) |
| C(19)-N(2) | 1.331(5) | C(22)-N(2) | 1.469(5) | C(19)-N(1)-C(18) | 124.6(3) |
| C(20)-N(1) | 1.347(6) | C(6)-P(1) | 1.823(4) | C(19)-N(2)-C(22) | 125.5(4) |
| C(21)-N(2) | 1.379(5) | C(7)-P(1) | 1.835(3) | C(6)-P(1)-C(7) | 104.6(2) |
| C(20)-C(21) | 1.347(6) | C(13)-P(1) | 1.841(3) | C(6)-P(1)-C(13) | 102.5(2) |
| | | | | C(7)-P(1)-C(13) | 99.4(3) |

An analogous process to that described above was followed for the synthesis of phosphine-imidazolium salt **17,** which was isolated in good yield (71.9%) as a pale tan solid. The product was again fully characterised including MS and elemental analysis. The characteristic peaks in $d_6$-DMSO were observed as follows: the $_{im}C_2$-H proton at 9.79 ppm, the $CH_2$ at 5.47 ppm and a singlet in the $^{31}$P-NMR spectra at -16.79 ppm.

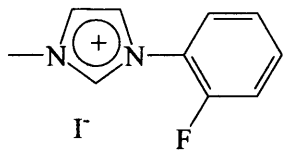
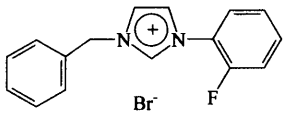
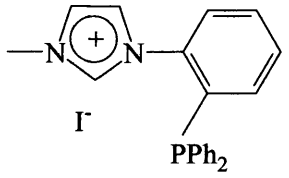
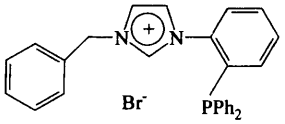
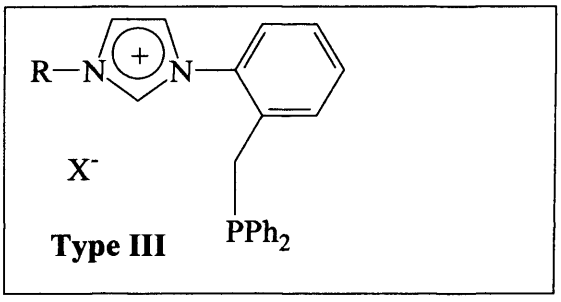
| Imidazolium salts | Number | Characteristic peaks in the $^1$H-NMR (ppm) | $^{31}$P-NMR (ppm) | Yield |
|---|---|---|---|---|
|  | **14** | 10.14, s, $_{im}C_2$-*H*,<br>4.24, s, C*H*$_3$ | — | 97.1% |
|  | **15** | 10.31, s, $_{im}C_2$-*H*,<br>5.82, s, C*H*$_2$, | — | 93.3% |
|  | **16** | 9.16, s, $_{im}C_2$-*H*,<br>3.97, s, C*H*$_3$ | -16.86 | 74.1% |
|  | **17*** | 9.79, s, $_{im}C_2$-*H*,<br>5.48, s, C*H*$_2$, | -16.79 | 71.9% |

Table 2.16: Summary of imidazolium salts synthesised in Section **2.3**.

All NMR spectra were recorded in $CDCl_3$ except **17*** which was recorded in $d_6$-DMSO.

## 2.4: Preparation and characterisation of functionalised phosphine-imidazolium salts of Type III

Several methodologies were attempted for the formation of the novel ligands of **Type III** structure before an effective method was established.




**Route 1**

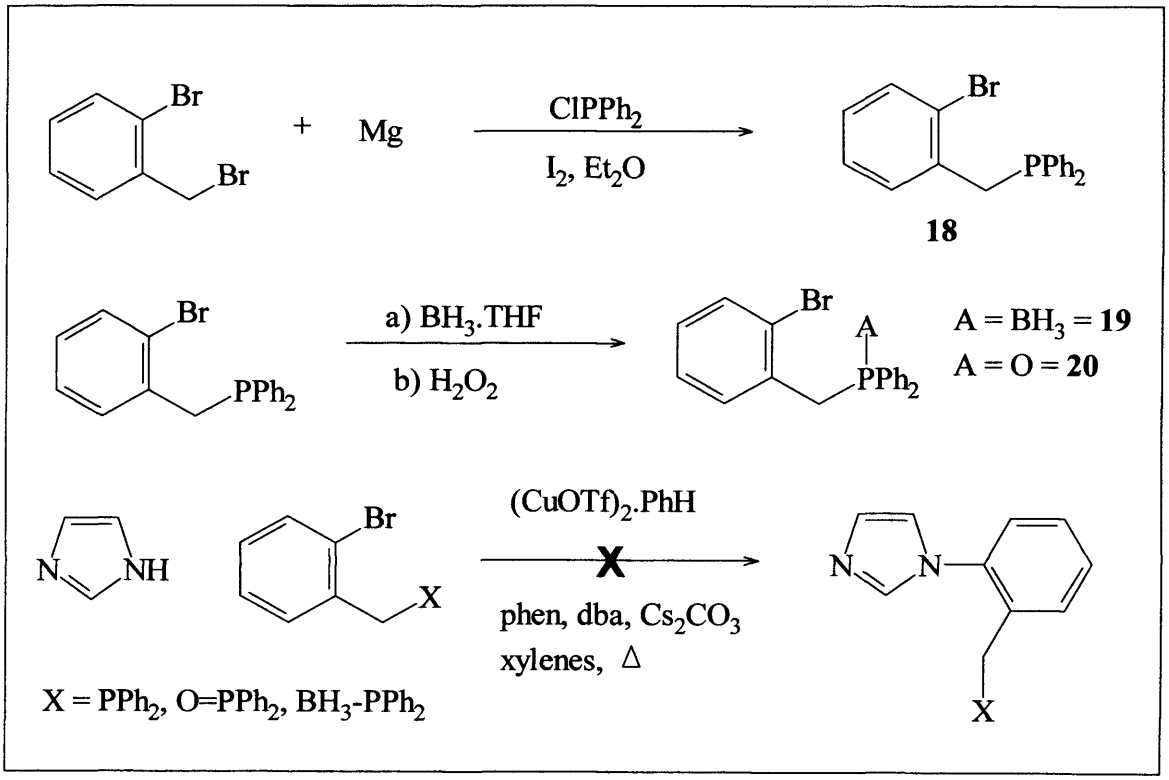



Figure 2.17: Synthesis of compounds **18**, **19**, and **20**.

The Buchwald[24] coupling method was applied in order to couple imidazole with a functionalised aryl halide. The synthesis of compound **18** was achieved by following the adapted synthetic methodology of a previous paper.[27] The attempted synthesis of 1-(phenyl-*o*-diphenylphosphino)imidazole by the cross-coupling method was not successful. The phosphine group on compound **18** was then protected to give compounds **19** and **20**, then both were reacted with imidazole in the cross-coupling reaction, however the desired product could not be isolated from the reaction work-up and therefore more viable methods were sought for the synthesis of these phosphine-imidazolium salts, **(Type III)**. Due to the fact that the desired product could not be isolated using this method the experimental details are not given in this work.

**Route 2**

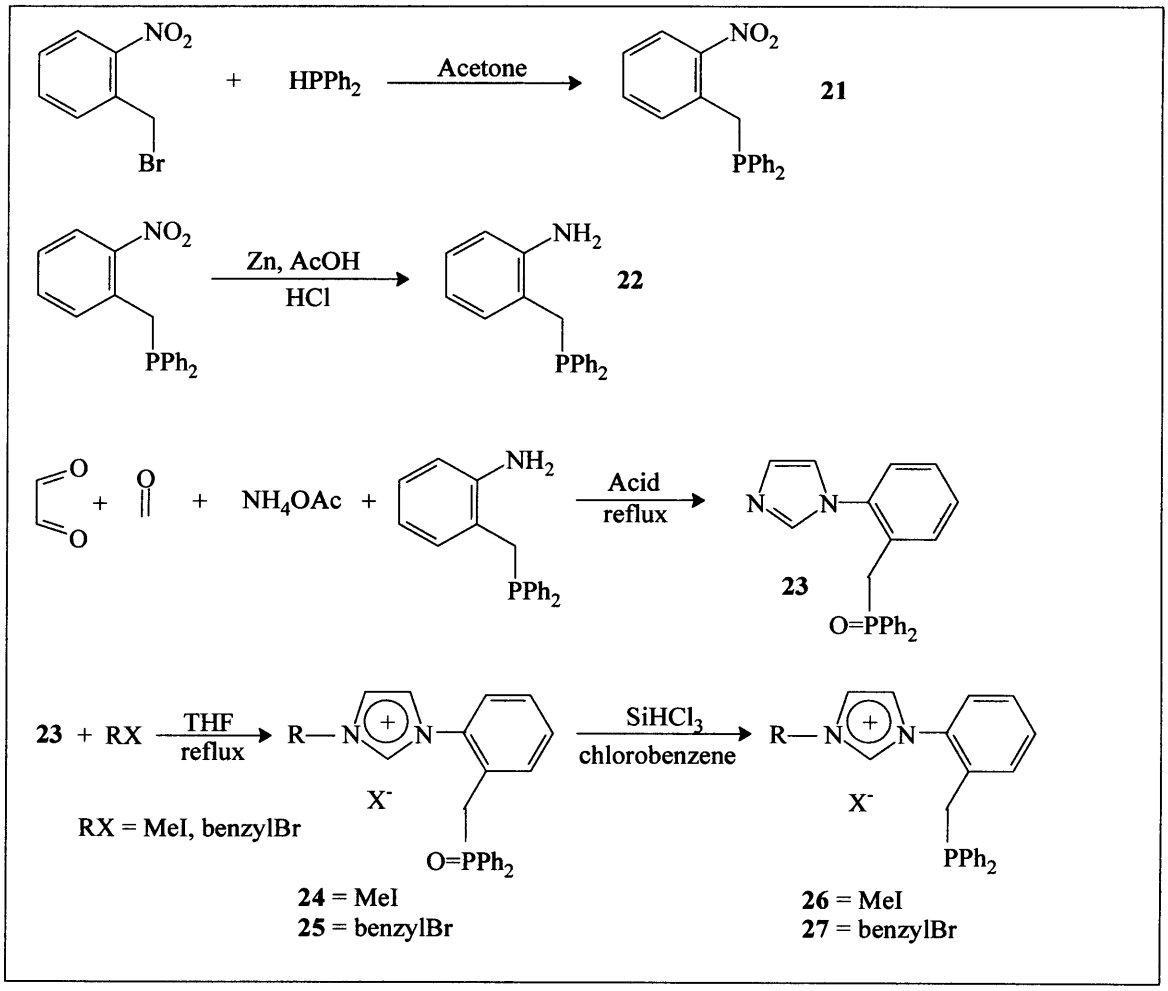



Figure 2.18: Synthesis of compounds **21-27**.

In a second approach, compound **21** was afforded in high yield (78.0%) by the reaction of 2-nitrobenzyl bromide with diphenylphosphine at 0 °C. The phosphine salt [$PHRPh_2$] Br of 2-nitrobenzyl diphenylphosphine, **21**, precipitated out of the acetone solution during the course of the reaction. Reduction of the nitro-group was achieved by reacting compound **21** with metallic zinc in the presence of acid, following the method of a previous paper in which a similar nitro-phosphine salt was reduced.[28] After an organic work-up the product, **22**, was isolated as a pale yellow solid (yield 81.7%). The product, **22**, was characterised by $^{1}H$ and $^{31}P$-NMR and the product was found to be a mixture of free phosphine at -19.91 ppm and phosphine salt at 35.64 ppm. The amine was then converted into the N-functionalised imidazole, again adapting the literature method for the formation for N-substituted imidazoles.[5,6] The product, **23**, was isolated in moderate yield as a mixture of desired product and oxide and characterised by $^{1}H$ and $^{31}P$-NMR. The imidazole-functionalised phosphine oxide was then reacted with aryl halides methyl iodide and benzyl bromide to give the corresponding imidazolium salts (1-phenyl-*o*-diphenylphosphino-oxide-3-methyl)imidazolium iodide, **24**, and (1-phenyl-*o*-diphenylphosphino-oxide-3-benzyl)imidazolium bromide, **25**, in high yield, (84.1%-79.8%). The oxide was then reduced to the corresponding free phosphine following the published method for similar phosphine-oxide imidazolium salts.[18] Imidazolium salts **26** and **27** were both characterised by $^{1}H$ $^{13}C$ and $^{31}P$-NMR, the $_{im}C_2$-H protons were observed at 9.53 ppm and 9.85 ppm respectively for **26** and **27** and singlets were observed in the $^{31}P$-NMR spectra at -17.05 ppm and -16.96 for **26** and **27** respectively, which is in the range of similar phosphine-imidazolium salts.[2,9,18] This synthesis is relatively laborious and was not considered the best route to these salts.

**Route 3**

This route provided the most convenient synthesis of the desired phosphine-imidazolium salts **26** and **27**. The functionalised imidazole 1-(phenyl-*o*-alcohol)imidazole, **28**, was again formed by the reaction of the corresponding amine, ammonium acetate, glyoxal and formaldehyde to give the desired product in

moderate yield, (43.5%), figure 2.19. The characteristic peaks in the $^1$H-NMR spectra were a broad singlet at 5.40 ppm which corresponded to the OH group, and a singlet for the $CH_2$ group at 4.30 ppm.

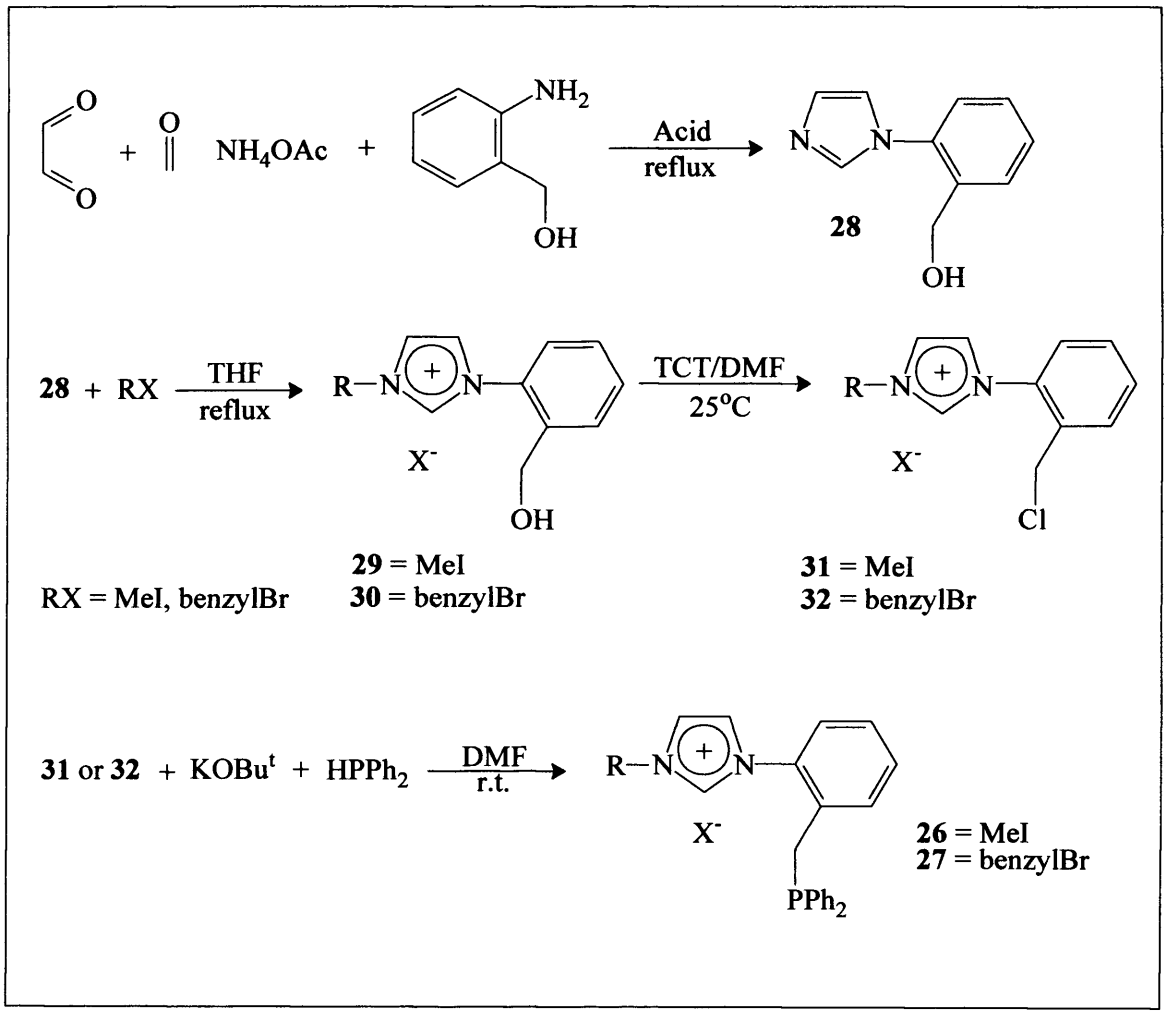
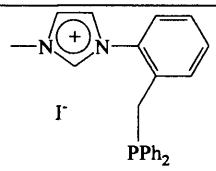
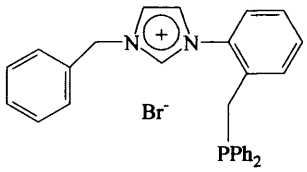
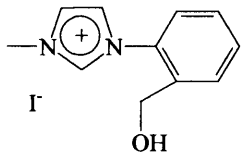



Figure 2.19: Synthesis of compounds **26-32**.

The 1-(phenyl-*o*-alcohol)imidazole, was then reacted with alkyl halides to give imidazolium salts **29** and **30** in almost quantitative yields. In both $^1$H-NMR spectra the OH proton is observed around 5.0 ppm and the benzylic $CH_2$ group at around 4.4 ppm. The $_{im}C_2$-H of compound **29** was at 9.46 ppm, whereas for **30** it was further downfield at 9.76 ppm as expected. The (1-phenyl-*o*-alcohol)imidazolium salts were then converted into (1-phenyl-*o*-chloride)imidazolium salts by reacting them with

2,4,6-trichloro[1,3,5]triazine (TCT) and DMF.[22] The reaction of TCT with DMF afforded the formation of a white solid which was then reacted with one equivalent of the alcohol in a DCM/DMF mixture. The mixture of DCM/DMF was needed because the alcohols, **29** and **30**, are not soluble in DCM, whereas the corresponding chlorides are, meaning that the product can be extracted in DCM at the end of the reaction. Imidazolium salts **31** and **32** were isolated as yellow/orange solids in high yields, and were characterised by $^{1}H$ and $^{13}C$-NMR spectroscopy. In the $^{1}H$-NMR spectra of the two imidazolium salts, the $CH_2$ group had shifted downfield from about 4.4 ppm in the alcohol to around 4.8 ppm in the halide, there was little effect on the $_{im}C_2$-H shift in both cases. Imidazolium salts **31** and **32** were then reacted with diphenylphosphide in the manner described in Section **2.2.1** and **2.3** (**Route 2**) to give the corresponding phosphine-imidazolium salt, (1-phenyl-*o*-diphenylphosphino-3-methyl)imidazolium iodide, **26**, and (1-phenyl-*o*-diphenylphosphino-3-benzyl)imidazolium bromide, **27**, in moderate yields (70.7%, 68.7%). The products were characterised by $^{1}H$ $^{13}C$ and $^{31}P$-NMR, which were discussed in **Route 2** (page 66).

| Imidazolium salts | Number | Characteristic peaks in the $^{1}H$-NMR (ppm) | $^{31}P$-NMR (ppm) | Yield |
|---|---|---|---|---|
|  | **26** | 9.79, s, $_{im}C_2$-*H*, 5.22, s, $CH_2$, 4.16, s, $CH_2$. | -17.05 | 70.7% |
|  | **27** | 9.85, s, $_{im}C_2$-*H*, 5.60, s, $CH_2$benzyl, 5.10, s, $CH_2PPh_2$ | -16.96 | 68.7% |
|  | **29** | 9.46, s, $_{im}C_2$-*H*, 5.05, br.s, OH, 4.44, s, $CH_2$, 3.96, s, $CH_3$ | ___ | 91.0% |

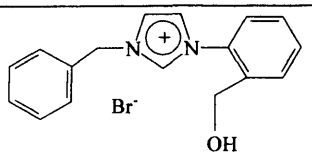
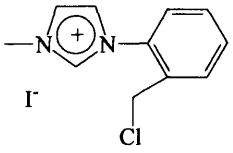
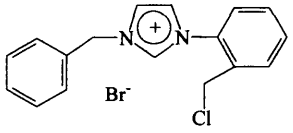
| | | | | |
|---|---|---|---|---|
|  | **30** | 9.76, s, $_{im}C_2$-*H*, 5.55, s, NC*H*$_2$benzyl, 4.73 br.s, OH, 4.42, s, C*H*$_2$OH. | ___ | 88.2% |
|  | **31** | 9.32 (s, 1H, $_{im}C_2$-*H*), 4.89, s, C*H*$_2$Cl, 3.81, s, C*H*$_3$. | ___ | 74.8% |
|  | **32** | 9.82, s, $_{im}C_2$-*H*, 5.56, s, NC*H*$_2$benzyl, 4.80, s, C*H*$_2$Cl. | ___ | 71.5% |

Table 2.20: Summary of imidazolium salts synthesised in Section **2.4**.

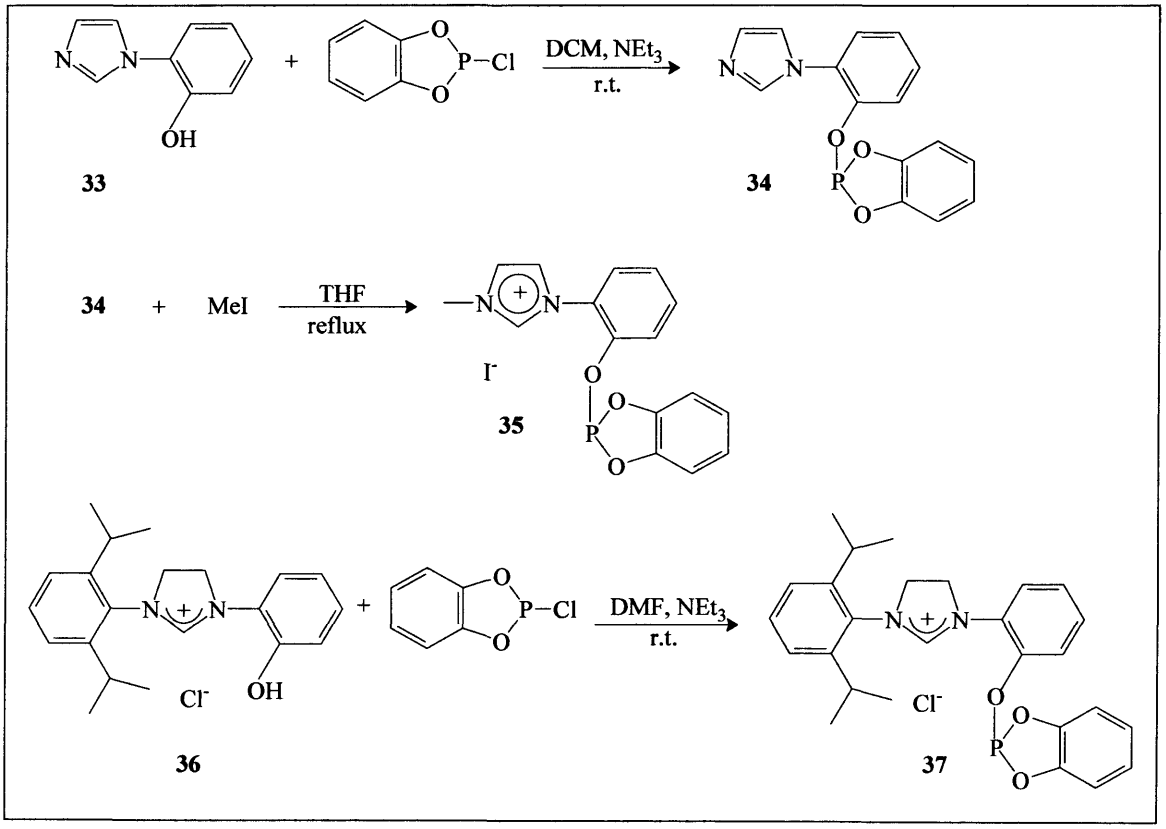
All NMR spectra were recorded in $d_6$-DMSO.

## 2.5: The synthesis of functionalised phosphite-imidazolium salts

The synthesis of two phosphite-imidazolium salts was attempted by the reaction of alcohol-functionalised imidazoles and imidazolium salts with *o*-1,2-phenylenephosphite chloride (scheme 2.21).

1-(2-phenol)imidazole, **33**, was formed from the corresponding amine by adapting the literature method for the formation of N-substituted imidazoles.[5,6] Imidazolium **33** was then reacted with one equivalent of *o*-1,2-phenylenephosphite chloride and triethylamine ($NEt_3$) in THF to give the desired product as a yellow/orange solid. The phosphite imidazole, **34**, was characterised by $^1H$, $^{13}C$ and $^{31}P$-NMR spectroscopy with the peak at 126.9 ppm in the $^{31}P$-NMR corresponding to the desired product, which is similar to that observed for $P(OPh)_3$ (~120 ppm).

The phosphine imidazole was then reacted with one equivalent of methyl iodide in refluxing THF for two days to give the corresponding phosphite-imidazolium salt (1-*o*-1-phenylenephosphitebenzene)-3-(methyl)imidazolium iodide, **35**, which was isolated as a yellow/orange solid and characterised by $^{1}H$ and $^{31}P$-NMR. The $^{1}H$-NMR of **35** showed the $_{im}C_2$-H proton at 9.47 ppm and the $CH_3$ group at 3.91 ppm (DMSO) which is characteristic for the formation of an imidazolium salt. However, in the $^{31}P$-NMR spectra two peaks were observed, one of which was the desired product at 129.9 ppm and the other was an unknown peak at 174.3 ppm in a ratio of 5:1 respectively. (The unknown peak at 174.3 ppm was not thought to be the oxide or a salt of the phosphite because they would appear much further up-field in the spectra).[29,30] Attempts to isolate the phosphite-imidazolium salt, **35**, as a pure compound failed.




Scheme 2.21: Synthesis of compounds **33-37**. Imidazolium salt **36** was previously synthesised by Grubbs *et al.*[11]

Imidazolium salt **36** was previously synthesised by Grubbs *et al.*[11] and was reacted further in an attempt to form the phosphite-imidazolium salt **37** by the reaction of **36** with secondary chlorophosphite (*o*-1,2-phenylenephosphite). The reaction was carried out at r.t. in the presence of base ($NEt_3$) following the general methodology.[29] Phosphite-imidazolium salt **37** was isolated as a yellow solid and was characterised by $^1H$ and $^{31}P$-NMR spectroscopy. However, from the NMR it is clear that although the desired product has formed, the product was not isolated cleanly. The $^1H$-NMR showed a mixture of the starting imidazolium salt **36** and the desired phosphite-imidazolium salt **37** in a ratio of approximately 1:1. The $^{31}P$-NMR showed several peaks at 137.1 ppm, 75.1 ppm, and 21.8 ppm in a ratio of 1:2:1. The peak at 137.1 ppm corresponds to the desired product and the two other significant peaks are unknown. Attempts to recrystalise the phosphite-imidazolium salt **37** were unsuccessful.

Evaporation of a DCM solution of **36** yielded crystals suitable for a single crystal X-ray crystallographic determination (figure 2.23). Selected bond lengths and angles for imidazolium salt **36** are given in table 2.22. The plane of the imidazolium and phenyl ring of imidazolium salt **36** make an angle of approximately 82.8°, with $_{im}C_2$-H and the hydroxyl group directed towards the same side of the molecule. Steric crowding between O(1) and H(1) is the most likely cause of the divergence from ring coplanarity. The dihedral angle between the plane of the imidazolium ring and the plane of the bulky 2,6-(diisopropylphenyl) substituent is 95.8°. The hydroxyl group hydrogen approaches the chloride counterion with H(1)·····Cl = 2.99(9)Å (approx); the $_{im}C_2$-H proton does not contact any other atoms.

Table 2.22: Selected bond lengths (Å) and angles (degrees) for imidazolium salt **36**.

| | | | | | |
|---|---|---|---|---|---|
| C(1)-N(1) | 1.300(8) | C(2)-C(3) | 1.526(9) | N(1)-C(1)-N(2) | 113.4(5) |
| C(1)-N(2) | 1.314(8) | C(4)-N(2) | 1.427(8) | C(1)-N(1)-C(10) | 124.7(5) |
| C(2)-N(2) | 1.480(9) | C(10)-N(1) | 1.451(8) | C(1)-N(2)-C(4) | 126.7(5) |
| C(3)-N(1) | 1.485(8) | C(9)-O(1) | 1.354(8) | | |

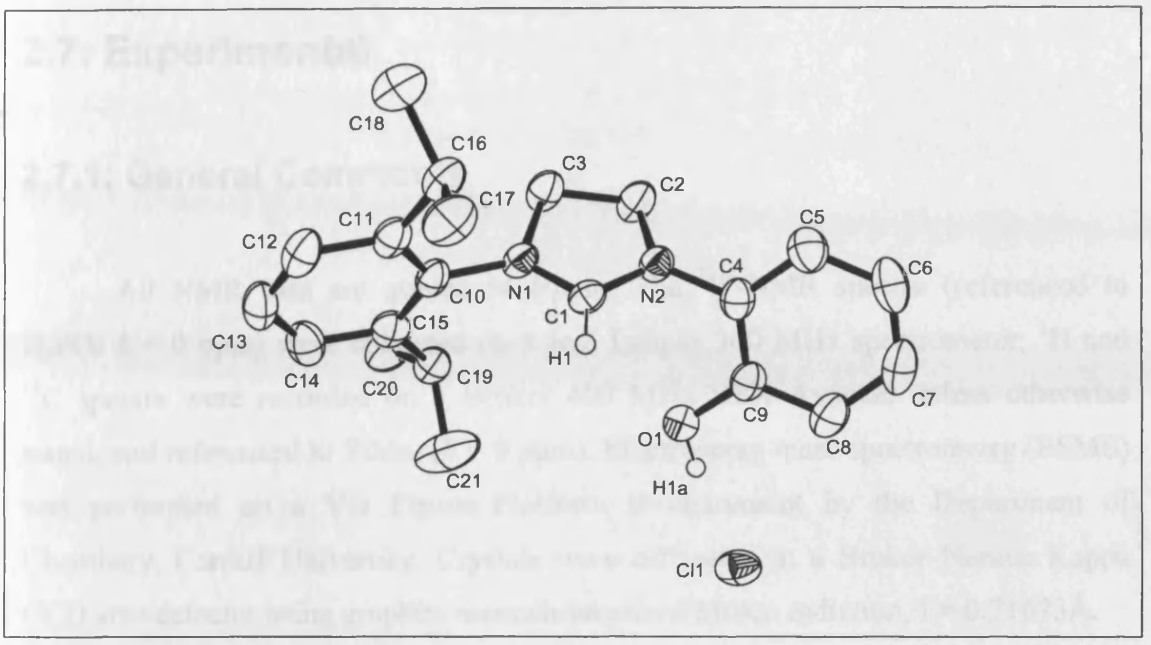



Figure 2.23: ORTEP projection of imidazolium salt **36**. Hydrogen atoms (except H 1 and H 1a), one dichloromethane molecule and one water molecule are omitted for clarity. First synthesised by Grubbs *et al.*[11].

## 2.6: Conclusion

A series of imidazolium salts, many of which combine an imidazolium moiety with a functional group, have been synthesised and characterised as precursors to the corresponding phosphine-NHC ligands. Three main types of phosphine-imidazolium salt have been formed, giving a range of chelating ligands with varying degrees of steric bulk on the imidazolium ring and different chelate sizes. Additional examples reported include a number of alcohol functionalised imidazolium salts and the synthesis of phosphite-imidazolium salts, although the phosphite-imidazolium salts could not be isolated cleanly. All compounds were characterised by spectroscopic means, including $^{1}H$, $^{13}C$ and $^{31}P$-NMR, mass spectrometry and in some cases elemental analysis. Crystalographically characterised examples include a phosphine-imidazolium salt, **16**, and a phenol-functionalised imidazolium salt, **36**.

# 2.7: Experimental

## 2.7.1: General Comments

All NMR data are quoted in δ/ppm. The $^{31}$P-NMR spectra (referenced to $H_3PO_4$ δ = 0 ppm) were collected on a Jeol Eclipse 300 MHz spectrometer; $^{1}$H and $^{13}$C spectra were recorded on a Bruker 400 MHz DPX Avance, unless otherwise stated, and referenced to $SiMe_4$ (δ = 0 ppm). Electrospray mass spectrometry (ESMS) was performed on a VG Fisons Platform II instrument by the Department of Chemistry, Cardiff University. Crystals were diffracted in a Bruker Nonius Kappa CCD area detector using graphite monochromatised MoKα radiation, I = 0.71073Å.

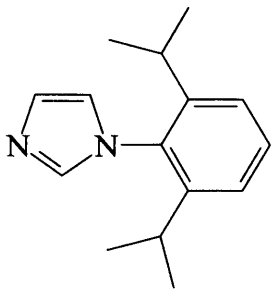
All manipulations were carried out using standard Schlenk techniques under dry argon or dinitrogen. Tetrahydrofuran (THF), diethyl ether ($Et_2O$), and *n*-hexane were dried and degassed by refluxing under dinitrogen over sodium wire and benzophenone. Dichloromethane (DCM), ethanol (EtOH), methanol (MeOH), and acetonitrile (MeCN) were dried over calcium hydride. All other anhydrous solvents were obtained by distillation from the appropriate drying agents under dinitrogen, except *N,N*-dimethylformamide and dimethysulfoxide, which were AR grade solvents dried over 3Å molecular sieves. Deoxygenation of solvents and reagents was carried out by three freeze-pump-thaw cycles. Water used during the work-up of all compounds was carefully deoxygenated by several cycles of heating at reflux and cooling to room temperature under a dinitrogen purge. All NMR solvents were purchased from Aldrich and Goss, freeze-pump-thaw degassed three times and dried over 3Å molecular sieves. $KOBu^t$ was sublimed twice. All reagents were purchased from commercial sources and used without purification, unless otherwise stated.

## 2.7.2: Preparation of compounds

The following compounds were prepared by literature methods. 1-(mesityl)imidazole, 1-(2,6-diisopropylphenyl)imidazole and 1-

(cyclopentyl)imidazole.[6] The methods for the latter two compounds were modified; the aniline starting material was dissolved in 50 ml of glacial acetic acid and the mixture was heated at 70 °C for 18h.

**1-(2,6-diisopropylphenyl)imidazole**[6]



Formaldehyde (10.7ml of 37% aqueous sol$^{n}$, 0.143 mol), glyoxal (16.4 ml of 40% aqueous sol$^{n}$, 0.143 mol) and glacial acetic acid (50 ml) were heated to 70 $^{0}$C. To the solution was added drop-wise with stirring over a period of 3h a solution of $NH_4OAc$ (11.0 g, 0.143 mol) and 2,6-diisopropylanile (28.0 ml, 0.141 mol) in $H_2O$ (6 ml) and glacial acetic acid (50 ml). The solution rapidly became orange/red then black and was stirred for 18h. The solution was cooled to r.t., then added drop-wise with stirring to a suspension of $NaHCO_3$ (151.00 g, 1.80 mol) in $H_2O$ (1 L). The solution was made alkaline to pH 9 with NaOH, and the resultant solid was then filtered on a Buchner funnel and washed with $H_2O$ (3 x 50 ml) sucked dry on the frit, then extracted with hot hexane (6 x 200 ml). The resulting brown hexane solution was filtered and the solvent removed under vacuum. The crude product was dissolved in a minimum amount of boiling *n*-hexane, allowed to cool slowly to r.t., then put in the fridge for 12h. The solution was filtered and washed with ice-cold hexane (3 x 10 ml) and sucked dry under vacuum. The product was a pale brown crystalline solid, yield (9.73 g, 29.8%).

**$^{1}$H NMR** (400.13 MHz, $d_6$-DMSO, δ): 7.71 (s, 1H, $_{im}C$-*H*), 7.50 (t, *J* = 8.4 Hz, 1H, $_{dipp}C_4$-*H*), 7.39 (d, *J* = 8.3 Hz, 1H, $_{dipp}C_{3,5}$-*H*), 7.37 & 7.13 (s x 2, each 1H, $_{im}C_{4,5}$-*H*), 2.25 (sep, *J* = 6.9 Hz, 2H, 2C*H*$Me_2$), 1.10 (d, *J* = 7.0 Hz, 12H, 2CH*Me*$_2$).

**1-(Mesityl)imidazole**[6]

(10.8 g, 40.6%).

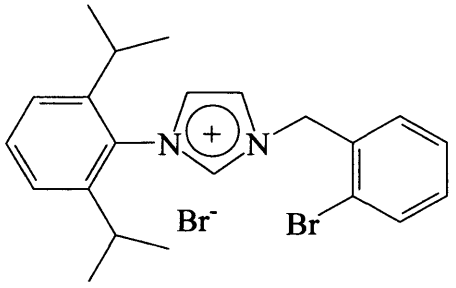
**$^1$H NMR** (400.13 MHz, $d_6$-DMSO, δ): 7.84 (s, 1H, $_{im}$C-*H*), 7.39 & 7.31 (s x 2, 1H, $_{im}C_{4,5}$-*H*), 7.25 (s, 2H, $_{mesityl}C_{3,5}$-*H*), 2.50 (s, 3H, $_{mes}C_4CH_3$) 2.13 (s, 6H, $_{mesityl}C_{2,6}CH_3$).

**1-(cyclopentyl)imidazole**[6]

(8.86 g, 45.5%).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 7.45 (s, 1H, $_{im}$C-*H*), 6.94 & 6.86 (s x 2, 1H, $_{im}C_{4,5}$-*H*), 4.38 (quint, $J$ = 7.4 Hz, 1H $_{cyclopent}C_1$-*H*) 2.21-1.54 (m, 8H, $_{cyclopent}C_{2\text{-}5}$-$H_2$).

**1-(*o*-Bromobenzyl-(3)- 2,6-diisopropylphenyl)imidazolium bromide (1)**




To a solution of 2-bromobenzyl bromide (8.25 g, 33.0 mmol) in THF (10 ml) was added 2,6-diisopropylphenylimidazole (2.51 g, 11.0 mmol) and the mixture was refluxed for 48h. The solvent was removed under filtration and the solid residue was washed with 20 ml of THF and the off-white solid was dried under vacuum. (5.06 g, 96.2%).

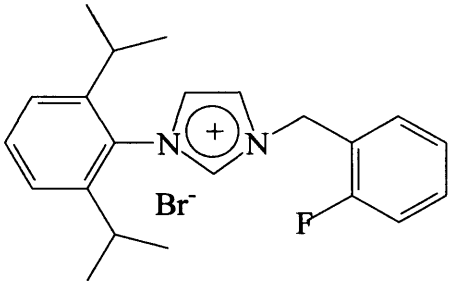
**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 10.22 (s, 1H, $_{im}C_2$-*H*), 8.07 (d, $J$ = 1.6 Hz, 1H, $_{im}C_{4or,5}$-*H*), 7.71 ( s, 1H, Ar-*H*), 7.58 (d, $J$ = 8.0 Hz, 1H, Ar-*H*), 7.50-7.34 (m, 2H, Ar-

*H*), 7.28-7.20 (m, 2H, Ar-*H*), 7.13 (d, $J$ = 1.6 Hz, 1H, $_{im}C_{4or,5}$-*H*), 6.12 (s, 2H, $CH_2$), 2.24 (sep, $J$ = 6.8 Hz 2H, 2C*H*$Me_2$), 1.16 (d, $J$ = 6.8 Hz, 6H, 2CH*Me*$_2$) 1.07 (d, $J$ = 6.8 Hz, 6H, 2CH*Me*$_2$).

**$^{13}$C NMR** (100.03 MHz, $CDCl_3$, δ): 145.4, 138.3, 133.49, 133.1, 132.8, 131.9, 131.57, 130.1, 128.87, 124.7, 124.5, 122.9 (Ar-*CH*), 53.4 (*C*$H_2$), 28.7 (2*C*H$Me_2$), 24.5 (2CH*Me*$_2$), 24.1 (2CH*Me*$_2$).

**MS** (ES): 397.1280 $[M-Br]^+$ ($C_{22}H_{26}N_2Br$ requires 397.1279).

**1-(*o*-Fluorobenzyl-(3)-2,6-diisopropylphenyl)imidazolium bromide (3)**



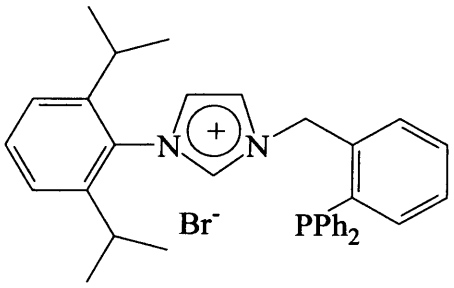

To a solution of 2-fluorobenzyl bromide (6.24 g, 33.0 mmol) in THF (10 ml) was added 2,6-diisopropylphenylimidazole (2.51 g, 11.0 mmol) (20 ml), the mixture was then gently refluxed for 48h. The solvent was removed under filtration and the solid product was washed with 20 ml of THF and the off-white solid was dried under vacuum. (4.43 g, 96.6%).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 10.60 (s, 1H, $_{im}C_2$-*H*), 8.03 (m, 1H, Ar-*H*), 7.78 (d, $J$ = 1.8 Hz, 1H, $_{im}C_4$-*H*), 7.45 (t, $J$ = 7.8 Hz, 1H, Ar-*H*), 7.36-7.14 (m, 5H, Ar-*H*), 7.05 (t, $J$ = 9.2 Hz, 1H, Ar-*H*), 6.10 (s, 2H, $CH_2$), 2.15 (sep, $J$ = 6.8 Hz 2H, 2C*H*$Me_2$), 1.13 (d, $J$ = 6.8 Hz, 6H, 2CH*Me*$_2$) 1.10 (d, $J$ = 6.8 Hz, 6H, 2CH*Me*$_2$).

**$^{13}$C NMR** (100.03 MHz, $CDCl_3$, δ): 145.7, 132.8, 132.3, 132.2, 130.5, 125.9, 125.1, 124.7, 123.3, 116.2, 116.0 (Ar-*CH*), 47.7 (*C*$H_2$), 29.1 (2*C*$HMe_2$), 24.8 (2CH*Me*$_2$), 24.4 (2CH*Me*$_2$).

**MS** (ES): *M/z* 337.2065 $[M\text{-}Br]^+$ ($C_{22}H_{26}N_2F$ requires 337.2080).

**1-(*o*-Benzyldiphenylphosphino-(3)-2,6-diisopropylphenyl) imidazolium bromide (2)**




To 1-(*o*-fluorobenzyl-(3)-2,6-diisopropylphenyl)imidazolium bromide (1.0 g, 2.40 mmol) in DMSO (5 ml) was added $KPPh_2$ (freshly prepared from $KOBu^t$ (0.28 g, 2.52 mmol) and $HPPh_2$ (0.50 ml, 2.52 mmol) in DMSO (5 ml)). The solution was allowed to stir for 24 h at r.t., then the solvent was removed under vacuum. Methanol (10 ml) was added to quench excess $KPPh_2$. The methanol was then removed under vacuum. DCM (10 ml) was added, the mixture was filtered to remove any inorganic salts formed. The solvent was removed completely under vacuum and washed with ether (10 ml x 3). The solid was dissolved in the minimum amount of DCM and THF was added drop-wise until a precipitate formed, the mixture was cooled in an ice-bath, the solid was collected by decanting off the liquid. The recrystalisation was repeated twice to give the product as white solid, which was dried under vacuum. Yield (0.57 g, 41.0%).

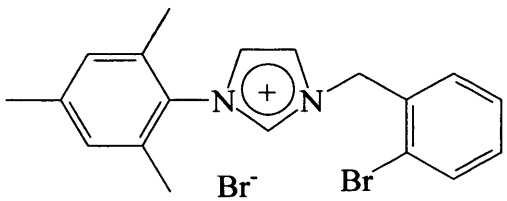
**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 10.73 (s, 1H, $_{im}C_2$-*H*), 8.02 (m, 1H, Ar-*H*), 7.66 (s, 1H, Ar-H), 7.44-7.17 (m, 15H, Ar-*H*), 7.00 (s, 1H, Ar-*H*), 6.87 (m, 1H, Ar-*H*), 6.16 (s, 2H, C*H*$_2$), 2.17 (sep, $J$ = 6.8 Hz 2H, 2C*H*$Me_2$), 1.14 (d, $J$ = 6.8 Hz, 6H, 2CH*Me*$_2$) 1.03 (d, $J$ = 6.8 Hz, 6H, 2CH*Me*$_2$).

**$^{13}$C NMR** (100.03 MHz, $CDCl_3$, δ): 145.7, 139.4, 138.7, 138.5, 136.9, 136.7, 135.1, 135.1, 134.6, 134.3, 134.1, 132.2, 132.2, 130.9, 130.6, 130.3, 129.9, 129.4, 129.3, 125.0, 124.0, 122.9, 122.9 (Ar-*C*H), 51.4, 51.2, (*C*H2), 29.0 (2*C*H$Me_2$), 24.8 (2CH*Me*$_2$), 24.5 (2CH*Me*$_2$).

