The Synthesis of Novel Aryl and Alkyl Phosphine-Imidazolium Salts

by

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Abstract

Several chelating phosphine-imidazolium salts have been synthesised and their activity tested in the hydrosilylation of styrene with triethylsilane and the Heck coupling of aryl bromides and chlorides with butyl acrylates.

A number of synthetic routes have been established to synthesise aryl substituted phosphine-imidazolium salts. New synthetic routes have been established to synthesise borane-protected alkyl substituted phosphine-imidazolium salts. These methodologies have increased the scope to synthesise new alkyl substituted phosphine-imidazolium salts.

Several group 9 and 10 complexes of these new aryl substituted phosphine-NHC ligands have been synthesised and characterised. The NHC's were generated *in situ* and reacted with suitable metal precursors. Platinum (0) complexes of these ligands were tested in the hydrosilylation of styrene with triethylsilane. Pd(0) complexes of these ligands were tested in the Heck coupling of aryl bromides and chlorides with butyl acrylate.

Contents

Acknowledgements

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Thanks to my parents for all their help and support throughout my degree as well as my PhD. It has taken me a while to get it all done but you never once doubted me and I'll never forget that. Also thanks to all the rest of the family- your interest and support kept me going.

And last but not least a huge thank you to Isla. Without your love, help and encouragement I would not be where I am today. Thank you.

Glossary

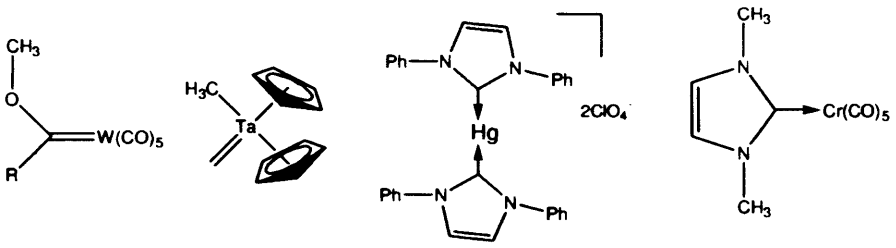
BARF	$B[3,5\text{-}(CF_3)C_6H_3]_4$
br	Broad (NMR)
BQ	1,4-benzoquinone
Bz	benzyl
COD	1, 5-cyclooctadiene
dba	Dibenzylidineacetone
DAB	Diazabutadiene
DCM	Dichloromethane
DMAc	N,N-dimethylacetamide
DMF	N,N-dimethylformamide
DMFU	Dimethylfumarate
DMSO	Dimethylsulfoxide
dipp	2,6-bis(diisopropyl)phenyl
Et_2O	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
Neopentyl	2,2-dimethylpropyl
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. Phosphine and Carbene Ligands- A Historical Perspective.

Both phosphines and carbenes have found useful applications as ligands in organometallic reactions for many years. The electronic and steric properties of these ligands can be controlled by varying the substituents. This can increase reaction rates and give a much greater control of the types of products formed.

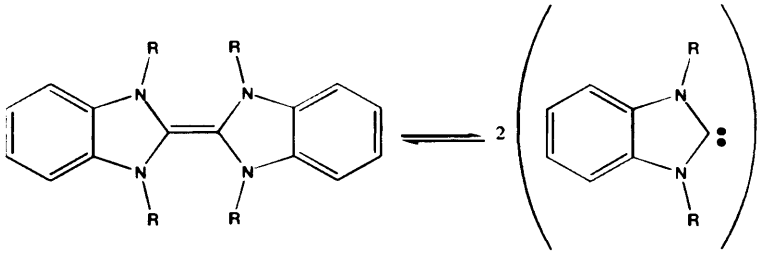
Carbenes are neutral divalent carbon species featuring two non-bonding electrons and have long played the role of reactive intermediates in organic chemistry without being isolated. Examples of carbene complexes (Figure 1.1) have been known since the 1960's. For example Fischer,[1] **1.1**, and Schrock-type,[2] **1.2**, carbenes as well as complexes of mercury,[3] **1.3**, and chromium,[4] **1.4**, were synthesised (see section 1.5 for discussion of different metal-carbon bonding). The first persistent carbene was isolated in 1988 by Bertrand *et* al[5] but it wasn't until 1991 that a stable crystalline N-nucleophilic heterocyclic carbene (NHC) was isolated by Arduengo *et al*, **1.8** (R= adamantly, R'= H).[6] This NHC was formed by deprotonation of 1,3-bis(1'-adamantyl)imidazolium chloride by NaH or KO^{t}Bu under oxygen free anhydrous conditions to give a thermally stable free carbene. This landmark discovery has allowed the synthesis of a wide range of stable NHC's with different nitrogen and imidazole backbone substituents that have been successfully coordinated to most metals of the periodic table in a variety of oxidation states.[7]



1.1 **1.2** **1.3** **1.4**

Figure 1.1.

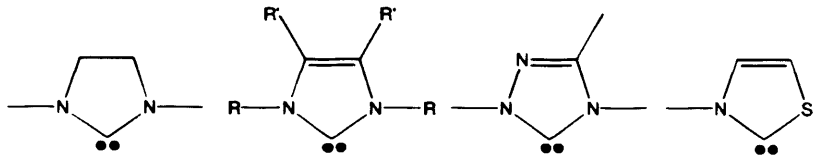
Wanzlick and co-workers carried out extensive studies on the imidazole ring system in the 1960's.[8] They focused on saturated systems and tried to synthesise substituted benzimidazolidin-2-ylidenes but never successfully managed to isolate these species, only the electron rich tetraaminoethylenes, **1.5**, formally formed by the dimerisation of two NHC's. Wanzlick proposed that the dimerisation process was an equilibrium as shown in Equation 1.1 and performed *in situ* trapping experiments with oxygen and water. While the results suggested that they had in fact generated the free carbenes, **1.6**,[9,10] some workers of that era discounted the "Wanzlick Equilibrium" and attributed all reactivity to tetraaminoethylenes. Recent studies have shown that the Wanzlick Equilibrium holds true for some benzimidazolin-2-ylidenes.[11-13]



1.5 **1.6**

Equation 1.1.

It should be noted that imidazolin-2-ylidenes, **1.8**, only form dimers if there are strong electron withdrawing groups, e.g. CF_3, attached to the unsaturated imidazole backbone (Figure 1.2).[11]



1.7 **1.8** **1.9** **1.10**

Figure 1.2.

A number of stable aminocarbenes have been isolated including cyclic imidazolidin-2-ylidenes, **1.7**;[12] 1, 2, 4-triazolin-5-ylidenes, **1.9**,[13] 1, 3-thiazolin-2-ylidenes, **1.10**,[14] as well as acyclic diamino-,[15] aminooxy-[16] and aminothiocarbenes.[16] All these carbene species bear two π-donor substituents, at least one of which is an amino group. The π-donor ability of the substituents is a major factor in the stability of these types of NHC's.

Phosphines have been used as ligands in homogeneous catalysis for many years. One of the first examples of this was in 1948 when Reppe *et al* discovered that a complex of $Ni(CO)_2(PPh_3)_2$ increased the rate of olefin and acetylene polymerisation.[17] A major breakthrough was the discovery by Wilkinson that $RhCl(PPh_3)_3$ promoted the hydrogenation of alkenes under mild conditions.[18]

In recent years NHC's have begun to replace phosphines in many reactions as they can form stronger metal-carbon bonds which are stable at much higher temperatures and pressures. Also, some processes demand that an excess of phosphine is present for reaction rates to be acceptable which can be expensive and detrimental to the environment. NHC's can be used in stoichiometric quantities and are thus much more environmentally benign.