**$^{31}$P NMR** (121.65 MHz, $CDCl_3$, δ): -15.49.

**MS** (ES): *M/z* 503.2645 $[M\text{-}Br]^+$ ($C_{34}H_{36}N_2P$ requires 503.2616).

**1-(*o*-Bromobenzyl-3-mesityl)imidazolium bromide (4)**

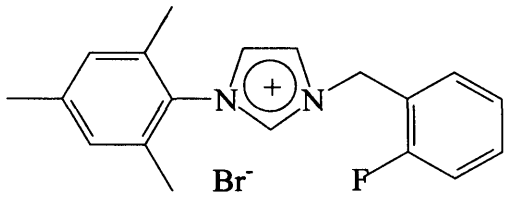



To a solution of 2-bromobenzyl bromide (8.25 g, 33.0 mmol) in THF (10 ml) was of mesitylimidazole (2.05 g, 11.0 mmol), the mixture was then gently refluxed for 48h. The solvent was removed under filtration and the solid product was washed with 20 ml of dry THF and the off-white solid was dried under vacuum. Yield (4.39 g, 91.5%).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 10.35 (s, 1H, $_{im}C_2$-*H*), 8.02 (dd, *J* = 7.6, 1.6 Hz, 1H, Ar-*H*), 7.58 (dd, *J* = 8.0, 1.1 Hz, 1H, Ar-*H*), 7.53 (d, *J* = 1.74 Hz, 1H, $_{im}C_{4or5}$-H), 7.38 (dt, *J* = 8.0, 1.2 Hz, Ar-*H*), 7.28-7.23 (m, 1H, Ar-*H*), 7.03 (d, *J* = 1.75 Hz, 1H, $_{im}C_{4or5}$-H), 6.93 (s, 2H, $_{mesityl}$C-H), 6.06 (s, 2H, C$H_2$), 2.32 (s, 3H, C$H_3$), 2.02 (s, 6H, 2C$H_3$).

**MS** (ES): *M/z* 355.1 & 357.1 $[M\text{-}Br]^+$.

**1-(*o*-Fluorobenzyl-3-mesityl)imidazolium bromide (5)**



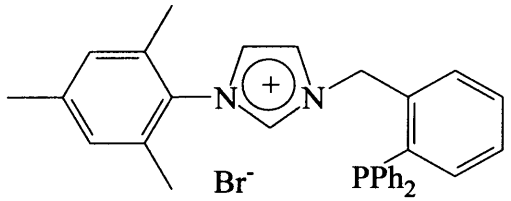

To a solution of 2-fluorobenzyl bromide (6.25 g, 33.0 mmol) in THF (10 ml) was mesitylimidazole (2.05 g, 11.0 mmol), the mixture was then gently refluxed for 48h. The solvent was removed under filtration and the solid product was washed with 20 ml of dry THF and the off-white solid was dried under vacuum. Yield (3.87 g, 93.9%).

**$^1$H NMR** (400.13 MHz, $d_6$-DMSO, δ): 9.77 (s, 1H, $_{im}C_2$-*H*), 8.11 + 8.01 (dd x 2, $J$ = 1.75 Hz, 1H each, $_{im}C_{4,5}$-*H*), 7.59 (m, 1H, Ar-*H*), 7.50 (m, 1H, Ar-*H*), 7.33 (m, 1H, Ar-*H*), 7.16 (s, 1H $_{mesityl}$C-*H*).

**$^{13}$C NMR** (100.03 MHz, $d_6$-DMSO, δ): 161.4, 159.4, 140.2, 138.0, 134.2, 131.5, 130.9, 129.2, 128.7, 125.1, 124.3, 121.6, 115.9 (Ar-*C*H), 47.0 (*C*H$_2$), 20.6 (*C*H$_3$), 16.9 (2*C*H$_3$).

**MS** (ES): *M/z* 295.1606 $[M\text{-}Br]^+$ ($C_{19}H_{20}N_2F$ requires 295.1610).

**1-(*o*-Benzyldiphenylphosphine-3-mesityl)imidazolium bromide (6)**



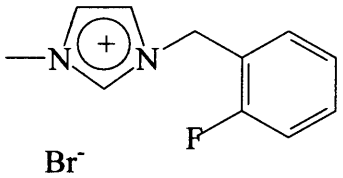
To 1-(*o*-benzyldiphenylphosphine-3-mesityl)imidazolium bromide (0.9 g, 2.40 mmol) in DMSO (5 ml) was added $KPPh_2$ (freshly prepared from $KOBu^t$ (0.28 g, 2.52 mmol) and $HPPh_2$ (0.50 ml, 2.52 mmol) in DMSO (5 ml)). The solution was allowed to stir for 24h at r.t., then the solvent was removed under vacuum and methanol (10 ml) was added to quench excess $KPPh_2$. The methanol was then removed under vacuum. DCM (10 ml) was added, the mixture was filtered to remove any inorganic salts formed. The solvent was removed completely under vacuum and washed with ether (10 ml x 3). The solid was dissolved in the minimum amount of DCM and THF was added drop-wise until a precipitate formed, the mixture was cooled in an ice-bath and the solid was collected by decanting off the liquid. The recrystalisation was repeated twice to give the product as a white solid, which was dried under vacuum. Yield (0.56 g, 43.1%).

**$^1$H NMR** (400.13 MHz, $d_6$-DMSO, δ): 10.53 (s, 1H, $_{im}C_2$-*H*), 8.11 (s, 1H, Ar-*H*), 7.99 (s, 1H, Ar-*H*), 7.83-7.56 (m, 12H, Ar-H), 7.19 (m, 2H, Ar-*H*), 7.15 (s, 1H, Ar-*H*), 7.10 (s, 1H, Ar-H), 6.18 (s, 2H, $CH_2$), 2.33 (s, 3H, $CH_3$), 2.01 (s, 6H, $2CH_3$).

**$^{13}$C NMR** (100.03 MHz, $d_6$-DMSO, δ): 162.8, 159.5, 141.4, 138.2, 134.2, 132.5, 132.0, 131.9, 130.7, 129.9, 129.0, 125.5, 125.5, 123.4, 122.8, 121.1, 120.8, 116.0, 115.7 (Ar-*C*H), 47.5, 47.4, (*C*$H_2$), 21.2 (*C*$H_3$), 17.7 (2*C*$H_2$).

**$^{31}$P NMR** (121.65 MHz, $d_6$-DMSO, δ): -15.56.

**1-(*o*-Fluorobenzyl-3-methyl)imidazolium bromide (7)**



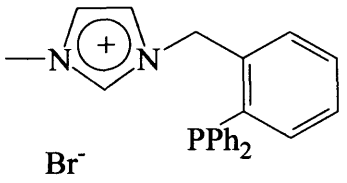
To a solution of 2-fluorobenzyl bromide (6.25 g, 33.0 mmol) in THF (10 ml) was methylimidazole (0.90 g, 11.0 mmol) and the mixture was gently refluxed for 48h. The solvent was removed under filtration and the solid product was washed with 20 ml of THF and the off-white solid was dried under vacuum. Yield (2.84 g, 96.2%).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 10.23 (s, 1H, $_{im}C_2$-*H*), 7.70 (m, 1H, Ar-*H*), 7.69 & 7.41 (s x 2 each 1H, $_{im}C_{4,5}$-*H*), 7.32 (m, 1H, Ar-*H*), 7.10 (t, $J$ = 7.5 Hz, 1H, Ar-*H*), 7.01 (t, $J$ = 9.2 Hz, 1H, Ar-*H*), 5.66 (s, 2H, C$H_2$), 4.02 (s, 3H, C$H_3$).

**$^{13}$C NMR** (100.03 MHz, $CDCl_3$, δ): 162.3, 159.8, 137.3, 132.1, 125.5, 124.5, 122.4, 120.9, 116.2 (Ar-*C*H), 47.3 (*C*$H_2$) 37.1 (*C*$H_3$).

**MS** (ES): *M/z* 191.0987 $[M\text{-}Br]^+$ ($C_{11}H_{12}N_2F$ requires 191.0985).

**1-(*o*-benzyldiphenylphosphino-3-methyl)imidazolium bromide (8)**




To 1-(*o*-fluorobenzyl-(3)-methyl)imidazolium bromide (0.65 g, 2.40 mmol) in DMSO (5 ml) was added $KPPh_2$ (freshly prepared from $KOBu^t$ (0.28 g, 2.52 mmol) and $HPPh_2$ (0.50 ml, 2.52 mmol) in DMSO (5 ml)). The solution was allowed to stir for 24h at r.t. The solvent was then removed under vacuum. Methanol (10 ml) was added to quench excess $KPPh_2$. The methanol was then removed under vacuum. DCM (10 ml) was added and the mixture was filtered to remove any inorganic salts formed. The solvent was removed completely under vacuum and washed with ether (10 ml x 3). The solid was dissolved in the minimum amount of DCM and THF was added drop-wise until a precipitate formed, the mixture was cooled in an ice-bath and the

solid was collected by decanting of the liquid. The recrystalisation was repeated twice to give the product as white solid, which was dried under vacuum. Yield (0.44 g, 42.0%).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 10.13 (s, 1H, $_{im}C_2$-*H*), 7.77 (m, 1H, Ar-*H*), 7.45-6.98 (m, 14H, Ar-*H*), 5.70 (s, 2H, C*H*$_2$), 3.81 (s, 3H, C*H*$_3$).

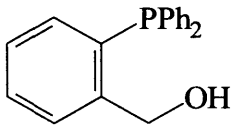
**$^{13}$C NMR** (100.03 MHz, $CDCl_3$, δ): 164.0, 137.8, 135.2, 135.0, 134.2, 133.9, 132.2, 131.9, 130.8, 129.7, 129.2, 125.8, 124.2, 123.6, 122.4, 121.9, 116.3, 116.1 (Ar-*C*H), 52.2, 52.0 (*C*H$_2$), 36.9 (*C*H$_3$).

**$^{31}$P NMR** (121.65 MHz, $CDCl_3$, δ): -16.71.

**MS** (ES): *M/z* 357.1508 $[M\text{-}Br]^+$ ($C_{23}H_{22}N_2P$ requires 357.1521).

The following compound was prepared by literature method: 2-diphenylphosphinobenzylalcohol (9).[17]

**2-Diphenylphosphinobenzylalcohol (9)**



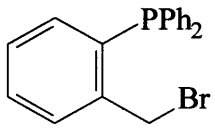

Diphenylphosphine (5.81 g, 28.7 mmol) and 2-iodobenzyl alcohol (6.72 g, 28.7 mmol) were dissolved in DMAc (40 ml), to which was added KOAc (2.94 g, 30.0 mmol) and a $Pd(OAc)_2$ stock solution in DMAc (10 μmol ml$^{-1}$). The reaction mixture was heated to 130 °C for 12h. The reaction was then added to an ice-water mixture and extracted with DCM (10 ml x 3). The organic phase was then washed with water (20 ml x 2) and dried over $Na_2SO_4$. The solvent was removed under vacuum to give the crude product as a yellow solid. The solid was treated with excess

$HN(SiMe_3)_2$ (2.4 g, 14.9 mmol) and a small amount of $CF_3COOH$ (0.1 g). The mixture was heated to 150 °C for 10 min. All volatiles were removed under vacuum and *O*-trimethylsilyether was obtained as a colourless oil after a short path distillation under reduced pressure. The oil was then dissolved in THF (30 ml) and treated with $NEt_4F$ for 30min. The volume of the reaction mixture was reduced to ca. 10 ml under vacuum, water (100 ml) was added and the resulting precipitate was extracted into DCM (20 ml x 3). The organic mixture was washed with water and dried over $Na_2SO_4$. The solvent was removed under vacuum to give the desired product as a colourless oil. Yield (8.41 g, 97.0%).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 7.49-7.33 (m, 2H, Ar-*H*), 7.28-7.09 (m, 11H, Ar-*H*), 6.83-6.81 (m, 1H, Ar-*H*), 4.74 (s, 2H, $CH_2OH$) 2.81 (b.s, 1H, OH).

**$^{31}$P NMR** (121.65 MHz, $CDCl_3$, δ): -15.54.

**2-diphenylphosphinobenzylbromide (10)**

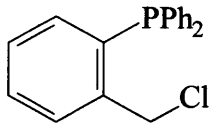



2-Diphenylphosphinobenzylalcohol (2.0 g, 6.84 mmol) was dissolved in AcOH (10 ml) and hydrogen bromide (45% w/v in AcOH 5ml) was added drop-wise to the mixture. The reaction mixture was stirred for 24h. The pH of the mixture was then brought to 9 by the additon of a NaOH solution. The mixture was extracted with DCM (20 ml x 3) and the organic phase was washed with water (10 ml). The organic layer was dried over $MgSO_4$, the solvent was removed under vacuum to give the product as a white solid. Yield (2.19 g, 90.1%).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 7.41-7.38 (m, 1H, Ar-*H*), 7.30-6.88 (m, 12H, Ar-*H*), 6.89-6.85 (m, 1H, Ar-*H*), 5.27 (s, 2H, $CH_2Br$).

**$^{31}$P NMR** (121.65 MHz, $CDCl_3$, δ): -15.39.

**2-Diphenylphosphinobenzylchloride (11)**

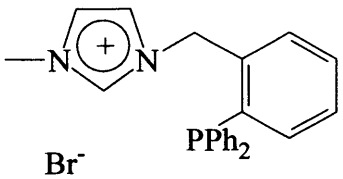



2,4,6-Trichloro[1,3,5]triazine (1.26 g, 6.84 mmol) was added to DMF (1.5 ml) at 25 °C. After the formation of a white solid DCM (10 ml) was added, followed by 2-diphenylphosphinobenzyl alcohol (2.0 g, 6.48 mmol) in DMF (10 ml). The mixture was stirred at r.t. for 4h, water (20 ml) was added and the organic phase was then washed with saturated solution of $Na_2CO_3$ (15 ml), followed by brine. The organic layers were dried over $Na_2SO_4$ and the solvent was removed under vacuum to give the product as a white solid. Yield (2.13 g, 93.2%).

**$^{1}$H NMR** (400.13 MHz, $CDCl_3$, δ): 7.41-7.38 (m, 1H, Ar-*H*), 7.30-6.88 (m, 12H, Ar-*H*), 6.89-6.85 (m, 1H, Ar-*H*), 5.27 (s, 2H, $CH_2Cl$).

**$^{31}$P NMR** (121.65 MHz, $CDCl_3$, δ): -15.41.

**1-(*o*-Benzyldiphenylphosphino-3-methyl)imidazolium bromide (8)**




2-Diphenylphosphinobenzylbromide (0.12g, 1.40 mmol) and methylimidazole (1.00g, 2.82 mmol) were dissolved in EtOH (10 ml), the solution was then refluxed for 7 days. The solvent was removed under vacuum and the mixture was washed with

THF (3 x 10 ml). The crude solid was recrystalised twice by dissolving the solid in minimum amount of DCM and THF was added drop-wise until a precipitate formed. The solid was collected by filtration. The product was a white solid which was dried under vacuum. Yield (0.33 g, 54.5%)

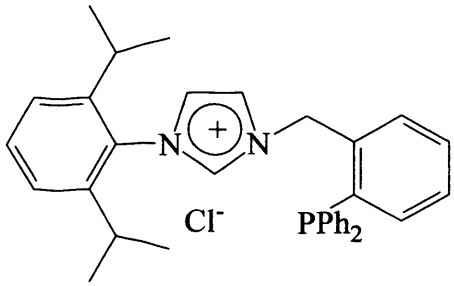
**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 10.13 (s, 1H, $_{im}C_2$-*H*), 7.77 (m, 1H, Ar-*H*), 7.45 (m, 14H, Ar-*H*), 5.70 (s, 2H, $CH_2$), 3.81 (s, 3H, $CH_3$).

**$^{13}$C NMR** (100.03 MHz, $CDCl_3$, δ): 164.0, 137.8, 135.2, 135.0, 134.2, 133.9, 132.2, 131.9, 130.8, 129.7, 129.2, 125.8, 124.2, 123.6, 122.4, 121.9, 116.3, 116.1 (Ar-*C*H), 52.2, 52.0 ($CH_2$), 36.9 ($CH_3$).

**$^{31}$P NMR** (121.65 MHz, $CDCl_3$, δ): -16.71.

**MS** (ES): *M/z* 357.1508 $[M\text{-}Br]^+$ ($C_{23}H_{22}N_2P$ requires 357.1521).

**1-(*o*-Benzyldiphenylphosphino-(3)-2,6-diisopropylphenyl)imidazolium chloride (2)**




2-Diphenylphosphinobenzylchoride (0.37g, 1.61 mmol) and diisopropylphenyl imidazole (1g, 3.22 mmol) were dissolved in EtOH (10 ml), the solution was then refluxed for 7 days. The solvent was removed under vacuum and the mixture was washed with THF (3 x 10 ml). The crude solid was recrystalised twice by dissolving the solid in minimum amount of DCM and the THF was added drop-wise until a precipitate formed. The solid was collected by filteration. The product was a white solid which was dried under vacuum. Yield (0.46g, 53.3 %).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 10.73 (s, 1H, $_{im}C_2$-*H*), 8.02 (m, 1H, Ar-*H*), 7.66 (s, 1H, Ar-H), 7.44-7.17 (m, 15H, Ar-*H*), 7.00 (s, 1H, Ar-*H*), 6.87 (m, 1H, Ar-*H*), 6.16 (s, 2H, C$H_2$), 2.17 (sep, $J$ = 6.8 Hz 2H, 2C*H*Me$_2$), 1.14 (d, $J$ = 6.8 Hz, 6H, 2CH*Me*$_2$) 1.03 (d, $J$ = 6.8 Hz, 6H, 2CH*Me*$_2$).

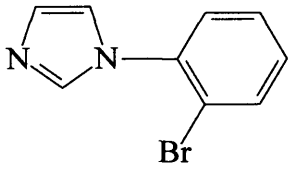
**$^{13}$C NMR** (100.03 MHz, $CDCl_3$, δ): 145.7, 139.4, 138.7, 138.5, 136.9, 136.7, 135.14, 135.1, 134.6, 134.3, 134.1, 132.2, 132.2, 130.9, 130.6, 130.3, 129.9, 129.4, 129.3, 125.0, 124.0, 122.9, 122.9 (Ar-*C*H), 51.4, 51.2 (*C*H$_2$), 29.0 (2*C*HMe$_2$), 24.8 (2CH*Me*$_2$), 24.5 (2CH*Me*$_2$).

**$^{31}$P NMR** (121.65 MHz, $CDCl_3$, δ): -15.49.

**MS** (ES): *M/z* 503.2645 $[M\text{-}Cl]^+$($C_{34}H_{36}N_2P$ requires 503.2616).

**Elemental Analysis** Calc. for $C_{34}N_2PClH_{36}$: C, 75.75; H, 6.73; N, 5.20; found: C, 75.37; H 6.77; N, 5.21.

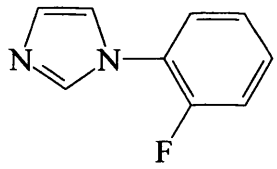
**1-(2-Bromobenzene)imidazole (12)**




Imidazole (0.20 g, 3.0 mmol), $(CuOTf)_2$·benzene (0.1 mmol), 1,10-phenanthroline (2.0 mmol), $Cs_2CO_3$ (0.72 g, 2.2 mmol) were charged in a Schlenk under argon to which was added 1,2-dibromobenzene (0.47 g, 2.0 mmol) and xylenes (0.8 ml). The dark brown mixture was heated at 110°C for 30h, the mixture was then cooled to r.t. and DCM (35 ml) and $NH_4Cl$ (5 ml) was added. The organic layer was separated, washed with brine and dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography on silica gel (1:4 hexane-ethyl acetate) to give the desired product as a yellow oil. Yield (0.15 g, 34.2%).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 7.63-7.53(m, 3H, $_{im}$C-*H*), 7.33-7.12 (m, 4H, Ar-H).

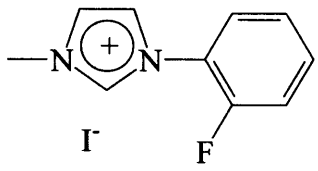
**1-(2-Fluorobenzene)imidazole (13)**




Formaldehyde (10.7 ml of 37 % sol$^n$, 0.143 mol), glyoxal (16.4 ml of 40 % sol$^n$, 0.143 mol) and glacial acetic acid (35 ml) was heated to 70 $^0$C, under $CaCl_2$ drying tube. To the solution was added drop-wise with stirring over a period of 3h a solution of $NH_4OAc$ (11.0 g, 0.143 mol) 2-fluorobenzeneaniline (10.4 ml, 0.143 mmol) in $H_2O$ (6 ml) and glacial acetic acid (30 ml). The solution which rapidly became orange/red, was stirred for 12h. The solution was cooled to r.t., then added drop-wise with stirring to a suspension of $NaHCO_3$ (151.00 g, 1.80 mol in $H_2O$ (1 L). The solution was made alkaline to pH 9 with NaOH, and the resultant solid was then filtered on a Buchner funnel and washed with $H_2O$ (3 x 50 ml) sucked dry on the frit, then extracted with hot hexane (6 x 200 ml). The resulting solvent was removed under vacuum. The product was a yellow oil. Yield (9.11 g, 39.3 %).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, 7.71 (s, 1H, $_{im}$C-*H*), 7.20 & 7.13 (s x 2 each 1H, $_{im}C_{4,5}$-*H*), 7.33-7.12 (m, 4H, Ar-H).

**(1-Fluorobenzene-3-methyl)imidazolium iodide (14)**



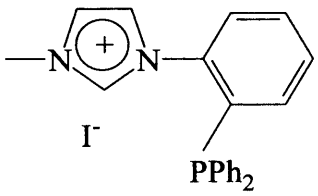
A mixture of 1-(2fluorobenzene)imidazole (4.50 g, 27.7 mmol) and iodomethane (11.8 g, 83.3 mmol) in THF (30 ml) was gently refluxed for 12h. During the reaction a pale yellow solid was formed. The solid was collected by filtration washed with THF and dried under vacuum to give the product as a yellow solid. Yield (8.18 g, 97.1%).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 10.14 (s, 1H, $_{im}C_2$-*H*), 8.50 (s, 1H, $_{im}C_{4or5}$-H), 7.92 (t, $J$ = 6.8 Hz, 1H, Ar-*H*), 7.62 (s, 1H, $_{im}C_{4or5}$-H), 7.50 (m, 1H, Ar-*H*), 7.35-722 (m, 2H, Ar-*H*), 4.24 (s, 3H, $CH_3$).

**$^{13}$C NMR** (100.03 MHz, $CDCl_3$, δ): 136.7, 132.4, 126.1, 124.8, 122.7, 122.3, 117.7, 117.4 (Ar-*C*H), 37.9 (*C*$H_3$).

**MS** (ES): *M/z* 177.1 $[M\text{-}I]^+$.

**(1-Benzene-*o*-diphenylphosphine-3-methyl)imidazolium iodide (16)**



To (1-fluorobenzene-3-methyl)imidazolium iodide (0.70 g, 2.30 mmol) in DMF (5 ml) was added $KPPh_2$, which was freshly prepared from $KOBu^t$ (0.26 g, 2.34

mmol) and $HPPh_2$ (0.20 ml, 2.30 mmol) in DMF (5 ml). The solution was allowed to stir for 24h at r.t. The solvent was then removed under vacuum to give a brown soild and methanol (10 ml) was added to quench excess $KPPh_2$. The methanol was then removed under vacuum. The residue was extracted into DCM (3 x 10ml), the mixture was filtered through celite. The volume of the DCM was reduced and $Et_2O$ was added to give the product as an orange precipitate. The solid was collected by filtration, washed with $Et_2O$ (3 x 10ml) and dried under vacuum to give the product as an orange/red solid. Yield (0.84 g, 74.1%).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 9.16 (s, 1H, $_{im}C_2$-*H*), 7.74 (m, 1H, Ar-*H*), 7.45 (s, 1H, $imC_{4or5}$-H), 7.48-7.31 (m, 8H, Ar-*H*), 7.23-7.11 (m, 4H, Ar-*H*), 7.06 (s, 1H, Ar-*H*), 6,96 (m, 1H, Ar-*H*), 3.97 (s, 3H, C*H*$_3$).

**$^{13}$C NMR** (100.03 MHz, $CDCl_3$, δ): 137.8, 137.5, 136.1, 135.9, 134.6, 134.4, 133.8, 133.7, 131.7, 131.2, 130.5, 129.7, 129.5, 128.6, 128.6, 128.1, 123.8, 123.6, (Ar-*C*H), 37.8 (*C*H$_3$).

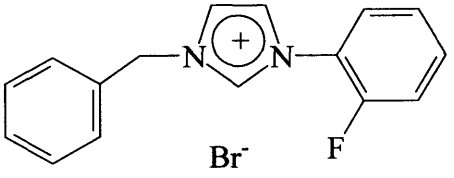
**$^{31}$P NMR** (121.65 MHz, $CDCl_3$, δ): -16.86.

**MS** (ES): *M/z* 343.1360 $[M-I]^+$ ($C_{22}H_{20}N_2P$ requires 343.1364).

**Elemental Analysis** Calc. for $C_{22}N_2PIH_{20}$: C, 56.18; H, 4.28; N, 5.96; found: C, 56.41; H, 4.60; N, 6.48.

Single crystals were obtained by layering a DCM solution of **16** with hexane at 5° C.

**(1-Fluorobenzene-3-benzyl)imidazolium bromide (15)**



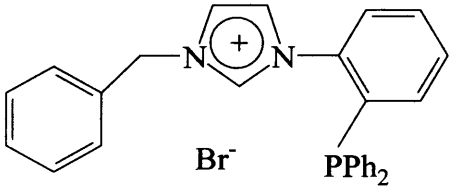
A mixture of 1-(2-Fluorobenzene)imidazole (4.50 g, 27.7 mmol) and bromobenzyl (14.2 g, 83.3 mmol) in THF (30 ml) was gently refluxed for 12h. During the reaction a pale brown solid was formed. The solid was collected by filtration washed with THF and dried under vacuum to give the product as a tan brown solid. Yield (8.61 g, 93.3%).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 10.31 (s, 1H, $_{im}C_2$-*H*), 7.88-7.84 (m, 2H, Ar-*H*), 7.65-7.60 (m, 3H, Ar-*H*), 7.44-7.30 (m, 1H, Ar-*H*), 7.28-719 (m, 5H, Ar-*H*), 5.82 (s, 2H, $CH_2$).

**$^{13}$C NMR** (100.03 MHz, $CDCl_3$, δ): 156.0, 153.5, 137.0, 133.6, 133.5, 132.6, 129.8, 126.4, 126.3, 123.4, 123.1, 122.8, 120.7, 118.0, 117.7 (Ar-*C*H), 53.7 (*C*$H_2$)

**MS** (ES): *M/z* 253.1139 $[M\text{-}Br]^+$ ($C_{16}H_{14}N_2F$ requires 253.1141).

**(1-Benzene-*o*-diphenylphosphine-3-benzyl)imidazolium bromide (17)**




To (1-fluorobenzene-3-benzyl)imidazolium iodide (0.80 g, 2.40 mmol) in DMF (5 ml) was added $KPPh_2$ (freshly prepared from $KOBu^t$ (0.28 g, 2.52 mmol) and $HPPh_2$ (0.50 ml, 2.52 mmol) in DMF (5 ml)). The solution was allowed to stir for 24h at r.t. The solvent was then removed under vacuum to give a brown soild and methanol (10 ml) was added to quench excess $KPPh_2$. The methanol was then removed under vacuum. The residue was extracted into DCM (3 x 10ml), the mixture was filtered through celite. The volume of the DCM was reduced and $Et_2O$ was added to give the product as an orange precipitate. The solid was collected by filtration,

washed with $Et_2O$ (3 x 10ml) and dried under vacuum to give the product as an orange/brown solid. Yield (0.86 g, 71.9%).

**$^1$H NMR** (400.13 MHz, $d_6$-DMSO, δ): 9.79 (s, 1H, $_{im}C_2$-*H*), 7.94-7.89 (s x 2, each 1H, $_{im}C_{4,5}$-*H*), 7.75-7.65 (m, 4H, Ar-*H*), 7.50-7.36 (m, 10H, Ar-*H*), 7.17-713 (m, 4H, Ar-*H*), 7.03-7.01 (m, 1H, Ar-*H*), 5.48 (s, 2H, $CH_2$).

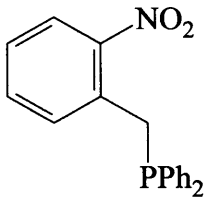
**$^{13}$C NMR** (100.03 MHz, $d_6$-DMSO, δ): 138.6, 138.4, 137.8, 135.1, 135.0, 134.9, 134.1, 133.9, 133.7, 131.6, 131.2, 130.2, 129.5, 129.4, 129.3, 129.1, 128.5, 128.1, 125.1, 122.7 (Ar-*C*H), 52.3 (*C*$H_2$).

**$^{31}$P NMR** (121.65 MHz, $d_6$-DMSO, δ): -16.79.

**MS** (ES): *M/z* 419.2 $[M\text{-}Br]^+$

**Elemental Analysis** Calc. for $C_{28}N_2PBrH_{24}$: C, 67.34; H, 4.84; N, 5.61; found: C, 66.00; H, 4.92; N, 5.47.

**2-Nitrobenzyl diphenylphosphine (21)**



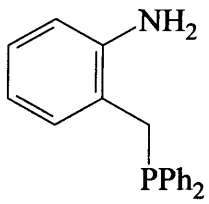

2-Nitrobenzyl bromide (5 g, 22.1 mmol) was stirred in acetone (50 ml), the solution was then cooled to 0 $^0$C and diphenylphosphine (4.4 ml, 22.1 mmol) was added slowly. The solution was allowed to warm to r.t. and stirred for 24h. The mixture was filtered, washed with NaOH solution and extracted in DCM, then dried

over $MgSO_4$. The solvent was removed under vacuum to give an off-white solid that was dried under vacuum. Yield (5.13 g, 78.0%).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 7.41-7.38 (m, 1H, Ar-*H*), 7.30-6.88 (m, 12H, Ar-*H*), 6.89-6.85 (m, 1H, Ar-*H*), 5.27 (s, 2H, $CH_2$).

**$^{31}$P NMR** (121.65 MHz, $CDCl_3$, δ): -10.85.

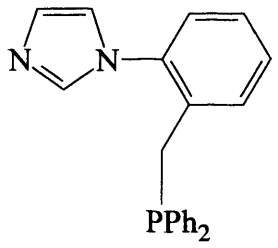
**2-Diphenylphosphine benzylamine (22)**




A stirred suspension of the 2-Nitrobenzyl diphenylphosphine (4.00 g, 13.4 mmol) and excess powdered zinc metal (5.25 g, 80.4 mmol) in AcOH (100 ml) was brought to reflux then conc. HCl (35 %, 30 ml) was added with care and the mixture refluxed under $N_2$ for 2h The solution was filtered to remove the excess zinc and the solvent was removed under vacuum, the residue was stirred with water (100 ml) and DCM (50 ml) for 10 min., the phase separated and the aqueous phase extracted twice with DCM (50 ml). The organic phases were combined, dried over $MgSO_4$ and the solvent removed under vacuum to give the product as a yellow solid. Yield (3.19 g, 81.7%).

**$^{31}$P NMR** (121.65 MHz, $CDCl_3$, δ): -19.91.

**1(Phenyl-o-diphenylphosphine)imidazole (23)**

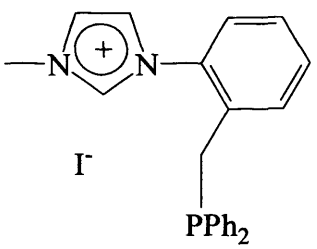



Solution of aq. formaldehyde (0.5 ml, of 37 % sol$^n$, 6.31 mmol), aq. glyoxal (0.75 ml, of 40 %, sol$^n$, 6.31 mmol) and glacial acetic acid (10 ml) was heated to 70 °C. To this solution was added drop-wise with stirring over a period of 2-3h, a solution of $NH_4OAc$ (0.487 g, 6.31 mol), 2-diphenylphosphine benzylamine (2.35 g, 6.31 mmol) in water (0.5 ml) and glacial acetic acid (10 ml). The mixture was refluxed at 70 °C for 16h. The solution was cooled to r.t., then added drop-wise with stirring to a suspension of $NaHCO_3$ (10.0 g) in water (44.5 ml). The solution was made alkaline to pH 9 with NaOH, then filtered and washed with water (5 ml) and sucked to dryness. The resulting brown oil was taken up in DCM (min. amount) and ether was added until the sticky solid came back out of solution. The solution was then filtered and the solvent removed under vacuum. Yield (0.76 g, 37.9%).

**$^1$H NMR** (400.13 MHz, $d_6$-DMSO, δ): 8.09-7.32 (m, 19H, Ar-H), 5.77 (s, 2H, C$H_2$).

**$^{31}$P NMR** (121.65 MHz, $d_6$-DMSO, δ): -5.12 ($PRPh_2$), 28.60 ($O{=}PRPH_2$).

**(1-Phenyl-*o*-diphenylphosphine-3-methyl)imidazolium iodide (26)**



A mixture of 1-(phenyl-*o*-diphenylphosphine oxide) imidazole (0.4 g, 1.2 mmol) and iodomethane (0.5 g, 3.6 mmol) in THF (30 ml) was stirred for 12h. During the reaction an yellow/orange solid was formed. The solid was collected by filtration, washed with THF and dried under vacuum. Yield (0.48 g, 84.8%).

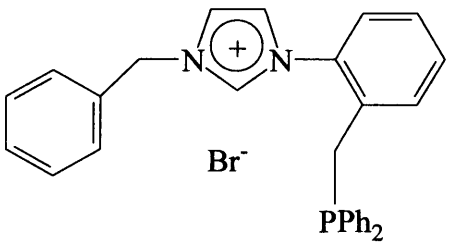
The phosphine oxide (0.40 g, 0.82 mmol) was placed in a three-neck flask (Schlenk adapter, double-jacket condenser, and a pressure-equalising dropping funnel) and was dissolved in chlorobenzene (40 ml) by heating to reflux temperature under a dinitrogen atmosphere. The temperature was then maintained at 120 °C and excess trichlorosilane in small portions (1.4 ml, 9.87 mmol, 12-fold excess). The reaction mixture was heated at 120 °C for 3h and then cooled to r.t. After the addition of DCM (40 ml), the excess trichlorosilane was quenched by the careful addition of 10% NaOH (30 ml) at 0 °C. The organic phase was separated, and washed with DCM (3 x 15 ml). After the combined organic extracts were dried over $MgSO_4$, the solvent was removed under vacuum and the solid was washed with $Et_2O$ (2 x 50 ml) and dried under vacuum overnight. Yield (0.27 g, 70.7 %)

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 9.79 (s, 1H, $_{im}C_2$-*H*), 7.96-7.25 (m, 14H, Ar-*H*), 6.72-6.68 (m, 2H, Ar-*H*), 5.22 (s, 2H, $CH_2$), 4.16 (s, 1H, $CH_3$).

**$^{13}$C NMR** (100.03 MHz, $CDCl_3$, δ): 137.9, 135.7, 135.3, 132.9, 132.7, 131.7, 131.6, 130.9, 130.7, 130.6, 129.3, 129.6, 129.2, 127.9, 125.0, 124.3, (Ar-*C*H), 68.3 ($CH_2$), 25.9 ($CH_3$).

**$^{31}$P NMR** (121.65 MHz, $CDCl_3$, δ): -17.05.

**1-Phenyl-*o*-diphenylphosphine- 3-benzyl)imidazolium bromide (27)**



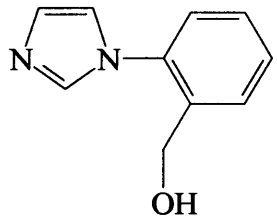

A mixture of 1-(Phenyl-*o*-diphenylphosphine oxide) imidazole (0.4 g, 1.2 mmol) and bromobenzyl (0.61 g, 3.6 mmol) in THF (30 ml) was stirred for 12h. During the reaction an yellow/orange solid was formed. The solid was collected by filtration, washed with THF and dried under vacuum. Yield (0.51 g, 79.8%).

The phosphine oxide (0.45 g, 0.85 mmol) was placed in a three-neck flask (Schlenk adapter, double-jacket condenser, and a pressure-equalising dropping funnel) and was dissolved in chlorobenzene (40 ml) by heating to reflux temperature under a dinitrogen atmosphere. The temperature was then maintained at 120 °C and excess trichlorosilane was added in small portions (1.4 ml, 10.00 mmol, 12-fold excess). The reaction mixture was heated at 120 °C for 3h and then cooled to r.t. After the addition of DCM (40 ml), the excess trichlorosilane was quenched by the careful addition of 10% NaOH (30 ml) at 0 °C. The organic phase was separated, and washed with DCM (3 x 15 ml). After the combined organic extracts were dried over $MgSO_4$, the solvent was removed under vacuum and the solid was washed with $Et_2O$ (2 x 50 ml) and dried under vacuum overnight. Yield (0.30 g, 68.7 %).

**$^1$H NMR** (400.13 MHz, $d_6$-DMSO, δ): 9.85 (s, 1H, $_{im}C_2$-*H*), 8.32-8.09 (m, 2H, Ar-*H*), 7.83-7.15 (m, 19H, Ar-*H*), 5.60 (s, 2H, C*H*$_2$benzyl), 5.10 (s, 2H, $CH_2PPh_2$).

**$^{31}$P NMR** (121.65 MHz, $CDCl_3$, δ): -16.96.

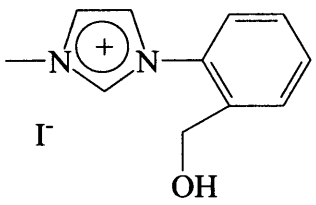
**1-(Phenyl-*o*-alcohol)imidazole (28)**



Formaldehyde (10.7 ml of 37 % sol$^n$, 0.143 mol), glyoxal (16.4 ml of 40 % sol$^n$, 0.143 mmol) and glacial acetic acid (35 ml) were heated to 70 $^0$C, under $CaCl_2$ drying tube. To the solution was added drop-wise with stirring over a period of 3h a solution of $NH_4OAc$ (11.0 g, 0.143 mmol) 1-phenyl-*o*-alcoholaniline (17.6 g, 0.143mmol) in $H_2O$ (6 ml) and glacial acetic acid (30 ml). The solution which rapidly became orange/red was stirred for 12h. The solution was cooled to r.t., then added drop-wise with stirring to a suspension of $NaHCO_3$ (151.00 g, 1.80 mol in $H_2O$ (1 L). The solution was made alkaline to pH 9 with NaOH, and the resultant solid then filtered on a Buchner funnel and washed with $H_2O$ (3 x 50 ml) sucked dry on the frit, then extracted with hot THF (6 x 200 ml). The resulting solvent was removed under vacuum. The product was a brown oil. Yield (10.8 g, 43.5%).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 7.56-6.57 (m, 8H, Ar-*H*), 5.40 (b.s, 1H, O*H*), 4.30 (s, 2H, C$H_2$OH).

**(1-Phenyl-*o*-alcohol-3-methyl)imidazolium iodide (29)**

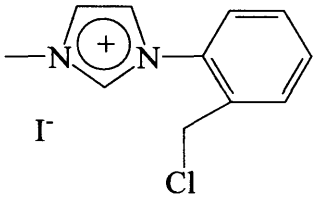


A mixture of 1-(phenyl-*o*-alcohol)imidazole (3.0 g, 17.2 mmol) and iodomethane (7.33 g, 51.7 mmol) in THF (30 ml) was gently refluxed for 12h. During the reaction an off-white solid was formed. The solid was collected by filtration washed with THF and dried under vacuum. Yield (4.95 g, 91.0%)

**$^1$H NMR** (400.13 MHz, $d_6$-DMSO, δ): 9.46 (s, 1H, $_{im}C_2$-*H*), 8.04 (s, 1H, Ar-*H*), 7.69 (m, 1H, Ar-*H*), 7.62-7.50 (m, 4H, Ar-*H*), 5.05 (b.s, 1H, O*H*), 4.44 (s, 2H, C$H_2$OH), 3.96 (s, 3H, $CH_3$).

**$^{13}$C NMR** (100.03 MHz, $d_6$-DMSO, δ): 137.6, 137.2, 133.2, 130.6, 129.5, 128.5, 126.5, 123.7, 123.7 (Ar-*C*H), 58.8 ($CH_2$), 36.2 ($CH_3$).

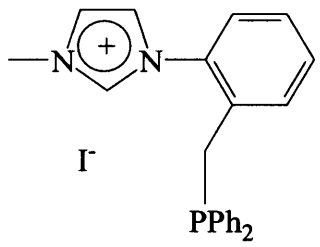
**(1-Phenyl-*o*-chloride-3-methyl)imidazolium iodide (31)**




2,4,6-Trichloro[1,3,5]triazine (0.58 g, 3.16 mmol) was added to DMF (1.5 ml) at 25 °C. After the formation of a white solid, DCM (10 ml) was added, followed by (1-phenyl-*o*-chloride-3-methyl) imidazolium iodide (1.0 g, 3.16 mmol) in DMF (10 ml). The mixture was stirred at r.t. for 4h, water (20 ml) was added and the organic phase was then washed with saturated solution of $Na_2CO_3$ (15 ml), followed by brine. The organic layers were dried over $Na_2SO_4$ and the solvent was removed under vacuum to give the product as a pale yellow solid. Yield (0.78 g, 73.8%).

**$^1$H NMR** (400.13 MHz, $d_6$-DMSO, δ): 9.32 (s, 1H, $_{im}C_2$-*H*), 7.90 δ 7.80 (d x 2, *J* = 1.7 Hz, 1H each, $_{im}C_{4\text{-}5}$-*H*), 7.56-7.40 (m, 4H, Ar-*H*1, 4.89 (s, 2H C$H_2$Cl), 3.81 (s, 3H, C$H_3$).

**(1-Phenyl-*o*-diphenylphosphine- 3-methyl)imidazolium iodide (26)**



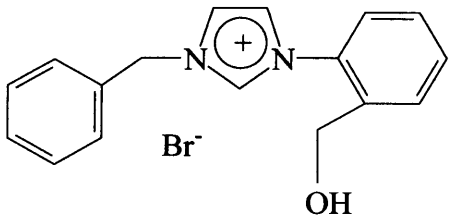

To (1-phenyl-*o*-chloride-3-methyl) imidazolium iodide (0.80 g, 2.40 mmol) in DMF (5 ml) was added $KPPh_2$, (freshly prepared from $KOBu^t$ (0.28g, 2.52 mmol) and $HPPh_2$ (0.5 ml, 2.52 mmol) in DMF (5 ml)). The solution was allowed to stir for 24h at r.t. The solvent was then reduced under vacuum to give a brown soild and methanol (10 ml) was added to quench excess $KPPh_2$. The methanol was then removed under vacuum. The residue was extracted into DCM (3 x 10ml) and the mixture was filtered through celite. The volume of the DCM was reduced and $Et_2O$ was added to give the product as an orange precipitate. The solid was collected by filtration, washed with $Et_2O$ (3 x 10ml) and dried under vacuum to give the product as an orange solid. Yield (0.84 g, 72.2%).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 9.79 (s, 1H, $_{im}C_2$-*H*), 7.96-7.25 (m, 14H, Ar-*H*), 6.72-6.68 (m, 2H, Ar-*H*), 4.16 (s, 1H, C*H*$_3$).

**$^{13}$C NMR** (100.03 MHz, $CDCl_3$, δ): 137.9, 135.7, 135.3, 132.9, 132.7, 131.7, 131.6, 130.9, 130.7, 130.6, 129.3, 129.6, 129.2, 127.9, 125.0, 124.3, (Ar-*C*H), 68.3 (*C*$H_2$), 25.9 (*C*$H_3$).

**$^{31}$P NMR** (121.65 MHz, $CDCl_3$, δ): -17.05.

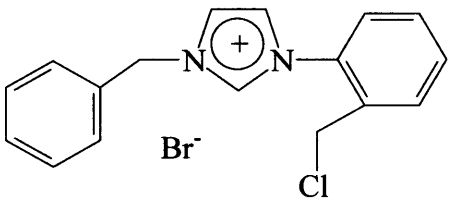
**(1-Phenyl-*o*-alcohol-3-benzyl)imidazolium bromide (30)**




A mixture of 1-(phenyl-*o*-alcohol)imidazole (3 g, 17.2 mmol) and benzylbromide (8.84 g, 51.7 mmol) in THF (30 ml) was gently refluxed for 12h. During the reaction an off-white solid was formed. The solid was collected by filtration, washed with THF and dried under vacuum. Yield (5.24 g, 88.2%).

**$^1$H NMR** (400.13 MHz, $d_6$-DMSO, δ): 9.76 (s, 1H, $_{im}C_2$-*H*), 8.10-8.01 (m, 2H, Ar-*H*), 7.72-7.40 (m, 9H, Ar-*H*), 5.55 (s, 2H, NC*H*$_2$ben), 4.73 (b.s, 1H, O*H*), 4.42 (s, 2H, C*H*$_2$OH).

**(1-Phenyl-*o*-chloride-3-benzyl)imidazolium bromide (32)**

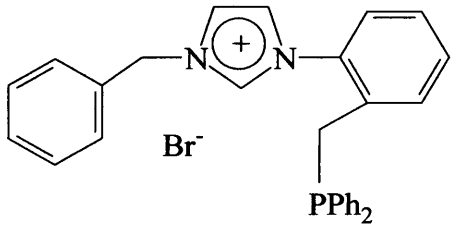



2,4,6-Trichloro[1,3,5]triazine (0.53 g, 2.89 mmol) was added to DMF (1.5 ml) at 25 °C. After the formation of a white solid, DCM (10 ml) was added, followed by (1-phenyl-*o*-chloride-3-benzyl) imidazolium bromide (1.0 g, 2.89 mmol) in DMF (10 ml). The mixture was stirred at r.t. for 4h, water (20 ml) was added and the organic phase was then washed with saturated solution of $Na_2CO_3$ (15 ml), followed by brine.

The organic layers were dried over $Na_2SO_4$ and the solvent was removed under vacuum to give the product as a pale yellow solid. Yield (0.75g, 71.5%).

**$^1$H NMR** (400.13 MHz, $d_6$-DMSO, δ): 9.82 (s, 1H, $_{im}C_2$-*H*), 8.09 (s, 1H, Ar-*H*), 8.00 (s, 1H, Ar-*H*), 7.80-7.38 (m, 9H, Ar-*H*), 5.56 (s, 2H, $CH_2$benzyl), 4.80 (s, 2H, C*H*$_2$Cl).