1.2. N-Heterocyclic Carbene Ligands

The stability of imidazolin-2-ylidenes was initially thought to be due to a combination of electronic factors and steric bulk protecting the carbene centre.[5] However, the synthesis of 1,3,4,5-tetramethylimidazolin-2-ylidene, **1.8** (R= CH_3, R'= CH_3)[17] and the somewhat less stable 1,3-dimethylimidazolin-2-ylidene, **1.8** (R= CH_3, R'= H)[17] showed that these sterically unencumbered species could be isolated. The major reason for the stability of the imidazole-based NHC systems is electronic in nature and due to the two nitrogen atoms vicinal to the sp^2-hybridised, divalent carbon atom. The filled nitrogen p_π-orbitals donate π-electron density into the formally empty carbon p_π-orbital while the more electronegative nitrogen atoms also withdraw σ-electron density from the carbene carbon *via* the inductive effect such that the carbene lone pair is stabilised in a singlet electronic configuration (Figure 1.3).[20a]

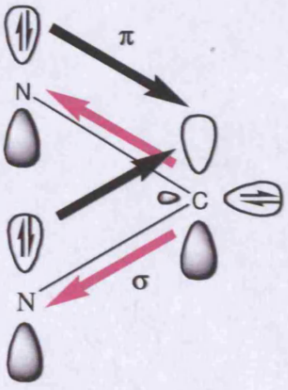


Figure 1.3.

The stability of this singlet configuration can be rationalised by considering the molecular orbitals involved and the changes in energy of these orbitals. The σ-electron withdrawing substituents inductively stabilise the σ nonbonding orbital by increasing its s character but do not affect the energy of the p_π-orbital. The σ-p_π gap is thus increased favouring the singlet state. Changing the substituents to σ-electron donating species

would cause a small σ-p_π gap which favours the triplet state.[20b] The energy of the vacant p_π carbon orbital is raised by interaction with the substituent lone pairs. The carbon σ-orbital remains almost unchanged increasing the σ-p_π gap and favouring the singlet state. Theoretical studies have shown that changing the vicinal substituents on the carbon to more electropositive atoms such as lithium results in the triplet state being favoured.[20b]

The extent to which aromaticity helps stabilise **1.8** has been the subject of some debate. Various theoretical[21-25] and experimental[19, 20] studies have shown that there is more π-delocalisation in imidazolin-2-ylidenes in comparison to saturated imidazolidin-2-ylidenes, **1.7**, but the "aromatic character" is significantly smaller compared to the imidazolium salt precursors.[25b] Reaction of **1.8** (R=Mes, R'=H) with CCl_4 in THF resulted in chlorination of the imidazolin-2-ylidene ring at the C4 and C5 positions. The resulting carbene is air stable and this has been attributed to the fact that the chlorines can donate π-electron density and withdraw σ-electron density from the imidazolin-2-ylidene ring.[27] This reduces the basicity and hence the reactivity of the carbene lone pair.

The basicity of the carbene influences the reactivity of the catalytic systems in which they are employed. For example, using saturated imidazolidin-2-ylidenes instead of unsaturated imidazolin-2-ylidenes results in an increase in catalytic activity of ruthenium-based olefin metathesis catalysts.[26] This increase in activity has been attributed to the higher basicity of the carbene. Both the saturated and unsaturated NHC systems are considerably more basic than even the most basic phosphines. For example, **1.7** (R=Me, R'=H) and **1.8** (R=Ph, R'=H) are calculated to have pK_a's of 28.5 ± 0.4 and 22.0 ± 0.1 respectively, compared to a pK_a of 11.40 for $P(^tBu)_3$ in water.[28] Substitution of the imidazole ring at the 4 and 5 positions was found to significantly alter the pK_a of the carbenes. Substitution by chlorine caused a decrease in pK_a while substitution with methyl groups caused an increase in pK_a.[28] This effect is similar to that observed in phosphines where more electron withdrawing groups cause a decrease in pK_a while more electron donating groups cause an increase in the pK_a.

The NCN bond angle observed in these NHC's is between 100-110° which is in good agreement for singlet carbenes. The amino groups are always in a planar environment and the N-C bonds are quite short (1.32-1.37Å) and seem to have some multiple bond character, consistent with donation from the nitrogen lone pairs. This has been confirmed by variable temperature solution NMR experiments in which a large barrier to rotation about the N-C bond has been shown in acyclic systems.[29,30]

While steric, kinetic and aromatic factors undoubtedly have an influence on the stability of NHC's, it is the electronic push, mesomeric-pull, inductive effect of the carbene carbon substituents that dominates.