**(1-Phenyl-*o*-diphenylphosphine- 3-benzyl)imidazolium bromide (27)**

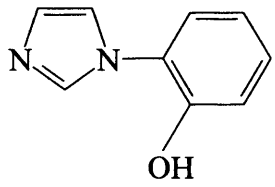



To (1-phenyl-*o*-chloride-3-benzyl) imidazolium bromine (0.87 g, 2.40 mmol) in DMF (5 ml) was added $KPPh_2$ (freshly prepared from $KOBu^t$ (0.28g, 2.52 mmol) and $HPPh_2$ (0.5 ml, 2.52 mmol) in DMF (5 ml)). The solution was allowed to stir for 24h at r.t. The solvent was then reduced under vacuum to give a brown soild and methanol (10 ml) was added to quench excess $KPPh_2$. The methanol was then removed under vacuum. The residue was extracted into DCM (3 x 10ml) and the mixture was filtered through celite. The volume of the DCM was reduced and $Et_2O$ was added to give the product as an orange precipitate. The solid was collected by filtration, washed with $Et_2O$ (3 x 10ml) and dried under vacuum to give the product as an orange solid. Yield (0.82, 66.3%).

**$^1$H NMR** (400.13 MHz, $d_6$-DMSO, δ): 9.85 (s, 1H, $_{im}C_2$-*H*), 8.21-8.09 (m, 2H, Ar-*H*), 7.83-7.15 (m, 19H, Ar-*H*), 5.60 (s, 2H, $CH_2$ben), 5.10 (s, C*H*$_2$$PPh_2$).

**$^{31}$P NMR** (121.65 MHz, $d_6$-DMSO, δ): -16.96.

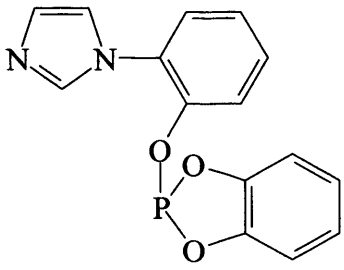
**1-(2-Phenol)imidazole (33)**



Formaldehyde (10.7 ml of 37 % sol$^{n}$, 0.143 mol), glyoxal (16.4 ml of 40 % sol$^{n}$, 0.143 mol) and glacial acetic acid (35 ml) was heated to 70 $^{0}$C. To the solution was added drop-wise with stirring over a period of 3h, a solution of $NH_4OAc$ (11.0 g, 0.143 mol), 2-phenolaniline (0.143 mol) in $H_2O$ (6 ml) and glacial acetic acid (30 ml). The solution which rapidly became orange/red, was stirred for 12h. The solution was cooled to r.t., then added drop-wise with stirring to a suspension of $NaHCO_3$ (151.00 g, 1.80 mol in $H_2O$ (1 L). The solution was made alkaline to pH 9 with NaOH, and the resultant solid then filtered on a Buchner funnel and washed with $H_2O$ (3 x 50 ml), sucked dry on the frit, then extracted with hot THF (6 x 200 ml). The resulting solvent was removed under vacuum. The product was a brown soild. (Yield 9.35 g, 40.8 %).

**$^{1}$H NMR** (400.13 MHz, $d_6$-DMSO, δ): 7.96 (s, 1H, imC$_2$*H*), 7.47 (s, 1H, Ar-*H*), 7.42-6.75 (m, 5H, Ar-*H*).

**(1-*o*-1,2-Phenylene phosphite-benzene)imidazole (34)**



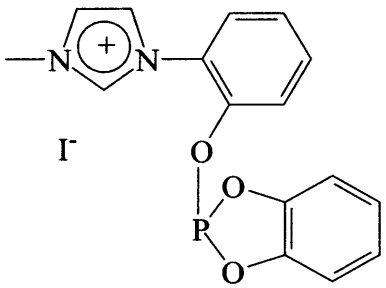
1-(2-Phenol)imidazole (0.29 g, 2.11 mmol) was dissolved in DCM (20 ml) and was added to a solution of *o*-1,2-phenylene phosphite chloride (0.275 ml, 2.11 mmol) and $Et_3N$ (0.30 ml, 211 mmol) in DCM (20 ml). The solution was stirred at r.t. for 24h. The solvent was removed under vacuum and then taken up into DCM (30 ml) and filtered. The solvent was then removed to give a yellow/orange solid. Yield (0.49g, 85.7%).

**$^1$H NMR** (400.13 MHz, $d_6$-DMSO, δ): 7.64 (s, 1H, $_{im}C_2$-*H*), 7.54 (s, 1H, Ar-*H*), 7.09-7.78 (m, 9H, Ar-*H*).

**$^{13}$C NMR** (100.03 MHz, $d_6$-DMSO, δ): 129.6, 129.0, 126.0, 123.1, 122.0, 120.2, 113.3, 113.0, 112.8, 112.7.

**$^{31}$P NMR** (121.65 MHz, $d_6$-DMSO, δ): 126.9

**(1-2-Phenylene phosphite-benzene)-3-(methyl)imidazolium iodide (35)**



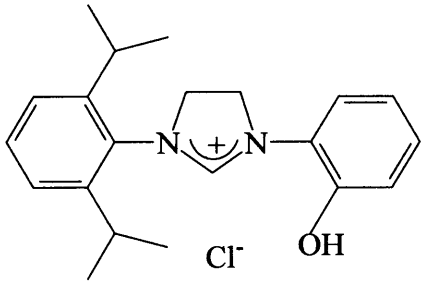

A mixture of (1-*o*-1,2-Phenylene phosphite-benzene)imidazole (0.30 g, 1.10 mmol) and iodomethane (0.16 g, 1.10 mmol) in THF (30 ml) was gently refluxed for 12h. During the reaction an off-white solid was formed. The solid was collected by filtration washed with THF and dried under vacuum. (Yield 0.25 g, 53.6 %).

**$^1$H NMR** (400.13 MHz, $d_6$-DMSO, δ): 9.47 (s, 1H, $_{im}C_2$-*H*), 7.97 & 7.85 (s x 2, each 1H, $_{im}C_{4,5}$-*H*), 7.45-6.72 (br m, 8H, Ar-*H*), 3.91 (s, 3H, $CH_3$).

**$^{31}$P NMR** (121.65 MHz, $d_6$-DMSO, δ): 174.3 (unknown), 129.9 (imidazolium salt **35**) in a ratio of 1:5.

The following compounds were prepared by literature methods.[11] Note: The below synthesis is only the final step of the reaction for the formation of compound **36**. For full preparation see literature method.

**1-(2,6-Diisopropylphenyl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolium chloride (36)**




$BH_3$-THF (1M in THF) (20.0 ml, 19.5 mmol, 8 equiv.) was added to (N-(2,6-Diisopropylphenyl)-N'-(2-hydroxyphenyl)-oxalamide (0.74g, 2.5 mmol) and the mixture was refluxed for 12h. The solution was allowed to cool to r.t. and then methanol was added very slowly, until all bubbling ceased. Conc. HCl solution (0.75 ml) was then added and the solvent was removed under reduced pressure. The resulting solid was dissolved in method, and then the solvent was again removed under reduced pressure. This process was repeated twice more. The resulting solid material was the dihydrochloride salt of the diimine. To this solid was added triethylorthoformate (7.5 ml). The resulting suspension was heated to 100 °C. As it heated, the solid slowly went into solution. After approx. 1 min. at high temperature, a white solid precipitated. The reaction was stirred for 5min. more, and then filtered. The resulting solid was washed with diethyl ether to provide the desired product as a pale yellow solid. Yield (0.42g, 47.1%).

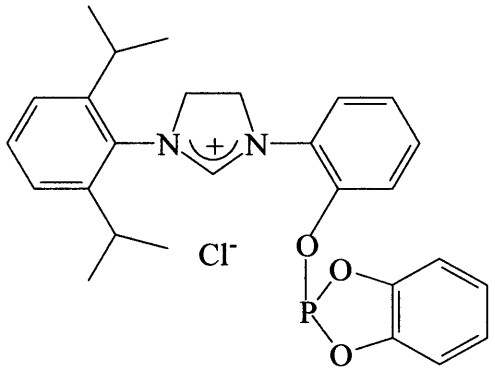
**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 9.02 (s, 1H, $_{im}C_2$-*H*), 7.54 (dd, *J* = 8.8, 1.0 Hz, 1H, Ar-*H*), 7.40 (t, *J* = 7.8 Hz, 1H, Ar-*H*), 7.18 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 7.11 (dd, *J* = 8.2, 1.3 Hz, 1H, Ar-*H*), 6.93 (dt, *J* = 7.8, 1.3 Hz, 1H, Ar-*H*), 6.75 (dt, *J* = 7.8, 1.2 Hz, 1H, Ar-*H*), 4.85 (t, *J* = 10.7 Hz, 2H, C*H*$_2$), 4.34 (t, *J* = 10.6 Hz, 2H, C*H*$_2$), 2.91 (sep, *J* = 6.7 Hz, 2H, 2CH), 1.21 (d, *J* = 6.8 Hz, 6H, $CH_3$), 1.12 (d, *J* = 6.7 Hz, 6H, $CH_3$).

**$^{13}$C NMR** (100.03 MHz, $CDCl_3$, δ): 156.8, 149.6, 146.4, 131.5, 129.8, 128.5, 125.0, 122.5, 120.1, 119.8, 118.4 (Ar-*C*H), 52.5, 51.0 ($_{im}C_{4,5}$-H), 28.8 (*C*H), 24.9 (*C*H$_3$), 24.1 (*C*H$_3$).

**MS** (ES): *M/z* 323.2 $[M\text{-}Cl]^+$

Single crystals were obtained by slow evaporation of a DCM solution of **36** in air.

**1-(2,6-Diisopropylphenyl)-3-(1-*o*-1,2-phenylene phosphite-benzene)-4,5-dihydro-imidazolium chloride (37)**




1-(2,6-Diisopropylphenyl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolium chloride (0.29 g, 2.11 mmol) was dissolved in DMF (20 ml) and was added to a solution of *o*-1,2-phenylene phosphite chloride (0.275 ml, 2.11 mmol) and $Et_3N$ (0.30 ml, 211 mmol) in DMF (20 ml). The solution was stirred at r.t. for 24h. The solvent

was removed under vacuum and then taken up into DCM (30 ml) and filtered. The solvent was then removed to give a yellow solid. Yield (cannot be calcd. because product was not isolated cleanly).

**$^{31}$P NMR** (121.65 MHz, $d_6$-DMSO, δ): 137.1 (imidazolium salt **37**), 75.1 (unknown), 21.8 (unknown) in a ratio of 1:2:1.

## 2.8: References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# CHAPTER THREE
# Phosphine-NHC Complexes

## 3.1: Introduction

### 3.1.1: Reported phosphine-NHC complexes

Upon starting this project only one palladium phosphine-carbene complex, **3.1**, synthesised by the group of Lappert in 1998, had been reported in the literature.[1] Subsequently while this project was undertaken, a series of functional NHC-phosphine complexes (**3.2** to **3.6**) were synthesised by the group of Danopoulos in 2003.[2] In 2004 Helmschen reported the synthesis of a Rh(I) phosphine-NHC complex, **3.8**, via transmetallation from the corresponding silver(I) complex, **3.7**, and the subsequent use of complex **3.8** in the asymmetric hydrogeneration. This shows how, with thoughtful design, phosphine-carbene ligands may be excellent ligands when used with other transition metals than palladium for the use in catalysis.

Recently the group of Zhon and Lee independently synthesised tridentate phosphine-imidazolium pincer ligands. Lee *et al.* set out to synthesise the corresponding silver(I), **3.9**, palladium(II), **3.10-3.11**, and ruthenium complexes with his phosphine-imidazolium pincer, whereas Zhon tested his pincer ligand, along with three phosphine-imidazolium salts, *in-situ* in the Heck coupling reaction with mixed results. The spectroscopy data of complex **3.12** was reported showing the coordination of the phosphine function via the significant shift in the singlet observed in the $^{31}$P-NMR from the free phosphine (Pd-$PRPh_2$ 16.52 ppm, $PRPh_2$ -14.48 ppm). However, in the $^{1}$H-NMR spectra, they reported no splitting for the $CH_2$ bridge (between the NHC-group and the phenyl ring, **3.12**) from a singlet in the phosphine-imidazolium salt to two doublets in the complex, which is characteristic of these chelating complexes. Such splitting was seen throughout this work in related complexes and has been reported in numerous papers.[2-4]

The synthesis and characteristic properties of these phosphine-NHC complexes was described in more detail in Chapter One and a summary of known complexes is given in figure 3.1.

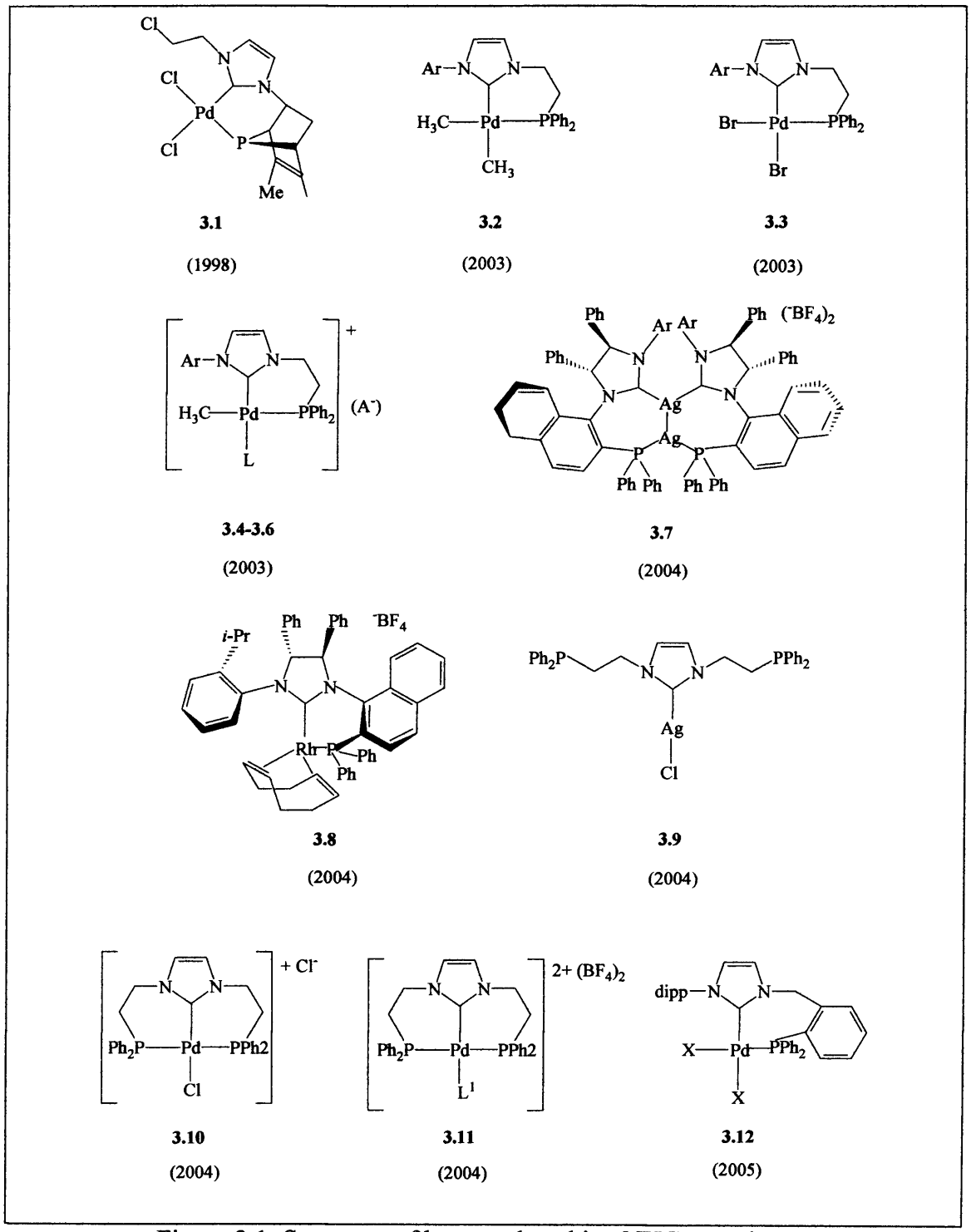


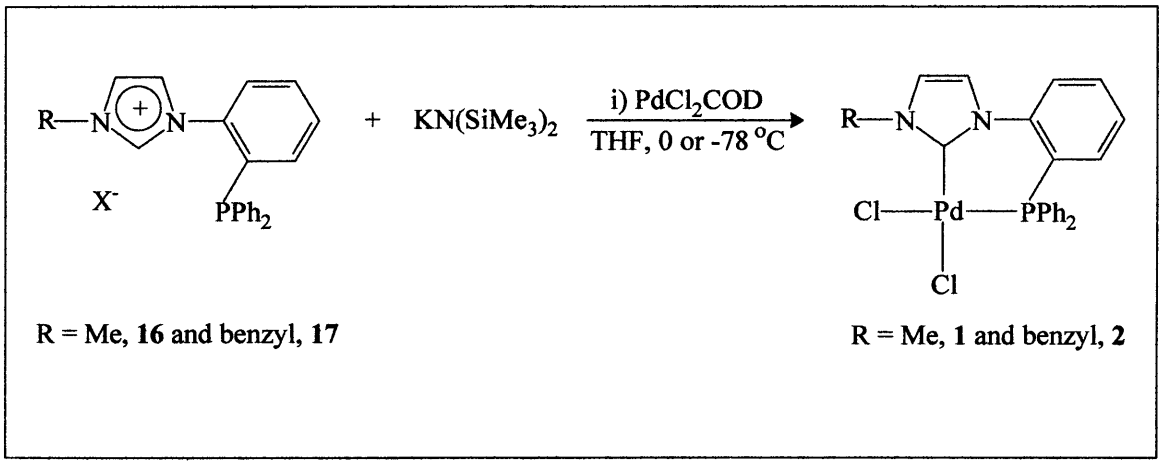

Figure 3.1: Summary of known phosphine-NHC complexes.

Ar = dipp **3.2-3.6**, Mes **3.2** and **3.3**. L = Py, $PMe_3$, NCMe **3.4-3.6**. $L^1$ =Py, NCMe.

# 3.2: Results and discussion

## 3.2.1: Formation of Pd(II) via the free carbene route

The synthesis of palladium(II) complexes was achieved via the formation of the free carbene, which was generated *in-situ* and then trapped by reacting the free chelating ligand with the palladium metal precursor. When phosphine-imidazolium salt **16** was reacted with one equivalent of $KN(SiMe_3)_2$ in THF at 0 °C, the imidazolium salt was rapidly deprotonated by the base to form the carbene, (scheme 3.2). After ten minutes the deprotonation was complete and the solution was filtered, removed again inorganic salts and into a second Schlenk containing one equivalent of $PdCl_2COD$. The resulting red solution was then stirred at room temperature (r.t.) for two hours.




Scheme 3.2: Formation of palladium complexes **1** and **2**.

After the reaction, the solvent was removed under vacuum, dissolved in DCM and filtered through celite. Concentration of this solution and the addition of $Et_2O$ led to the precipitation of a sticky red solid which was stirred vigorously with *n*-hexane for 10 minutes. The crude product was then recrystalised from DCM/$Et_2O$ twice to

give phosphine-NHC complex **1** as an orange solid in 78% yield. Complex **1** was stable both in the solid state and in solution, e.g. there was no sign of degradation when a solution of complex **1** was exposed to air over a period of several days (NMR). Complex **1** was characterised by satisfactory NMR spectroscopy and MS data. The $^{1}$H-NMR spectra of **1** shows the coordination of the carbene to the palladium metal centre by the absence of $_{im}C_2$-H, which usually appears at 9.16 ppm in the corresponding imidazolium salt. The palladium-phosphine bond appears in the $^{31}$P-NMR spectra as a singlet at 17.48 ppm, with the corresponding free ligand at -16.86 ppm.

The formation of complex **2** was also achieved by the *in-situ* deprotonation for phosphine-imidazolium salt **17**, with one equivalent of $KN(SiMe_3)_2$ in THF. However, this time the reaction was carried out at -78 °C, to insure that only the $_{im}C_2$-H position was deprotoned by the base and no other acidic protons (e.g. $CH_2$ protons between the imidazolium ring and the phenyl ring) were removed. After the deprotonation was complete the solution was filtered onto one equivalent of $PdCl_2COD$ and stirred at r.t. for two hours. The reaction was worked up in the same way as above (complex **1**) and led to the isolation of phosphine-NHC palladium complex **2** in 71% yield. Complex **2** was an orange/yellow solid and was freely soluble in organic solvents such as THF and DCM.

The phosphine-NHC palladium complex **2** was characterised by spectroscopic and analytical means. In the $^{1}$H-NMR the absence of the $_{im}C_2$-H appeared at 9.79 ppm in the corresponding phosphine-imidazolium salt and the fact that the $CH_2$ bridge linker of the benzyl group moved from a singlet at 5.47 ppm in the free imidazolium salt to two doublets at 6.10 and 5.58 ppm (J = ~15 Hz) shows that the formation of the NHC-palladium bond has occurred. The palladium-phosphine bond appears in the $^{31}$P-NMR spectra as a singlet at 16.35 ppm, with the corresponding free phosphine at -16.8 ppm. Again complex **2** was stable both in the solid state and in solution when exposed to air; subsequently slow evaporation of a DCM solution of palladium complex **2** in air yielded crystals suitable for a single crystal x-ray crystalographic determination. Suitable elemental analysis and MS data was also achieved for complex **2**. The structure and numbering scheme for complex **2** is shown in figure 3.3 and selected bond lengths and angles are collected in table 3.4.

Complex **2** exhibits a square-planar geometry, which is slightly distorted around the palladium metal centre where the chelating ligand occupies the two *cis*-positions. The six-membered ring is twisted; the dihedral angle between the plane of the imidazolium ring and the plane of the phenyl ring is approximately 63.2°. The ligand bite angle is 82.8 °, which was significantly smaller than the bite angle in a similar six-membered palladium phosphine-NHC complex, **3.3**, in which the bite angle was 89.2 °.[2] Whilst both complexes (**2** and **3.3**, page 108) form six-membered chelating rings, the difference in bite angles maybe accounted for by the fact that the linkers between the phosphine-NHC ligands are very different. In complex **3.5** reported by Danoponlos *et al.*,[2] the linker is a more flexible ethylene bridge, whereas in complex **2** the linker between the two functional groups is a much more rigid phenyl ring. Thus, in complex **2** the chelating ligand is unable to rotate and pucker as 'freely' as the ethylene bridged chelate. This was one of the primary aims of the design of these chelating ligands.

Both the Pd(1)-P(1) and Pd(1)-C(1) bond lengths in complex **2** are typical at 2.210(3) Å and 1.961(1) Å respectively, and are similar to related complexes.[2,5] Notably the Pd-Cl bond *trans* to the phosphine is longer than that *trans* to the NHC by approximately 0.065 Å. Although this is not unique as two other phosphine-NHC palladium complexes (e.g. complex **3.1**[5], and complex **3.3**[2], page 108) have both shown the same trend, the differences in both cases was only about 0.03 Å. As noted in the introduction to Chapter One by the work of Danopoulos,[2] this observation is unexpected due to the fact that NHC ligands are even stronger σ-donors than trialkylphosphine.[2] The stronger σ-donor ligands weaken the σ-donor contribution of the ligand *trans* to themselves and therefore lengthens the ligand bonded opposite. The fact that Cl ligands can donate π-electron density to the metal and phosphines can also accept electron density from the metal should only go to strengthen the fact that the Cl bond *trans* to the phosphine should be stronger and therefore shorter than that *trans* to the NHC, which does not accept π-electron density from the metal. It is important to remember that *trans* influence is a purely thermodynamic phenomenon and affects only the ground state properties of the complex; the 'labilising effect,' which affects the substitution/reactivity of a ligand *trans* to a particular group, is

called the *trans* effect and is a kinetic phenomenon, and may be affected by the stabilisation of a particular transition state.

The formation of the functionalised free phosphine-NHC ligand, which was formed from the corresponding imidazolium salt, **16**, was achieved using the same methodology as described in the synthesis of complex **1**. However, after the deprotonation was complete, the phosphine-NHC ligand was then reacted with one equivalent of PdClMeCOD. The resulting solution was stirred at r.t. for two hours. The reaction was worked up in the same was as above (complex **1**), however, the dichloromethane used during the work-up was cold (0 °C).[2] The product was isolated as a red/brown solid (yield 68%), which showed signs of decomposition in DCM under a dinitrogen atmosphere over a period of several hours.

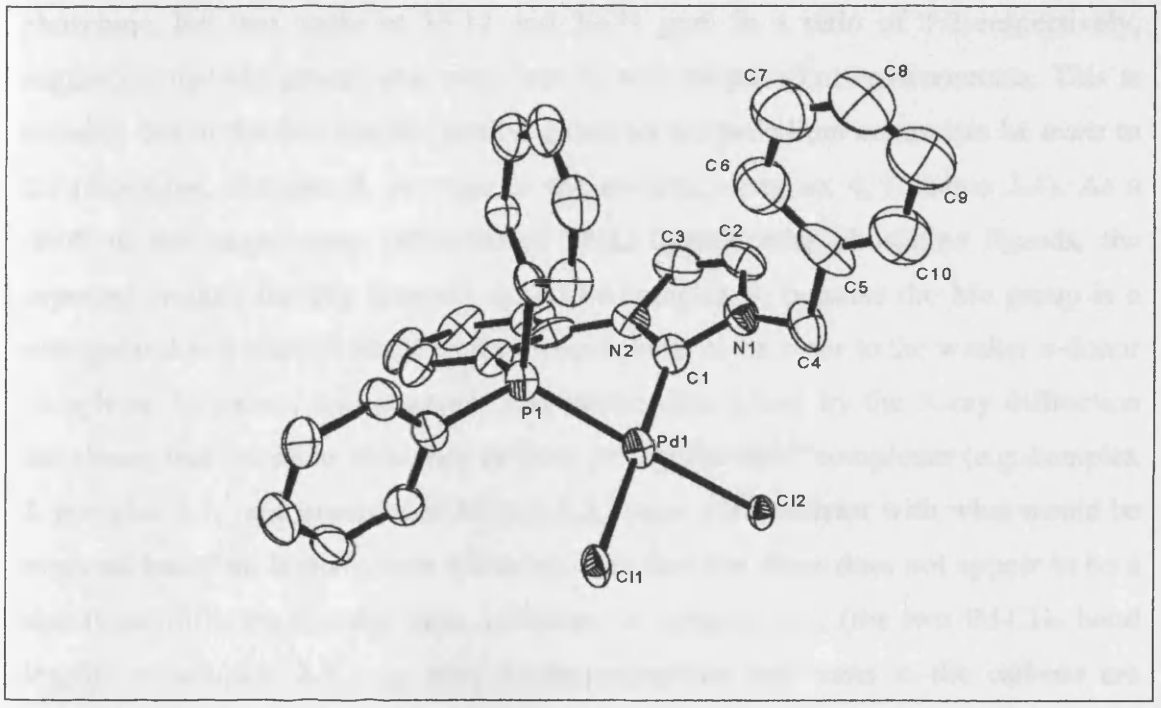
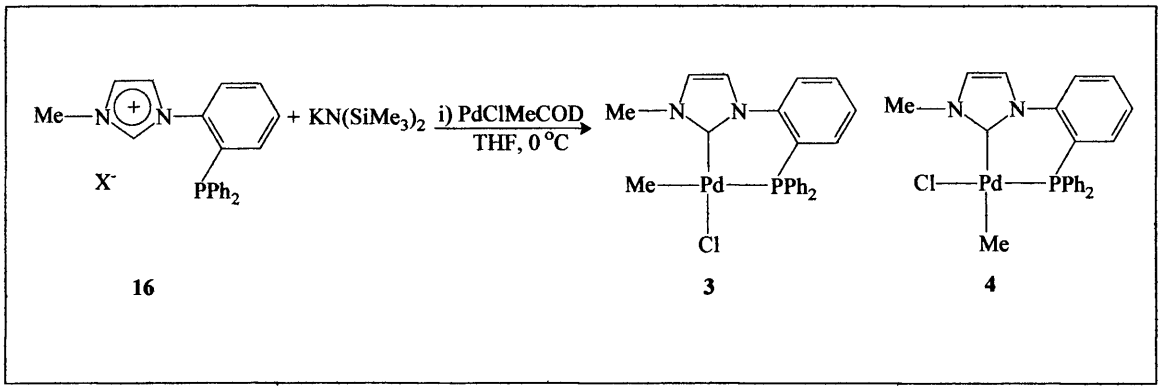



Figure 3.3: ORTEP projection of phosphine-NHC palladium complex **2**. Hydrogen atoms and one water molecule are omitted for clarity.

Table 3.4: Selected bond lengths (Å) and angles (deg) for complex **2**.

| | | | | | |
|---|---|---|---|---|---|
| Pd(1)-C(1) | 1.961(1) | N(1)-C(4) | 1.441(5) | N(1)-C(1)-Pd(2) | 127.7(8) |
| Pd(1)-P(1) | 2.210(3) | N(2)-C(1) | 1.469(5) | N(2)-C(1)-Pd(1) | 128.1(8) |
| Pd(1)-Cl(1) | 2.356(2) | N(2)-C(3) | 1.823(4) | C(1)-Pd(1)-P(1) | 82.8 |
| Pd(1)-Cl(2) | 2.421(2) | N(2)-C(11) | 1.835(3) | C(1)-Pd(1)-Cl(2) | 89.5(3) |
| N(1)-C(1) | 1.350(1) | C(2)-C(3) | 1.841(3) | Pd(1)-P(1)-Cl(11) | 96.01(1) |
| N(1)-C(2) | 1.364(1) | | | C(1)-Pd(1)-Cl(2) | 92.12(8) |

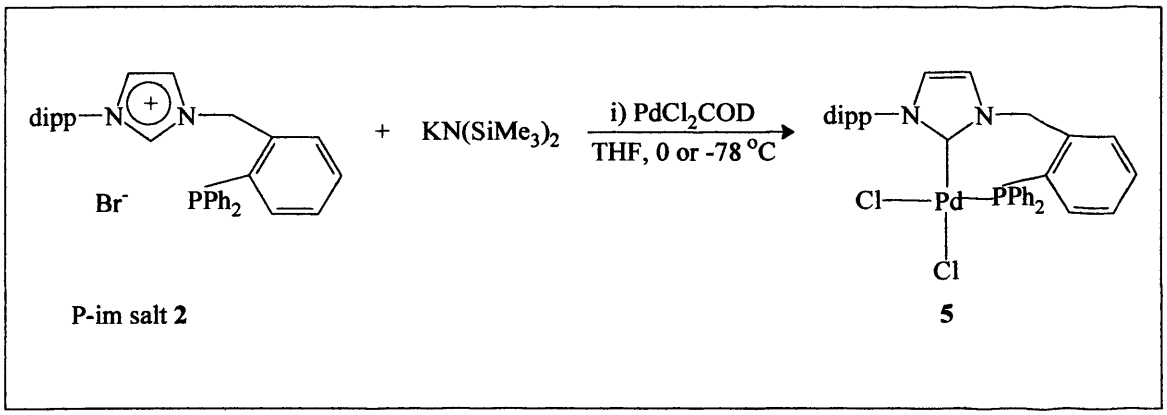
Although there was no $_{im}C_2$-H proton in the $^1$H-NMR, impurities in the spectra made it hard to interpret. However, the $^{31}$P-NMR showed no sign of the free phosphine, but two peaks at 35.12 and 32.71 ppm in a ratio of 1:2 respectively, suggesting that the phosphorus atom was in two inequivalent environments. This is possibly due to the fact that the methyl group on the palladium centre can be *trans* to the phosphine, complex **3**, or *trans* to the carbene, complex **4**, (scheme 3.4). As a result of the larger *trans* influence of NHC ligands over phosphine ligands, the expected product for this reaction would be complex **3**, because the Me group is a stronger σ-donor than Cl and therefore would prefer to be *trans* to the weaker σ-donor phosphine. However, the structure information determined by the X-ray diffraction has shown that the *trans* influence in these phosphine-NHC complexes (e.g. complex **2**, complex **3.1**,[5] and complexes **3.2** and **3.3**,[2] page 108) contrast with what would be expected based on known *trans* influence. The fact that there does not appear to be a significant difference in the *trans* influence in complex **3.2**, (the two Pd-$CH_3$ bond lengths in complex **3.2**, e.g. *trans* to the phosphine and *trans* to the carbene are 2.111(5) and 2.098(5) Å respectively), and the *trans* influence showed in complex **2** is the opposite to what would be expected (Pd-Cl bond *trans* to the phosphine is longer than that *trans* to the NHC), may account for the fact that the two isomers are formed.




Scheme 3.4: Formation of palladium(II) complexes **3** and **4**.

Attempts to separate complexes **3** and **4** via recrystalisation failed. The formation of palladium black, which is visible in a DCM solution of complexes **3** and **4** after a few hours, is evidence that the complexes may undergo a facile reductive elimination process resulting in the formation of an alkyl imidazolium salt. The reductive elimination of complex **3**, in which the methyl group on the palladium is *cis* to the NHC, would occur much more rapidly than the more stable *trans* complex **4**. This reductive elimination could be monitored by $^{31}$P-NMR ($CD_2Cl_2$) by slowly heating a solution of the two isomers (**8** and **9**) and seeing how the integration of these two peaks changed over a period of time.

When one equivalent of the phosphine-imidazolium salt, **2**, was reacted with one equivalent of $KN(SiMe_3)_2$ in THF at -78 °C, the corresponding phosphine-NHC ligand formed rapidly. After the deprotonation was complete, the reaction was filtered into a second Schlenk flask containing one equivalent of $PdCl_2COD$. The resulting yellow solution was then stirred at r.t. for two hours. After the reaction, the solvent was removed under vacuum; subsequent solid was dissolved in DCM and filtered through celite to remove any inorganic salts. The DCM was then removed and the crude product was triturated with *n*-hexane.




Scheme 3.5: Formation of palladium(II) complex **5**.

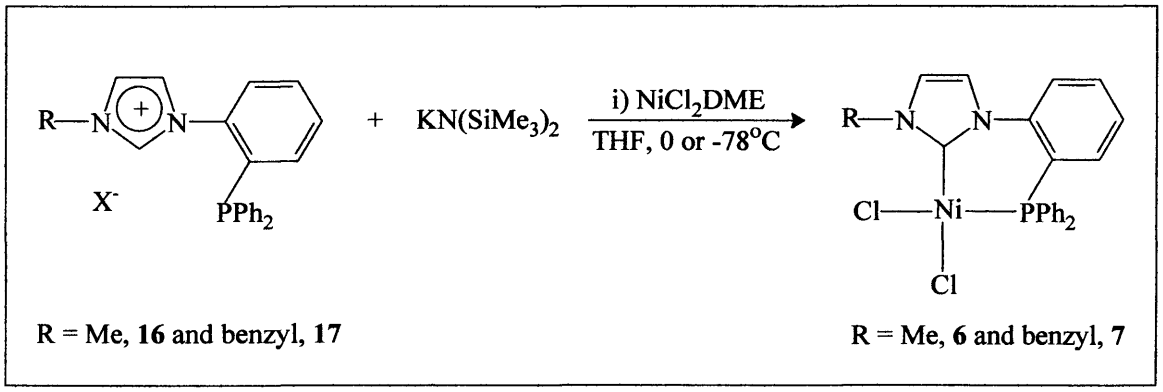
The crude product was recrystalised twice from DMC by the drop-wise addition of $Et_2O$ which led to the isolation of the phosphine-NHC complex, **5**, as a yellow solid in 70% yield. The palladium(II) complex, **5**, was found to be stable both as a solid and in solution with respect to air and moisture. Complex **5** dissolved freely in solvent such as chloroform, dichloromethane and tetrahydrofuran. Characteristic changes to both the $^1H$ and $^{31}P$-NMR, along with satisfactory MS data, confirmed that the desired product had been formed. The palladium-phosphine bond appeared in the $^{31}P$-NMR spectra as a singlet at 12.51 ppm, and the corresponding free ligand appeared at 15.49 ppm. The chemical shift value of the coordinated phosphine bond was in the same range as that of related complexes.[2,6]

The $^1H$-NMR spectra of **5** shows the coordination of the carbene to the metal centre by the absence of the $_{im}C_2$-H (at 10.73 ppm), and the splitting of the $CH_2$ bridging protons (between the two functional groups) from a singlet at 6.16 ppm in the phosphine-imidazolium salt, **2**, into two doublets in the corresponding chelating complex, **5**, at 5.87 ppm and 4.70 ppm ($J$ = 14.4 Hz). This splitting of the $CH_2$ bridging protons is characteristic for such chelating complexes[2-4] and is due to the fact that one proton points towards the metal and the other points away from the metal, and as a result the protons are rendered inequivalent.

## 3.3: Formation of Ni(II) complexes via the free carbene route

An analogous approach to that used in the synthesis of a series of palladium(II) complexes, was applied to form the corresponding chelating Ni(II) complexes. Once again *in-situ* deprotonation of phosphine-imidazolium salts **16** and **17** was carried out at low temperature (0 °C to -78 °C) by the reaction with one molar equivalent of $KN(SiMe_3)_2$. The use of $KN(SiMe_3)_2$ as a base in the deprotonation of imidazolium salts has proven to be highly effective due to the fact that the base is strong enough to deprotonate a range of imidazolium salts cleanly, but mild enough to be compatible with imidazolium salts that contain acidic protons when used at low temperatures.[2,7] The by-product of the reaction between $KN(SiMe_3)_2$ and the imidazolium salt is easily removed (KX may be filtered and $HN(SiMe_3)_2$ can be removed under vacuum), making the reaction work-up uncomplicated.

When equimolar quantities of the free ligand (**16** or **17**) were stirred at room temperature with $NiCl_2COD$, the synthesis of the two new phosphine-NHC nickel(II) complexes, **6** and **7**, was achieved (scheme 3.6). The isolation of these complexes (68% and 65% yield respectively) was achieved using the same methodology as previously reported for complex **1**. Both complexes were found to be stable in solution as well as in the solid state with respect to air and moisture and may be stored unchanged under an inert atmosphere for an extended period of time. The nickel(II) complexes **6** and **7** were pale yellow solids and freely soluble in several organic solvents (i.e. DCM, THF, $CHCl_3$).

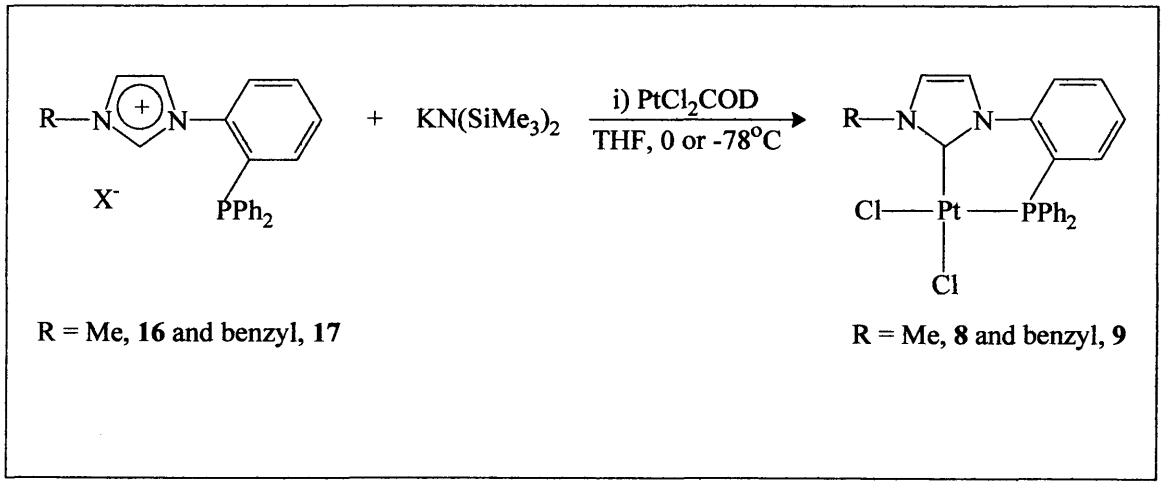



Scheme 3.6: Formation of nickel(II) complexes **6** and **7**.

Both complexes were characterised by NMR spectroscopy and MS. The $^{1}$H-NMR spectra of the nickel(II) complexes **6** and **7** showed similar trends to those seen in the $^{1}$H-NMR spectra of the analogous palladium(II) complexes **1** and **2** (however both nickel complexes gave broader peaks in the $^{1}$H-NMR spectra). The $^{31}$P-NMR spectra of **6** and **7** appeared as singlets at 7.88 ppm and 8.30 ppm respectively and showed no sign of the free phosphine, which appears around -16.0 ppm for both phosphine- imidazolium salts, indicating that all the phosphorous atoms are in the same electronic environment, e.g. coordinated to the metal centre.

## 3.4: Synthesis of phosphine-NHC Pt(II) complexes

Using the same synthetic methodologies as for the related palladium and nickel complexes (**1** and **2**, **6** and **7**), the analogous platinum(II) phosphine-carbene bis-chloride complexes (**8** and **9**) were prepared, (scheme 3.7).




Scheme 3.7: Formation of platinum(II) complexes **8** and **9**.

Following this synthetic process and after the work-up the isolation of platinum(II) complexes **8** and **9** were achieved in a yield of 84% and 79% respectively. Both **8** and **9** were isolated as red solids and like their analogous palladium and nickel complexes were found to be stable when exposed to air (no

visible sign of decomposition when a solution of complexes **8** and **9** were left open to air over a period of several days). Both compound **8** and **9** were characterised by $^{1}H$ and $^{31}P$-NMR and MS data was obtained for complex **9**. The characteristic peaks in the $^{1}H$-NMR for the platinum complex **8** was the absence of the $_{im}C_2$-H, which appears at 9.16 ppm in the corresponding phosphine-imidazolium salt **16**, and the $_{im}C_{4\text{-}5}$ –H protons, which come as two doublets at 7.4 ppm and 6.8 ppm ($J$ = 1.93 Hz).The $^{31}P$-NMR is characteristic for such complexes, showing a singlet at 5.24 ppm and platinum satellites at 20.34 ppm and -9.86 ppm ($J$ = 9060.0 Hz); the spectra also showed no sign of the free phosphine of compound **16** which comes at -15.49 ppm.

The characteristic peaks in the $^{1}H$-NMR of complex **9** are two doublets corresponding to the $CH_2$ protons (e.g. between the NCH and the phenyl ring), which come at 6.08 ppm and 4.37 ppm ($J$ = 14.2 Hz), and again the absence of the imidazolium proton which appears at 9.79 ppm in the corresponding imidazolium salt **17**. Like complex **7** the $^{31}P$-NMR of complex **9** shows the characteristic peaks which indicate that only one product has formed from this reaction; the platinum(II) phosphine-carbene complex **9** with a singlet at 10.29 ppm and the two platinum satellites at 20.06 and 0.76 ppm ($J$ = 5741.4 Hz).

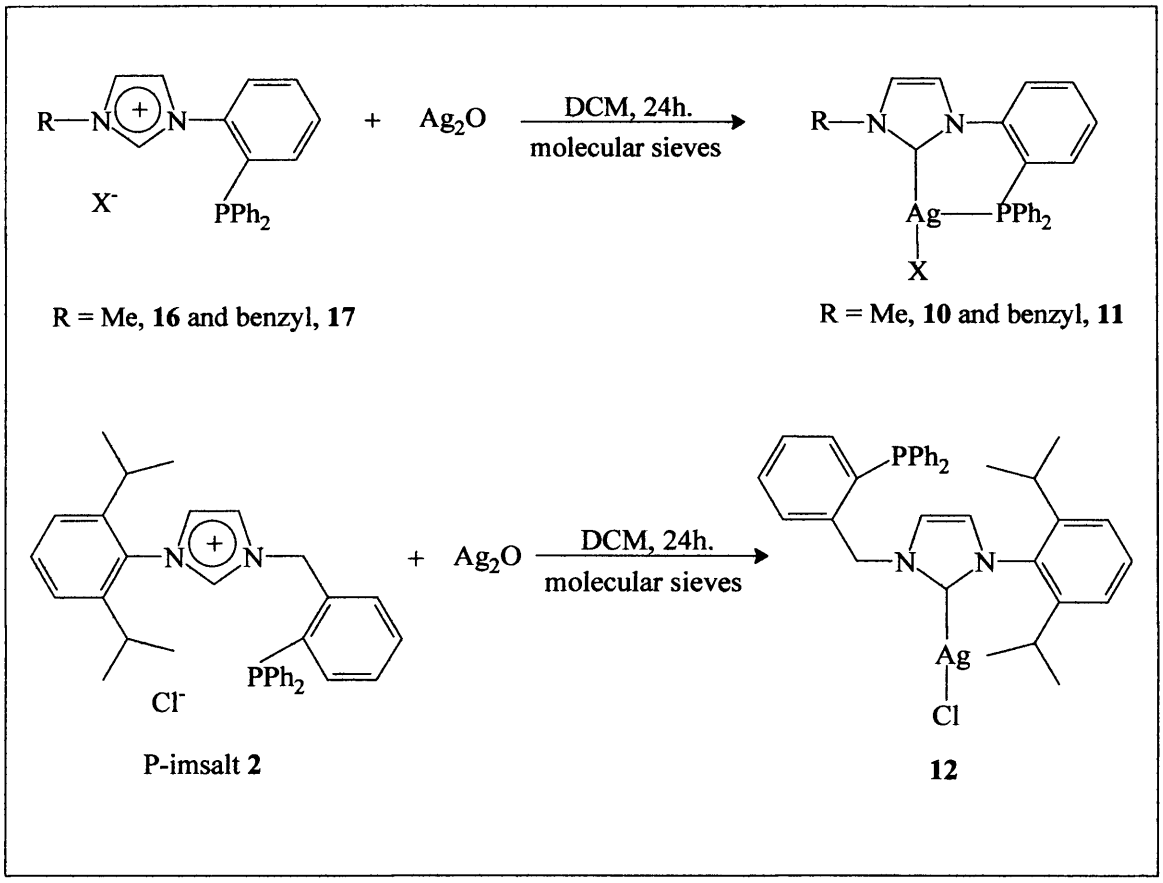
## 3.5: Synthesis of silver(I) phosphine-NHC's

The synthesis of silver complexes **10-12** was achieved via the reaction of $Ag_2O$ with the corresponding phosphine-imidazolium salts. Imidazolium salts **2**, **16** and **17** were reacted with one molar equivalent of $Ag_2O$ in refluxing DCM for 24h in the presence of 4 Å molecular sieves, (scheme 3.8), following the method of Wang and Lin.[8] Notably, when the reaction of imidazolium salt **16** was carried out with only half the equivalent of $Ag_2O$, the $_{im}C_2$-H proton in the $^{1}H$-NMR was still visible, indicating that the reaction did not go to completion. The same observation was supported by the work of Helmschen *et al.* in the synthesis of the related phosphine-NHC silver(I) complex **3.7** (page 108).[1]

After the reaction the mixture was cooled to r.t. and filtered through celite to remove any unreacted $Ag_2O$. The solvent was reduced under vacuum and the addition of $Et_2O$ yielded the corresponding silver(I) complexes **10**, **11** and **12**, yields 67-73%. Complexes **10** and **11** were isolated as red solids and complex **12** was isolated as a grey-white solid. All three complexes readily dissolved in dichloromethane and chloroform and showed signs of decomposition (e.g. visible formation of silver halide after approximately one hour, $CDCl_3$) under an atmosphere of di-nitrogen when exposed to light.