1.3. Phosphine Ligands

Phosphines can act as σ-base or π-acid ligands and form a synergic metal-phosphine bond that can stabilise metal complexes in low oxidation states. Phosphines act as σ-bases by σ-donation of a lone pair of electrons to the metal centre and as π-acids by back donation of electron density from filled metal d-orbitals into either σ* antibonding molecular orbitals or empty d-orbitals on the phosphorous atom[31-33] (Figure 1.4).

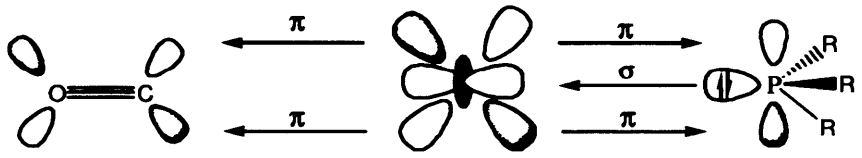


Figure 1.4: Shows back-bonding from metal d-orbitals to phosphine and carbonyl ligands. Also shows σ-bond formed by donation of phosphorous lone pairs.

The metal-phosphine σ-bond is very similar in nature to that of a metal-NHC σ-bond and this is why NHC's have sometimes been called "phosphine mimics".

Phosphines have found use as ligands in organometallic reactions due to the ease with which the electronic and steric properties of the ligand can be tuned. The steric properties of a phosphine can be defined by the cone angle (Figure 1.5) which was first described by Tolman.[34]

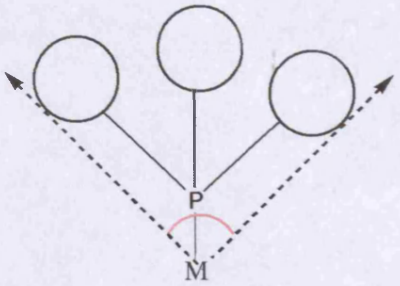


Figure 1.5.

Different substituents on phosphorus cause a change in the size of the phosphine ligand as "seen" by the metal centre. More bulky substituents will increase this angle while less sterically demanding substituents will decrease the angle. Using suitable substituents allows us to tailor the stability and reactivity of any metal complexes formed.

The electronic interaction of the phosphine ligand with the metal can be tuned by varying the π-acidity of the phosphine. Phosphines with higher π-acidity accept more electron density from the metal which lessens the electron density shared with other coordinated ligands. Tolman qualified this by looking at the CO stretching frequency of ancillary carbonyl ligands in the infra-red spectrum for the complex $Ni(CO)_3L$.[36] As electron density is removed by the phosphine there is less back-bonding to the carbonyl. This strengthens the C=O bond (acceptor orbitals of the carbonyl are antibonding) and so shifts the A_1 band to a lower wavenumber. Comparison of different phosphines can give us the relative π-acidity of these phosphines.

Ligand (L)	CO Stretch (v, cm^{-1})	pKa (H_2O)[35]
PPh_3	2068.9	2.73
PMe_3	2064.1	8.65
PCy_3	2056.4	9.70
P^tBu_3	2056.1	11.40

Table showing CO stretching frequencies and relative aqueous pKa's for complexes of the formula $Ni(CO)_3L$.

NHC's form strong σ-bonds with metals that are comparable with phosphine-metal bonds. However, one difference of the phosphine-metal bond compared to the NHC-metal bond is that it is synergic and there is appreciable back-donation of electron density from the metal to the phosphorus whereas commonly, this does not happen to the same extent in NHC-metal bonds. The σ-basicity of phosphines can be examined by measuring the pKa's of the conjugate acids (the phosphonium salts). The higher the pKa the more basic the phosphine. This does not describe M-PR_3 bonding fully as it does not take into account the π-acceptor nature of the phosphine but is a useful method to make comparisons between phosphines.