Complex **11** and **12** were characterised by $^{1}H$, $^{13}C$ and $^{31}P$-NMR and suitable MS data, however, complex **9** was characterised by $^{1}H$ and $^{31}P$-NMR only and then reacted further to form a rhodium(I) complex, *vide infra*. The absence of the $_{im}C_2$-H proton from the $^{1}H$-NMR from all three complexes **10**, **11** and **12** signified the formation of the carbene-silver bond. The $^{31}P$-NMR of **9** and **11** showed the phosphorus atom in the complexes had shifted downfield from ~ -16 ppm in the phosphine-imidazolium salts to -3.87 and -4.81 ppm in the corresponding silver(I) complexes **9** and **11**, indicating that the formation of the phosphine was coordinated to the metal centre, which was found to be the same in the case of complex **3.12** synthesised by Helmschen *et al.*[1] However, in the $^{31}P$-NMR of complex **12**, the phosphorus signal remained at -15.79 ppm which was the same as in the free phosphine-imidazolium precursor ligand. This means that the silver(I) complex formed in this reaction only contains a carbene bound to the metal centre and the phosphine ligand remains uncoordinated. This was shown to be the case in other NHC functionalised silver(I) complexes in which only the NHC is bound to the metal and not the steric functional group[9]. It may be that the phosphine in silver complex **12** can rotate more freely than in complexes **10** and **11** (due to the methyl linker) and the coordination of the phosphine is unfavoured due to steric factors.

The MS data for silver complexes **11** and **12** only show peaks corresponding to the mono-silver complex (e.g. one phosphine-NHC molecule, one silver atom and one halide atom) and the low fragment compound. However, that does not mean that the structures drawn in scheme 3.8 are the right structures as it is difficult to know the precise formula of such silver complexes without crystal structure data.

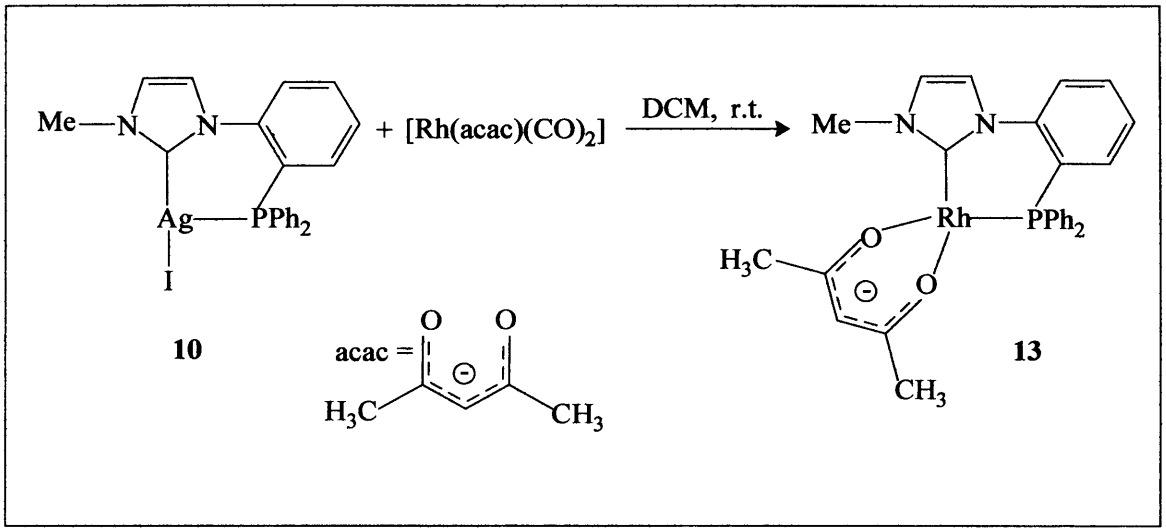



Scheme 3.8: Formation of silver(I) complexes **10-12.**

## 3.6: Synthesis of group nine phosphine-NHC complexes

The synthesis of rhodium(I) complex **13** was achieved via transmetallation from the corresponding silver(I) complex **10**. The synthesis of the silver(I) complex **10** was achieved via the reaction of phosphine-imidazolium salt **11** and $Ag_2O$, as described above (scheme 3.8). Half a molar quantities of complex **11** and the rhodium(I) precursor complex, $[Rh(acac)(CO)_2]$, (scheme 3.9), was stirred together in dichloromethane for two hours at r.t., in the dark. After the reaction, silver halide was visible in the reaction mixture, indicating that transmetallation had occurred. The mixture was then filtered through celite to remove the silver halide and the solution

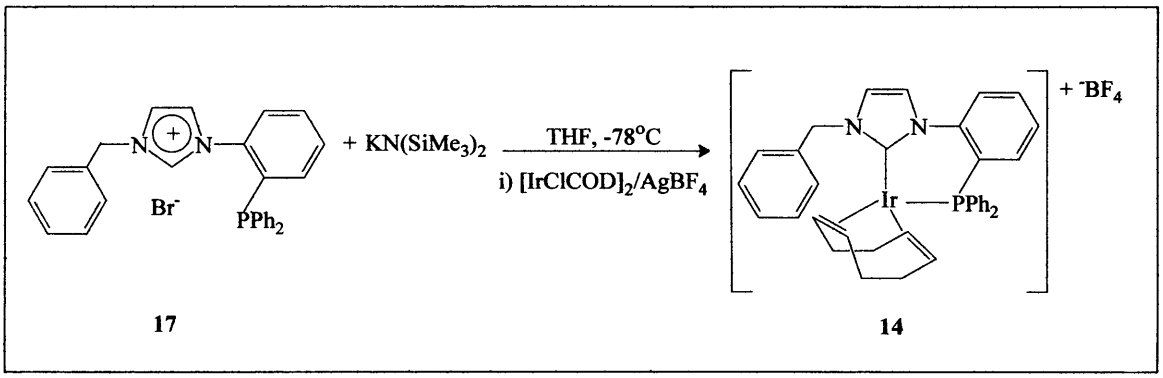
was reduced under vacuum. Diethyl ether was added and the crude product precipitated out of solution as an orange/red solid. The solid was washed with $Et_2O$, then stirred in *n*-hexane for ten minutes. The resulting solid was recrystalised from DCM/$Et_2O$ twice and dried under vacuum.




Scheme 3.9: Synthesis of rhodium(I) complexes **13**.

The product was characterised by $^1H$ and $^{31}P$-NMR and the spectra of the latter, showed that three different products had formed. The major product, complex **13**, was characterised by a doublet at 31.10 ppm with a $J_{RhP}$ = 145.44 Hz. The two minor products appeared at 42.35 ppm ($J_{RhP}$ = 125.24 Hz.) and 27.84 ppm ($J_{RhP}$ = 131.30 Hz.) respectively. The two peaks in the $^{31}P$-NMR of the minor products are found at the same intensity and are in a ratio of 8:1 with the desired product complex **13**. The minor products may be due to the formation of two different five coordinate rhodium(I) compounds in which a carbon monoxide molecule is taking up the five coordination sites in two different positions.

When phosphine-imidazolium salt **17** was reacted with one equivalent of $KN(SiMe_3)_2$ in THF at 0° C, the imidazolium salt was rapidly deprotonated by the base to form the carbene, (scheme 3.10). After ten minutes the deprotonation was complete and the solution was added via a cannula into a second Schlenk containing one equivalent of an iridium precursor complex. The iridium precursor complex was freshly prepared from the reaction of $[IrClCOD]_2$ and $AgBF_4$ in refluxing THF for 30 minutes. One silver atom is required to extract a chloride atom from the iridium dimer, therefore the $[IrClCOD]_2$ and $AgBF_4$ was reacted in a ratio of 1:2. After the extraction, the mixture was filtered through celite to remove the silver halide and cooled to 0° C. It was at this stage that the free phosphine-NHC ligand was added to the iridium(I) precursor which was then stirred together for two hours at r.t.




Scheme 3.10: Attempted synthesis of iridium(I) complex **15**.

After the reaction the solvent was removed and the product was extracted into DCM and filtered. The volume of DCM was reduced and the addition of $Et_2O$ led to the isolation of a green/brown solid, which was recrystalised from DCM/$Et_2O$ twice and dried under vacuum. However, the $^1H$ and $^{31}P$-NMR spectra were unclean, the $^1H$-NMR showed broad multiplets from 7.8 ppm to 6.2 ppm and although, the $CH_2$ group between the phenyl ring and the NHC ring appeared as two doublets at 4.80 ppm and 4.68 ppm with a $J$ = 13.7 Hz the integration of these peaks and those of the CH and $CH_2$ group on the coordinated COD are not correct, indicating that a significant amount of impurity is present. Attempts to isolate complex **14** as a pure compound via recrystalisation failed.

## 3.7: Conclusion

The preparation and characterisation of several new group 10 metal(II) phosphine-NHC complexes has been achieved. These complexes are readily synthesised via well established high yielding methods. The solid state structure of complex **1** has been obtained, giving an insight into the properties of these chelating ligands. The relative *trans* influences of the phosphine and carbene functions revealed that the Pd-Cl bond *trans* to the phosphine is longer than that *trans* to the NHC. This observation is not fully understood and has been observed in other related phosphine-carbene complexes. Three new silver(I) phosphine-NHC complexes have been synthesised and characterised and the rhodium(I) complex **13** was prepared via transmetallation from the corresponding silver(I) complex **10**.

# 3.8: Experimental

## 3.8.1: General Comments

All NMR data are quoted in δ/ppm. The $^{31}P$ NMR spectra (referenced to $H_3PO_4$ δ = 0 ppm) were collected on a Jeol Eclipse 300 MHz spectrometer; $^{1}H$ and $^{13}C$ spectra were recorded on a Bruker 400 MHz DPX Avance, unless otherwise stated, and referenced to $SiMe_4$ (δ = 0 ppm). Electrospray mass spectrometry (ESMS) was performed on a VG Fisons Platform II instrument by the Department of Chemistry, Cardiff University. Crystals were diffracted in a Bruker Nonius Kappa CCD area detector using graphite monochromatised MoKα radiation, I = 0.71073Å.

All manipulations were carried out using standard Schlenk techniques under dry argon or dinitrogen. Tetrahydrofuran (THF), diethyl ether ($Et_2O$), and *n*-hexane were dried and degassed by refluxing under dinitrogen over sodium wire and benzophenone. Dichloromethane (DCM), methanol (MeOH), and acetonitrile (MeCN) were dried over calcium hydride. All other anhydrous solvents were obtained by distillation from the appropriate drying agents under dinitrogen, except *N,N*-dimethylformamide and dimethysulfoxide, which were AR grade solvents dried over 3Å molecular sieves. Deoxygenation of solvents and reagents was carried out by three freeze-pump-thaw cycles. Water used during the work-up of all compounds was carefully deoxygenated by several cycles of heating at reflux and cooling to room temperature under a dinitrogen purge. All NMR solvents were purchased from Aldrich and Goss, dried over 3Å molecular sieves and freeze-pump-thaw degassed three times. All reagents were purchased from commercial sources and used without purification, unless otherwise stated.

## 3.8.2: Metal reagents

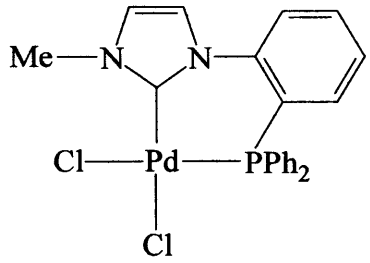
$PdCl_2$ was provided by Johnson Matthey PLC. $PdCl_2COD$, and PdMeClCOD were prepared by established procedures in high yield. $NiCl_2DME$ was formed by known methodology. $[RhClCOD]_2$ and $[IrClCOD]_2$ was prepared by the method of Giordano and Crabtree. $Ag_2O$ was purchased from Aldrich.

## 3.8.3: Preparation of complexes

## 3.8.4: General method for the synthesis of complexes 1-9

To a mixture of phosphine-imidazolium salt (1 equiv.) and $KN(SiMe_3)_2$ (1 equiv.) was added precooled THF (20 ml at 0 or -78 °C). The resulting mixture was stirred at this temperature for 10 min., then added to a solid metal precursor (1 equiv.) via a cannula. The mixture was allowed to reach r.t. and stirred for 2h. The solvent was removed under vacuum and the solid was extracted into DCM and filtered through celite. The solution was concentrated to 2 ml and $Et_2O$ was added to afford the crude product, which was washed with $Et_2O$ (10 ml) and vigorously stirred for 10 min with *n*-hexane. The solid was then recrystalised from DCM/ $Et_2O$ twice to give the product as a yellow to red/brown solid, which was dried under vacuum.

**$[L^{16}]PdCl_2$ (complex 1)**



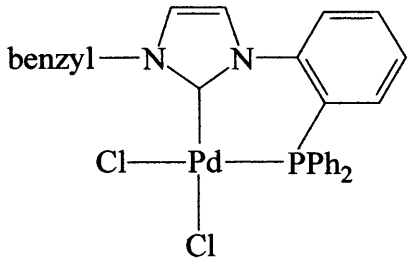
Palladium complex **1** was prepared according to the general method using phosphine-imidazolium salt, **16**, (0.30 g, 0.64 mmol), $KN(SiMe_3)_2$ (0.13 g, 0.64 mmol) and $PdCl_2COD$ (0.18 g, 0.64 mmol) in THF at 0°C and then r.t. Yield (0.26g, 78%).

**$^1$H NMR** (500.13 MHz, $CDCl_3$, δ): 8.06 (m, 1H, Ar-*H*), 7.45-6.75 (m, 13 H, Ar-*H*), 6.62 (m, 1H, Ar-*H*), 6.62 (m, 1H, Ar-*H*), 3.67 (s, 3H, C*H*$_3$).

**$^{31}$P NMR** (202.75 MHz, $CDCl_3$, δ): 17.48.

**MS** (ES): *M/z* (%); 521.1 (56) $[M+H]^+$, 357.1 (30) $[M-2C_6H_5-Me]^+$.

**$[L^{17}]PdCl_2$ (complex 2)**




Palladium complex **2** was prepared according to the general method using phosphine-imidazolium salt, **17**, (0.4 g, 0.80 mmol), $KN(SiMe_3)_2$ (0.15 g, 0.80 mmol) and $PdCl_2COD$ (0.23 g, 0.80 mmol) in THF at -78°C and then r.t. Yield (0.48 g, 71%).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 8.00-6.85 (m, H, Ar-*H*), 6.57 (d, $J$ = 1.9 Hz, 1H, $_{im}C_{4,5}$-*H*), 6.09 (d, $J$ = 15.1 Hz, 1H, C*H*$_2$benzyl), 5.58 (d, $J$ = 14.9 Hz, 1H, C*H*$_2$benzyl).

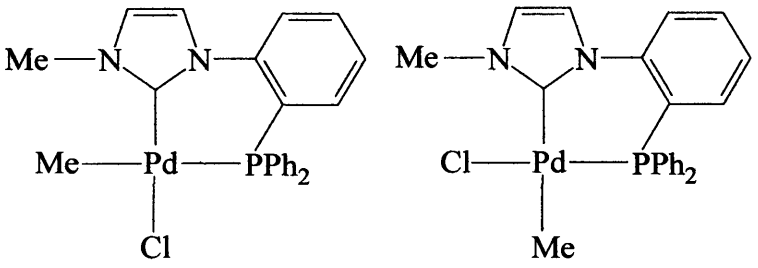
**$^{31}$P NMR** (202.75 MHz, $CDCl_3$, δ): 16.35.

**MS** (ES): *M/z* (%); 559.1 (5) $[M-Cl]^+$, 471.1 (100) $[M-Cl-Benzyl]^+$.

**Elemental Analysis** Calc. for $C_{28}N_2PCl_2H_{23}Pd$: C, 56.44; H, 3.89; N, 4.70; found: C, 52.69; H, 3.91; N, 4.48.

Single crystals were obtained by slow evaporation of a DCM solution of **2** in air.

**[L[16]]PdClMe (complex 3 + 4)**

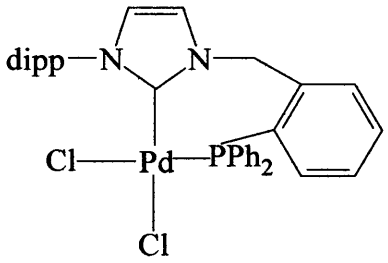



Palladium complex **3** + **4** was prepared according to the general method using phosphine-imidazolium salt, **16**, (0.20 g, 0.43 mmol), $KN(SiMe_3)_2$ (0.09 g, 0.43 mmol) and PdClMeCOD (0.11 g, 0.43 mmol) in THF at 0 °C and then r.t. Yield (0.14 g, 68%), mixture of **3** and **4**.

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 7.53-6.91 (m, Ar-*H*), 6.87 + 6.72 (d x 2, $J$ = 1.8, 1.7 Hz, $_{im}C_{4,5}$-*H*), 4.09 (s, NHC-C$H_3$ ), 4.00 (s, NHC-C$H_3$), 0.39 (d, $J$ = 3.8 Hz, 3H, Pd-C$H_3$), 0.24 (d, $J$ = 3.8 Hz, Pd-C$H_3$).

**$^{31}$P NMR** (121.65 MHz, $CDCl_3$, δ): 35.1, 32.2. (ratio 1:2).

**$[L^2]PdCl_2$ (complex 5)**



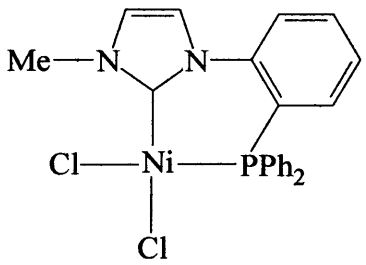

Palladium complex **5** was prepared according to the general method using phosphine-imidazolium salt, **2**, (0.10 g, 0.19 mmol) $KN(SiMe_3)_2$ (0.04 g, 0.19 mmol) and $PdCl_2COD$ (0.05 g, 0.19 mmol) in THF at 0°C and then r.t. Yield (0.09 g, 70%).

**$^1H$ NMR** (400.13 MHz, $CDCl_3$, δ): 8.07 (m, 1H, Ar-*H*), 7.70-7.12 (m, 16H, Ar-*H*), 6.78 (s, 1H, Ar-*H*), 6.49 (m, 1H, Ar-*H*), 5.87 and 4.70 (d x 2, 1H each, $J$ = 14.4 Hz), 2.32 (m, 2H, C*H*), 1.35 (d, $J$ = 6.6 Hz, 6H, $CH_3$), 1.05 (d, $J$ = 6.6 Hz, 6H, $CH_3$).

**$^{31}P$ NMR** (121.65 MHz, $CDCl_3$, δ): 12.51.

**MS** (ES): *M/z* (%); 643.2 (70) $[M\text{-}Cl]^+$, 461.1 (47) [P/NHC-isopropyl]$^+$.

**$[L^{16}]NiCl_2$ (complex 6)**



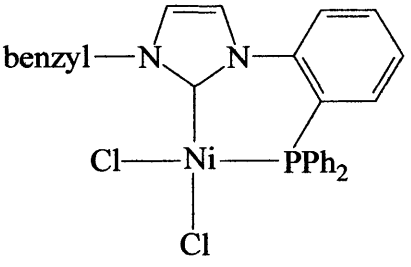
Nickel complex **6** was prepared according to the general method using phosphine-imidazolium salt, **16**, (0.20 g, 0.43 mmol), $KN(SiMe_3)_2$ (0.09 g, 0.43 mmol) and $NiCl_2DME$ (0.09 g, 0.43 mmol) in THF at 0 °C and then r.t. Yield (0.15 g, 68%).

**$^1$H NMR** (500.13 MHz, $CDCl_3$, δ): 7.93 (d, $J$ = 6.7 Hz, 1H, Ar-*H*), 7.76 (br. m, 1H, Ar-*H*), 7.66-7.22 (br. m, 10H, Ar-*H*), 6.57 (d, $J$ = 6.6 Hz, Ar-*H*), 6.45 (m, 1H, Ar-*H*), 3.57 (s, 3H, C*H*$_3$).

**$^{31}$P NMR** (121.65 MHz, $CDCl_3$, δ): 7.88.

**MS** (ES): *M/z* (%); 471.1 (30) $[M+H]^+$, 359.1 (71) $[M\text{-}Cl\text{-}C_6H_5]^+$, 341.4 (17) $[P/NHC+H]^+$.

**$[L^{17}]NiCl_2$ (complex 7)**




Nickel complex **7** was prepared according to the general method using phosphine-imidazolium salt, **17**, (0.50 g, 1.00 mmol), $KN(SiMe_3)_2$ (0.20 g, 1.00 mmol) and $NiCl_2DME$ (0.22 g, 1.00 mmol) in THF at -78 °C and then r.t. Yield (0.36 g, 65%).

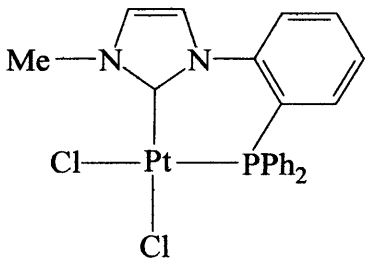
**$^1$H NMR** (500.13 MHz, $CDCl_3$, δ): 7.74-7.16 (br. m, 17H, Ar-H), 6.80 (br. m, 2H, Ar-*H*), 6.87 (br. m, 1H, Ar-*H*), 6.54 (br. m, 1H, Ar-*H*) 5.24 (br. s, 1H, C*H*$_2$).

**$^{13}$C NMR** (125.03 MHz, $CDCl_3$, δ): 134.2, 132.9, 132.4, 131.8, 131.3, 129.4, 129.0, 128.9, 128.9, 128.4, 128.3, 128.0 (Ar-*C*H), 54.91 (*C*$H_2$).

**$^{31}$P NMR** (121.65 MHz, $CDCl_3$, δ): 8.30.

**MS** (ES): *M/z* (%); 402.2 (94) $[M\text{-}2Cl\text{-}C_6H_5]^+$, 359.1 (45) $[M\text{-}Cl\text{-}2C_6H_5]^+$.

**[L$^{16}$]PtCl$_2$ (complex 8)**

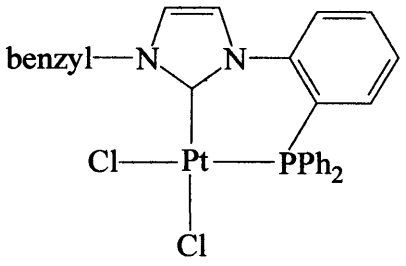



Platinum complex **8** was prepared according to the general method using phosphine-imidazolium salt, **16**, (0.20 g, 0.43 mmol), $KN(SiMe_3)_2$ (0.09 g, 0.43 mmol) and $PtCl_2COD$ (0.16 g, 0.43 mmol) in THF at 0 °C and then r.t. Yield (0.22 g, 84%).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 7.63-7.29 (m, H, Ar-*H*), 7.04 (d, *J* = 1.9 Hz, 1H, $_{im}C_{4\ or\ 5}$-*H*), 6.91 (m, 1H, Ar-*H*), 6.82 (d, *J* = 1.9 Hz, 1H, $_{im}C_{4\ or\ 5}$-*H*), 4.04 (s, 3H, $CH_3$).

**$^{31}$P NMR** (121.65 MHz, $CDCl_3$, δ): 20.3, 5.2, -9.9 (d, $J_{Pt\text{-}P}$ = 9060.0 Hz).

**[L[17]]$PtCl_2$ (complex 9)**




Platinum complex **9** was prepared according to the general method using phosphine-imidazolium salt, **17**, (0.4 g, 0.80 mmol), $KN(SiMe_3)_2$ (0.15 g, 0.80 mmol) and $PtCl_2COD$ (0.30 g, 0.80 mmol) in THF at -78 °C and then r.t. Yield (0.43 g, 79%).

**$^1H$ NMR** (400.13 MHz, $CDCl_3$, δ): 8.35 (d, $J$ = 8.0 Hz, 1H, Ar-*H*), 7.87 (d, $J$ = 2.0 Hz, 1H, $_{im}C_{4\ or\ 5}$-*H*), 7.47-6.77 (m, 18H, Ar-H), 6.55 (d, $J$ = 1.9 Hz, 1H, $_{im}C_{4\ or\ 5}$-*H*), 6.08 + 4.37 (d x 2, $J$ = 14.2 Hz, 1H each, C$H_2$).

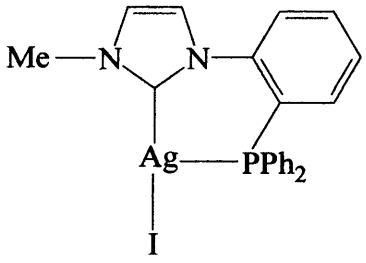
**$^{31}P$ NMR** (121.65 MHz, $CDCl_3$, δ): 19.9, 10.3, 0.8 (d, $J_{Pt\text{-}P}$ = 5741.4 Hz).

**MS** (ES): *M/z* (%); 649.1 (4) $[M\text{-}Cl]^+$, 515.1 (100) $[M\text{-benzyl-}C_6H_5]^+$, 435.1 (15) $[M\text{-benzyl-}2C_6H_5]^+$.

## 3.8.5: General method for the synthesis of complexes 10-12

To a mixture of phosphine-imidazolium salt (1 equiv.), $Ag_20$ (1 equiv.) and flamed 4Å molecular sieves was added DCM (20 ml). The resulting mixture was stirred at reflux in the dark for 24h. After the reaction was complete, the grey solid (silver halide) was filtered through celite and the volume of the solvent was reduced under vacuum (2-3 ml). The addition of $Et_2O$ isolated the crude product which was vigorously stirred for 10 min with *n*-hexane. The solid was then recrystalised from DCM/ $Et_2O$ to give the product as a white to red solid, which was dried under vacuum.

**[$L^{16}$]'AgCl' (complex 10)**

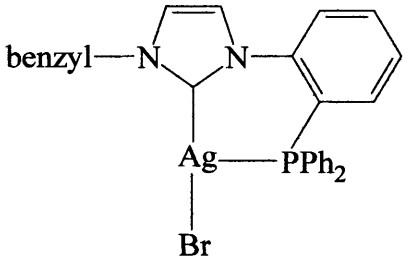



Silver complex **10** was prepared according to the general method using phosphine-imidazolium salt, **16**, (0.30 g, 0.64 mmol) and $Ag_2O$ (0.04 g, 0.64 mmol). Yield (0.27 g, 73%).

**$^1$H NMR** (400.13 MHz, $d_6$-DMSO, δ): 7.64-7.40 (m, 14H, Ar-*H*), 7.14 & 6.95 (s x 2, 1H each, $C_{4,5}$-*H*), 3.69 (s, 3H, $CH_3$).

**$^{31}$P NMR** (121.65 MHz, $d_6$-DMSO, δ): -3.87 (br, s).

**[$L^{17}$]'AgBr' (complex 10)**



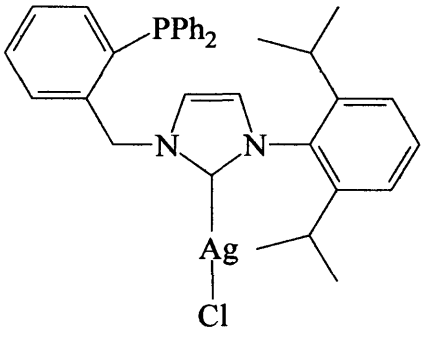

Silver complex **11** was prepared according to the general method using phosphine-imidazolium salt, **17**, (0.20 g, 0.40 mmol) and $Ag_2O$ (0.09 g, 0.04 mmol). Yield (0.17 g, 70%).

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 7.46-7.06 (m, 19H, Ar-H), 6.53 and 6.43 (s x 2, 1H each, $C_{4,5}$-*H*), 5.23 (s, 1H, C$H_2$), 5.15 (s, 1H, C$H_2$).

**$^{31}$P NMR** (60 MHz, $CDCl_3$, δ): -4.81 (s).

**MS** (ES): *M/z* (%); 607.0 (4) $[M-H]^+$, 419.2 (100) $[NHC + H]^+$.

**[$L^2$]'AgCl' (complex 12)**




Silver complex **12** was prepared according to the general method using phosphine-imidazolium salt, **2**, (0.09 g, 0.16 mmol) and $Ag_2O$ (0.04 g, 0.16 mmol). Yield (0.07 g, 67%).

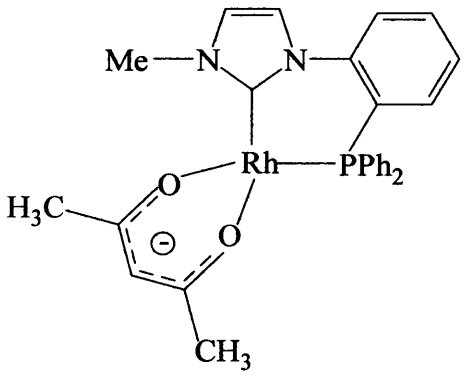
**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 7.87 (br.s, 1H, Ar-*H*), 7.53 (s, 1H, Ar-*H*), 7.46 and 7.20 (m, 15H, Ar-*H*), 7.00 (s, 1H, Ar-*H*), 6.91 (m, 1H, Ar-*H*), 2.18 (sep, J = 6.6 Hz, 2H (dipp C-*H*), 1.11 (d, J = 6.7 Hz, 6H, C$H_3$), 103 (d, J = 6.7 Hz, 6H C$H_3$).

**$^{13}$C NMR** (125 MHz, $CDCl_3$, δ): 144.6, 133.6, 133.5, 132.6, 129.7, 129.6, 129.4, 127.3, 123.3, 122.9, 119.9 (Ar-*C*H), 54.6 (*C*$H_2$), 27.29 (2*C*$H_3$), 23.7, 23.2 (2*C*$H_3$).

**$^{31}$P NMR** (60 MHz, $CDCl_3$, δ): -15.54

**MS** (ES): *M/z* (%); 647.2 (8) $[M-H]^+$, 503.2 (100) $[NHC + H]^+$.

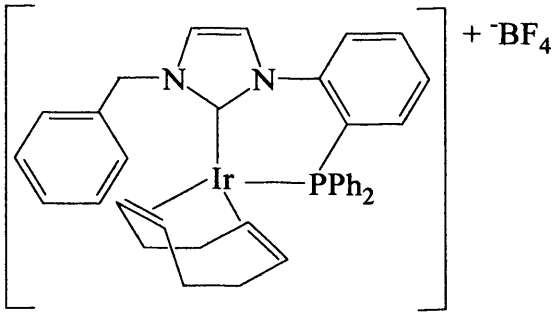
## 3.8.6: Method for the synthesis of complexes 13-14




[Rh(acac)(CO)$_2$] (0.13 g, 0.51 mmol) and complex **10** (0.15 g, 0.26 mmol) was dissolved in DCM (20 ml) and stirred at r.t. in the dark for 2h. The mixture was then filtered through celite to remove the silver halide. The volume of DCM was reduced under vacuum and $Et_2O$ was added. The resulting solid was washed with $Et_2O$ and stirred vigorously in *n*-hexane for 10 min. The resulting red solid was recrystalised form DCM/$Et_2O$ twice to give the product which was then dried under vacuum. Yield (0.18 g, 68 %).

**$^1$H NMR** (400.13 MHz, $CD_2Cl_2$, δ): 7.69 (m, Ar-*H*), 7.56-7.10 (m, Ar-*H*), 6.89 (d, $J$ = 2.0 Hz, $_{NHC}C_{4,5}$-*H*), 3.41 (s, C*H*$_3$), 2.14 (m, C*H*), 1.95 (s, $CH_3$).

**$^{31}$P NMR** (121.65 MHz, $CD_2Cl_2$, δ): 42.35 (d, $J_{RhP}$ = 125.2 Hz), 31.10 (d, $J_{RhP}$ = 145.44 Hz), 27.84 (d, $J_{RhP}$ = 131.30 Hz), ratio 1:8:1.




To a mixture of imidazolium salt **17** (0.20 g, 0.40 mmol) and $KN(SiMe_3)_2$ (0.08 g, 0.40 mmol) was added pre-cooled THF (20 ml, 0 °C). The resulting mixture was stirred at this temperature for 10 min. In a second Schlenk $[IrClCOD]_2$ (0.13 g, 0.20 mmol) and $AgBF_4$ (0.08g, 0.40 mmol) was refluxed in THF for 30 min. After the reaction the resulting silver halide was removed by filtration and the solution was cooled to 0 °C. The free NHC was then filtered into the Schlenk containing the iridium precursor complex. The resulting mixture was stirred for 2h. The solvent was then removed under vacuum and the product extracted into DCM and filtered. The volume of the DCM was reduced and $Et_2O$ was added to give a green/brown solid which was further recrystalised from DCM/$Et_2O$ twice. The resulting product was dried under vacuum.

**$^1$H NMR** (400.13 MHz, $CDCl_3$, δ): 7.58-70.8 (br.m, Ar-*H*), 7.01 and 6.89 (d x 2, $J$ = 2.1Hz, $_{NHC}C_{4,5}$-*H*), 6.87-6.61 (br.m, Ar-*H*), 4.77 and 4.68 ($J$ = 13.5 Hz, NHCC*H*$_2$benzyl), 2.95-1.32 (br.m CODC*H*$_2$).

# 3.9: References

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# CHAPTER FOUR
# Palladium-Catalysed Coupling Reactions

## 4.1: Introduction

### 4.1.1: Definition and significance of a catalyst

Catalysts are substances that accelerate the rates of chemical reactions by facilitating the establishment of equilibria, but they do not affect the position of the equilibrium.[1,2] Therefore a catalyst does not affect the overall thermodynamics of a reaction, only the kinetics.[1,2] If alternative routes exist, a catalyst can enhance product selectivity by accelerating just one of the competing reaction sequences.[3] Despite taking part in the chemical reaction, the catalyst remains largely unchanged (other than catalyst 'poisoning' or degeneration) and is regenerated during the catalyst cycle.[4]

In industry reactions rarely reach equilibrium, partly on account of the rates at which reactants mix. Hence, under these non-equilibrium conditions catalysts can have a significant role in industry.[2] It is therefore not surprising that the vast majority of products in chemical industry involve a catalyst at some stage in their manufacture.[1] This applies to bulk chemicals produced on a larger scale as the starting materials for numerous end-products such as alcohols, ketones, carboxylic acids, hydrocarbons such as olefins and dienes that can be polymerised to polyolefins (e.g., polyethene, polypropylene, and rubbers),[1] and also increasingly in fine chemical industries, where more than 80% of all current pharmaceuticals contain aromatic or heteroaromatic units as integral parts of their structure.[5]

Catalytic reactions can be divided into two types; heterogeneous and homogeneous catalysis depending on the phase relationship of the catalyst to the substrate. Most catalysts are heterogeneous,[1] in which the vacant coordination site is

located at a phase boundary (solid/liquid solid/gas), i.e. only the surface atoms are catalytically active.[3] A principal advantage is the easy recovery of the catalyst and disadvantages include low specificity, relatively high reaction temperatures and difficulties in the mechanistic studies.[3] Homogenous catalysis on the other hand can be tailor-made by ligand variation and is obtained reproducibly with high specificity and the catalysis can often be carried out at low temperatures.[3] The essential properties of homogeneous systems have been outlined by Cornils and Herrmann.[4]

1) Dispersion at the molecular level, i.e., the catalytically active species and the substrate molecules are in the same phase;
2) The catalyst can be unequivocally characterised by spectroscopic means and synthesised reproducibly;
3) New catalysts are able to rationally design for specific purposes according to known chemical principles.
4) Unequivocal reaction kinetics may be related to each metal atom of the catalyst.

The coordination of the reacting species to a transition metal brings the species in close proximity and can even activate them, thus promoting reactivity.[3] However, the coordinating ligands which are bound to the metal centre play a vital role in promoting and controlling catalytic activity; through preventing metal aggregation, stabilising reaction intermediates, providing vacant coordination sites via ligand dissociation, and modifying the steric and electronic environment around the metal centre.[4] The readiness of a particular metal to exist in a coordinatively unsaturated state is pronounced at the end of the transition series ($M = d^8$, $d^{10}$). Thus, the most commonly used metals in homogeneous catalysis are often those of the 'late transition metals' Ru, Co, Rh, Ni, Pd and Pt.[3] The growing interest in the development of transition metal complexes as catalysts over recent years has led to a large increase of new, high value organic molecules being procured from cheap starting materials and simple processes.[6]

The development of new catalysts which are more productive and active continues to be a main goal in the area of organometallic chemistry.[7] Future applications for cross-coupling reactions will rely on two key factors: (1) The development of more robust catalysts which are highly effective (active and selective), and (2) the availability of 'cheap' starting materials to generate new bonds in fundamental and novel compounds.[7]

## 4.1.2: The history of cross-coupling reactions

The core of the cross-coupling reaction was discovered in the late 1960's and early 1970's. Palladium- and nickel-catalysed cross-coupling reactions of aryl halides or more recent halide equivalent (i.e. triflate, tosylate and diazonium) with various nucleophiles have been shown to be highly effective and practical methods for the formation of C-C bonds.[8] Catalysed cross-coupling processes such as Suzuki,[7-10] Kumada,[8,11,12] Stille[8,13] and Negishi[8,14] make use of a variety of transmetalating agents (organoboron, organomagnesium, organostannane, and organozinc reagents)[8]. The amination reaction in which aryl halides are coupled with amines is also an important palladium- and nickel-catalysed reaction.[5,7,8,15-19]

One of the most important building blocks for the synthesis of biologically active substances (e.g. pharmaceuticals and herbicides) is biaryl.[10] Currently the Suzuki reaction is the most versatile method for the synthesis of substituted biaryls by the cross-coupling reaction of aryl halides and arylboronic acid (Suzuki reaction). A cross-coupling methodology employing organoboron reagents is attractive since a wide variety of air and thermally stable low toxicity organoboron reagents are available, either commercially or via straightforward synthesis.[8]

Unlike the other coupling methods, Heck coupling does not utilise an organometallic substrate as a coupling reagent. The term Heck chemistry is associated initially with the catalytic arylation and alkenylation of olefins.[20] Originating in the late 1960's, the reaction involved stoichiometric Pd-mediated olefin arylation reaction using arylmercury substrates.[4] There were some major problems associated with the

availability, toxicity and stability of organomercury compounds. Then came the discovery of a mercury free method in which the olefination of aryl iodides in the presence of base was catalysed by simple Pd(II) salts. This Heck or Mizoroki-Heck reaction was discovered independently by Mizoroki[21] and Heck.[22]

Due to the expense of aryl iodides the Heck reaction did not have a great impact until the late 1980's, however, Alwyn Spencer in the group of Hans-Ulrich Blaser investigated the effect of reaction conditions on Heck olefinations of aryl bromide and was able to report turnover number (TON) > 100000 for the first time in 1983.[23]

Interest in palladium-catalysed C-N coupling reactions has grown constantly over the last few years.[15,18,24-39] The palladium catalysed reactions of aryl halides with amines, indoles and imines play a key role in both bulk and fine chemical industries[5] and N-aryl halides are attractive synthetic targets since they can be biologically active.[8] The pioneering work in the development of this methodology came from the groups of Buchwald and Hartwig,[15,18,27-36,39] and the reaction in its present form was first reported in 1995 and is now known as the Buchwald-Hartwig amination.[39,40] The Buchwald-Hartwig amination has significant advantages over classical organic methodologies (which often involve protection and deprotection steps) in terms of generality and mild conditions.[8]

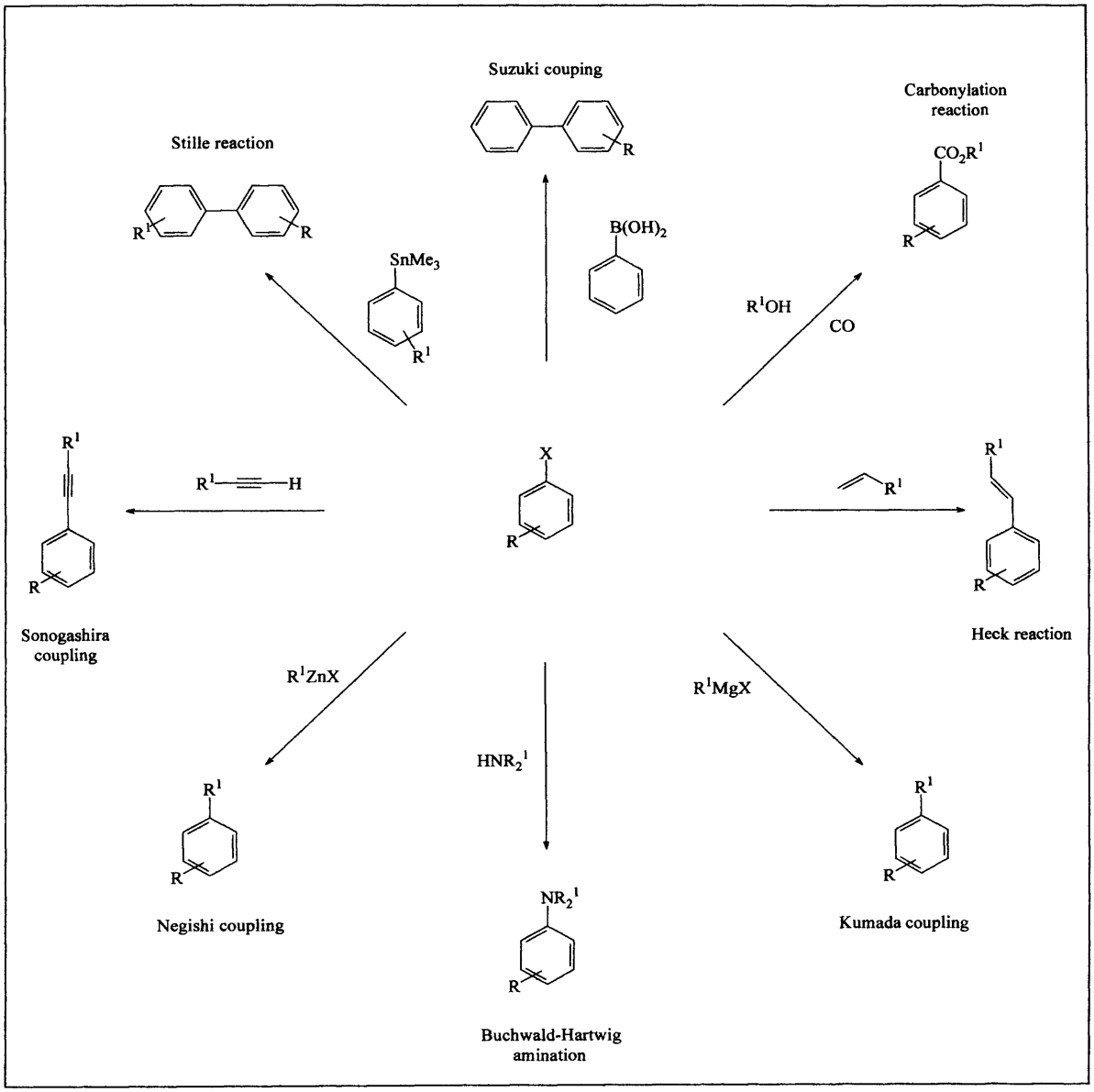



Figure 4.1: Selected examples of palladium-catalysed coupling reactions of aryl-X derivatives. Several recent papers and reviews cover these coupling reactions in detail.[7-9,15-20,41,42]

## 4.1.3: Mechanistic aspects of cross-coupling reactions

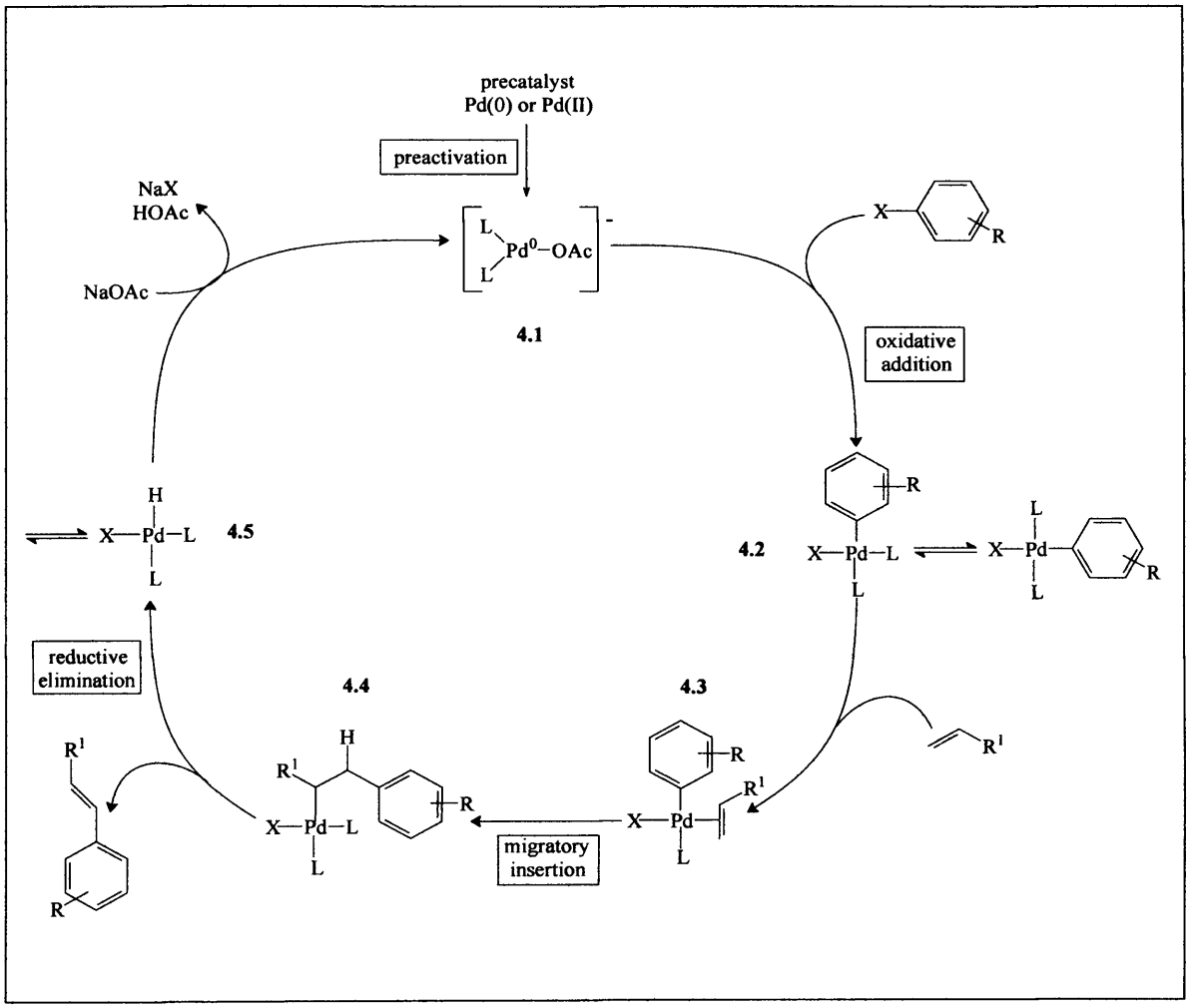
### Palladium catalysed Heck reaction

The generally accepted methodology for the Pd-catalysed C-C coupling reaction is one in which the oxidation state of the palladium in the cycle goes between 0 and +2.[43-48] In some cases, like that of phosphalladacycles, a Pd(II)/Pd(IV) catalyst system have been suggested.[48-50] A review by Herrmann *et al.* discussed the possible mechanisms involved; Pd(0)/Pd(II) versus Pd(II)/Pd(IV) for palladocycle catalysts,[51] but later Herrmann ruled out a palladium(IV) intermediate for his phosphalladacycles.[52]

The classical textbook interpretation mechanism for the reaction discovered by Heck[45] can be broken into some fundamental steps; preactivation, oxidation addition, migratory insertion and reductive elimination. The active catalyst is assumed to be a coordinatively unsaturated 14-electron palladium(0) species,[20,43,53] which can be generated *in-situ* from an 18-electron palladium(II) moiety. In 2000 Amatore and Jutand put forward a proposal for $Pd/PR_3$ systems that involved acetate anions, which were present from the NaOAc employed as the base in the system, that coordinated to the unsaturated Pd(0) species to give an anionic Pd(0) species.[43,53] This mechanism also gives a better explanation of how the hydride is removed from the palladium[20] (scheme 4.2).