The use of chelating bidentate phosphines can markedly change the rate of reaction and type of product formed. Having two phosphines linked "locks" the geometry around the metal centre so that substrate molecules can only coordinate to the metal at certain sites, and in certain orientations i.e. forces *cis* coordination. This can result in a faster rate and greater selectivity of product type when compared to monodentate phosphines.

The bite angle of bidentate phosphine ligands can be manipulated so that a particular geometric change at the metal centre is favoured. For example, if the change of the metal coordination geometry from square planar to tetrahedral is the rate determining step in a reaction, a bidentate ligand with a bite angle of 110° increases the rate as this is closer to the optimum angle for a tetrahedral complex. This effect was demonstrated by van Leeuwen *et al* in the nickel catalysed hydrocyanation of alkenes.[37]

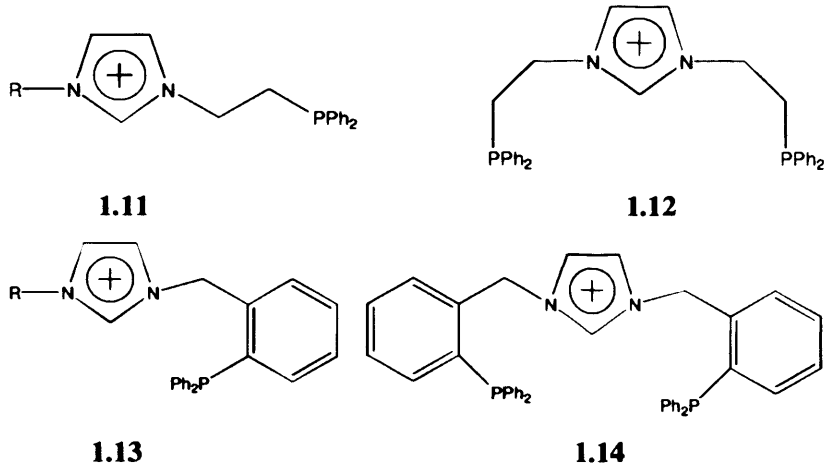
1.4. Mixed Donor Ligands

Ligands containing more than one donor atom that can coordinate to a metal are of considerable interest as these can be tailored to suit the requirements of a particular reaction. Strong σ-donor ligands can cause a weakening of the bonds of ligands *trans* to them while another weaker donor could dissociate during the reaction to generate a vacant coordination site.

Theoretical calculations show that a chelating ligand that consists of a carbene and phosphine moiety is suitable for the Pd-catalysed Heck reaction.[38] The mixed phosphine-carbene ligand combines the stabilising effect of the carbene with a labile Pd-P bond that can be broken reversibly allowing for a facile coordination of the olefin to the Pd centre.[38]

The first mixed donor phosphine-carbene ligand with alkyl linkers to be catalytically tested was synthesised by Nolan *et al* (Figure 1.6, **1.11**). *In situ* reactions showed that the ligand was highly efficient in the Heck coupling of various aryl bromides with n-butyl acrylates. However, the ligand proved to be ineffective in aryl chloride coupling reactions.[39]

Metal complexes of the ligand, **1.11**, were synthesised by Danopoulos *et al* by deprotonation of the imidazolium salt with an inorganic base. The Pd(P-NHC)Me_2 species formed were susceptible to reductive elimination. X-Ray structures of the complexes showed that the stronger σ-donor NHC moiety does not always exert a higher *trans* influence than the phosphine as evidenced by bond lengths, but the methyls *cis* and *trans* to the NHC were kinetically different. Studies of Heck coupling reactions with preformed complexes showed only moderate activity with both aryl bromides and aryl chlorides.[40] A more detailed discussion of the *trans* influence and reductive elimination of NHC's appears in section 1.5.



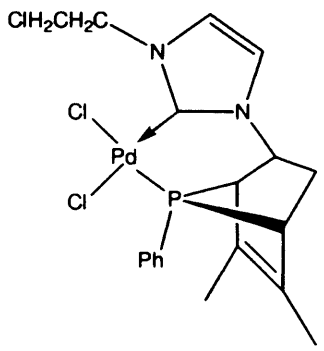
1.11 **1.12**

1.13 **1.14**

Figure 1.6.