The preliminary step before the catalytic cycle includes the reduction of Pd(II) complexes to Pd(0) and the generation of the active species **4.1** through multiple ligand exchange equilibria.[20] When Pd(0) complexes are used as the catalyst, the initial reduction is not needed, however, ligand dissociation from the pre-catalyst may be required to form the coordinatively unsaturated active catalyst **4.1**.[20] The oxidative addition proceeds as a concerted process in which the C–X bond breaks and corresponds with the formation of M–C and M–X bonds. The order of reactivity for oxidative addition is I >> OTf > Br >> Cl.[20,54] The strength of the $C_{aryl}$–Cl bond compared to the $C_{aryl}$–Br and $C_{aryl}$–I bonds is 402, 339, and 272 kJ/mol in PhCl,

PhBr, and PhI, respectively.[85] But aryl chloride substrates are ultimately still preferred due to the fact that they are readily available, cost effective, and highly stabile.[42]

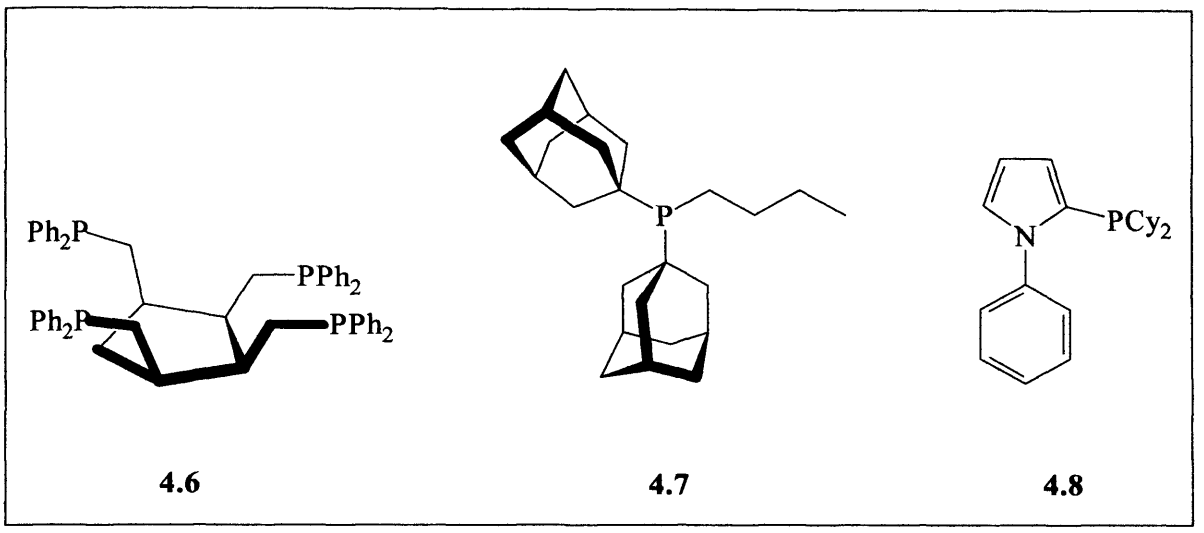



Scheme 4.2: The Heck mechanism.[43,55]

## 4.2: Catalysts based on phosphine ligands

Due to their ability to stabilise metal centres in a variety of oxidation states, phosphines have been used as ligands in a wide range of metal complexes.[56-60] Many of these complexes play a key role in homogenous catalysis and a large number of coupling reactions are catalysed by palladium-phosphine complexes.[7,52,57-62] The palladium-tetraphosphine system has one of the highest catalyst turnover numbers (TON) for the Suzuki coupling reaction.[63] Ligand **4.6** (figure 4.3) with $[PdCl(C_3H_5)]_2$ gives a system which catalyses 4-bromobenzophenone and phenylboronic acid with a TON of 28,000,000 and a palladium-phosphine system such as $Pd_2(dba)_3/P(^tBu)_3$ can catalyse the Sonogashira coupling even at room temperature.[64] A recent paper published in 2002 by Beller and coworkers reported a new ligand di-(1-adamantyl)-*n*-butylphosphine, **4.7**, which was superior to all other previously known ligands in the Buchwald-Hartwig amination of bulky 2,6-disubstituted anilines and congested aryl chlorides.[7,65] The same group also showed that sterically demanding and electron rich monodentate 2-phosphino-1-arylpyrrole ligands (PAP ligands, e.g. **4.8**), are easy to prepare and are highly efficient in the Suzuki coupling of electron rich as well as electron poor aryl chlorides under mild conditions and very low catalyst loading.[10]

Transition metals such as rhodium, ruthenium and iridium are also useful in catalysis when they form complexes with phosphines. Wilkinson's catalyst, $RhCl(PPh_3)_3$,[66] Grubb's catalyst, $Ru(PCy_3)_2Cl_2(CHPh)$[67] and Crabtree's catalyst, $[Ir(COD)(pyridine)(PCy_3)]PF_6$[68] are all important phosphine catalysts. Rhodium and iridium complexes of bis and tris(phosphines) catalyse hydrogenation of alkenes,[69,70] hydrogenolsis reactions,[71] and hydroformylation reactions.[72] Grubb's ruthium phosphine catalysts are active in ring open methathesis polymerisation (ROMP).[67]




**4.6** **4.7** **4.8**

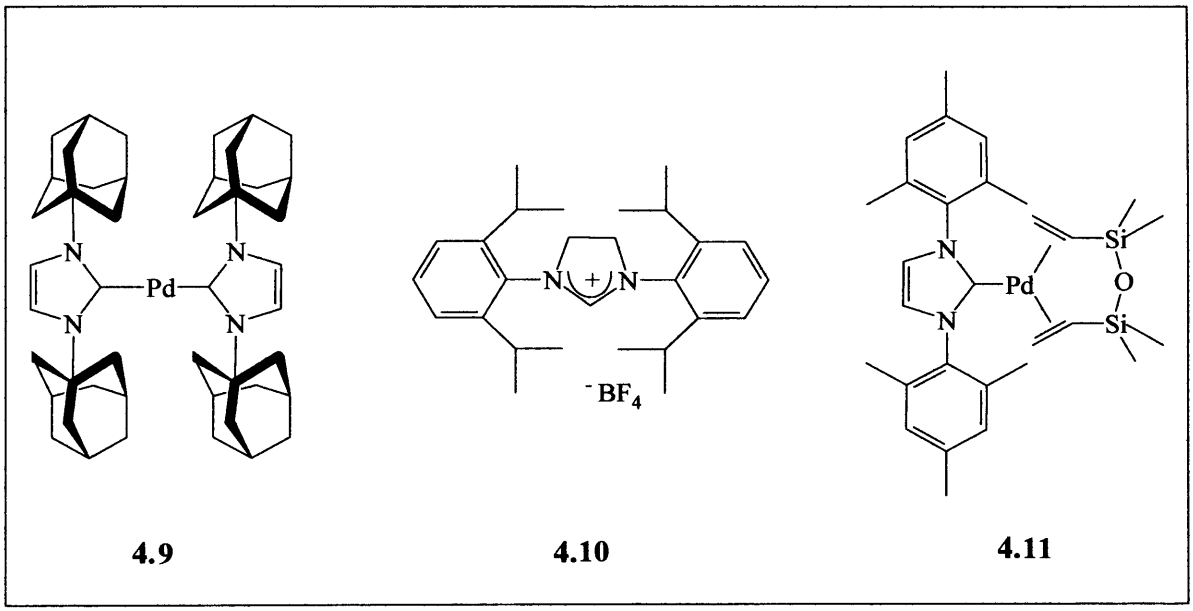
Figure 4.3: Highly active phosphine ligands in cross-coupling reactions.[10,63,65]

## 4.2.1: Catalysts based on carbene ligands

The use of N-heterocyclic carbenes as ligands in catalysis has received a great deal of interest over the last decade or so, primarily due to the strength of the metal-carbene bond relative to the usual metal-phosphine bond.[8,41,73] This inherent stability gives rise to catalysts that are active for long periods at elevated temperatures, often without using specially purified solvents or inert atmospheres. P-$C_{aryl}$ bond cleavage and aryl scrambling is often observed in triarylphosphine systems at elevated temperatures and can cause catalyst decomposition and the generation of unwanted by-products,[8,55,74] which is often the reason for high ligand:Pd ratios.[20,46,75] Initially, palladium(II) complexes with two carbene ligands were described by Herrmann *et al.* for the Heck reaction of aryl bromide and activated aryl chlorides.[46,76] Subsequently, Herrmann,[77-79] Cavell,[48,80,81] Nolan,[82-84] and others[85-93] described various applications of palladium carbene catalysts for aryl-X functionalisation.

Herrmann's NHC catalyst, **4.9**, either as the isolated complex or generated *in-situ*, proved to be a most effective coupling agent in the Suzuki reaction.[41,94] The bulky saturated imidazolium, **4.10**, was used in the Buchwald-Hartwig amination of morpholine with unactivated aryl chloride giving near quantitative yields,[25] and Pd(0)

complex **4.11** turned out to be the most efficient catalyst known to date in the telomerisation of 1,3-butadiene with various alcohols.[7,95,96] Nickel NHC complexes have also been used in the Kumada cross-coupling and these catalysts were found to be active at room temperature (r.t.) where all previous catalysts required much higher temperatures, resulting in numerous side products.[41]



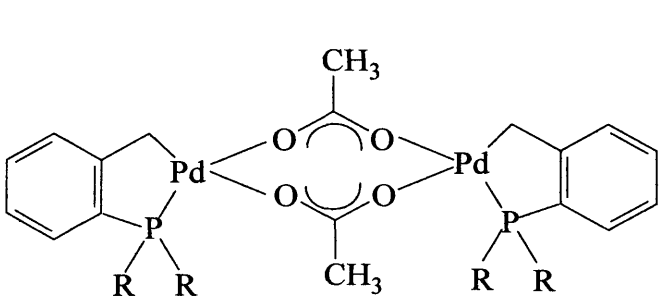

**4.9** **4.10** **4.11**

Figure 4.4: Examples of highly active catalysts in cross-coupling reactions.

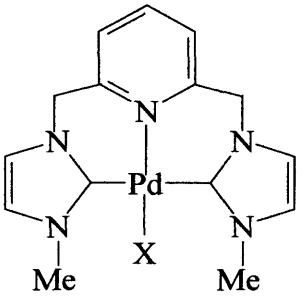
Ruthenium(II) NHC complexes have been reviewed by Fürstner,[97] Grubbs,[98] Buchmeiser,[99] and Herndon[100] on the olefin metathesis reactions. The imidazolium salt can also play a role as ionic liquid, acting as both reaction medium and a source of imidazol-2-ylidene unit for the Pd-NHC complex prepared *in-situ*[101-103] that catalyses Heck[101,104,105] and Suzuki[106] coupling reactions. The introduction of asymmetric centres onto NHC-metal complexes has also led to the use of chiral complexes in asymmetric homogenous catalysis.[47,107]

## 4.2.2: Catalytically active metal complexes with mixed donor atom ligands

One important class of ligands in catalysing coupling reactions is the phospha-palladocycles.[49-51,108] The work in 1995 by Herrmann and coworkers reported a family of phosphapalladocycles, **4.12** (R = *o*-tolyl, phenyl, cyclohexyl, t-butyl, mesityl).[109] His work received great attention[50,110] and the unique catalytic activity of these dimeric complexes set a milestone in palladium catalysis. These complexes were formed by the *in-situ* reaction of the respective phosphine (*o*-TolPR$_2$) with Pd(OAc)$_2$ and proved very effective catalysts in a wide range of reactions.




**4.12**




**4.13** X = Cl
**4.14** X = Me

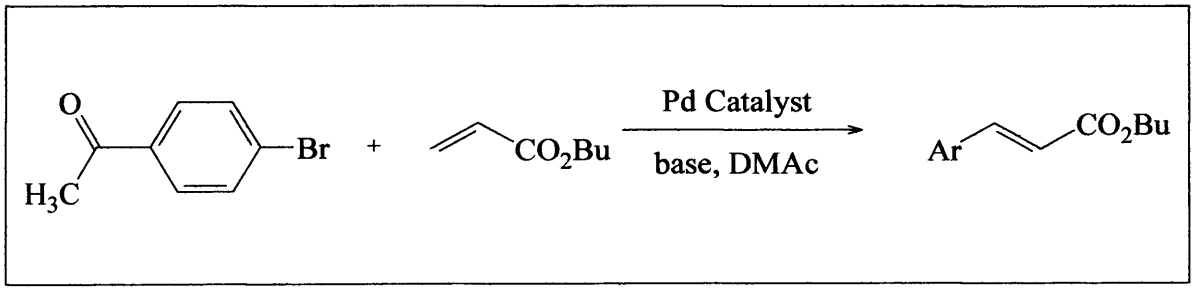
Figure 4.5: Examples of highly activate catalysts in cross-coupling reactions.

Mixed donor carbene complexes have been the topic of many papers and reviews;[41,42,75,80,90-93,111,112] whilst the carbene ligand stabilises the catalytic centres, the other ligand has the potential to be a hemi-labile ligand, creating a degree of coordinative and electronic unsaturation for incoming substrates. Pyridine-functional carbene complexes of palladium have been shown to be active in catalysing Heck coupling reactions[80,81,111,113-115] and these 'pincer' complexes are more thermally

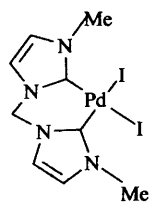
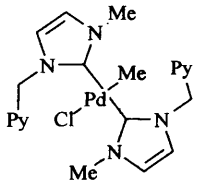
stable than bidenate non-pincer counterparts.[42] Cavell found complex **4.14** to be highly active and reasonably stable for the Heck reaction.[113] Interestingly the chloro complex **4.13** was consistently more active than the methylated derivative in terms of maximum turnover rate (the addition of $Pr_4NBr$ to the methyl derivative brought the reactivity of **4.14** close to that of **4.13**), but the chloride complex actually lost more activity than the methyl species as the catalytic cycle continued.[112,113]

## 4.2.3: Reactivity of Pd-NHC and palladocycle complexes in the Heck reaction

### Heck Reaction




Scheme 4.6: The Heck reaction of 4-bromoacteopheone (BAP) and *n*-butyl acrylate (BA) catalysed by functionalised palladium complexes.

| Entry | Catalyst | Condition/Additives | TON[a] (TOF)[b] |
|---|---|---|---|
| 1 |  | 100°C | >200 |
| 2 |  | 120°C/$Pr_4NBr$ | 1,700,000 (14,166) |

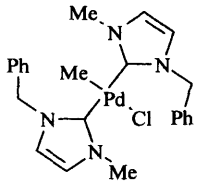
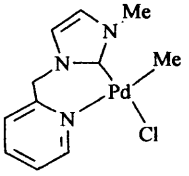
| | | | |
|---|---|---|---|
| 3 |  | 120°C/$Pr_4NBr$ and $NH_2NH_2{\cdot}H_2O$ | 980,000 (10,000) |
| 4 |  | 120°C | 610,000 (5,080) |
| 5 | **4.12** | 130°C/TBAB | 1,000,000 (42,000) |
| 6 | **4.13** | 120°C/$Pr_4NBr$ | 34,330 (10,430) |
| 7 | **4.14** | 120°C and $NH_2NH_2{\cdot}H_2O$ | 40,160 (1,980) |

Table 4.7: Result of the Heck reaction of 4-bromoacteopheone (BAP) and *n*-butyl acrylate (BA) catalysed by functionalised palladium complexes. This table was adapted from the review by Crudden and Allen.[112]

[a] Total yield of coupled products. [b] mol(product)/mol(Pd).

## 4.3: Palladium-catalysed carbonylation reactions

Homogeneous catalytic carbonylation first emerged during the late 1930's when Otto Røelen discovered that in the presence of a cobalt catalyst and at elevated pressures of CO and $H_2$, alkenes could be converted to aldehydes.[1] This process is known as hydroformylation and the name refers to the fact that effectively it is the addition of a hydrogen atom and a formyl (CHO) group to a carbon double bond.[1] The original reaction required high temperatures (150-180°C) and pressures (>200 bar) and gave linear and branched-chain aldehydes.[1] The main steps of the reaction mechanism, first elucidated by Breslow and Heck, involves; (a) $\beta$-hydrogen transfer to the coordinated olefin, (b) the insertion of CO to form an acyl intermediate, and (c) the hydrogenolysis of the acyl, with formation of the aldehyde product.[1]

The carbonylation of methanol to actetic acid and methyl acetate was found by Reppe, using iodide-promoted cobalt salts as catalyst precursors.[1] This process also required very high pressure (600 bar) as well as high temperature (230°C), however, the use of rhodium allowed much milder conditions, which was also the case for hydroformylation.[1] Such a process was started by Monsanto in 1996; it operates at 30-60 bar and 150-200 °C and is now the world's largest process for acetic acid production (>5 million tons per year).[1] Reppe showed that group 8, 9 and 10 metal carbonyl complexes catalyse a wide range of carbonylation reactions involving alkenes, alkynes and alcohols (figure 4.8).[1]

(I) $HC{\equiv}CH + CO + H_2O \rightarrow H_2C{=}CHCOOH$

(II) $HC{\equiv}CH + CO + ROH \rightarrow H_2C{=}CHCOOR$

(III) $R'C{\equiv}CH + CO + ROH \rightarrow H_2C{=}C(`R)COOR$

(IV) $R'C{\equiv}CH + CO + H_2O \rightarrow H_2C{=}C(`R)COOH$

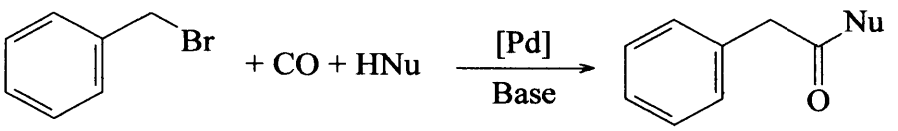
(V) $HCR{=}CH_2 + CO + R'OH \rightarrow RCH_2CH_2COOR'$

(VI) $HCR{=}CH_2 + CO + R'NH_2 \rightarrow RCH_2CH_2CONHR'$

(VII) $RCH_2OH + CO \rightarrow RCH_2COOH$

Figure 4.8.

Palladium-catalysed carbonylation of organic halides to give carboxylic acids, esters, and amides has been extensively used for production of carbonyl-containing compounds in laboratory synthesis as well as in industrial processes.[116-120] The use of substrates such as benzyl halides for the carbonylation reaction (scheme 4.9), were found to be excellent substrates for the synthesis of very valuable carbonyl compounds used in medicines or fragrances.[121]

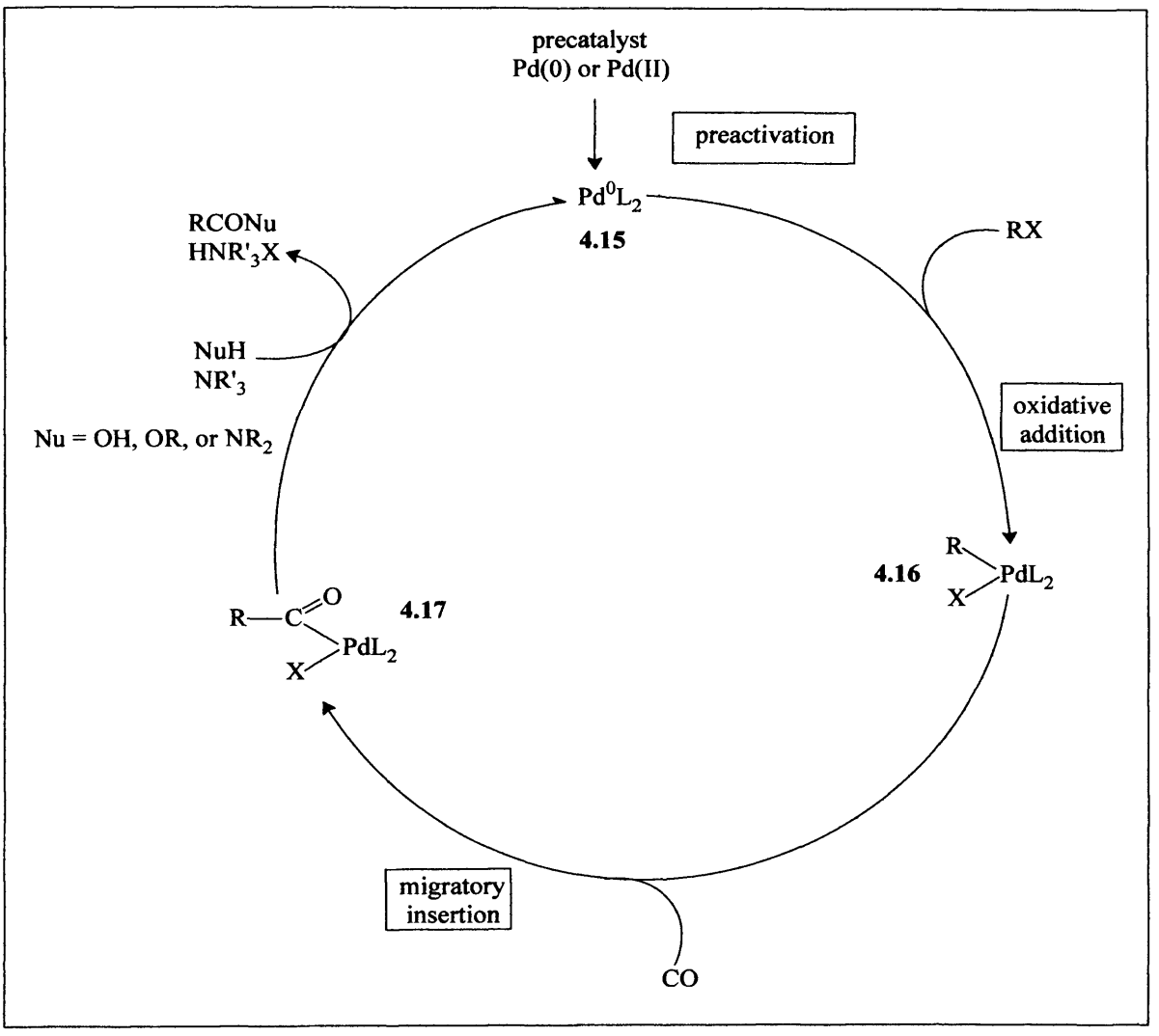



HNu = $H_2O$, HOR, or $HNR_2$

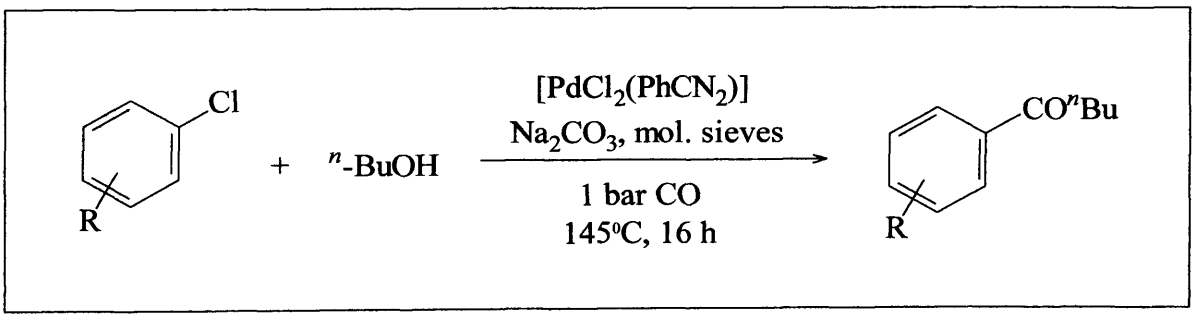
Scheme 4.9: Carbonylation of benzyl bromide.

The synthesis of benzeneacetic acid via the carbonylation reaction was found to be a less expensive and an easier method in comparison to the traditional synthesis based on a two-step process converting of benzyl chloride to benzyl cyanide and subsequent hydrolysis of cyanide with sulphuric acid.[121] The kind of carbonylation products obtained depends on the kind of nucleophilic agent used; when water is the nucleophile, carboxylic acids are produced, alcohols give esters, whereas amides are produced when amines are applied.[122] The catalytic cycle of carbonylation of organic halides is shown below (scheme 4.10).

Heck type carbonylation coupling can be 'more difficult' than some coupling reactions. In contrast to most palladium coupling reactions, the reaction partner (CO) strongly deactivates the metal centre due to their π-acidic nature.[7] However, the use of a bidentate ligand can offer significant advantages for the carbonylation of aryl bromides and chlorides.[7] In 2001 Beller developed a new and efficient catalyst system based on the cyclohexyl-substituted ferrocenylphosphine ligand for the carbonylation of activated and deactivated aryl chloride (scheme 4.11).[7] However, the activation of $C(sp^3)$–Cl bonds has been less studied in palladium-catalysed reactions, although bulky phosphines and some NHC's have been used as suitable ligands for the coupling of alkyl chloride with aryl Grignards.[7]




Scheme 4.10: Mechanism of palladium-catalysed carbonylation of organic halides. This scheme was adapted from Yamamoto *et al.*[122]




Scheme 4.11: Carbonylation of aryl chloride.[7]

**Ligand structures**

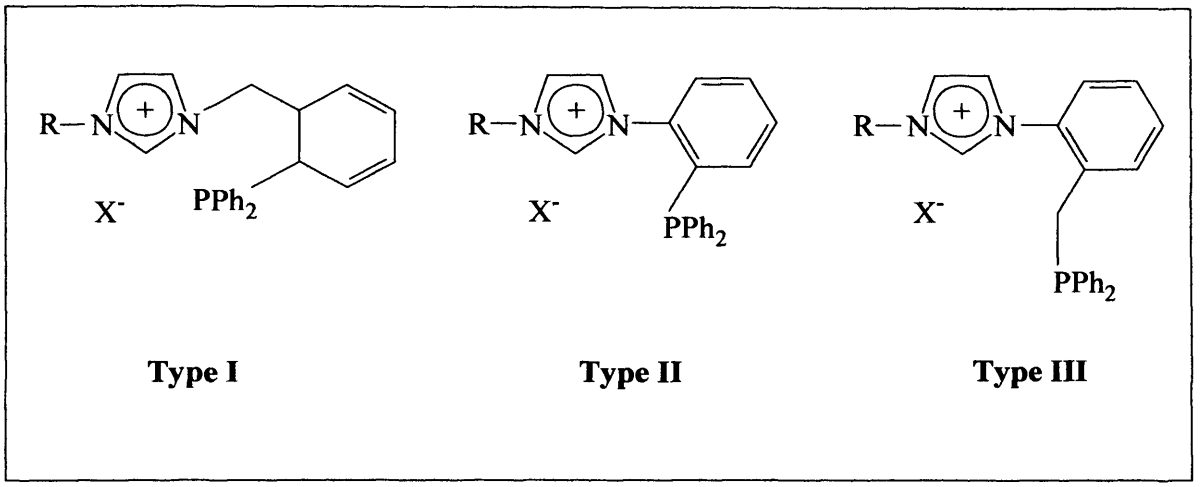



Figure 4.12: Phosphine-imidazolium salts.

| | |
|---|---|
| **Type I** | Phosphine-imidazolium salt with a methyl linker between the imidazolium ring and the benzyl ring. |
| **Type II** | Phosphine-imidazolium salt with no methyl linker. |
| **Type III** | Phosphine-imidazolium salt with a methyl linker between the phosphine and the benzyl ring. |

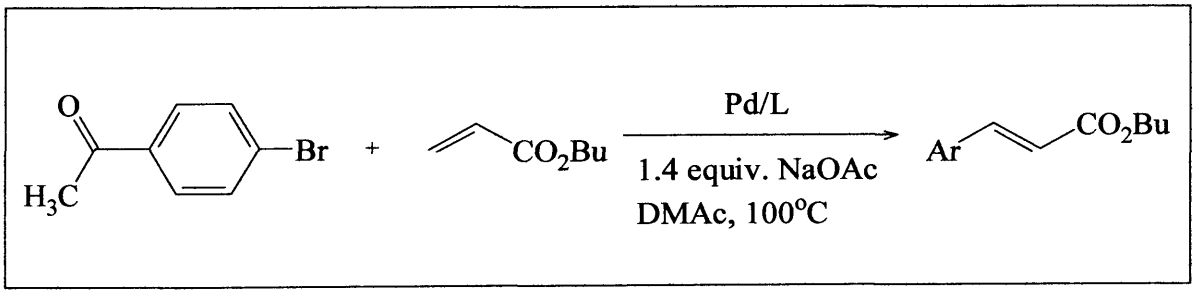
# 4.4: Results and discussion

The *in-situ* catalyst testing of all ligands was carried out at Johnson-Matthey (JM) Technology Centre at Sonning Common in a purpose-built parallel screening Radley's carousel reactor (which was designed to mimic the completely oxygen-free atmosphere inside a Schlenk flask). However, less care was taken in the purification and the degassing of solvents and reagents than what would be common when using standard Schlenk line technique, hence there was a possibility of contamination by air and moisture. All reactions (e.g. reagents and conditions) in the *in-situ* catalyst testing

were chosen by JM to obtain the relevant information they required. The pre-formed catalyst testing was carried out in the University laboratory and N,N-dimethylacetamide (AR grade) and reagents were freeze-thawed degassed three times and dried over 3 Å molecular sieves. Caesium carbonate and potassium carbonate were dried in an oven at 120°C.

## 4.4.1: Palladium-catalysed *in-situ* testing of the Heck reaction

The *in-situ* catalyst testing of functionalised imidazolium salts in the Heck reaction focussed on the coupling of the activated aryl bromide 4-bromoactophenone (BAP) with *n*-butyl acrylate (BA), scheme 4.13, under standardised conditions. Sodium acetate was used as the base as it has a proven suitability for the Heck reaction across a range of substrates and catalyst systems.[78,79,81,123] With the exception of imidazolium salts **14** and **16a** (figure 4.15), the available ligands all comprised of phosphine-imidazolium salts that varied both due to the nature of the ligands' N-substituents and in the presence or otherwise of the methyl bridge (between either the phenyl ring and the NHC moiety **(Type I)**, or the phenyl ring and the phosphine **(Type III)**). The results of the Heck reactions of 4-bromoactophenone (BAP) and *n*-butyl acrylate (BA) in which these imidazolium salts were tested are listed in table 4.14 with their structures shown in figure 4.15.




Scheme 4.13: The Heck reaction of 4-bromoacteopheone (BAP) and *n*-butyl acrylate (BA) catalysed with functionalised imidazolium salts.

Performed at 0.5 mol % Pd/L (1:1), $Pd(OAc)_2$.

| Entry | Catalyst (ligand) | Amount of catalyst (mol%) | Time (h) | Yield [a] (%) | TON |
|---|---|---|---|---|---|
| 1 | **8** | 0.5 | 5 | 25 | 50 |
| 2 | **6** | 0.5 | 5 | 96 | 192 |
| 3 | **2** | 0.5 | 5 | 30 | 60 |
| 4 | **2a** | 0.5 | 5 | 42 | 84 |
| 5 | **14** | 0.5 | 5 | 6 | 12 |
| 6 | **16a** | 0.5 | 5 | 5 | 10 |
| 7 | **16** | 0.5 | 5 | 97 | 194 |
| 8 | **16b** | 0.5 | 5 | 98 | 196 |
| 9 | **26** | 0.5 | 5 | 3 | 6 |
| 10 | **27** | 0.5 | 5 | 2 | 4 |

Table 4.14: Results of the *in-situ* Heck reaction of 4-bromoacteopheone (BAP) and *n*-butyl acrylate (BA) catalysed with functionalised imidazolium salts.

1.4 equiv. of NaOAc, performed at 0.5 mol % Pd/L (1:1), $Pd(OAc)_2$, preformed at 100°C.

[a] GC yield.

From the data presented in table 4.14 it is clear that there is a significant difference in the yield of the desired product (determined by GC), which ranges from 2 to 98% for the coupling of BAP and BA. Of the ligands where the methyl bridge is between the phenyl ring and the NHC moiety **(Type I)**, the N-mesityl substituted ligand gives the best yield of the four ligands tested (96% conversion), whereas the less bulky methyl and the more bulky diisopropyl showed relatively low yields of 25% and 30% respectively. When the counter ion was exchanged from bromide to the BARF counter ion in imidazolium salt **2** the yield increased from 30% to 42%, and maybe a result of the increased solubility of the ligand. The phosphine-imidazolium salt with no methyl bridge **(Type II)** performed slightly better than imidazolium salts **2**, **6** and **8** with a yield of 97% and once again changing the counter ion to the BARF ion slightly increased the activity. Imidazolium salt **14**, which is a precursor to **16**, and

imidazolium salt **16a**, which is the oxide of **16**, were also tested. Both ligands gave poor yields (6% and 5% respectively) in the Heck coupling reaction and indicated that the activity of these imidazolium salts in the coupling reactions are not just due to the *in-situ* formation of the carbene, but a combination of the chelating phosphine-carbene. However, it is important not to assume that this is the case with *in-situ* catalyst testing as it may be due to the fact that different types of imidazolium salts deprotonate with varying efficiency. The major disadvantage with *in-situ* catalyst testing of imidazolium salts is that one can never be certain to what extent the imidazolium salt has been deprotonated, unlike in the case of phosphines where *in-situ* catalyst testing can sometimes be as successful as pre-formed catalyst testing. The final two imidazolium salts tested were imidazolium salts where the methyl bridge was between the phenyl ring and the phosphine **(Type III)**. Both imidazolium salts **26** and **27** proved to have very poor activity in the coupling of BAP and BA. However, these phosphine-imidazolium salts are particularly oxygen and water sensitive and may have oxidised due to contamination by air and moisture in the reaction mixture, thus the full potential of these ligands may not have been measured. Three of the imidazolium salts tested in these reactions (imidazolium salts **6**, **16**, and **16b**) had yields close to 100% conversion and give better results than the standard ligands used by Johnson Matthey (JM) ($PPh_3$ and $PCy_3$), however, the fact that the catalyst loading was 0.5% meant that the maximum TON was 200. This is not good enough when compared to known catalysts (see table 4.7 page 149-150).

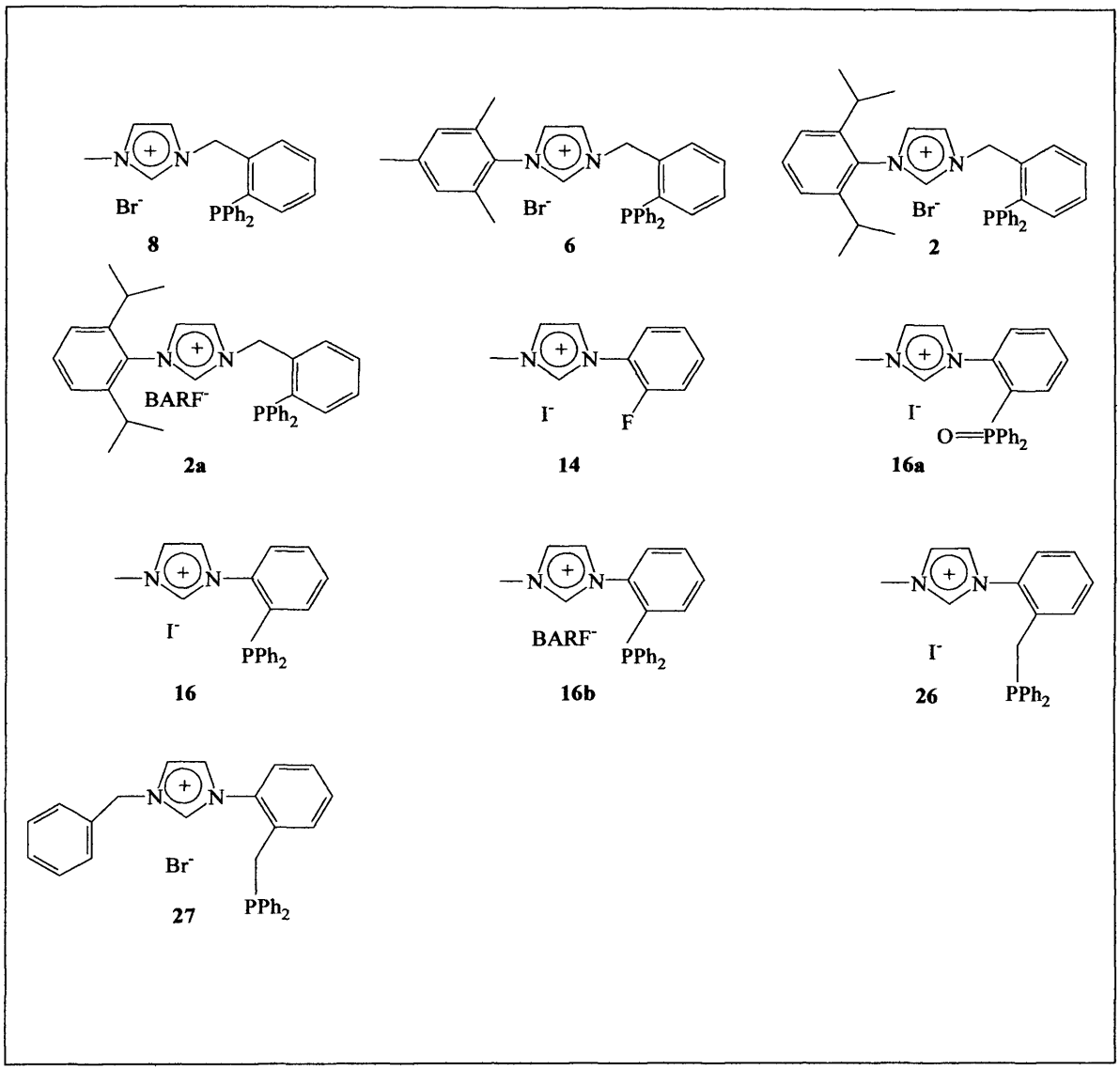



Figure 4.15: Imidazolium salts tested in the coupling reactions of 4-bromoacteopheone (BAP) and *n*-butyl acrylate (BA), (table 4.14), and 4-bromoanisole (BAS) and phenylboronic acid (PA),(table 4.19).

In a paper published by Nolan, a phosphine-imidazolium salt (page 29) was tested in the *in-situ* catalyst Heck coupling reaction with a range of different aryl halides.[75] Although the paper reported the imidazolium salts to be highly efficient in the Heck coupling reaction of aryl bromides with *n*-butyl acrylate and 100% conversion was achieved for the activated BAP (0.25h) in addition to a 99%

conversion of the deactivated 4-bromoanisole (BAS) (3h), the fact that the catalyst loading was also a high 0.5% meant that the TON was only 200 which is not particularly good activity.[75] However, in some pharmaceutical processes where 100% conversion is the main concern and not catalytic loading, these ligands may have potential when applied *in-situ*. Nolan and coworkers also attempted the coupling of the electron-deficient aryl chlorides, such as 4-chlorobenzaldehyde (CBA) and 4-chloroacetophenone (CAP). However, no desired coupled products were obtained and for the electron-neutral chlorobenzene (CB) only a low yield of 13% was obtained.[75] Subsequently, a report by Danopoulos *et al.* published findings on the catalytic study they carried out using fully characterised phosphine-NHC palladium(II) complexes of the same and similar ligands to that of Nolan.[93] Danopoulos reported that the same activity could not be achieved with the pre-formed catalysts that Nolan reported with his *in-situ* catalyst testing. Danopoulos also met with limited success when repeating Nolan's exact methodology under identical conditions.[93] Danopoulos proposed that the synthesis of analogous chelating phosphine-NHC Pd(0) complexes may provide an explanation for the reduction in catalytic activity observed in the Pd(II) complexes.[93]

The effect of base was tested by Nolan and shown to have an immense impact on the yield and the reaction rate, the latter being very dependent on the amount of base employed (table 4.16).[75] A remarkable increase in activity was observed with $Cs_2CO_3$, and the use of 2 equiv. rather than 1.4 equiv. was found to be optimal (e.g. 1.4 equiv. $Cs_2CO_3$ yielded 96% conversion (4 h) and 2.0 equiv. $Cs_2CO_3$ yeilded 100% conversion (1.5 h)). The difference between the use of NaOAc as the base compared to $Cs_2CO_3$ was significant with the yield increasing from 12% to 96%.[75] In the above Heck catalyst runs (table 4.14) the base employed was NaOAc and given that the imidazolium salts were all based on phosphine-imidazolium salts, one might expect the use of $Cs_2CO_3$ (2.0 equiv.) to have a positive effect on the catalytic ability of the imidazolium salts synthesised in this thesis. However, Danopoulos reported that in the pre-formed catalyst testing he carried out the product increased with $NEt_3$ rather than $Cs_2CO_3$ with the same complex (complex **1.26**, page 31) under identical conditions (66% conversion $NEt_3$ and 54% $Cs_2CO_3$). This indicates that best base for *in-situ*

catalyst testing of any given imidazolium salt may not prove to be the best base for the pre-formed catalyst of the same imidazolium salt.

| Entry | Base | Amount of base (equiv.) | Time (h) | Yield [a] (%) |
|---|---|---|---|---|
| 1 | None | 1.4 | 4 | 0 |
| 2 | $NEt_3$ | 1.4 | 4 | 5 [b] |
| 3 | $KOBu^t$ | 1.4 | 4 | 0 [c] |
| 4 | NaOAc | 1.4 | 4 | 12 |
| 5 | $K_2CO_3$ | 1.4 | 4 | 6 |
| 6 | $Cs_2CO_3$ | 1.4 | 4 | 96 |
| 7 | $Cs_2CO_3$ | 2.0 | 1.5 | 100 |

Table 4.16: Nolan's base screen test of the Heck reaction with 1-(ethylenediphenylphosphine)-3-(mesityl)imidazolium bromide (page 29).[75]

Reaction conditions: 1 mmol of 4-bromotoluene, 1.4 mmol of *n*-butyl acrylate. [a] GC yield (an average of two runs). [b] Biphenyl as the major product. [c] Decomposition.

| Entry | Base | Amount of base (equiv.) | Time (h) | Yield [a] (%) |
|---|---|---|---|---|
| 1 | $Cs_2CO_3$ | 2.0 | 6 | 54 |
| 2 | $NEt_3$ | 2.0 | 6 | 66 |

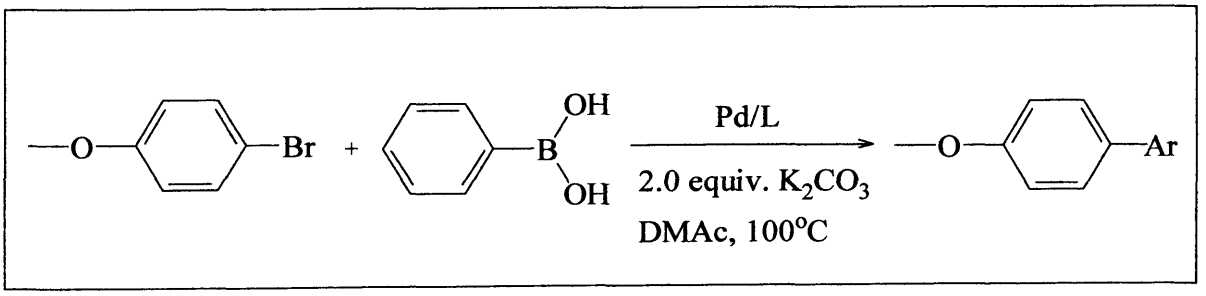
Table 4.17: Danopoulos' catalytic data for the Heck coupling reaction of 4-bromoacetophenone (BAP) and with methyl acrylate in the presence of Pd(II) phosphine-carbene complex 1.26 (page 31).[93]

Reaction conditions: 1 mmol of 4-bromoacetophenone, 1.4 mmol of methyl acrylate. [a] GC yield (an average of two runs).

Subsequently in 2005 Wang *et al.* published a report on the Heck coupling reactions of triaryl phosphine-functionalised imidazolium salts which have the same structure as the **Type I** ligands synthesised in this work.[90] Wang proved that under the right conditions these ligands were highly effective for the coupling of a wide range

of aryl bromides and iodides with acrylates. A variety of palladium compounds such as $Pd(dba)_2$, $Pd(OAc)_2$, $[Pd(n\text{-}C_3H_5)Cl]_2$ and $Pd_2(dba)_3{\cdot}CHCl_3$ were compared as catalyst precursors under the same reaction conditions and the $Pd(dba)_2$ gave the highest conversion in the shortest reaction time. Under identical reaction conditions with the same phosphine-imidazolium salt the conversion yield (GC) increased from 54% to 100% when $Pd(dba)_2$ replaced $Pd(OAc)_2$ as the source of palladium, the reaction time was also halved.[90] The base was found to have a significant effect on both reaction rate and yield of product which was also found by Nolan and Danopoulos in their system.[75,93] However, in the work of Wang *et al.*, the highest yield was achieved by the use of two equivalents of $K_2CO_3$. Increasing the temperature from 120 °C to 140 °C accelerated the rate of the reaction and increased the yield. Wang also allowed a 30 minute initiation period in which the phosphine-imidazolium salt, base and Pd precursor were stirred at 25 °C before adding the reagents and heating to the required reaction temperature.[90] This may have helped to ensure that the catalyst complex was formed, thus measuring the true potential of these ligands. It is believed that with further screening tests to find the optimum conditions and with a truly oxygen and moisture free environment, the activity of all the phosphine-imidazolium salts tested in the Heck coupling reaction (table 4.14) have the potential to increase.

## 4.4.2: Palladium-catalysed *in-situ* testing of the Suzuki reaction




Scheme 4.18: The Suzuki reaction of 4-bromoanisole (BAS) and phenylboronic acid (PA) catalysed with functionalised imidazolium salts.

Performed at 0.5 mol % Pd/L (1:1), $Pd(OAc)_2$.

The *in-situ* catalyst testing of functionalised imidazolium salts in the Suzuki reaction focussed on the coupling of the deactivated aryl bromide 4-bromoanisole (BAS) with phenylboronic acid (PA), scheme 4.18, and the activated aryl chloride 4-chloroacetopheone (CAP) with phenylboronic acid (PA), scheme 4.20, under standardised conditions. Potassium carbonate was used as the base (in the coupling of BAS and PA), as it has a proven suitability of the Suzuki reaction across a range of substrates and catalyst systems.[80,124,125] The results of the Suzuki reaction of 4-bromoanisole (BAS) and phenylboronic acid (PA) in which these imidazolium salts were tested are listed in table 4.19 with the ligand structures shown in figure 4.15.

| Entry | Catalyst | Amount of catalyst (mol%) | Time (h) | Yield [a] (%) | TON |
|---|---|---|---|---|---|
| 1 | **8** | 0.5 | 2 | 43 | 86 |
| 2 | **6** | 0.5 | 2 | 48 | 96 |
| 3 | **2** | 0.5 | 2 | 54 | 108 |
| 4 | **2a** | 0.5 | 2 | 50 | 100 |
| 5 | **14** | 0.5 | 2 | 16 | 32 |
| 6 | **16a** | 0.5 | 2 | 17 | 34 |
| 7 | **16** | 0.5 | 2 | 39 | 78 |
| 8 | **16b** | 0.5 | 2 | 31 | 62 |
| 9 | **26** | 0.5 | 2 | 27 | 54 |
| 10 | **27** | 0.5 | 2 | 30 | 60 |

Table 4.19: Results of the *in-situ* Suzuki reaction of 4-bromoanisole and phenylboronic acid catalysed with functionalised imidazolium salts.

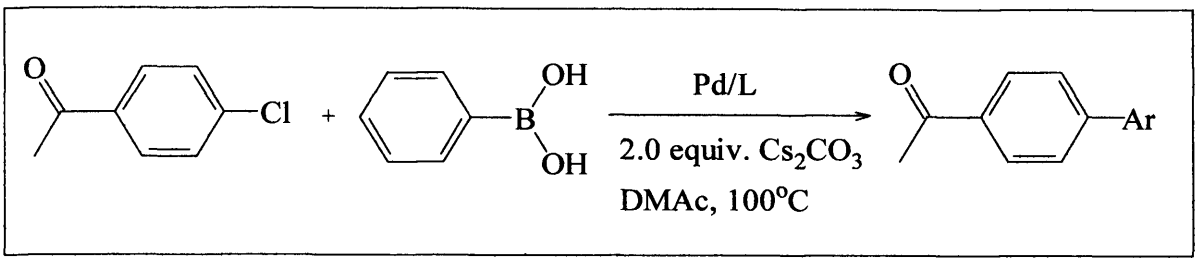
2.0 equiv. of $K_2CO_3$ performed at 0.5 mol % Pd/L (1:1), $Pd(OAc)_2$ preformed at 100°C.

[a] GC yield.

The results of the coupling of BAS and PA show a similar pattern to those of the earlier Heck reaction (table 4.14), in which the three distinct types of imidazolium salts show significant differences in activity. The **Type I** imidazolium salts all showed similar activity, with the less active being the least bulky N-substituted methyl (**8**) and the more active being the most bulky N-substituted diisopropal (**2**). On exchanging the counter ion of imidazolium salt **2** from bromide to the BARF counter ion to give imidazolium salt **2a**, there was a slight decrease in the yield by 4%.

The phosphine-imidazolium salt with no methyl bridge **(Type II)** performed less well than imidazolium salts **2**, **6** and **8** this time. However, the activity of imidazolium salts **8 (Type I)** and **16 (Type II)** show similar activity and if a bulkier electron donating group replaced the methyl group on imidazolium salt **16**, it is thought that the activity would increase. This is due to the fact that bulky, electron donating substituents in the $N_3$-position of NHC's are known to strengthen the NHC-metal bond whilst activating substituents in the *trans* position, and may also help stabilise the complex from reductive elimination through steric bulk.

Imidazolium salt **14**, which is a precursor to **16**, and imidazolium salt **16a**, which is the oxide of **16**, were also tested. Again both ligands showed poor activity in the Suzuki coupling reaction and in fact gave the poorest yields of all ligands tested. This result was also expected and indicates that the activity of these coupling reactions is increased by the chelating ligand (phosphine-NHC). Imidazolium salts **26** and **27** were still the worse out of the three types of phosphine-imidazolium salts tested, with both giving yields around 30%, however, they performed better in the Suzuki reaction with respect to the other two types of ligands than in the Heck reaction, but again the phosphine may have oxidised (due to non-ideal degassing and purification techniques). Again ligands **2**, **3**, and **4** proved to be as active as or more active in this reaction than the standard ligand tested ($PPh_3$). However, the fact that the highest yield was 54% and the catalyst loading was 0.5% meant that the TON was low for all these ligands. The one positive result to be taken from this reaction is that although the yield was not as high as in the previous Heck reaction (BAP and BA), the substrate was the deactivated BAS and the reaction time was only 2h, meaning that some of the ligands gave higher TOF in the Suzuki reaction than the Heck reaction.




Scheme 4.20: The Suzuki reaction of 4-chloroacetophenone and phenylboronic acid catalysed with functionalised imidazolium salts.

Performed at 0.5 mol % Pd/L (1:1), $Pd(OAc)_2$.

Given the increase in activity that Nolan achieved with the use of two equivalents of $Cs_2CO_3$ as a base in the Heck reaction[75] (table 4.16), caesium carbonate was chosen as the base in the Suzuki coupling reactions of 4-chlororactephenone and phenylboronic acid. However, Nolan's base screening was in the Heck reaction and not the Suzuki so it should not be automatically assumed that $Cs_2CO_3$ will give the best results in the Suzuki reaction. It should also be noted that different types of phosphine-imidazolium salts may show higher activity with different bases and therefore blanket assumptions should be avoided.

| Entry | Catalyst | Amount of catalyst (mol%) | Time (h) | Yield [a] (%) | TON |
|---|---|---|---|---|---|
| 1 | **8** | 0.5 | 8 | 28 | 56 |
| 2 | **6** | 0.5 | 8 | 26 | 52 |
| 3 | **2** | 0.5 | 8 | 30 | 60 |
| 4 | **2a** | 0.5 | 8 | 30 | 60 |
| 5 | **16** | 0.5 | 8 | 27 | 54 |
| 6 | **17** | 0.5 | 8 | 30 | 60 |
| 7 | **26** | 0.5 | 8 | 25 | 50 |

Scheme 4.21: Results of the *in-situ* Suzuki reaction of 4-chloroacetophenone (CAP) and phenylboronic acid (PA) catalysed with functionalised phosphine-imidazolium salts.

2.0 equiv. of $Cs_2CO_3$ performed at 0.5 mol % Pd/L (1:1), $Pd(OAc)_2$ preformed at 100°C.

[a] GC yield.

The results of the coupling of CAP and PA are presented in table 4.21 and they show that all the ligands tested gave poor results for the coupling for the activated aryl chloride. Again the imidazolium salts which gave the best results were the bulky N-substituted diisopropal **2** and **2a**, and the phosphine-imidazolium salt **17** without the methyl bridge, however the yield (GC) was still only around 30%.

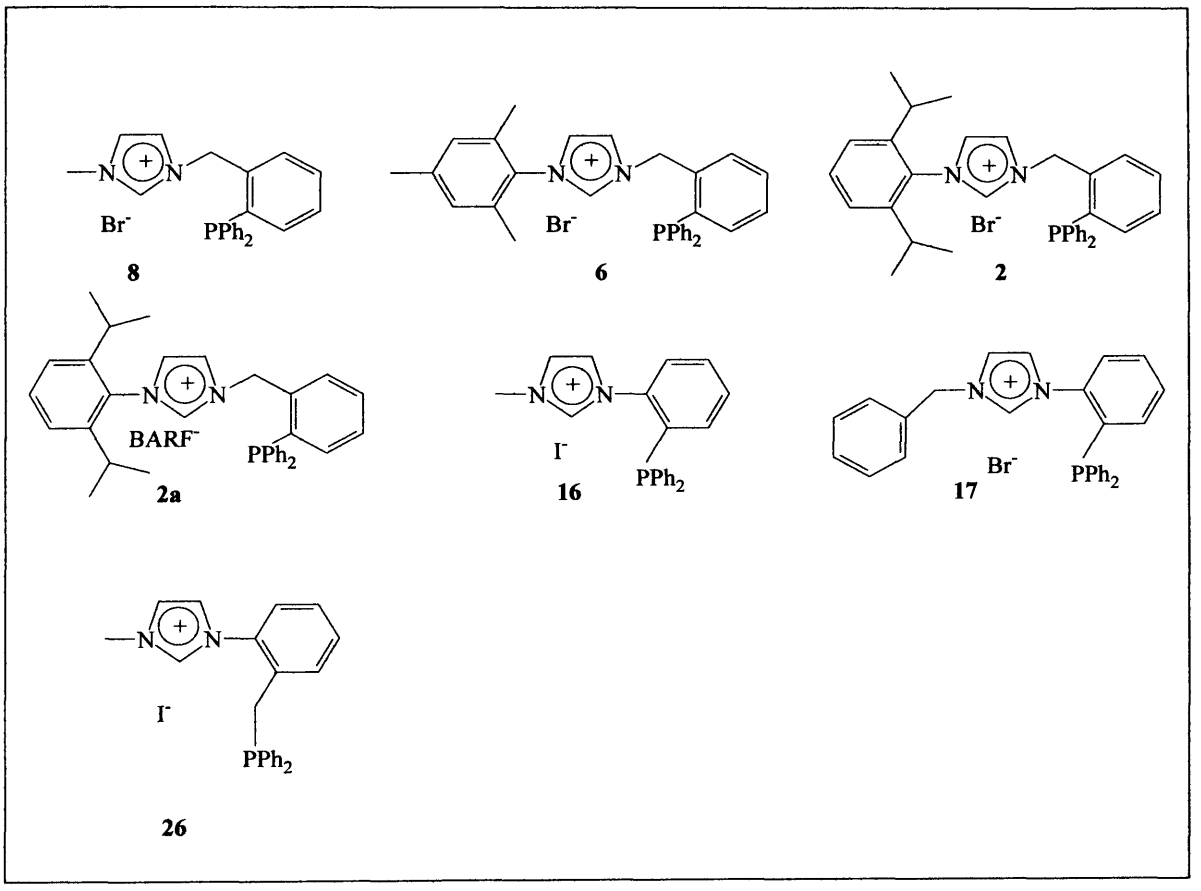


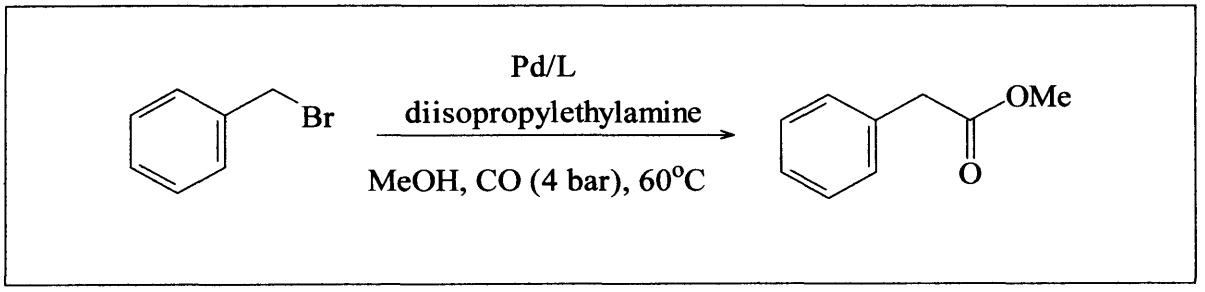

Figure 4.22: Ligands tested in the coupling reactions of 4-chloroacetophenone (CAP) and phenylboronic acid (PA), and the carbonylation of benzyl bromide (BB).

Subsequently, the group of Wang *et al.* showed that phosphine-imidazolium salt which had the same structure as **Type 1** ligands can be successfully used for the Suzuki cross-coupling reaction of aryl bromide and activated chloride with phenylboronic acid. The optimum conditions were found to be when $[Pd(\eta\text{-}C_3H_5)Cl]_2$

was the palladium precursor compound, 2 equiv. of $K_3PO_4$ was used as the base and dioxane was the solvent used. Again Wang also allowed a 30 minute initiation period in which the phosphine-imidazolium salt, base and Pd precursor were stirred at 25 °C before adding the reagents and heating to the required reaction temperature.[90]

## 4.4.3: Palladium-catalysed *in-situ* testing of carbonylation reaction

The *in-situ* catalyst testing of funtionalised imidazolium salts in the carbonylation reaction focussed on the carbonylation of the benzyl bromide (BB) to give the product methyl phenyl acetate, scheme 4.23, under standardised conditions.




Scheme 4.23: The carbonylation reaction of benzyl bromide (BB) catalysed with functionalised phosphine-imidazolium salts.

Performed at 1.0 mol % Pd/L (1:1), $Pd(OAc)_2$.

The results of the reaction in which these phosphine-imidazolium salts were tested are listed in table 4.24 with their structures shown in figure 4.22. The data shows that all of the phosphine-imidazolium salts tested in the above reaction showed similar activation in the carbonylation reaction of BB. The majority of ligands tested gave a conversion of the desired product between 60-63%, similar to the standard (JM) ligand $PPh_3$ tested in this reaction which gave a conversion of 64%. This was disappointing due to the fact that bidentate ligands offer significant advantages for carbonylation.[29]

| Entry | Catalyst | Amount of catalyst (mol%) | Time (h) | Yield (%) |
|---|---|---|---|---|
| 1 | **8** | 1 | 3 | 58 |
| 2 | **6** | 1 | 3 | 63 |
| 3 | **2** | 1 | 3 | 61 |
| 4 | **2a** | 1 | 3 | 48 |
| 5 | **16** | 1 | 3 | 62 |
| 6 | **17** | 1 | 3 | 61 |

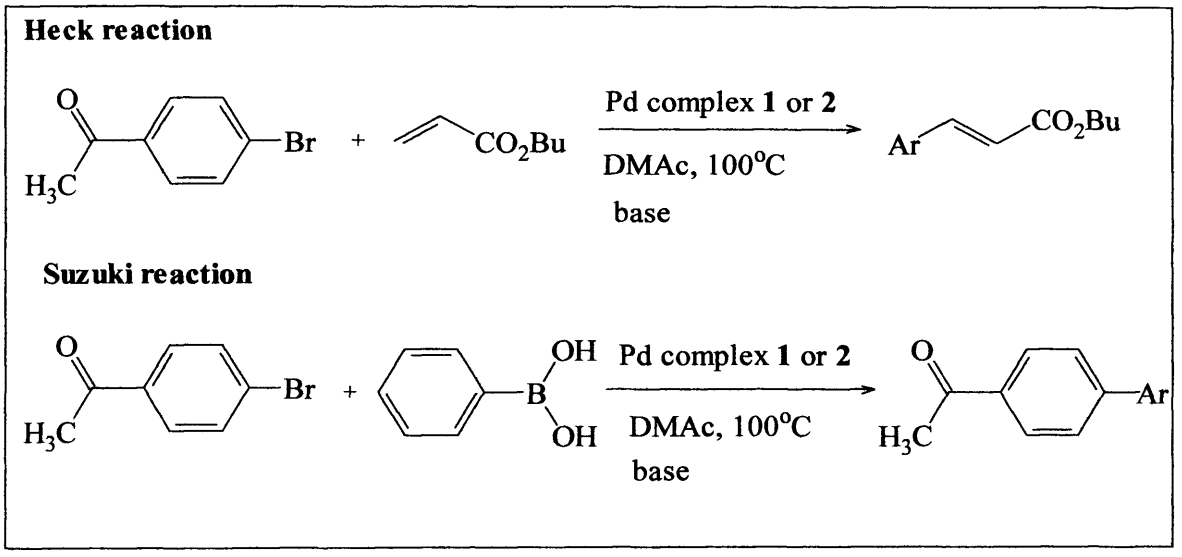
Table 4.24: Results of the *in-situ* carbonylation reaction of benzyl bromide catalysed with functionalised phosphine-imidazolium salts.

1.1 equiv. of diisopropylethylamine, performed at 1 mol % Pd/L (1:1), $Pd(OAc)_2$, preformed at 60°C.

[a] GC yield.

## 4.5: Heck and Suzuki cross-coupling reaction with Pd(II) phosphine-NHC complexes

The pre-formed catalyst testing of palladium complexes **1** and **2** in the Heck and Suzuki reactions focussed on the coupling of the activated aryl bromide 4-bromoactepheone (BAP) with *n*-butyl acrylate (BA), and phenylboronic acid (PA), scheme 4.25, under standardised conditions.




Scheme 4.25: The Heck and Suzuki reaction of 4-bromoactepheone (BAP) with *n*-butyl acrylate (BA), and phenylboronic acid (PA) catalysed by Pd(II) functionalised phosphine-NHC complexes **1** and **2**.

Performed at 0.5 mol % Pd complex **1** or **2**.

The results of the coupling reaction in which Pd(II) complexes **1** and **2** were tested are listed in table 4.26 with their structure shown in figure 4.27. The data showed that both complexes **1** and **2** had good activity producing a high yield (GC) of the desired product when applied in the Heck and Suzuki coupling. Again, the chosen of base had a significant impact on the activity of the complex, in the Heck reaction 100 % conversion was achieved when 2 equiv. of $K_2CO_3$ was used (entry 3), whereas

in the Suzuki reaction $Cs_2CO_3$ was by far the best base giving 97 % (entry 5) conversion after five hours. Although complex **2** gave 100% conversion in the Heck reaction and 97% in the Suzuki reaction, the fact that the substrate was the activated aryl bromide (BAP) and the catalyst loading was 0.5%, means that these complexes (**1** and **2**) are not particularly activate when compared to known catalysts (see table 4.7 page 149-150). The above catalyst runs should also be repeated to obtain an average value of the two runs. The activity of these complexes may further increase if conditions were optimised and with the addition of bulky groups on the both the phosphine and NHC ($N_3$-position)

The pre-formed palladium complexes **1** and **2** were also tested in the Heck and Suzuki reactions of the aryl chloride chloroanisole (CAS), under the same conditions as above, however no coupling product was obtain.

| Entry | Catalyst (complex) | Coupling reagents | Base | Time (h) | Yield % | TON |
|---|---|---|---|---|---|---|
| 1 | **1** | BAP + BA | $Cs_2CO_3$ | 5 | 73 | 146 |
| 2 | **2** | BAP + BA | $Cs_2CO_3$ | 5 | 61 | 122 |
| 3 | **2** | BAP + BA | $K_2CO_3$ | 5 | 100 | 200 |
| 4 | **1** | BAP + PA | $Cs_2CO_3$ | 5 | 79 | 158 |
| 5 | **2** | BAP + PA | $Cs_2CO_3$ | 5 | 97 | 196 |
| 6 | **2** | BAP + PA | $K_2CO_3$ | 5 | 0 | 0 |

Table 4.26: Results of the Heck and Suzuki reaction of BAP with BA, and PA catalysed by Pd(II) functionalised phosphine-NHC complexes **1** and **2**.

Performed at 0.5 mol % Pd complex **1** or **2** and at 100°C.

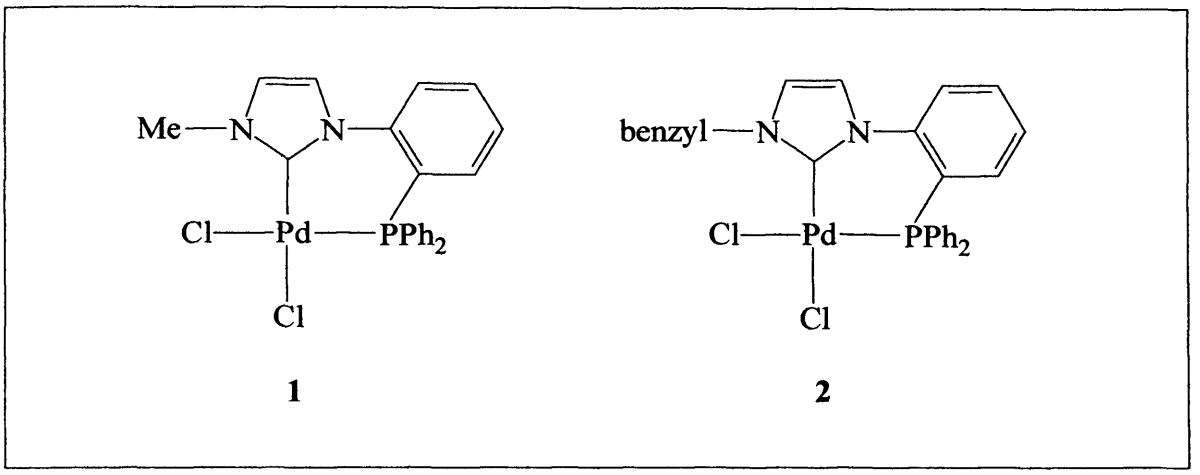



Figure 4.27: Complexes tested in the coupling reactions of 4-bromoactepheone (BAP) with *n*-butyl acrylate (BA), and phenylboronic acid (PA).

## 4.6: Conclusion

The *in-situ* catalyst testing of a range of phosphine-imidazolium salts has been carried out in a number of palladium catalysed cross-coupling reactions. Phosphine-imidazolium salts **2**, **6** and **16** gave the best results of the ligands tested, showing moderate catalytic activity in the Heck coupling of activated aryl bromides with *n*-butyl acrylate and in the Suzuki coupling of deactivated aryl bromides with phenylboronic acid. The pre-formed catalyst testing of palladium(II) complexes **1** and **2** showed good activity in the Heck and Suzuki coupling of activated aryl bromides when used with a specific base. The activity of these complexes may further increase if conditions are optimised. The introduction of bulky groups on both the phosphine and carbene functions in these complexes may also have a positive effect on their catalytic potential.

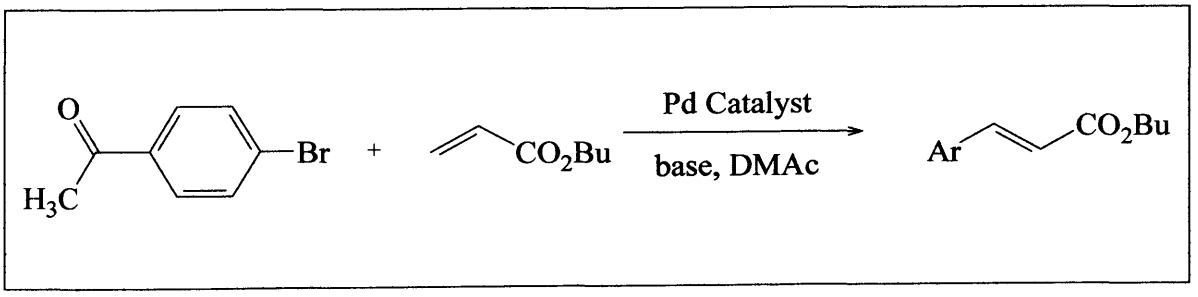
# 4.7: Experimental

## 4.7.1: General comments

All the ligands and complexes synthesised were prepared using standard Schlenk techniques under an atmosphere of either dinitrogen or argon as discussed in Chapters Two and Three. The *in-situ* catalyst testing of all ligands was carried out at Johnson-Matthey (JM) Technology Centre at Sonning Common, N,N-dimethylacetamide was purged with dinitrogen for one hour before being used and all other reagent were used without any other purification. The pre-formed catalyst testing was carried out in the University laboratory and N,N-dimethylacetamide (AR grade) and all liquid reagents were freeze-thawed degassed three times and dried over 3 Å molecular sieves. Caesium carbonate and potassium carbonate were dried in an oven at 120 °C. The catalytic runs were carried out in a Radley's carousel reactor or Schlenk techniques. GC-MS data were acquired on a Perkin Elmer Autosystem XL GC/MS with a 'CPSIL5' (10m x 0.53mm) column.

## 4.7.2: Palladium-catalysed *in-situ* testing

**Heck Reaction: 4-Bromoacephenone and butyl acrylate**



**Reagents**

**Stock Solution A:** -0.4M bromoacetophenone, 0.56M butyl acrylate and 0.4 mesitylene (internal standard) in DMAc.

**Stock Solution B:** -0.002M $Pd(OAc)_2$ (with respect to metal) in DMAc.

**Base:** NaOAc (0.0014mol, 0.115g).

**Ligand:** 0.5 mol % bidentate ligand and 1 mol % monodentate $PPh_3$ (standard ligand).

**Method**

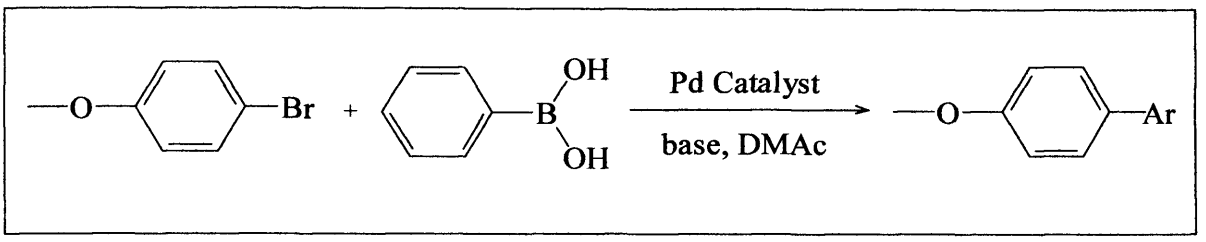
Into each tube was added the ligand and base as a solid, then 2.5 ml of each of the stock solutions was added. The carousel was heated to 100 °C and stirred for five hours. The tubes were allowed to cool to r.t. and an aliquot was taken from each tube and centrifuged to remove any precipitate. The samples were loaded into GC using method 'Heck 1' and column 'CPSIL5' and the samples were run against a solution of 1:1 Stock Solution A: DMAc.

GC Method Heck One:

$$130^\circ\,C\ (2\ min) \xrightarrow{30^\circ\,C} 300^\circ\,C\ (2\ min)$$

Attenuation: -6, Split: 25:1, Range 20, Detector and injector temp: 320° C.

**Suzuki reaction: Bromoanisole and phenylboronic acid**




**Reagents**

**Stock Solution A:** -0.4M bromoanisole, and 0.4 mesitylene (internal standard) in DMAc.

**Stock Solution B:** -0.002M $Pd(OAc)_2$ (with respect to metal) in DMAc.

**Boronic Acid:** $PhB(OH)_2$ (0.0012mol, 0.146g).

**Base:** $K_2CO_3$ (0.0014mol, 0.276g).

**Ligand:** 0.5 mol % bidentate ligand and 1 mol % monodentate $PPh_3$ (standard ligand).

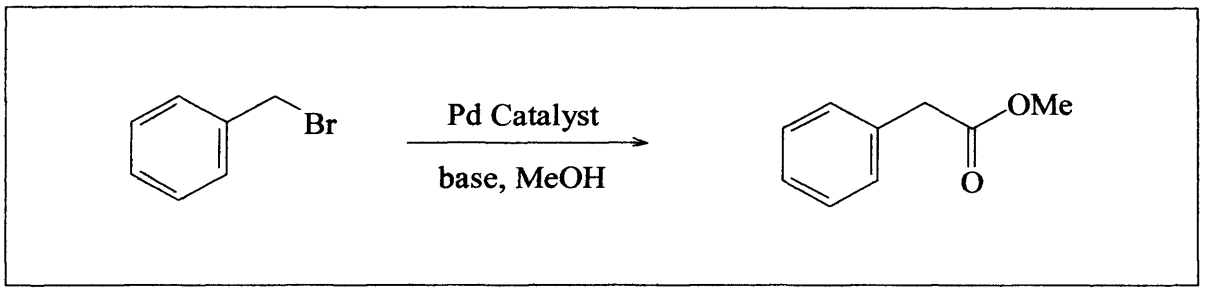
**Method**

Into each tube was added the ligand, base and boronic acid as a solid, then 2.5 ml of each of the stock solutions was added. The carousel was heated to 100 °C and stirred for two hours. The tubes were allowed to cool to r.t. and an aliquot was taken from each tube and centrifuged to remove any precipitate. The samples were loaded into GC suing method 'Heck 1' and column 'CPSIL5' and the samples were run against a solution of 1:1 Stock Solution A: DMAc.

**Suzuki reaction: Chloroacetophenone and phenylboronic acid**

The same methodology was used as above, but this time bromoanisole was replaced by chloroaectophenone, $Cs_2CO_3$ was used as the base and the reaction was stirred for eight hours.

**Carbonylation of benzyl bromide**




**Reagents**

**Stock Solution A:** -0.2M benzyl bromide, 0.22M diisopropylethylamine and 0.2 mesitylene (internal standard) in MeOH.

**Palladium Source:** $Pd(OAc)_2$ (0.00001mol).

**Ligand:** 1 mol % bidentate ligand and 2 mol % monodentate $PPh_3$ (standard ligand).

**Method**

Into each tube was added the ligand and palladium as a solid, then 5 ml of the stock solution was added. The Baskerville was placed at 4 bar CO, heated to 60 °C and stirred for three hours. The tubes were depressurised and allowed to cool to r.t. and an aliquot was taken from each tube and centrifuged to remove any precipitate. The samples were loaded into GC suing method 'Carb01' and column 'CPSIL5' and the samples were run against a solution of 1:1 Stock Solution A.

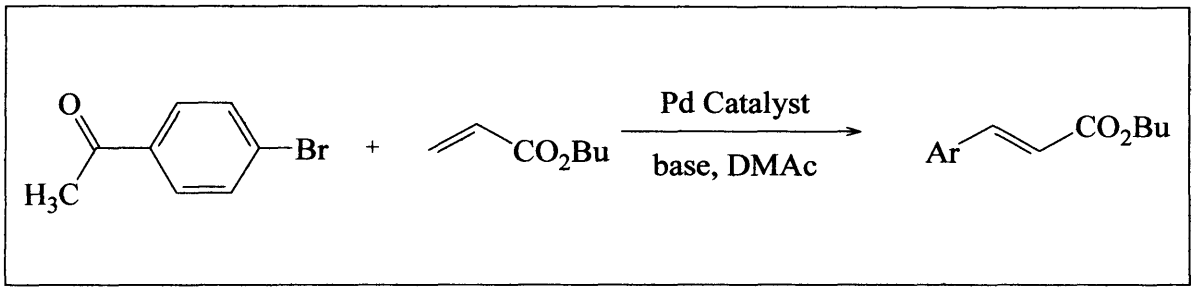
GC Method Carb01:

| | 20° C | |
|---|---|---|
| 50° C | → | 250° C |
| 1 min | | 5 min |

Attenuation: -8, Split: 25:1, Range 20, Detector and injector temp: 300° C.

## 4.7.3: Palladium-catalysed pre-formed testing

**Heck Reaction: Bromoacephenone and butyl acrylate**




**Reagents**

**Stock Solution A:** -0.4M bromoacetophenone, 0.56M butyl acrylate and 0.4 naphthalene (internal standard) in DMAc.

**Stock Solution B:** -0.002M Pd(II) phosphine-NHC Complex **1** or **2** in DMAc.

**Base:** $Cs_2CO_3$ (0.0014mol, 0.4g) or $K_2CO_3$ (0.0014mol, 0.146g).

**Method**

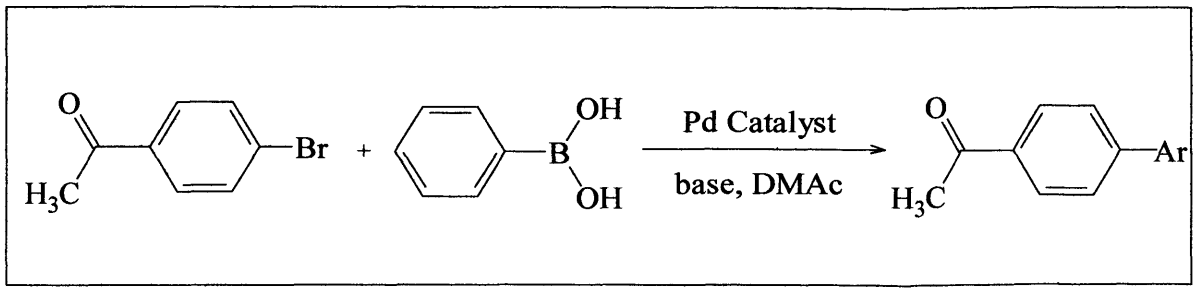
Into each Schlenk was added the base as a solid, then 2.5 ml of each of the stock solutions was added. The mixtures were immediately put into an oil bath pre-heated to 100 °C and stirred for five hours. The reactions were allowed to cool to r.t.

and DCM was added to precipitate any inorganic salts. An aliquot of samples were loaded into GC suing.

**Heck Reaction: Chloroanisole and butyl acrylate**

The same methodology was used as above this time bromoacetophenone was replaced by chloroanisole.

**Suzuki reaction: Bromoacetophenone and phenylboronic acid**




**Reagents**

**Stock Solution A:** -0.4M bromoacetophenone, and 0.4 naphthalene (internal standard) in DMAc.

**Stock Solution B:** -0.002M Pd(II) phosphine-NHC Complex **1** or **2** in DMAc

**Boronic Acid:** $PhB(OH)_2$ (0.0012mol, 0.146g).

**Base:** $Cs_2CO_3$ (0.002mol, 0.657g) or $K_2CO_3$ (0.002mol, 0.270g).

**Method**

Into each Schlenk was added the base and boronic acid as a solid, then 2.5 ml of each of the stock solutions was added. The mixtures were immediately put into an oil bath preheated to 100° C and stirred for five hours. The reactions were allowed to

cool to r.t. and DCM was added to precipitate any inorganic salts. An aliquot of samples were loaded into GC suing.

**Suzuki reaction: Chloroanisole and phenylboronic acid**

The same methodology was used as above this time bromoacetophenone was replaced by chloroanisole.

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# CHAPTER FIVE
# Conclusion

## 5.1: Conclusion and suggestions for further work

Several synthetic routes have been successfully established which have provided viable paths into a series of functional imidazolium salts. A variety of phosphine-imidazolium salts were presented in this work, giving a range of chelating ligands with varying degrees of steric bulk on the imidazolium ring and different chelating sizes.

Of the three main **Types** of chelating ligands targeted in this thesis, the synthesis of **Type I** and **II**, were achieved via the nucleophilic attack of potassium diphenylphosphine on an aryl fluoride bond. This method proved to be relatively straightforward, due to the *ortho* imidazolium function acting as an electron-withdrawing group, which is the key in the success of these types of reactions, and in suitable solvents a number of phosphine-imidazolium salts were synthesised in moderate to high yields. An alterative method for the synthesis of **Type I** ligands was also established and involved the reaction of 2-diphenylphosphinobenzyl halide with N-substituted imidazoles, which will enable the synthesis of a large range of these phosphine-imidazolium salts with one simple reaction.

The synthesis of **Type III** chelating ligands was also achieved in two different ways. The first was a relatively laborious synthesis involving several steps, including the reduction of the phosphine oxides, and was not considered the best route to these salts. The second involved the synthesis and subsequent reaction of (1-phenyl-*o*-chloride-3-alkyl-N-substituted)imidazolium salts, which was found to be the easier and most productive way. In this method the reaction was a simple nucleophilic attack of the alkyl-chloride by potassium diphenylphosphine, which is easier than on an aryl fluoride bond, to yield the desired phosphine-imidazolium salts in high yields.

The preparation of several new group 10 metal(II) phosphine-NHC complexes has been achieved via the deprotonation of the chelating imidazolium salt by $KN(SiMe_3)_2$ and subsequent reaction with a suitable metal precursor. These complexes show that even with ligands containing acidic protons, with a milder base and the right temperatures these complexes could readily be synthesised with this high-yielding method. The solid state structure of complex **1** has been obtained, giving an insight into the properties of these chelating ligands. The relative *trans* influences of the phosphine and carbene functions revealed that the Pd-Cl bond *trans* to the phosphine is longer than that *trans* to the NHC. This observation is not fully understood and has been observed in other related phosphine-carbene complexes. Given the known *trans* effects of phosphines and carbenes the opposite outcome would be expected and this is one area where more investigation is needed to understand the full properties of these ligands. Three new silver(I) phosphine-NHC complexes have been synthesised and characterised, and the rhodium(I) complex **13** was prepared via transmetallation from the corresponding silver(I) complex **10**.

The capability of both phosphines and/or carbenes as catalysts has been proven in a wide range of catalytic reactions, however, the results obtained from the testing carried out in this work showed only limited success in both *in-situ* and pre-formed testing. In the *in-situ* catalyst testing the best results were obtained, in both the Heck and Suzuki coupling reaction, with the **Type I** and **II** ligands. However, as discussed in this thesis, less care was taken in the purification and degassing of solvents and reagents than what would be common when using standard Schlenk line techniques. Hence there was a possibility of contamination by air and moisture, which may have led to the formation of the phosphine oxide in solution and therefore the full potential of these ligands may not have been measured. The pre-formed catalyst testing of palladium(II) complexes **1** and **2** showed good activity in the Heck and Suzuki coupling of activated aryl bromides when used with a specific base, although the TON were still poor compared to known ligands.

The activity of both the ligands and the complexes may further increase if conditions are optimised. The optimisation of catalyst systems is key in getting the best results out of the ligands/complexes; the solvent, palladium source, base, etc. can

all have a major effect on the yield of the product obtained. In *in-situ* catalyst systems when NHC's are employed as ligands, the base plays two roles in the reaction; not only to regenerate and stabilise active species in the catalytic cycle, but also to deprotonate the imidazolium salt in solution to form the free NHC. It is important to realise that the best base for one role in the reaction may not be the best for the other roles in the reaction. This is one of the major disadvantages with *in-situ* catalyst testing of imidazolium salts in that one can never be certain to what extent the imidazolium salt has been deprotonated, unlike in the case of phosphines where *in-situ* catalyst testing can sometimes be as successful as pre-formed catalyst testing. It is therefore vital for further catalyst testing be carried out on these ligands and complexes before drawing firm conclusions about their catalytic potential.

Now that such well-established routes have been achieved in the synthesis of all three **Types** of ligands, further extensions of this work could explore the large scope of synthetic design. The 'tuneability' of these ligands and ultimately metal complexes which are used in homogeneous catalysis, is one of the main goals in the long-term success of such a project. Varying the substituents on both the phosphine and NHC will affect the steric and electronic properties of the resulted complex, which in turn may have an influence on particular rate-determining steps in the reaction cycle and also how labile the chelating ligand is. The introduction of different groups on both the phosphine and carbene functions in these complexes may also have a positive effect on their catalytic potential.

The strength of both the σ- and π-donor ability of the phosphine can be changed by replacing the R groups on the phosphine. For example, the Ph groups which were used in this project could be changed to $^{t}$Bu, Cy and Ad groups, which would increase the strength of the σ-bond to the metal. This may discourage these types of ligands from being hemi-labile and provide two strong *trans* effecting ligands (e.g. phosphine and NHC) *cis* to the two reacting species in a square planar complex. Alternatively replacing the phosphine function with a phosphite would weaken the σ-bond to the metal which may encourage the chelating phosphite to dissociate, leaving a free coordination site during some stages of the catalytic cycle. The phosphite would also be a stronger π-accepter ligand which may help to stabilise an electron rich metal centre and also have a strong *trans* effect on reacting substrates.

The steric and electronic properties of the carbene may be altered by changing the R group on one of the nitrogens of the carbene. The addition of a large, strongly electron donating group on the nitrogen may help to stabilise the metal-NHC bond in two ways. Firstly by increasing the σ-donor ability of the carbene, making the metal-NHC bond stronger and thus having a larger *trans* effect on the ligand opposite, and secondly by reducing the risk of reductive elimination of the carbene from an intermediate catalytic complex bearing a hydrocarbyl ligand, by blocking the path for this reaction to occur due to its steric bulk. Some examples of possible synthetic targets are given below (figure 5.1).

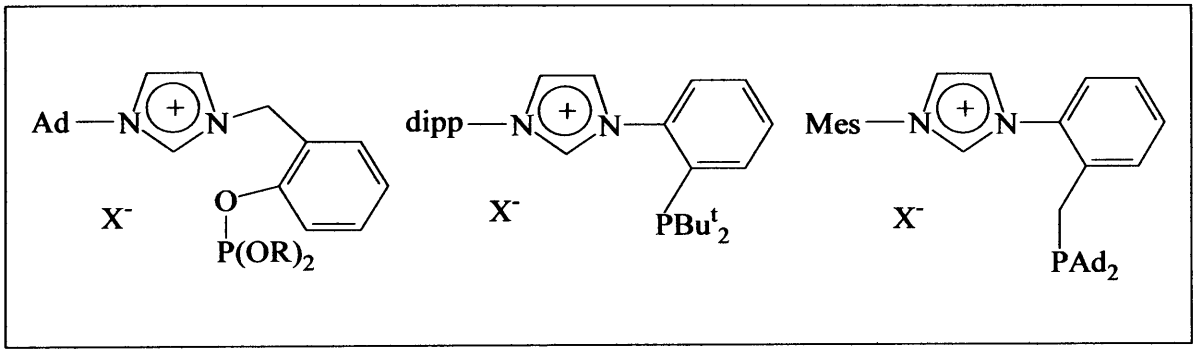
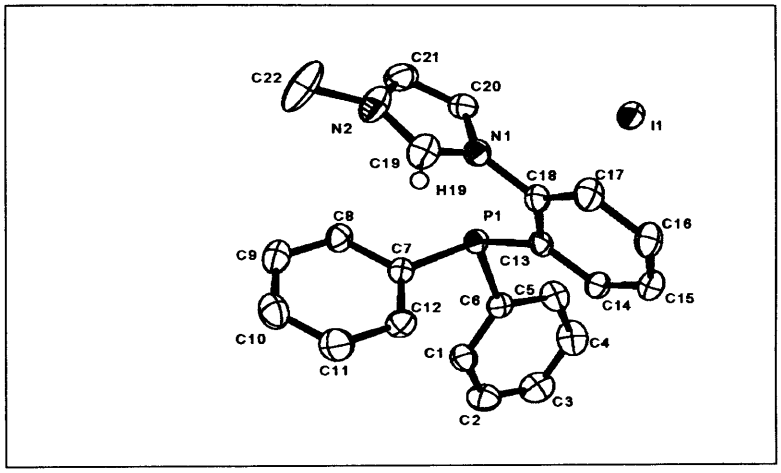



Figure 5.1

# APPENDIX

## Crystal data

Table 1: Crystal data and structure refinement for phosphine-imidazolium salt **16**.




| | | |
|---|---|---|
| Identification code | Phosphine-imidazolium salt **16** | |
| Empirical formula | $C_{23}$ $H_{22}$ $Cl_2$ I $N_2$ P | |
| Formula weight | 555.20 | |
| Temperature | 150(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | a = 8.5040(2) Å | α = 83.2620(10)°. |
| | b = 11.4720(2) Å | β= 72.4170(10)°. |
| | c = 13.0560(3) Å | γ = 86.0640(10)°. |
| Volume | 1205.08(4) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.530 $Mg/m^3$ | |
| Absorption coefficient | 1.629 $mm^{-1}$ | |
| F(000) | 552 | |
| Crystal size | 0.33 x 0.15 x 0.10 $mm^3$ | |
| Theta range for data collection | 2.98 to 29.99°. | |
| Index ranges | -11<=h<=11, -15<=k<=16, -18<=l<=18 | |

| | |
|---|---|
| Reflections collected | 24121 |
| Independent reflections | 6974 [R(int) = 0.1243] |
| Completeness to theta = 29.99° | 99.4 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.8541 and 0.6155 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 6974 / 12 / 282 |
| Goodness-of-fit on $F^2$ | 1.029 |
| Final R indices [I>2sigma(I)] | R1 = 0.0484, wR2 = 0.1073 |
| R indices (all data) | R1 = 0.0755, wR2 = 0.1257 |
| Largest diff. peak and hole | 0.985 and -0.902 e.$Å^{-3}$ |

Table 2: Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for phosphine-imidazolium salt **16**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 8146(4) | 945(4) | 4455(3) | 33(1) |
| C(2) | 8236(5) | 1766(4) | 5140(3) | 42(1) |
| C(3) | 7974(5) | 2940(4) | 4886(4) | 47(1) |
| C(4) | 7638(5) | 3319(4) | 3917(4) | 47(1) |
| C(5) | 7596(5) | 2517(3) | 3212(3) | 36(1) |
| C(6) | 7821(4) | 1312(3) | 3480(3) | 27(1) |
| C(7) | 8011(4) | -1138(3) | 3102(3) | 24(1) |
| C(8) | 9406(4) | -1834(3) | 2632(3) | 31(1) |
| C(9) | 9623(5) | -2962(4) | 3066(4) | 39(1) |
| C(10) | 8437(6) | -3429(4) | 3978(4) | 43(1) |
| C(11) | 7015(5) | -2784(4) | 4435(4) | 41(1) |
| C(12) | 6799(5) | -1629(3) | 4004(3) | 33(1) |
| C(13) | 5662(4) | 393(3) | 2491(3) | 25(1) |
| C(14) | 4438(4) | 1107(3) | 3099(3) | 26(1) |
| C(15) | 2814(4) | 1122(3) | 3081(3) | 30(1) |
| C(16) | 2396(4) | 412(4) | 2431(3) | 36(1) |
| C(17) | 3576(4) | -332(3) | 1808(3) | 34(1) |
| C(18) | 5181(4) | -318(3) | 1844(3) | 27(1) |
| C(19) | 6402(5) | -2249(4) | 1340(3) | 36(1) |
| C(20) | 7774(5) | -736(4) | 358(3) | 34(1) |
| C(21) | 8613(5) | -1726(4) | 18(3) | 40(1) |
| C(22) | 8218(6) | -3913(4) | 544(5) | 67(2) |
| C(23) | 6457(6) | 5561(5) | -2011(5) | 71(2) |
| N(1) | 6399(3) | -1080(3) | 1193(2) | 28(1) |
| N(2) | 7743(4) | -2665(3) | 635(3) | 40(1) |
| P(1) | 7845(1) | 355(1) | 2454(1) | 24(1) |
| I(1) | 6960(1) | 2843(1) | -20(1) | 36(1) |
| Cl(1A) | 8631(11) | 5964(9) | -2421(6) | 71(2) |
| Cl(2A) | 5820(20) | 5059(14) | -2899(15) | 81(3) |
| Cl(1B) | 8407(13) | 5915(10) | -2778(7) | 76(2) |
| Cl(2B) | 5550(30) | 4887(13) | -3004(15) | 71(3) |

Table 3. Bond lengths [Å] and angles [°] for phosphine-imidazolium salt **16**.

| | | | |
|---|---|---|---|
| C(1)-C(2) | 1.394(5) | C(14)-C(15) | 1.388(4) |
| C(1)-C(6) | 1.394(5) | C(14)-H(14) | 0.9500 |
| C(1)-H(1) | 0.9500 | C(15)-C(16) | 1.377(5) |
| C(2)-C(3) | 1.369(7) | C(15)-H(15) | 0.9500 |
| C(2)-H(2) | 0.9500 | C(16)-C(17) | 1.395(5) |
| C(3)-C(4) | 1.394(6) | C(16)-H(16) | 0.9500 |
| C(3)-H(3) | 0.9500 | C(17)-C(18) | 1.381(4) |
| C(4)-C(5) | 1.385(6) | C(17)-H(17) | 0.9500 |
| C(4)-H(4) | 0.9500 | C(18)-N(1) | 1.441(5) |
| C(5)-C(6) | 1.401(5) | C(19)-N(2) | 1.331(5) |
| C(5)-H(5) | 0.9500 | C(19)-N(1) | 1.333(5) |
| C(6)-P(1) | 1.823(4) | C(19)-H(19) | 0.9500 |
| C(7)-C(12) | 1.398(5) | C(20)-C(21) | 1.347(6) |
| C(7)-C(8) | 1.403(5) | C(20)-N(1) | 1.380(5) |
| C(7)-P(1) | 1.835(3) | C(20)-H(20) | 0.9500 |
| C(8)-C(9) | 1.375(5) | C(21)-N(2) | 1.379(5) |
| C(8)-H(8) | 0.9500 | C(21)-H(21) | 0.9500 |
| C(9)-C(10) | 1.386(6) | C(22)-N(2) | 1.469(5) |
| C(9)-H(9) | 0.9500 | C(22)-H(22A) | 0.9800 |
| C(10)-C(11) | 1.382(6) | C(22)-H(22B) | 0.9800 |
| C(10)-H(10) | 0.9500 | C(22)-H(22C) | 0.9800 |
| C(11)-C(12) | 1.400(5) | C(23)-Cl(2A) | 1.596(17) |
| C(11)-H(11) | 0.9500 | C(23)-Cl(1B) | 1.706(12) |
| C(12)-H(12) | 0.9500 | C(23)-Cl(1A) | 1.838(11) |
| C(13)-C(14) | 1.386(5) | C(23)-Cl(2B) | 1.947(17) |
| C(13)-C(18) | 1.401(5) | C(23)-H(23A) | 0.9900 |
| C(13)-P(1) | 1.841(3) | C(23)-H(23B) | 0.9900 |

| | | | |
|---|---|---|---|
| C(2)-C(1)-C(6) | 120.3(4) | C(14)-C(13)-C(18) | 116.5(3) |
| C(2)-C(1)-H(1) | 119.8 | C(14)-C(13)-P(1) | 124.6(3) |
| C(6)-C(1)-H(1) | 119.8 | C(18)-C(13)-P(1) | 118.9(3) |
| C(3)-C(2)-C(1) | 121.0(4) | C(13)-C(14)-C(15) | 122.3(3) |
| C(3)-C(2)-H(2) | 119.5 | C(13)-C(14)-H(14) | 118.8 |
| C(1)-C(2)-H(2) | 119.5 | C(15)-C(14)-H(14) | 118.8 |
| C(2)-C(3)-C(4) | 119.2(4) | C(16)-C(15)-C(14) | 119.2(3) |
| C(2)-C(3)-H(3) | 120.4 | C(16)-C(15)-H(15) | 120.4 |
| C(4)-C(3)-H(3) | 120.4 | C(14)-C(15)-H(15) | 120.4 |
| C(5)-C(4)-C(3) | 120.4(4) | C(15)-C(16)-C(17) | 120.8(3) |
| C(5)-C(4)-H(4) | 119.8 | C(15)-C(16)-H(16) | 119.6 |
| C(3)-C(4)-H(4) | 119.8 | C(17)-C(16)-H(16) | 119.6 |
| C(4)-C(5)-C(6) | 120.6(4) | C(18)-C(17)-C(16) | 118.3(3) |
| C(4)-C(5)-H(5) | 119.7 | C(18)-C(17)-H(17) | 120.9 |
| C(6)-C(5)-H(5) | 119.7 | C(16)-C(17)-H(17) | 120.9 |
| C(1)-C(6)-C(5) | 118.3(3) | C(17)-C(18)-C(13) | 122.8(3) |
| C(1)-C(6)-P(1) | 125.1(3) | C(17)-C(18)-N(1) | 118.1(3) |
| C(5)-C(6)-P(1) | 116.3(3) | C(13)-C(18)-N(1) | 119.1(3) |
| C(12)-C(7)-C(8) | 118.7(3) | N(2)-C(19)-N(1) | 108.4(3) |
| C(12)-C(7)-P(1) | 123.8(3) | N(2)-C(19)-H(19) | 125.8 |
| C(8)-C(7)-P(1) | 117.5(3) | N(1)-C(19)-H(19) | 125.8 |
| C(9)-C(8)-C(7) | 121.2(4) | C(21)-C(20)-N(1) | 106.6(4) |
| C(9)-C(8)-H(8) | 119.4 | C(21)-C(20)-H(20) | 126.7 |
| C(7)-C(8)-H(8) | 119.4 | N(1)-C(20)-H(20) | 126.7 |
| C(8)-C(9)-C(10) | 119.6(4) | C(20)-C(21)-N(2) | 107.7(3) |
| C(8)-C(9)-H(9) | 120.2 | C(20)-C(21)-H(21) | 126.2 |
| C(10)-C(9)-H(9) | 120.2 | N(2)-C(21)-H(21) | 126.2 |
| C(11)-C(10)-C(9) | 120.7(4) | N(2)-C(22)-H(22A) | 109.5 |
| C(11)-C(10)-H(10) | 119.7 | N(2)-C(22)-H(22B) | 109.5 |
| C(9)-C(10)-H(10) | 119.7 | H(22A)-C(22)-H(22B) | 109.5 |
| C(10)-C(11)-C(12) | 119.8(4) | N(2)-C(22)-H(22C) | 109.5 |
| C(10)-C(11)-H(11) | 120.1 | H(22A)-C(22)-H(22C) | 109.5 |
| C(12)-C(11)-H(11) | 120.1 | H(22B)-C(22)-H(22C) | 109.5 |
| C(7)-C(12)-C(11) | 120.0(4) | Cl(2A)-C(23)-Cl(1B) | 99.7(8) |
| C(7)-C(12)-H(12) | 120.0 | Cl(2A)-C(23)-Cl(1A) | 116.8(8) |
| C(11)-C(12)-H(12) | 120.0 | Cl(1B)-C(23)-Cl(1A) | 17.8(4) |

| | | | |
|---|---|---|---|
| Cl(2A)-C(23)-Cl(2B) | 4.4(12) | Cl(1A)-C(23)-Cl(2B) | 120.7(7) |
| Cl(1B)-C(23)-Cl(2B) | 103.8(7) | Cl(2A)-C(23)-H(23A) | 108.1 |
| Cl(1B)-C(23)-H(23A) | 120.8 | C(19)-N(1)-C(18) | 124.6(3) |
| Cl(1A)-C(23)-H(23A) | 108.1 | C(20)-N(1)-C(18) | 126.4(3) |
| Cl(2B)-C(23)-H(23A) | 104.4 | C(19)-N(2)-C(21) | 108.3(3) |
| Cl(2A)-C(23)-H(23B) | 108.1 | C(19)-N(2)-C(22) | 125.5(4) |
| Cl(1B)-C(23)-H(23B) | 112.0 | C(21)-N(2)-C(22) | 126.1(4) |
| Cl(1A)-C(23)-H(23B) | 108.1 | C(6)-P(1)-C(7) | 104.62(16) |
| Cl(2B)-C(23)-H(23B) | 107.5 | C(6)-P(1)-C(13) | 102.52(15) |
| H(23A)-C(23)-H(23B) | 107.3 | C(7)-P(1)-C(13) | 99.43(15) |
| C(19)-N(1)-C(20) | 108.9(3) | | |

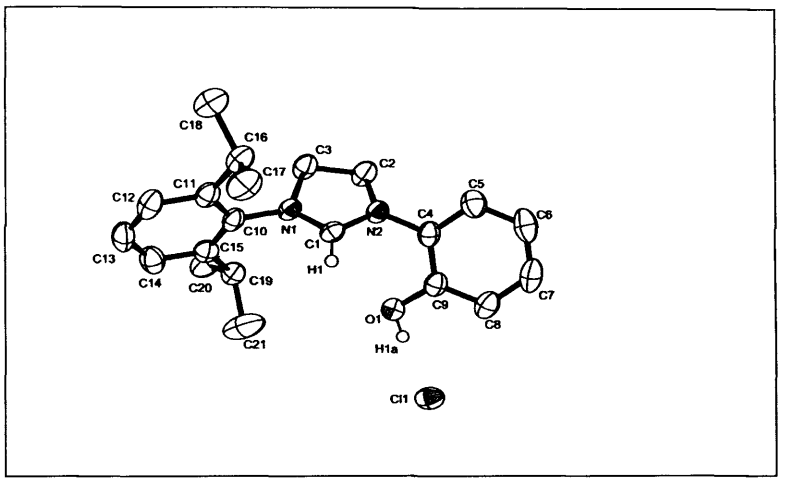
Table 4: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for phosphine-imidazolium salt **16**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 32(2) | 35(2) | 35(2) | -3(2) | -14(2) | -1(2) |
| C(2) | 51(2) | 43(2) | 38(2) | -10(2) | -17(2) | -7(2) |
| C(3) | 44(2) | 51(3) | 51(3) | -17(2) | -15(2) | -10(2) |
| C(4) | 45(2) | 35(2) | 68(3) | -7(2) | -27(2) | -8(2) |
| C(5) | 38(2) | 31(2) | 46(2) | -3(2) | -21(2) | -6(2) |
| C(6) | 15(1) | 34(2) | 31(2) | -4(2) | -6(1) | -3(1) |
| C(7) | 23(2) | 24(2) | 30(2) | -6(1) | -12(1) | -2(1) |
| C(8) | 21(2) | 36(2) | 36(2) | -6(2) | -11(1) | 3(1) |
| C(9) | 35(2) | 36(2) | 51(2) | -12(2) | -17(2) | 8(2) |
| C(10) | 54(3) | 29(2) | 51(3) | -1(2) | -24(2) | 1(2) |
| C(11) | 50(2) | 29(2) | 42(2) | -1(2) | -10(2) | -7(2) |
| C(12) | 33(2) | 30(2) | 33(2) | -5(2) | -6(2) | -2(2) |
| C(13) | 16(1) | 32(2) | 26(2) | 2(1) | -8(1) | 1(1) |
| C(14) | 22(2) | 26(2) | 30(2) | -4(1) | -7(1) | -1(1) |
| C(15) | 24(2) | 29(2) | 37(2) | -5(2) | -6(1) | 2(1) |
| C(16) | 19(2) | 42(2) | 48(2) | -6(2) | -14(2) | 2(2) |
| C(17) | 27(2) | 36(2) | 45(2) | -12(2) | -20(2) | 1(2) |
| C(18) | 23(2) | 30(2) | 30(2) | -2(1) | -10(1) | 3(1) |
| C(19) | 27(2) | 35(2) | 48(2) | -9(2) | -11(2) | -3(2) |
| C(20) | 33(2) | 42(2) | 26(2) | -3(2) | -8(2) | 4(2) |
| C(21) | 32(2) | 53(3) | 31(2) | -9(2) | -5(2) | 4(2) |
| C(22) | 52(3) | 38(3) | 107(5) | -45(3) | -7(3) | 6(2) |
| C(23) | 54(3) | 57(3) | 70(4) | 15(3) | 16(3) | 20(2) |
| N(1) | 24(1) | 34(2) | 30(2) | -7(1) | -13(1) | 3(1) |
| N(2) | 33(2) | 33(2) | 56(2) | -21(2) | -13(2) | 5(1) |
| P(1) | 17(1) | 28(1) | 27(1) | -4(1) | -8(1) | -1(1) |
| I(1) | 36(1) | 32(1) | 37(1) | -6(1) | -8(1) | 5(1) |
| Cl(1A) | 55(3) | 43(2) | 91(4) | 5(3) | 5(3) | 10(2) |
| Cl(2A) | 90(5) | 87(6) | 58(4) | 3(4) | -18(3) | 19(4) |
| Cl(1B) | 58(3) | 42(2) | 102(5) | 14(3) | 6(3) | 9(2) |
| Cl(2B) | 98(7) | 53(3) | 54(4) | 4(2) | -15(3) | 11(3) |

Table 5: Hydrogen coordinates (x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for phosphine-imidazolium salt **16**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 8308 | 132 | 4652 | 40 |
| H(2) | 8483 | 1506 | 5795 | 51 |
| H(3) | 8020 | 3492 | 5365 | 56 |
| H(4) | 7437 | 4131 | 3739 | 56 |
| H(5) | 7413 | 2787 | 2539 | 44 |
| H(8) | 10216 | -1519 | 2002 | 37 |
| H(9) | 10580 | -3420 | 2742 | 47 |
| H(10) | 8603 | -4199 | 4292 | 52 |
| H(11) | 6186 | -3123 | 5041 | 49 |
| H(12) | 5831 | -1180 | 4323 | 39 |
| H(14) | 4721 | 1605 | 3544 | 31 |
| H(15) | 2000 | 1616 | 3512 | 36 |
| H(16) | 1289 | 428 | 2405 | 43 |
| H(17) | 3282 | -835 | 1372 | 40 |
| H(19) | 5585 | -2708 | 1861 | 43 |
| H(20) | 8071 | 47 | 78 | 41 |
| H(21) | 9623 | -1771 | -546 | 47 |
| H(22A) | 9270 | -4081 | 704 | 100 |
| H(22B) | 8338 | -4094 | -191 | 100 |
| H(22C) | 7364 | -4397 | 1059 | 100 |
| H(23A) | 6274 | 4964 | -1378 | 85 |
| H(23B) | 5763 | 6264 | -1771 | 85 |

Table 6: Crystal data and structure refinement for imidazolium salt **36**.




| | |
|---|---|
| Identification code | Imidazolium salt **36** |
| Empirical formula | $C_{22}$ $H_{31}$ $Cl_3$ $N_2$ $O_2$ |
| Formula weight | 461.84 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P 21/c |
| Unit cell dimensions | a = 11.6015(3) Å α= 90°. |
| | b = 14.2272(4) Å β= 102.416(2)°. |
| | c = 15.9647(5) Å γ = 90°. |
| Volume | 2573.45(13) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.192 $Mg/m^3$ |
| Absorption coefficient | 0.375 $mm^{-1}$ |
| F(000) | 976 |
| Crystal size | 0.15 x 0.15 x 0.10 $mm^3$ |
| Theta range for data collection | 3.60 to 26.37°. |
| Index ranges | -14<=h<=14, -17<=k<=17, -19<=l<=19 |
| Reflections collected | 37484 |
| Independent reflections | 5237 [R(int) = 0.0809] |
| Completeness to theta = 26.37° | 99.6 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9635 and 0.9459 |

| | |
|---|---|
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 5237 / 12 / 267 |
| Goodness-of-fit on $F^2$ | 1.104 |
| Final R indices [I>2sigma(I)] | R1 = 0.1216, wR2 = 0.3422 |
| R indices (all data) | R1 = 0.1530, wR2 = 0.3668 |
| Largest diff. peak and hole | 1.913 and -1.105 e.$Å^{-3}$ |

Table 7: Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for imidazolium salt **36**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 4071(5) | 433(4) | 7666(4) | 32(1) |
| C(2) | 3387(7) | 1840(5) | 7053(4) | 46(2) |
| C(3) | 4150(7) | 1360(5) | 6508(4) | 44(2) |
| C(4) | 2741(6) | 1257(4) | 8397(4) | 38(1) |
| C(5) | 1548(6) | 1461(5) | 8237(5) | 48(2) |
| C(6) | 1004(7) | 1622(6) | 8922(6) | 59(2) |
| C(7) | 1651(7) | 1589(6) | 9743(6) | 59(2) |
| C(8) | 2850(7) | 1401(5) | 9918(5) | 47(2) |
| C(9) | 3415(6) | 1235(4) | 9239(4) | 37(1) |
| C(10) | 5425(6) | -136(4) | 6785(4) | 36(1) |
| C(11) | 4962(6) | -868(4) | 6221(4) | 39(1) |
| C(12) | 5783(7) | -1458(4) | 5960(4) | 45(2) |
| C(13) | 6967(7) | -1336(5) | 6251(5) | 48(2) |
| C(14) | 7393(7) | -618(5) | 6825(5) | 48(2) |
| C(15) | 6631(6) | 13(4) | 7096(4) | 39(1) |
| C(16) | 3649(6) | -1042(4) | 5929(4) | 41(2) |
| C(17) | 3302(8) | -1962(5) | 6302(5) | 54(2) |
| C(18) | 3293(8) | -1064(6) | 4944(5) | 58(2) |
| C(19) | 7108(6) | 815(5) | 7694(4) | 42(2) |
| C(20) | 8024(8) | 1388(6) | 7378(5) | 58(2) |
| C(21) | 7557(12) | 462(7) | 8606(5) | 85(3) |
| C(22) | 1342(10) | -1091(8) | 8583(9) | 93(3) |
| N(1) | 4608(5) | 525(3) | 7034(3) | 34(1) |
| N(2) | 3317(5) | 1113(3) | 7704(3) | 35(1) |
| O(1) | 4583(4) | 1063(3) | 9360(3) | 39(1) |
| Cl(3) | 921(3) | -912(2) | 7475(3) | 115(1) |
| Cl(1) | 5707(2) | 1588(1) | 11177(1) | 49(1) |
| Cl(2) | 575(4) | -2017(3) | 8959(3) | 139(1) |
| O(2) | -708(6) | -4248(5) | 9587(6) | 96(2) |

Table 8: Bond lengths [Å] and angles [°] for imidazolium salt **36**.

| | | | |
|---|---|---|---|
| C(1)-N(1) | 1.300(8) | C(10)-C(11) | 1.405(9) |
| C(1)-N(2) | 1.314(8) | C(10)-N(1) | 1.450(8) |
| C(2)-N(2) | 1.481(8) | C(11)-C(12) | 1.398(9) |
| C(2)-C(3) | 1.529(9) | C(11)-C(16) | 1.515(10) |
| C(3)-N(1) | 1.486(8) | C(12)-C(13) | 1.363(11) |
| C(4)-C(5) | 1.383(10) | C(13)-C(14) | 1.391(11) |
| C(4)-C(9) | 1.402(9) | C(14)-C(15) | 1.392(10) |
| C(4)-N(2) | 1.426(8) | C(15)-C(19) | 1.515(9) |
| C(5)-C(6) | 1.394(11) | C(16)-C(17) | 1.528(9) |
| C(6)-C(7) | 1.363(13) | C(16)-C(18) | 1.537(10) |
| C(7)-C(8) | 1.385(11) | C(19)-C(20) | 1.510(10) |
| C(8)-C(9) | 1.402(9) | C(19)-C(21) | 1.522(11) |
| C(9)-O(1) | 1.350(8) | C(22)-Cl(3) | 1.750(14) |
| C(10)-C(15) | 1.397(10) | C(22)-Cl(2) | 1.766(12) |

| | | | |
|---|---|---|---|
| N(1)-C(1)-N(2) | 113.4(5) | C(13)-C(12)-C(11) | 121.6(6) |
| N(2)-C(2)-C(3) | 102.3(5) | C(12)-C(13)-C(14) | 120.5(6) |
| N(1)-C(3)-C(2) | 102.5(5) | C(13)-C(14)-C(15) | 121.3(7) |
| C(5)-C(4)-C(9) | 120.7(6) | C(14)-C(15)-C(10) | 116.5(6) |
| C(5)-C(4)-N(2) | 120.3(6) | C(14)-C(15)-C(19) | 120.8(6) |
| C(9)-C(4)-N(2) | 118.9(6) | C(10)-C(15)-C(19) | 122.8(6) |
| C(4)-C(5)-C(6) | 119.6(7) | C(11)-C(16)-C(17) | 110.6(6) |
| C(7)-C(6)-C(5) | 120.0(7) | C(11)-C(16)-C(18) | 110.5(6) |
| C(6)-C(7)-C(8) | 121.5(7) | C(17)-C(16)-C(18) | 110.2(6) |
| C(7)-C(8)-C(9) | 119.5(7) | C(20)-C(19)-C(15) | 112.6(6) |
| O(1)-C(9)-C(8) | 122.8(6) | C(20)-C(19)-C(21) | 112.2(7) |
| O(1)-C(9)-C(4) | 118.5(5) | C(15)-C(19)-C(21) | 111.0(6) |
| C(8)-C(9)-C(4) | 118.7(6) | Cl(3)-C(22)-Cl(2) | 113.6(7) |
| C(15)-C(10)-C(11) | 123.8(6) | C(1)-N(1)-C(10) | 126.7(5) |
| C(15)-C(10)-N(1) | 117.9(5) | C(1)-N(1)-C(3) | 110.2(5) |
| C(11)-C(10)-N(1) | 118.3(6) | C(10)-N(1)-C(3) | 122.6(5) |
| C(12)-C(11)-C(10) | 116.4(6) | C(1)-N(2)-C(4) | 124.7(5) |
| C(12)-C(11)-C(16) | 121.0(6) | C(1)-N(2)-C(2) | 110.1(5) |
| C(10)-C(11)-C(16) | 122.6(6) | C(4)-N(2)-C(2) | 123.4(5) |

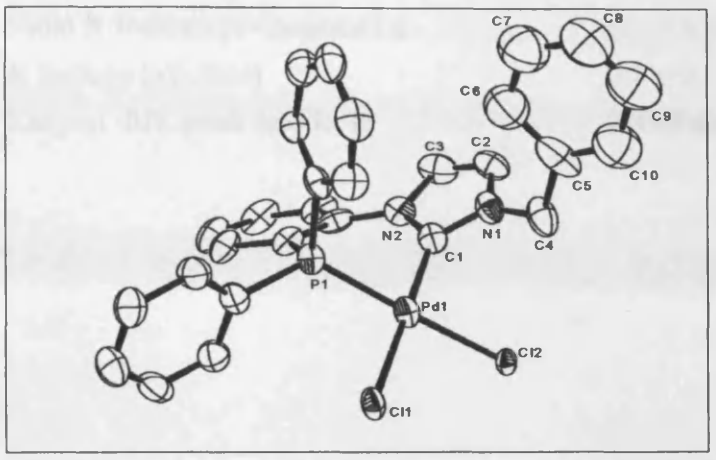
Table 9: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for imidazolium salt **36**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 39(3) | 30(3) | 28(3) | 1(2) | 8(2) | -3(2) |
| C(2) | 72(5) | 32(3) | 40(3) | 5(3) | 23(3) | 10(3) |
| C(3) | 64(4) | 32(3) | 40(3) | 5(3) | 23(3) | 6(3) |
| C(4) | 39(3) | 34(3) | 44(3) | 1(3) | 18(3) | -3(3) |
| C(5) | 41(4) | 49(4) | 55(4) | -7(3) | 12(3) | -2(3) |
| C(6) | 36(4) | 62(5) | 85(6) | -5(4) | 27(4) | -3(3) |
| C(7) | 59(5) | 61(5) | 70(5) | -3(4) | 42(4) | -2(4) |
| C(8) | 58(4) | 43(4) | 45(4) | 1(3) | 24(3) | -3(3) |
| C(9) | 42(4) | 32(3) | 39(3) | 2(3) | 16(3) | -3(3) |
| C(10) | 51(4) | 28(3) | 32(3) | 4(2) | 20(3) | 4(3) |
| C(11) | 55(4) | 30(3) | 35(3) | 3(2) | 18(3) | 2(3) |
| C(12) | 70(5) | 27(3) | 45(4) | -2(3) | 28(3) | -3(3) |
| C(13) | 62(5) | 35(3) | 57(4) | 5(3) | 32(4) | 10(3) |
| C(14) | 51(4) | 39(4) | 60(4) | 7(3) | 22(3) | 6(3) |
| C(15) | 48(4) | 34(3) | 38(3) | 7(3) | 14(3) | 1(3) |
| C(16) | 57(4) | 32(3) | 36(3) | -2(3) | 16(3) | -5(3) |
| C(17) | 68(5) | 51(4) | 49(4) | 10(3) | 23(4) | -12(4) |
| C(18) | 75(5) | 57(5) | 42(4) | -1(3) | 12(4) | -6(4) |
| C(19) | 45(4) | 43(4) | 39(3) | -1(3) | 12(3) | 0(3) |
| C(20) | 64(5) | 62(5) | 48(4) | -6(4) | 13(4) | -19(4) |
| C(21) | 146(10) | 58(5) | 44(4) | 6(4) | 6(5) | -4(6) |
| C(22) | 72(7) | 83(7) | 133(10) | 3(7) | 44(7) | 5(5) |
| N(1) | 48(3) | 28(2) | 29(2) | 1(2) | 12(2) | 1(2) |
| N(2) | 43(3) | 31(3) | 33(3) | 2(2) | 14(2) | 2(2) |
| O(1) | 39(2) | 43(2) | 36(2) | 0(2) | 10(2) | 4(2) |
| Cl(3) | 97(2) | 95(2) | 146(3) | -20(2) | 13(2) | 27(2) |
| Cl(1) | 66(1) | 35(1) | 42(1) | 2(1) | 5(1) | 3(1) |
| Cl(2) | 137(2) | 130(2) | 188(2) | -8(2) | 118(2) | -2(2) |
| O(2) | 72(4) | 63(3) | 148(5) | 39(4) | 12(4) | 2(3) |

Table 10: Hydrogen coordinates (x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for imidazolium salt **36**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 4211 | -75 | 8061 | 39 |
| H(2A) | 3766 | 2420 | 7323 | 56 |
| H(2B) | 2595 | 1995 | 6707 | 56 |
| H(3A) | 3674 | 1173 | 5941 | 52 |
| H(3B) | 4801 | 1775 | 6424 | 52 |
| H(5) | 1102 | 1491 | 7664 | 58 |
| H(6) | 183 | 1754 | 8817 | 71 |
| H(7) | 1271 | 1698 | 10205 | 71 |
| H(8) | 3287 | 1385 | 10494 | 56 |
| H(12) | 5509 | -1955 | 5571 | 54 |
| H(13) | 7505 | -1745 | 6060 | 58 |
| H(14) | 8220 | -557 | 7036 | 58 |
| H(16) | 3217 | -515 | 6140 | 49 |
| H(17A) | 3770 | -2479 | 6141 | 81 |
| H(17B) | 2461 | -2085 | 6076 | 81 |
| H(17C) | 3453 | -1913 | 6929 | 81 |
| H(18A) | 3570 | -491 | 4711 | 87 |
| H(18B) | 2431 | -1103 | 4765 | 87 |
| H(18C) | 3649 | -1614 | 4730 | 87 |
| H(19) | 6429 | 1245 | 7707 | 50 |
| H(20A) | 8731 | 1005 | 7399 | 87 |
| H(20B) | 8229 | 1942 | 7745 | 87 |
| H(20C) | 7706 | 1589 | 6787 | 87 |
| H(21A) | 8192 | 6 | 8615 | 127 |
| H(21B) | 6909 | 160 | 8810 | 127 |
| H(21C) | 7857 | 993 | 8981 | 127 |
| H(22A) | 1205 | -503 | 8880 | 111 |
| H(22B) | 2198 | -1227 | 8735 | 111 |
| H(1A) | 4903 | 1145 | 9879 | 59 |
| H(1O2) | -327 | -3779 | 9444 | 115 |
| H(2O2) | -1440 | -4123 | 9415 | 115 |

Table 11: Crystal data and structure refinement for complex **2**.




| | |
|---|---|
| Identification code | Complex **2** |
| Empirical formula | $C_{28}$ $H_{27}$ $Cl_2$ $N_2$ $O_2$ P Pd |
| Formula weight | 631.79 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P -1 |
| Unit cell dimensions | a = 10.0640(3) Å α= 91.8890(10)°. |
| | b = 10.4500(3) Å β= 101.8580(10)°. |
| | c = 13.8930(6) Å γ = 109.088(2)°. |
| Volume | 1343.36(8) $Å^3$ |
| Z | 2 |
| Density (calculated) | 1.562 $Mg/m^3$ |
| Absorption coefficient | 0.978 $mm^{-1}$ |
| F(000) | 640 |
| Crystal size | 0.18 x 0.15 x 0.05 $mm^3$ |
| Theta range for data collection | 3.51 to 26.37°. |
| Index ranges | -12<=h<=12, -13<=k<=13, -16<=l<=17 |
| Reflections collected | 19759 |
| Independent reflections | 5478 [R(int) = 0.1896] |
| Completeness to theta = 26.37° | 99.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9527 and 0.8436 |
| Refinement method | Full-matrix least-squares on $F^2$ |

| | |
|---|---|
| Data / restraints / parameters | 5478 / 42 / 325 |
| Goodness-of-fit on $F^2$ | 1.017 |
| Final R indices [I>2sigma(I)] | R1 = 0.1021, wR2 = 0.2478 |
| R indices (all data) | R1 = 0.1428, wR2 = 0.2767 |
| Largest diff. peak and hole | 2.113 and -2.330 e.$Å^{-3}$ |

Table 12: Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for complex **2**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Pd(1) | -3385(1) | 3991(1) | 2729(1) | 32(1) |
| Cl(1) | -5462(2) | 2366(3) | 1708(2) | 39(1) |
| Cl(2) | -4317(2) | 3470(2) | 4197(2) | 26(1) |
| P(1) | -2132(3) | 4462(3) | 1575(2) | 32(1) |
| N(1) | -1648(11) | 6462(9) | 4148(6) | 42(2) |
| N(2) | -254(9) | 5528(9) | 3662(6) | 37(2) |
| C(1) | -1681(12) | 5417(10) | 3535(8) | 37(2) |
| C(2) | -282(13) | 7187(12) | 4670(9) | 49(3) |
| C(3) | 582(14) | 6603(13) | 4390(9) | 54(3) |
| C(4) | -2895(16) | 6837(13) | 4206(9) | 56(3) |
| C(5) | -2775(15) | 8274(14) | 3907(12) | 70(4) |
| C(6) | -1780(20) | 8919(18) | 3306(13) | 88(5) |
| C(7) | -1760(20) | 10240(20) | 3026(15) | 98(6) |
| C(8) | -2640(20) | 10830(19) | 3297(14) | 87(5) |
| C(9) | -3400(20) | 10311(19) | 3879(16) | 96(5) |
| C(10) | -3530(20) | 8979(18) | 4150(15) | 90(5) |
| C(11) | 312(11) | 4772(11) | 3081(8) | 40(3) |
| C(12) | 1596(12) | 4605(12) | 3486(10) | 48(3) |
| C(13) | 2199(13) | 3908(14) | 2922(10) | 55(4) |
| C(14) | 1503(14) | 3397(14) | 1946(10) | 56(3) |
| C(15) | 214(11) | 3579(12) | 1531(9) | 43(3) |
| C(16) | -425(10) | 4242(11) | 2083(8) | 35(2) |
| C(17) | -1697(11) | 6207(10) | 1268(7) | 35(2) |
| C(18) | -2871(13) | 6696(12) | 1022(9) | 47(3) |
| C(19) | -2609(15) | 7991(13) | 740(9) | 54(3) |
| C(20) | -1258(16) | 8815(13) | 742(9) | 54(3) |
| C(21) | -93(15) | 8354(13) | 1031(9) | 54(3) |
| C(22) | -338(11) | 7036(10) | 1257(8) | 36(2) |
| C(23) | -2832(11) | 3399(11) | 395(8) | 38(2) |
| C(24) | -3061(12) | 3942(12) | -493(8) | 44(3) |
| C(25) | -3592(14) | 3075(14) | -1389(9) | 56(3) |

| | | | | |
|---|---|---|---|---|
| C(26) | -3930(15) | 1689(15) | -1384(10) | 61(4) |
| C(27) | -3662(13) | 1172(12) | -473(11) | 54(3) |
| C(28) | -3166(13) | 1972(12) | 389(9) | 46(3) |
| O(1) | 3001(13) | 8667(13) | 3485(9) | 100(4) |
| O(2) | 1373(16) | 10392(13) | 3426(10) | 110(4) |

Table 13: Bond lengths [Å] and angles [°] for complex **2**.

| | | | |
|---|---|---|---|
| Pd(1)-C(1) | 1.961(11) | C(11)-C(16) | 1.428(15) |
| Pd(1)-P(1) | 2.210(3) | C(12)-C(13) | 1.400(18) |
| Pd(1)-Cl(1) | 2.359(2) | C(12)-H(12) | 0.9500 |
| Pd(1)-Cl(2) | 2.421(2) | C(13)-C(14) | 1.389(19) |
| P(1)-C(16) | 1.809(10) | C(13)-H(13) | 0.9500 |
| P(1)-C(17) | 1.818(11) | C(14)-C(15) | 1.383(15) |
| P(1)-C(23) | 1.819(11) | C(14)-H(14) | 0.9500 |
| N(1)-C(1) | 1.350(13) | C(15)-C(16) | 1.393(15) |
| N(1)-C(2) | 1.364(15) | C(15)-H(15) | 0.9500 |
| N(1)-C(4) | 1.448(16) | C(17)-C(22) | 1.362(15) |
| N(2)-C(1) | 1.376(13) | C(17)-C(18) | 1.419(14) |
| N(2)-C(3) | 1.396(14) | C(18)-C(19) | 1.378(17) |
| N(2)-C(11) | 1.429(15) | C(18)-H(18) | 0.9500 |
| C(2)-C(3) | 1.322(18) | C(19)-C(20) | 1.350(19) |
| C(2)-H(2) | 0.9500 | C(19)-H(19) | 0.9500 |
| C(3)-H(3) | 0.9500 | C(20)-C(21) | 1.399(18) |
| C(4)-C(5) | 1.545(18) | C(20)-H(20) | 0.9500 |
| C(4)-H(4A) | 0.9900 | C(21)-C(22) | 1.377(16) |
| C(4)-H(4B) | 0.9900 | C(21)-H(21) | 0.9500 |
| C(5)-C(10) | 1.30(2) | C(22)-H(22) | 0.9500 |
| C(5)-C(6) | 1.45(2) | C(23)-C(24) | 1.383(15) |
| C(6)-C(7) | 1.44(2) | C(23)-C(28) | 1.416(15) |
| C(6)-H(6) | 0.9500 | C(24)-C(25) | 1.410(16) |
| C(7)-C(8) | 1.33(3) | C(24)-H(24) | 0.9500 |
| C(7)-H(7) | 0.9500 | C(25)-C(26) | 1.376(19) |
| C(8)-C(9) | 1.25(3) | C(25)-H(25) | 0.9500 |
| C(8)-H(8) | 0.9500 | C(26)-C(27) | 1.402(19) |
| C(9)-C(10) | 1.43(2) | C(26)-H(26) | 0.9500 |
| C(9)-H(9) | 0.9500 | C(27)-C(28) | 1.341(17) |
| C(10)-H(10) | 0.9500 | C(27)-H(27) | 0.9500 |
| C(11)-C(12) | 1.368(14) | C(28)-H(28) | 0.9500 |

| | | | |
|---|---|---|---|
| C(1)-Pd(1)-P(1) | 82.8(3) | C(7)-C(6)-C(5) | 117.1(17) |
| C(1)-Pd(1)-Cl(1) | 176.9(3) | C(7)-C(6)-H(6) | 121.4 |
| P(1)-Pd(1)-Cl(1) | 96.01(10) | C(5)-C(6)-H(6) | 121.4 |
| C(1)-Pd(1)-Cl(2) | 89.5(3) | C(8)-C(7)-C(6) | 121(2) |
| P(1)-Pd(1)-Cl(2) | 168.71(8) | C(8)-C(7)-H(7) | 119.4 |
| Cl(1)-Pd(1)-Cl(2) | 92.12(8) | C(6)-C(7)-H(7) | 119.4 |
| C(16)-P(1)-C(17) | 106.2(5) | C(9)-C(8)-C(7) | 120.7(19) |
| C(16)-P(1)-C(23) | 104.9(5) | C(9)-C(8)-H(8) | 119.7 |
| C(17)-P(1)-C(23) | 105.6(5) | C(7)-C(8)-H(8) | 119.7 |
| C(16)-P(1)-Pd(1) | 106.0(3) | C(8)-C(9)-C(10) | 121(2) |
| C(17)-P(1)-Pd(1) | 114.5(4) | C(8)-C(9)-H(9) | 119.6 |
| C(23)-P(1)-Pd(1) | 118.6(4) | C(10)-C(9)-H(9) | 119.6 |
| C(1)-N(1)-C(2) | 112.2(10) | C(5)-C(10)-C(9) | 124(2) |
| C(1)-N(1)-C(4) | 124.4(10) | C(5)-C(10)-H(10) | 117.9 |
| C(2)-N(1)-C(4) | 123.3(10) | C(9)-C(10)-H(10) | 117.9 |
| C(1)-N(2)-C(3) | 108.8(10) | C(12)-C(11)-C(16) | 120.6(11) |
| C(1)-N(2)-C(11) | 126.1(9) | C(12)-C(11)-N(2) | 118.9(11) |
| C(3)-N(2)-C(11) | 124.8(10) | C(16)-C(11)-N(2) | 120.5(9) |
| N(1)-C(1)-N(2) | 104.1(9) | C(11)-C(12)-C(13) | 120.1(12) |
| N(1)-C(1)-Pd(1) | 127.7(8) | C(11)-C(12)-H(12) | 120.0 |
| N(2)-C(1)-Pd(1) | 128.1(8) | C(13)-C(12)-H(12) | 120.0 |
| C(3)-C(2)-N(1) | 106.6(11) | C(14)-C(13)-C(12) | 120.1(10) |
| C(3)-C(2)-H(2) | 126.7 | C(14)-C(13)-H(13) | 120.0 |
| N(1)-C(2)-H(2) | 126.7 | C(12)-C(13)-H(13) | 120.0 |
| C(2)-C(3)-N(2) | 108.2(11) | C(15)-C(14)-C(13) | 120.0(12) |
| C(2)-C(3)-H(3) | 125.9 | C(15)-C(14)-H(14) | 120.0 |
| N(2)-C(3)-H(3) | 125.9 | C(13)-C(14)-H(14) | 120.0 |
| N(1)-C(4)-C(5) | 113.6(12) | C(14)-C(15)-C(16) | 121.1(12) |
| N(1)-C(4)-H(4A) | 108.8 | C(14)-C(15)-H(15) | 119.5 |
| C(5)-C(4)-H(4A) | 108.8 | C(16)-C(15)-H(15) | 119.5 |
| N(1)-C(4)-H(4B) | 108.8 | C(15)-C(16)-C(11) | 118.2(9) |
| C(5)-C(4)-H(4B) | 108.8 | C(15)-C(16)-P(1) | 122.3(8) |
| H(4A)-C(4)-H(4B) | 107.7 | C(11)-C(16)-P(1) | 119.5(8) |
| C(10)-C(5)-C(6) | 115.4(16) | C(22)-C(17)-C(18) | 119.8(10) |
| C(10)-C(5)-C(4) | 124.5(17) | C(22)-C(17)-P(1) | 123.8(8) |
| C(6)-C(5)-C(4) | 120.1(13) | C(18)-C(17)-P(1) | 116.4(9) |

| | | | |
|---|---|---|---|
| C(19)-C(18)-C(17) | 118.6(11) | C(28)-C(23)-P(1) | 118.9(9) |
| C(19)-C(18)-H(18) | 120.7 | C(23)-C(24)-C(25) | 119.8(11) |
| C(17)-C(18)-H(18) | 120.7 | C(23)-C(24)-H(24) | 120.1 |
| C(20)-C(19)-C(18) | 121.4(11) | C(25)-C(24)-H(24) | 120.1 |
| C(20)-C(19)-H(19) | 119.3 | C(26)-C(25)-C(24) | 120.5(12) |
| C(18)-C(19)-H(19) | 119.3 | C(26)-C(25)-H(25) | 119.7 |
| C(19)-C(20)-C(21) | 119.9(12) | C(24)-C(25)-H(25) | 119.7 |
| C(19)-C(20)-H(20) | 120.1 | C(25)-C(26)-C(27) | 118.3(12) |
| C(21)-C(20)-H(20) | 120.1 | C(25)-C(26)-H(26) | 120.8 |
| C(22)-C(21)-C(20) | 119.8(12) | C(27)-C(26)-H(26) | 120.8 |
| C(22)-C(21)-H(21) | 120.1 | C(28)-C(27)-C(26) | 122.2(12) |
| C(20)-C(21)-H(21) | 120.1 | C(28)-C(27)-H(27) | 118.9 |
| C(17)-C(22)-C(21) | 120.4(10) | C(26)-C(27)-H(27) | 118.9 |
| C(17)-C(22)-H(22) | 119.8 | C(27)-C(28)-C(23) | 119.9(12) |
| C(21)-C(22)-H(22) | 119.8 | C(27)-C(28)-H(28) | 120.0 |
| C(24)-C(23)-C(28) | 119.1(10) | C(23)-C(28)-H(28) | 120.0 |
| C(24)-C(23)-P(1) | 122.0(8) | | |

Table 14: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for complex **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

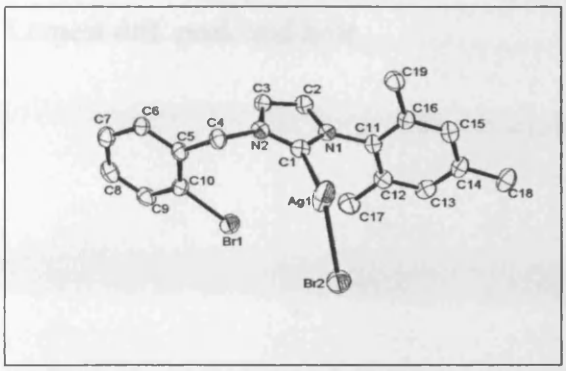
| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Pd(1) | 32(1) | 40(1) | 27(1) | -2(1) | 1(1) | 20(1) |
| Cl(1) | 22(1) | 56(2) | 33(1) | -20(1) | 2(1) | 12(1) |
| Cl(2) | 21(1) | 36(1) | 23(1) | -4(1) | 3(1) | 13(1) |
| P(1) | 33(1) | 41(1) | 28(1) | 4(1) | 3(1) | 22(1) |
| N(1) | 64(6) | 42(5) | 25(5) | 5(4) | 9(4) | 26(5) |
| N(2) | 37(5) | 43(5) | 31(5) | 7(4) | -2(4) | 17(4) |
| C(1) | 55(7) | 37(6) | 28(6) | 12(5) | 9(5) | 26(5) |
| C(2) | 53(7) | 40(6) | 43(7) | -3(5) | -4(5) | 12(6) |
| C(3) | 52(7) | 51(7) | 42(7) | 1(6) | -13(6) | 8(6) |
| C(4) | 94(10) | 55(7) | 34(7) | 8(6) | 18(6) | 44(7) |
| C(5) | 60(8) | 50(7) | 87(11) | -23(7) | -17(8) | 27(7) |
| C(6) | 112(8) | 78(7) | 80(8) | 10(6) | 27(6) | 37(6) |
| C(7) | 121(9) | 86(8) | 91(8) | 12(6) | 22(7) | 39(7) |
| C(8) | 96(8) | 83(7) | 84(8) | 9(6) | 2(6) | 43(6) |
| C(9) | 102(8) | 81(8) | 108(9) | 14(6) | 10(7) | 46(6) |
| C(10) | 94(8) | 80(7) | 103(9) | 9(6) | 19(6) | 39(6) |
| C(11) | 30(5) | 43(6) | 46(7) | 25(5) | 7(5) | 10(5) |
| C(12) | 42(6) | 58(7) | 54(8) | 28(6) | 8(5) | 28(6) |
| C(13) | 39(6) | 86(9) | 58(8) | 41(7) | 12(6) | 39(7) |
| C(14) | 61(8) | 73(9) | 63(9) | 34(7) | 36(7) | 44(7) |
| C(15) | 38(6) | 62(7) | 44(7) | 20(6) | 18(5) | 31(5) |
| C(16) | 30(5) | 46(6) | 35(6) | 16(5) | 7(4) | 19(5) |
| C(17) | 44(6) | 40(6) | 23(5) | -4(4) | -1(4) | 23(5) |
| C(18) | 44(6) | 55(7) | 47(7) | 7(6) | 7(5) | 26(6) |
| C(19) | 66(9) | 63(8) | 48(8) | 12(6) | 10(6) | 43(7) |
| C(20) | 90(10) | 54(7) | 40(7) | 15(6) | 27(7) | 46(7) |
| C(21) | 71(9) | 57(7) | 42(7) | 9(6) | 19(6) | 30(7) |
| C(22) | 43(6) | 41(6) | 31(6) | 5(5) | 7(4) | 24(5) |
| C(23) | 30(5) | 44(6) | 38(6) | -7(5) | 3(4) | 14(5) |
| C(24) | 47(6) | 45(6) | 34(6) | 2(5) | 4(5) | 11(5) |
| C(25) | 69(9) | 66(9) | 30(7) | 1(6) | 11(6) | 19(7) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(26) | 68(9) | 68(9) | 36(7) | -13(6) | 5(6) | 13(7) |
| C(27) | 43(7) | 40(6) | 76(10) | -17(6) | 18(6) | 9(5) |
| C(28) | 53(7) | 43(6) | 46(7) | 5(5) | 17(5) | 18(5) |
| O(1) | 91(5) | 115(5) | 83(5) | 17(4) | 44(4) | 8(4) |
| O(2) | 131(6) | 93(5) | 94(6) | 4(4) | 18(4) | 29(4) |

Table 15: Hydrogen coordinates (x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for complex **2**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | -5 | 7960 | 5142 | 59 |
| H(3) | 1596 | 6869 | 4641 | 65 |
| H(4A) | -3029 | 6794 | 4893 | 67 |
| H(4B) | -3764 | 6162 | 3770 | 67 |
| H(6) | -1171 | 8490 | 3103 | 106 |
| H(7) | -1110 | 10703 | 2641 | 118 |
| H(8) | -2679 | 11652 | 3044 | 104 |
| H(9) | -3904 | 10810 | 4146 | 115 |
| H(10) | -4211 | 8581 | 4532 | 108 |
| H(12) | 2079 | 4964 | 4150 | 58 |
| H(13) | 3085 | 3784 | 3206 | 67 |
| H(14) | 1912 | 2924 | 1564 | 67 |
| H(15) | -244 | 3245 | 859 | 52 |
| H(18) | -3819 | 6142 | 1051 | 56 |
| H(19) | -3394 | 8310 | 540 | 65 |
| H(20) | -1099 | 9706 | 548 | 65 |
| H(21) | 865 | 8949 | 1070 | 64 |
| H(22) | 445 | 6703 | 1406 | 43 |
| H(24) | -2863 | 4894 | -501 | 53 |
| H(25) | -3716 | 3451 | -2000 | 67 |
| H(26) | -4335 | 1097 | -1983 | 74 |
| H(27) | -3838 | 222 | -466 | 65 |
| H(28) | -3038 | 1583 | 994 | 5 |

Table 16: Crystal data and structure refinement for the below complex .




| | | |
|---|---|---|
| Empirical formula | $C_{38}\ H_{38}\ Ag_2\ Br_4\ N_4$ | |
| Formula weight | 1086.10 | |
| Temperature | 150(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P 21/n | |
| Unit cell dimensions | a = 11.4910(3) Å | α= 90°. |
| | b = 9.8700(3) Å | β= 93.494(2)°. |
| | c = 16.6780(4) Å | γ = 90°. |
| Volume | 1888.04(9) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.910 $Mg/m^3$ | |
| Absorption coefficient | 5.303 $mm^{-1}$ | |
| F(000) | 1056 | |
| Crystal size | 0.28 x 0.25 x 0.10 $mm^3$ | |
| Theta range for data collection | 3.55 to 26.37°. | |
| Index ranges | -14<=h<=14, -12<=k<=12, -20<=l<=20 | |
| Reflections collected | 26737 | |
| Independent reflections | 3852 [R(int) = 0.0969] | |
| Completeness to theta = 26.37° | 99.6 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.6191 and 0.3183 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3852 / 0 / 220 | |
| Goodness-of-fit on $F^2$ | 1.103 | |

| | |
|---|---|
| Final R indices [I>2sigma(I)] | R1 = 0.0561, wR2 = 0.1371 |
| R indices (all data) | R1 = 0.0645, wR2 = 0.1421 |
| Largest diff. peak and hole | 1.204 and -2.026 e.Å$^{-3}$ |

Table 17: Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for complex . U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 7322(5) | 3445(5) | 1398(3) | 30(1) |
| C(2) | 7965(5) | 2194(6) | 2475(3) | 33(1) |
| C(3) | 8882(5) | 2883(6) | 2215(3) | 31(1) |
| C(4) | 9195(5) | 4509(5) | 1084(3) | 30(1) |
| C(5) | 10268(5) | 3822(5) | 798(3) | 29(1) |
| C(6) | 11360(5) | 4345(5) | 1038(3) | 32(1) |
| C(7) | 12392(5) | 3789(6) | 775(4) | 37(1) |
| C(8) | 12331(5) | 2683(6) | 270(4) | 39(1) |
| C(9) | 11257(5) | 2132(6) | 24(3) | 37(1) |
| C(10) | 10247(5) | 2709(5) | 282(3) | 32(1) |
| C(11) | 5833(5) | 2058(5) | 2011(3) | 28(1) |
| C(12) | 5467(5) | 923(5) | 1548(3) | 33(1) |
| C(13) | 4315(5) | 511(6) | 1589(4) | 36(1) |
| C(14) | 3536(5) | 1181(6) | 2060(3) | 33(1) |
| C(15) | 3941(5) | 2285(5) | 2506(3) | 34(1) |
| C(16) | 5083(5) | 2755(5) | 2487(3) | 29(1) |
| C(17) | 6269(6) | 221(6) | 1015(4) | 46(2) |
| C(18) | 2286(5) | 749(6) | 2071(4) | 43(2) |
| C(19) | 5477(5) | 4030(6) | 2931(4) | 37(1) |
| N(1) | 7014(4) | 2551(4) | 1964(3) | 27(1) |
| N(2) | 8471(4) | 3627(4) | 1562(3) | 28(1) |
| Br(1) | 8791(1) | 1969(1) | -115(1) | 48(1) |
| Br(2) | 5175(1) | 3508(1) | -855(1) | 49(1) |
| Ag(1) | 6136(1) | 4215(1) | 511(1) | 71(1) |

Table 18: Bond lengths [Å] and angles [°] for complex .

| | | | |
|---|---|---|---|
| C(1)-N(2) | 1.344(7) | C(11)-C(12) | 1.410(8) |
| C(1)-N(1) | 1.354(7) | C(11)-N(1) | 1.448(7) |
| C(1)-Ag(1) | 2.092(5) | C(12)-C(13) | 1.391(8) |
| C(2)-C(3) | 1.348(8) | C(12)-C(17) | 1.490(8) |
| C(2)-N(1) | 1.390(7) | C(13)-C(14) | 1.393(9) |
| C(2)-H(2) | 0.9500 | C(13)-H(13) | 0.9500 |
| C(3)-N(2) | 1.374(7) | C(14)-C(15) | 1.384(8) |
| C(3)-H(3) | 0.9500 | C(14)-C(18) | 1.500(8) |
| C(4)-N(2) | 1.472(6) | C(15)-C(16) | 1.394(8) |
| C(4)-C(5) | 1.510(7) | C(15)-H(15) | 0.9500 |
| C(4)-H(4A) | 0.9900 | C(16)-C(19) | 1.515(8) |
| C(4)-H(4B) | 0.9900 | C(17)-H(17A) | 0.9800 |
| C(5)-C(6) | 1.393(8) | C(17)-H(17B) | 0.9800 |
| C(5)-C(10) | 1.395(7) | C(17)-H(17C) | 0.9800 |
| C(6)-C(7) | 1.402(8) | C(18)-H(18A) | 0.9800 |
| C(6)-H(6) | 0.9500 | C(18)-H(18B) | 0.9800 |
| C(7)-C(8) | 1.378(9) | C(18)-H(18C) | 0.9800 |
| C(7)-H(7) | 0.9500 | C(19)-H(19A) | 0.9800 |
| C(8)-C(9) | 1.387(9) | C(19)-H(19B) | 0.9800 |
| C(8)-H(8) | 0.9500 | C(19)-H(19C) | 0.9800 |
| C(9)-C(10) | 1.385(8) | Br(2)-Ag(1) | 2.5670(10) |
| C(9)-H(9) | 0.9500 | Br(2)-Ag(1)#1 | 2.7850(11) |
| C(10)-Br(1) | 1.907(5) | Ag(1)-Br(2)#1 | 2.7850(11) |
| C(11)-C(16) | 1.389(8) | | |

| | | | |
|---|---|---|---|
| N(2)-C(1)-N(1) | 103.9(4) | C(13)-C(12)-C(11) | 117.3(5) |
| N(2)-C(1)-Ag(1) | 133.2(4) | C(13)-C(12)-C(17) | 121.2(5) |
| N(1)-C(1)-Ag(1) | 122.9(4) | C(11)-C(12)-C(17) | 121.5(5) |
| C(3)-C(2)-N(1) | 106.0(5) | C(12)-C(13)-C(14) | 122.3(5) |
| C(3)-C(2)-H(2) | 127.0 | C(12)-C(13)-H(13) | 118.8 |
| N(1)-C(2)-H(2) | 127.0 | C(14)-C(13)-H(13) | 118.8 |
| C(2)-C(3)-N(2) | 106.6(5) | C(15)-C(14)-C(13) | 118.1(5) |
| C(2)-C(3)-H(3) | 126.7 | C(15)-C(14)-C(18) | 120.5(6) |
| N(2)-C(3)-H(3) | 126.7 | C(13)-C(14)-C(18) | 121.4(5) |
| N(2)-C(4)-C(5) | 113.9(4) | C(14)-C(15)-C(16) | 122.4(5) |
| N(2)-C(4)-H(4A) | 108.8 | C(14)-C(15)-H(15) | 118.8 |
| C(5)-C(4)-H(4A) | 108.8 | C(16)-C(15)-H(15) | 118.8 |
| N(2)-C(4)-H(4B) | 108.8 | C(11)-C(16)-C(15) | 117.8(5) |
| C(5)-C(4)-H(4B) | 108.8 | C(11)-C(16)-C(19) | 120.9(5) |
| H(4A)-C(4)-H(4B) | 107.7 | C(15)-C(16)-C(19) | 121.2(5) |
| C(6)-C(5)-C(10) | 116.8(5) | C(12)-C(17)-H(17A) | 109.5 |
| C(6)-C(5)-C(4) | 118.8(5) | C(12)-C(17)-H(17B) | 109.5 |
| C(10)-C(5)-C(4) | 124.4(5) | H(17A)-C(17)-H(17B) | 109.5 |
| C(5)-C(6)-C(7) | 122.0(5) | C(12)-C(17)-H(17C) | 109.5 |
| C(5)-C(6)-H(6) | 119.0 | H(17A)-C(17)-H(17C) | 109.5 |
| C(7)-C(6)-H(6) | 119.0 | H(17B)-C(17)-H(17C) | 109.5 |
| C(8)-C(7)-C(6) | 119.3(6) | C(14)-C(18)-H(18A) | 109.5 |
| C(8)-C(7)-H(7) | 120.4 | C(14)-C(18)-H(18B) | 109.5 |
| C(6)-C(7)-H(7) | 120.4 | H(18A)-C(18)-H(18B) | 109.5 |
| C(7)-C(8)-C(9) | 120.2(5) | C(14)-C(18)-H(18C) | 109.5 |
| C(7)-C(8)-H(8) | 119.9 | H(18A)-C(18)-H(18C) | 109.5 |
| C(9)-C(8)-H(8) | 119.9 | H(18B)-C(18)-H(18C) | 109.5 |
| C(10)-C(9)-C(8) | 119.6(5) | C(16)-C(19)-H(19A) | 109.5 |
| C(10)-C(9)-H(9) | 120.2 | C(16)-C(19)-H(19B) | 109.5 |
| C(8)-C(9)-H(9) | 120.2 | H(19A)-C(19)-H(19B) | 109.5 |
| C(9)-C(10)-C(5) | 122.2(5) | C(16)-C(19)-H(19C) | 109.5 |
| C(9)-C(10)-Br(1) | 118.0(4) | H(19A)-C(19)-H(19C) | 109.5 |
| C(5)-C(10)-Br(1) | 119.9(4) | H(19B)-C(19)-H(19C) | 109.5 |
| C(16)-C(11)-C(12) | 122.1(5) | C(1)-N(1)-C(2) | 111.3(4) |
| C(16)-C(11)-N(1) | 118.7(5) | C(1)-N(1)-C(11) | 122.9(4) |
| C(12)-C(11)-N(1) | 119.1(5) | C(2)-N(1)-C(11) | 125.8(4) |

| | | | |
|---|---|---|---|
| C(1)-N(2)-C(3) | 112.1(4) | C(1)-Ag(1)-Br(2) | 139.05(15) |
| C(1)-N(2)-C(4) | 123.3(4) | C(1)-Ag(1)-Br(2)#1 | 118.97(15) |
| C(3)-N(2)-C(4) | 124.5(5) | Br(2)-Ag(1)-Br(2)#1 | 101.15(2) |
| Ag(1)-Br(2)-Ag(1)#1 | 78.85(2) | | |

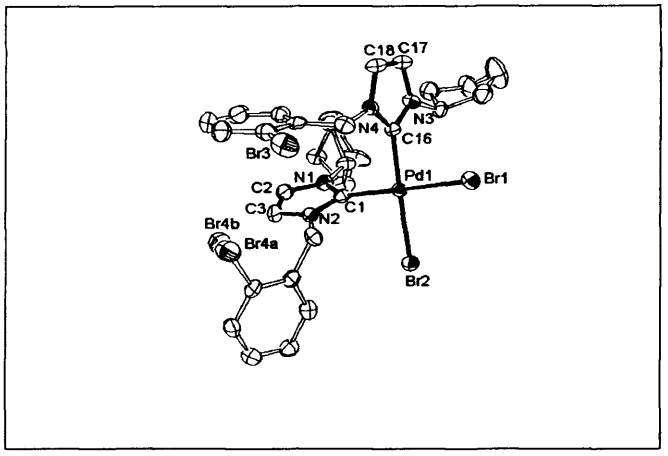
Table 19: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for complex. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 32(3) | 25(2) | 31(3) | 1(2) | 1(2) | 5(2) |
| C(2) | 33(3) | 32(3) | 34(3) | 6(2) | 4(2) | 2(2) |
| C(3) | 27(3) | 34(3) | 31(3) | -1(2) | 1(2) | 1(2) |
| C(4) | 31(3) | 23(2) | 37(3) | 2(2) | 8(2) | -4(2) |
| C(5) | 32(3) | 25(2) | 30(3) | 3(2) | 8(2) | -2(2) |
| C(6) | 32(3) | 30(3) | 33(3) | 2(2) | 5(2) | -7(2) |
| C(7) | 32(3) | 39(3) | 40(3) | 10(2) | 2(2) | -3(2) |
| C(8) | 39(3) | 38(3) | 43(3) | 6(3) | 15(3) | 9(3) |
| C(9) | 46(3) | 31(3) | 36(3) | -5(2) | 12(3) | -2(2) |
| C(10) | 34(3) | 29(3) | 33(3) | -1(2) | 5(2) | -10(2) |
| C(11) | 29(3) | 24(2) | 32(3) | 6(2) | 4(2) | 2(2) |
| C(12) | 39(3) | 24(2) | 35(3) | 3(2) | 6(2) | -3(2) |
| C(13) | 43(3) | 25(3) | 40(3) | 5(2) | -4(3) | -7(2) |
| C(14) | 29(3) | 30(3) | 41(3) | 13(2) | -2(2) | -4(2) |
| C(15) | 34(3) | 28(3) | 40(3) | 11(2) | 7(2) | 4(2) |
| C(16) | 29(3) | 25(3) | 32(3) | 7(2) | 2(2) | -1(2) |
| C(17) | 52(4) | 35(3) | 52(4) | -9(3) | 13(3) | -4(3) |
| C(18) | 36(3) | 37(3) | 56(4) | 13(3) | -2(3) | -10(3) |
| C(19) | 41(3) | 32(3) | 40(3) | -5(2) | 11(3) | -4(2) |
| N(1) | 29(2) | 24(2) | 28(2) | 2(2) | 3(2) | 1(2) |
| N(2) | 34(2) | 21(2) | 30(2) | -1(2) | 6(2) | 1(2) |
| Br(1) | 45(1) | 50(1) | 48(1) | -20(1) | 9(1) | -18(1) |
| Br(2) | 51(1) | 42(1) | 54(1) | -16(1) | 7(1) | -11(1) |
| Ag(1) | 38(1) | 105(1) | 69(1) | 56(1) | -12(1) | -18(1) |

Table 20: Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for complex.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 7968 | 1588 | 2917 | 39 |
| H(3) | 9662 | 2859 | 2440 | 37 |
| H(4A) | 9440 | 5307 | 1412 | 36 |
| H(4B) | 8716 | 4840 | 611 | 36 |
| H(6) | 11406 | 5101 | 1391 | 38 |
| H(7) | 13126 | 4170 | 943 | 44 |
| H(8) | 13026 | 2298 | 89 | 47 |
| H(9) | 11216 | 1363 | -320 | 45 |
| H(13) | 4049 | -256 | 1286 | 44 |
| H(15) | 3422 | 2740 | 2837 | 40 |
| H(17A) | 5987 | -702 | 906 | 69 |
| H(17B) | 7053 | 183 | 1280 | 69 |
| H(17C) | 6295 | 719 | 508 | 69 |
| H(18A) | 1873 | 1353 | 2423 | 65 |
| H(18B) | 2248 | -182 | 2271 | 65 |
| H(18C) | 1920 | 794 | 1525 | 65 |
| H(19A) | 6262 | 3893 | 3181 | 56 |
| H(19B) | 4937 | 4234 | 3347 | 56 |
| H(19C) | 5487 | 4787 | 2552 | 56 |

Table 21: Crystal data and structure refinement for complex .




| | |
|---|---|
| Empirical formula | $C_{31}$ $H_{34}$ $Br_4$ $Cl_2$ $N_4$ O Pd |
| Formula weight | 967.56 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P 21/c |
| Unit cell dimensions | a = 14.0540(3) Å α= 90°. |
| | b = 16.3570(4) Å β= 100.0640(10)°. |
| | c = 16.6910(5) Å γ = 90°. |
| Volume | 3777.91(17) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.701 $Mg/m^3$ |
| Absorption coefficient | 4.890 $mm^{-1}$ |
| F(000) | 1888 |
| Crystal size | 0.18 x 0.15 x 0.08 $mm^3$ |
| Theta range for data collection | 3.51 to 26.37°. |
| Index ranges | -17<=h<=17, -20<=k<=20, -20<=l<=20 |
| Reflections collected | 33311 |
| Independent reflections | 7702 [R(int) = 0.0739] |
| Completeness to theta = 26.37° | 99.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.6957 and 0.4731 |
| Refinement method | Full-matrix least-squares on $F^2$ |

| | |
|---|---|
| Data / restraints / parameters | 7702 / 0 / 407 |
| Goodness-of-fit on $F^2$ | 1.097 |
| Final R indices [I>2sigma(I)] | R1 = 0.0630, wR2 = 0.1456 |
| R indices (all data) | R1 = 0.0934, wR2 = 0.1568 |
| Largest diff. peak and hole | 1.691 and -0.652 e.$Å^{-3}$ |

Table 22: Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for complex . U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 10418(5) | 7308(4) | 3148(4) | 25(2) |
| C(2) | 11107(6) | 8309(5) | 3966(5) | 38(2) |
| C(3) | 11775(6) | 7719(5) | 3956(5) | 36(2) |
| C(4) | 9352(6) | 8481(4) | 3389(4) | 32(2) |
| C(5) | 9410(6) | 9336(4) | 3004(5) | 39(2) |
| C(6) | 8761(9) | 9883(5) | 3427(6) | 68(3) |
| C(7A) | 8234(13) | 9265(10) | 3989(8) | 63(5) |
| C(7B) | 9123(17) | 9636(13) | 4267(12) | 32(5) |
| C(8) | 9003(7) | 8635(5) | 4182(5) | 46(2) |
| C(9) | 11839(5) | 6368(5) | 3269(4) | 32(2) |
| C(10) | 12416(5) | 6005(4) | 4032(4) | 29(2) |
| C(11) | 11945(5) | 5657(4) | 4618(4) | 31(2) |
| C(12) | 12444(6) | 5334(4) | 5337(4) | 35(2) |
| C(13) | 13441(6) | 5355(5) | 5477(5) | 42(2) |
| C(14) | 13935(6) | 5678(5) | 4917(5) | 48(2) |
| C(15) | 13421(6) | 5990(5) | 4192(5) | 44(2) |
| C(16) | 9465(5) | 7483(4) | 1497(4) | 27(2) |
| C(17) | 8940(6) | 8401(4) | 524(4) | 34(2) |
| C(18) | 9851(6) | 8229(4) | 473(5) | 36(2) |
| C(19) | 7732(5) | 7891(4) | 1360(4) | 30(2) |
| C(20) | 7325(6) | 8723(5) | 1569(5) | 43(2) |
| C(21) | 6231(6) | 8599(7) | 1334(6) | 58(3) |
| C(22) | 6121(8) | 8104(7) | 552(8) | 81(4) |
| C(23) | 6983(6) | 7557(5) | 652(6) | 47(2) |
| C(24) | 11133(5) | 7292(5) | 1187(4) | 34(2) |
| C(25) | 11938(5) | 7838(4) | 1606(4) | 31(2) |
| C(26) | 11750(6) | 8554(5) | 2019(4) | 34(2) |
| C(27) | 12498(7) | 9022(5) | 2420(5) | 47(2) |
| C(28) | 13454(7) | 8797(6) | 2424(6) | 56(3) |
| C(29) | 13656(6) | 8092(6) | 2012(6) | 50(2) |

| | | | | |
|---|---|---|---|---|
| C(30) | 12893(6) | 7633(5) | 1621(5) | 38(2) |
| N(1) | 10278(4) | 8043(3) | 3483(4) | 31(1) |
| N(2) | 11340(4) | 7118(3) | 3451(3) | 27(1) |
| N(3) | 8697(4) | 7943(3) | 1163(3) | 29(1) |
| N(4) | 10175(4) | 7665(3) | 1078(3) | 28(1) |
| Br(1) | 8469(1) | 5782(1) | 1334(1) | 39(1) |
| Br(2) | 9403(1) | 5650(1) | 3484(1) | 34(1) |
| Br(3) | 13202(1) | 6668(1) | 1073(1) | 55(1) |
| Br(4A) | 14178(4) | 6261(3) | 3367(3) | 63(1) |
| Br(4B) | 14114(5) | 6620(4) | 3541(4) | 83(2) |
| Pd(1) | 9486(1) | 6644(1) | 2374(1) | 24(1) |
| Cl(1) | 15798(2) | 6170(2) | 2092(2) | 90(1) |
| Cl(2) | 16926(3) | 7162(2) | 3326(2) | 92(1) |
| C(31) | 16835(7) | 6224(6) | 2814(6) | 66(3) |
| O(1) | 6161(17) | 9438(14) | 3721(14) | 47(6) |
| O(2) | 13761(17) | 5422(14) | -309(14) | 48(6) |

Table 23: Bond lengths [Å] and angles [°] for complex .

| | | | |
|---|---|---|---|
| C(1)-N(2) | 1.342(9) | C(12)-C(13) | 1.379(11) |
| C(1)-N(1) | 1.356(9) | C(12)-H(12) | 0.9500 |
| C(1)-Pd(1) | 1.993(7) | C(13)-C(14) | 1.365(11) |
| C(2)-C(3) | 1.348(11) | C(13)-H(13) | 0.9500 |
| C(2)-N(1) | 1.367(10) | C(14)-C(15) | 1.393(11) |
| C(2)-H(2) | 0.9500 | C(14)-H(14) | 0.9500 |
| C(3)-N(2) | 1.367(9) | C(15)-Br(4B) | 1.888(10) |
| C(3)-H(3) | 0.9500 | C(15)-Br(4A) | 1.933(10) |
| C(4)-N(1) | 1.470(10) | C(16)-N(4) | 1.348(9) |
| C(4)-C(8) | 1.512(10) | C(16)-N(3) | 1.353(9) |
| C(4)-C(5) | 1.546(10) | C(16)-Pd(1) | 2.003(6) |
| C(5)-C(6) | 1.535(12) | C(17)-C(18) | 1.329(11) |
| C(5)-H(5A) | 0.9900 | C(17)-N(3) | 1.394(9) |
| C(5)-H(5B) | 0.9900 | C(17)-H(17) | 0.9500 |
| C(6)-C(7B) | 1.46(2) | C(18)-N(4) | 1.384(9) |
| C(6)-C(7A) | 1.643(18) | C(18)-H(18) | 0.9500 |
| C(6)-H(6A) | 0.9900 | C(19)-N(3) | 1.454(9) |
| C(6)-H(6B) | 0.9900 | C(19)-C(23) | 1.538(11) |
| C(7A)-C(8) | 1.487(16) | C(19)-C(20) | 1.539(11) |
| C(7A)-H(7A1) | 0.9900 | C(20)-C(21) | 1.532(12) |
| C(7A)-H(7A2) | 0.9900 | C(20)-H(20A) | 0.9900 |
| C(7B)-C(8) | 1.65(2) | C(20)-H(20B) | 0.9900 |
| C(7B)-H(7B1) | 0.9900 | C(21)-C(22) | 1.521(14) |
| C(7B)-H(7B2) | 0.9900 | C(21)-H(21A) | 0.9900 |
| C(8)-H(8A) | 0.9900 | C(21)-H(21B) | 0.9900 |
| C(8)-H(8B) | 0.9900 | C(22)-C(23) | 1.492(13) |
| C(9)-N(2) | 1.472(9) | C(22)-H(22A) | 0.9900 |
| C(9)-C(10) | 1.507(10) | C(22)-H(22B) | 0.9900 |
| C(9)-H(9A) | 0.9900 | C(23)-H(23A) | 0.9900 |
| C(9)-H(9B) | 0.9900 | C(23)-H(23B) | 0.9900 |
| C(10)-C(15) | 1.391(11) | C(24)-N(4) | 1.461(9) |
| C(10)-C(11) | 1.395(10) | C(24)-C(25) | 1.514(11) |
| C(11)-C(12) | 1.384(10) | C(24)-H(24A) | 0.9900 |
| C(11)-H(11) | 0.9500 | C(24)-H(24B) | 0.9900 |

| | | | |
|---|---|---|---|
| C(25)-C(30) | 1.380(11) | C(29)-H(29) | 0.9500 |
| C(25)-C(26) | 1.406(10) | C(30)-Br(3) | 1.912(8) |
| C(26)-C(27) | 1.377(11) | Br(1)-Pd(1) | 2.4861(9) |
| C(26)-H(26) | 0.9500 | Br(2)-Pd(1) | 2.4830(8) |
| C(27)-C(28) | 1.392(13) | Cl(1)-C(31) | 1.724(11) |
| C(27)-H(27) | 0.9500 | Cl(2)-C(31) | 1.750(11) |
| C(28)-C(29) | 1.396(13) | C(31)-H(31A) | 0.9900 |
| C(28)-H(28) | 0.9500 | C(31)-H(31B) | 0.9900 |
| C(29)-C(30) | 1.377(12) | | |

| | | | |
|---|---|---|---|
| N(2)-C(1)-N(1) | 104.4(6) | C(8)-C(7B)-H(7B1) | 111.7 |
| N(2)-C(1)-Pd(1) | 126.9(5) | C(6)-C(7B)-H(7B2) | 111.7 |
| N(1)-C(1)-Pd(1) | 128.7(5) | C(8)-C(7B)-H(7B2) | 111.7 |
| C(3)-C(2)-N(1) | 106.8(7) | H(7B1)-C(7B)-H(7B2) | 109.5 |
| C(3)-C(2)-H(2) | 126.6 | C(7A)-C(8)-C(4) | 105.1(8) |
| N(1)-C(2)-H(2) | 126.6 | C(7A)-C(8)-C(7B) | 52.5(10) |
| C(2)-C(3)-N(2) | 106.5(7) | C(4)-C(8)-C(7B) | 101.3(8) |
| C(2)-C(3)-H(3) | 126.7 | C(7A)-C(8)-H(8A) | 110.7 |
| N(2)-C(3)-H(3) | 126.7 | C(4)-C(8)-H(8A) | 110.7 |
| N(1)-C(4)-C(8) | 113.8(6) | C(7B)-C(8)-H(8A) | 147.3 |
| N(1)-C(4)-C(5) | 112.0(6) | C(7A)-C(8)-H(8B) | 110.7 |
| C(8)-C(4)-C(5) | 105.2(6) | C(4)-C(8)-H(8B) | 110.7 |
| C(6)-C(5)-C(4) | 105.0(6) | C(7B)-C(8)-H(8B) | 63.4 |
| C(6)-C(5)-H(5A) | 110.8 | H(8A)-C(8)-H(8B) | 108.8 |
| C(4)-C(5)-H(5A) | 110.8 | N(2)-C(9)-C(10) | 111.0(6) |
| C(6)-C(5)-H(5B) | 110.8 | N(2)-C(9)-H(9A) | 109.4 |
| C(4)-C(5)-H(5B) | 110.8 | C(10)-C(9)-H(9A) | 109.4 |
| H(5A)-C(5)-H(5B) | 108.8 | N(2)-C(9)-H(9B) | 109.4 |
| C(7B)-C(6)-C(5) | 98.2(10) | C(10)-C(9)-H(9B) | 109.4 |
| C(7B)-C(6)-C(7A) | 53.0(10) | H(9A)-C(9)-H(9B) | 108.0 |
| C(5)-C(6)-C(7A) | 105.5(7) | C(15)-C(10)-C(11) | 116.6(7) |
| C(7B)-C(6)-H(6A) | 150.4 | C(15)-C(10)-C(9) | 123.2(7) |
| C(5)-C(6)-H(6A) | 110.6 | C(11)-C(10)-C(9) | 120.2(7) |
| C(7A)-C(6)-H(6A) | 110.6 | C(12)-C(11)-C(10) | 122.2(7) |
| C(7B)-C(6)-H(6B) | 64.6 | C(12)-C(11)-H(11) | 118.9 |
| C(5)-C(6)-H(6B) | 110.6 | C(10)-C(11)-H(11) | 118.9 |
| C(7A)-C(6)-H(6B) | 110.6 | C(13)-C(12)-C(11) | 118.9(7) |
| H(6A)-C(6)-H(6B) | 108.8 | C(13)-C(12)-H(12) | 120.5 |
| C(8)-C(7A)-C(6) | 99.6(10) | C(11)-C(12)-H(12) | 120.5 |
| C(8)-C(7A)-H(7A1) | 111.9 | C(14)-C(13)-C(12) | 121.1(7) |
| C(6)-C(7A)-H(7A1) | 111.9 | C(14)-C(13)-H(13) | 119.5 |
| C(8)-C(7A)-H(7A2) | 111.9 | C(12)-C(13)-H(13) | 119.5 |
| C(6)-C(7A)-H(7A2) | 111.9 | C(13)-C(14)-C(15) | 119.2(8) |
| H(7A1)-C(7A)-H(7A2) | 109.6 | C(13)-C(14)-H(14) | 120.4 |
| C(6)-C(7B)-C(8) | 100.3(13) | C(15)-C(14)-H(14) | 120.4 |
| C(6)-C(7B)-H(7B1) | 111.7 | C(10)-C(15)-C(14) | 121.9(7) |

| | |
|---|---|
| C(10)-C(15)-Br(4B) | 119.3(6) |
| C(14)-C(15)-Br(4B) | 117.3(6) |
| C(10)-C(15)-Br(4A) | 121.8(6) |
| C(14)-C(15)-Br(4A) | 115.9(6) |
| Br(4B)-C(15)-Br(4A) | 20.1(2) |
| N(4)-C(16)-N(3) | 105.8(6) |
| N(4)-C(16)-Pd(1) | 127.8(5) |
| N(3)-C(16)-Pd(1) | 126.3(5) |
| C(18)-C(17)-N(3) | 107.6(6) |
| C(18)-C(17)-H(17) | 126.2 |
| N(3)-C(17)-H(17) | 126.2 |
| C(17)-C(18)-N(4) | 107.0(6) |
| C(17)-C(18)-H(18) | 126.5 |
| N(4)-C(18)-H(18) | 126.5 |
| N(3)-C(19)-C(23) | 112.8(6) |
| N(3)-C(19)-C(20) | 113.5(6) |
| C(23)-C(19)-C(20) | 104.9(6) |
| C(21)-C(20)-C(19) | 102.8(7) |
| C(21)-C(20)-H(20A) | 111.2 |
| C(19)-C(20)-H(20A) | 111.2 |
| C(21)-C(20)-H(20B) | 111.2 |
| C(19)-C(20)-H(20B) | 111.2 |
| H(20A)-C(20)-H(20B) | 109.1 |
| C(22)-C(21)-C(20) | 103.7(8) |
| C(22)-C(21)-H(21A) | 111.0 |
| C(20)-C(21)-H(21A) | 111.0 |
| C(22)-C(21)-H(21B) | 111.0 |
| C(20)-C(21)-H(21B) | 111.0 |
| H(21A)-C(21)-H(21B) | 109.0 |
| C(23)-C(22)-C(21) | 105.4(8) |
| C(23)-C(22)-H(22A) | 110.7 |
| C(21)-C(22)-H(22A) | 110.7 |
| C(23)-C(22)-H(22B) | 110.7 |
| C(21)-C(22)-H(22B) | 110.7 |
| H(22A)-C(22)-H(22B) | 108.8 |
| C(22)-C(23)-C(19) | 107.8(7) |
| C(22)-C(23)-H(23A) | 110.1 |
| C(19)-C(23)-H(23A) | 110.1 |
| C(22)-C(23)-H(23B) | 110.1 |
| C(19)-C(23)-H(23B) | 110.1 |
| H(23A)-C(23)-H(23B) | 108.5 |
| N(4)-C(24)-C(25) | 114.1(6) |
| N(4)-C(24)-H(24A) | 108.7 |
| C(25)-C(24)-H(24A) | 108.7 |
| N(4)-C(24)-H(24B) | 108.7 |
| C(25)-C(24)-H(24B) | 108.7 |
| H(24A)-C(24)-H(24B) | 107.6 |
| C(30)-C(25)-C(26) | 117.3(7) |
| C(30)-C(25)-C(24) | 120.8(7) |
| C(26)-C(25)-C(24) | 121.9(7) |
| C(27)-C(26)-C(25) | 120.6(7) |
| C(27)-C(26)-H(26) | 119.7 |
| C(25)-C(26)-H(26) | 119.7 |
| C(26)-C(27)-C(28) | 120.6(8) |
| C(26)-C(27)-H(27) | 119.7 |
| C(28)-C(27)-H(27) | 119.7 |
| C(27)-C(28)-C(29) | 119.7(8) |
| C(27)-C(28)-H(28) | 120.1 |
| C(29)-C(28)-H(28) | 120.1 |
| C(30)-C(29)-C(28) | 118.4(8) |
| C(30)-C(29)-H(29) | 120.8 |
| C(28)-C(29)-H(29) | 120.8 |
| C(29)-C(30)-C(25) | 123.4(8) |
| C(29)-C(30)-Br(3) | 117.0(6) |
| C(25)-C(30)-Br(3) | 119.5(6) |
| C(1)-N(1)-C(2) | 110.8(6) |
| C(1)-N(1)-C(4) | 125.3(6) |
| C(2)-N(1)-C(4) | 123.8(6) |
| C(1)-N(2)-C(3) | 111.4(6) |
| C(1)-N(2)-C(9) | 125.3(6) |
| C(3)-N(2)-C(9) | 123.3(6) |
| C(16)-N(3)-C(17) | 109.3(6) |

| | | | |
|---|---|---|---|
| C(16)-N(3)-C(19) | 125.7(6) | C(16)-Pd(1)-Br(1) | 86.81(19) |
| C(17)-N(3)-C(19) | 124.5(6) | Br(2)-Pd(1)-Br(1) | 93.04(3) |
| C(16)-N(4)-C(18) | 110.3(6) | Cl(1)-C(31)-Cl(2) | 111.5(6) |
| C(16)-N(4)-C(24) | 126.4(6) | Cl(1)-C(31)-H(31A) | 109.3 |
| C(18)-N(4)-C(24) | 123.1(6) | Cl(2)-C(31)-H(31A) | 109.3 |
| C(1)-Pd(1)-C(16) | 91.4(3) | Cl(1)-C(31)-H(31B) | 109.3 |
| C(1)-Pd(1)-Br(2) | 89.12(18) | Cl(2)-C(31)-H(31B) | 109.3 |
| C(16)-Pd(1)-Br(2) | 175.8(2) | H(31A)-C(31)-H(31B) | 108.0 |
| C(1)-Pd(1)-Br(1) | 173.94(19) | | |

Table 24: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for COMPLEX. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 31(4) | 26(3) | 20(4) | 3(3) | 9(3) | -2(3) |
| C(2) | 49(5) | 36(4) | 26(4) | 1(3) | 0(4) | -12(4) |
| C(3) | 37(5) | 37(4) | 30(4) | -1(3) | -1(3) | -9(4) |
| C(4) | 45(5) | 24(4) | 28(4) | 4(3) | 9(3) | 6(3) |
| C(5) | 50(5) | 31(4) | 33(4) | 5(3) | 3(4) | -5(4) |
| C(6) | 119(10) | 34(5) | 49(6) | -4(4) | 12(6) | 22(5) |
| C(7A) | 87(12) | 76(10) | 29(7) | 9(7) | 20(8) | 36(9) |
| C(7B) | 38(13) | 48(13) | 18(10) | 0(9) | 25(10) | 5(10) |
| C(8) | 59(6) | 46(5) | 39(5) | -1(4) | 24(4) | 5(4) |
| C(9) | 31(4) | 40(4) | 26(4) | -3(3) | 2(3) | 2(3) |
| C(10) | 32(4) | 24(3) | 32(4) | -2(3) | 9(3) | -1(3) |
| C(11) | 31(4) | 33(4) | 31(4) | -9(3) | 9(3) | 1(3) |
| C(12) | 46(5) | 35(4) | 26(4) | 1(3) | 10(4) | -3(4) |
| C(13) | 44(5) | 42(5) | 37(5) | 8(4) | -3(4) | 0(4) |
| C(14) | 29(4) | 66(6) | 46(5) | 21(4) | -6(4) | -13(4) |
| C(15) | 35(5) | 51(5) | 45(5) | 17(4) | 2(4) | -18(4) |
| C(16) | 31(4) | 27(3) | 23(4) | 4(3) | 4(3) | -5(3) |
| C(17) | 43(5) | 31(4) | 29(4) | 11(3) | 8(3) | 4(3) |
| C(18) | 47(5) | 33(4) | 31(4) | 12(3) | 11(4) | 1(4) |
| C(19) | 23(4) | 29(4) | 38(4) | 4(3) | 5(3) | -2(3) |
| C(20) | 36(5) | 49(5) | 43(5) | 3(4) | 8(4) | 3(4) |
| C(21) | 33(5) | 80(7) | 59(6) | 8(5) | 0(4) | 8(5) |
| C(22) | 54(7) | 84(8) | 94(9) | -28(7) | -19(6) | 22(6) |
| C(23) | 39(5) | 47(5) | 56(6) | 8(4) | 9(4) | -2(4) |
| C(24) | 39(5) | 41(4) | 24(4) | -1(3) | 10(3) | 4(4) |
| C(25) | 38(4) | 33(4) | 24(4) | 12(3) | 13(3) | 3(3) |
| C(26) | 34(4) | 40(4) | 29(4) | 6(3) | 11(3) | 2(3) |
| C(27) | 59(6) | 39(5) | 42(5) | 4(4) | 9(4) | -9(4) |
| C(28) | 46(6) | 62(6) | 56(6) | 15(5) | -7(5) | -21(5) |
| C(29) | 28(5) | 60(6) | 62(6) | 17(5) | 7(4) | -2(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(30) | 39(5) | 42(4) | 35(4) | 10(4) | 10(4) | 5(4) |
| N(1) | 39(4) | 28(3) | 26(3) | -3(3) | 5(3) | -4(3) |
| N(2) | 30(3) | 28(3) | 22(3) | 1(2) | 1(3) | -4(3) |
| N(3) | 30(3) | 31(3) | 26(3) | 6(3) | 2(3) | 6(3) |
| N(4) | 25(3) | 33(3) | 25(3) | 5(2) | 3(3) | -1(3) |
| Br(1) | 44(1) | 40(1) | 30(1) | 0(1) | -1(1) | -3(1) |
| Br(2) | 39(1) | 36(1) | 25(1) | 5(1) | 4(1) | -6(1) |
| Br(3) | 45(1) | 68(1) | 53(1) | 5(1) | 15(1) | 24(1) |
| Br(4A) | 36(1) | 96(3) | 60(2) | 37(2) | 15(1) | 0(2) |
| Br(4B) | 43(2) | 137(5) | 66(3) | 56(3) | 1(2) | -30(3) |
| Pd(1) | 28(1) | 24(1) | 19(1) | 2(1) | 4(1) | 0(1) |
| Cl(1) | 56(2) | 125(3) | 86(2) | -16(2) | 9(2) | -1(2) |
| Cl(2) | 107(3) | 112(3) | 63(2) | -18(2) | 34(2) | -22(2) |
| C(31) | 55(6) | 72(7) | 69(7) | 24(6) | 5(5) | -4(5) |

Table 25: Hydrogen coordinates (x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for complex.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 11196 | 8812 | 4254 | 46 |
| H(3) | 12422 | 7721 | 4243 | 43 |
| H(5A) | 10084 | 9540 | 3103 | 47 |
| H(5B) | 9173 | 9317 | 2410 | 47 |
| H(6A) | 8274 | 10166 | 3020 | 81 |
| H(6B) | 9151 | 10299 | 3769 | 81 |
| H(7A1) | 8097 | 9539 | 4486 | 75 |
| H(7A2) | 7628 | 9032 | 3681 | 75 |
| H(7B1) | 8726 | 9865 | 4648 | 39 |
| H(7B2) | 9807 | 9797 | 4445 | 39 |
| H(8A) | 8740 | 8128 | 4382 | 55 |
| H(8B) | 9537 | 8838 | 4602 | 55 |
| H(9A) | 12276 | 6496 | 2881 | 39 |
| H(9B) | 11357 | 5964 | 3009 | 39 |
| H(11) | 11259 | 5642 | 4522 | 38 |
| H(12) | 12106 | 5100 | 5726 | 42 |
| H(13) | 13789 | 5142 | 5973 | 51 |
| H(14) | 14621 | 5691 | 5020 | 58 |
| H(17) | 8528 | 8770 | 186 | 41 |
| H(18) | 10212 | 8450 | 93 | 44 |
| H(20A) | 7512 | 8847 | 2156 | 51 |
| H(20B) | 7551 | 9169 | 1249 | 51 |
| H(21A) | 5973 | 8296 | 1763 | 70 |
| H(21B) | 5892 | 9130 | 1241 | 70 |
| H(22A) | 5518 | 7779 | 476 | 97 |
| H(22B) | 6106 | 8467 | 76 | 97 |
| H(23A) | 7258 | 7547 | 145 | 57 |
| H(23B) | 6798 | 6992 | 773 | 57 |
| H(24A) | 11273 | 7137 | 646 | 41 |
| H(24B) | 11125 | 6785 | 1509 | 41 |
| H(26) | 11101 | 8716 | 2020 | 41 |
| H(27) | 12361 | 9503 | 2698 | 56 |

| | | | | |
|---|---|---|---|---|
| H(28) | 13966 | 9121 | 2705 | 68 |
| H(29) | 14304 | 7934 | 2002 | 60 |
| H(31A) | 17405 | 6151 | 2546 | 80 |
| H(31B) | 16835 | 5775 | 3211 | 80 |