Pd(II) complexes of tridentate ligands, **1.12**, with alkyl linkers between the NHC and phosphine groups were synthesised using a silver transfer method or by direct reaction of the imidazolium salt and $PdCl_2$.[41] The high acidity of the ligand favours the successful deprotonation of the imidazolium salt and the elimination of HCl without the need of a base. Pd(II) complexes of the ligands were efficient catalysts for the coupling of aryl bromides but ineffective with aryl chlorides.[41] Metal complexes of Ru(II) bearing ligands of type **1.12** have been synthesised.[42]

Bidentate, **1.13**, and tridentate, **1.14**, ligands with aryl linkers have been tested in *in situ* Heck coupling reactions. They show high activity for the coupling of aryl bromides.[43] An interesting *in situ* metal template synthesis of a chelating phosphine-carbene complex has been reported.[44]

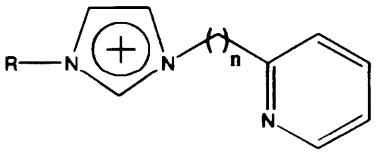


1.15

Figure 1.7.

Mixed donor ligands containing NHC groups and other donor groups have been synthesised. Bidentate ligands of the type **1.16** with the picolyl[45] functionality (n=1) and pyridyl[46,47] functionality (n=0) form stable complexes with Ag(I) and Pd(II). These palladium complexes are highly active catalysts in Heck, Suzuki and Sonogashira coupling reactions.[45] Bidentate bis-carbene ligands, **1.17**, have been synthesised and complexes of Pd(II), Ni(II)[48,49,50] and Ru(II)[51] formed.

Tridentate ligands with alkoxide,[52] pyridyl,[53,54] and picolyl[55,57,58] donors, **1.18**, have been formed. Pd(II) complexes of the picolyl donor ligands are active catalysts in Suzuki coupling reactions[56] and the Heck coupling of aryl bromides but are poor catalysts in the Heck coupling of aryl chlorides.[55] This is not too suprising as aryl chlorides are poor Heck substrates due to the stability of the Ar-Cl bond. Pd-methyl complexes have been shown to undergo reductive elimination[57] and migratory insertion reactions[58] to give 2-methyl substituted imidazolium salts, see Section 1.5. Ru(II) complexes of the pyridyl functionalized ligand are active hydrogen transfer catalyst[59] and Cr(III) complexes of **1.19** have been shown to be active ethylene oligomerisation catalysts.[60]



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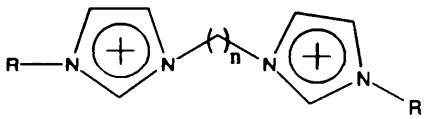

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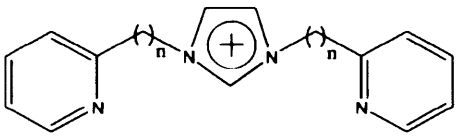

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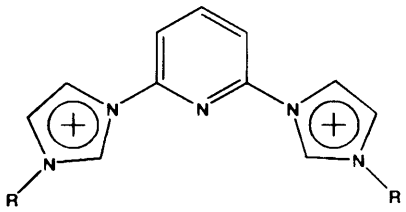

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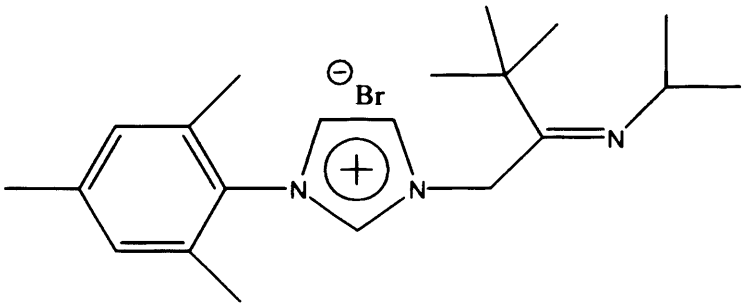

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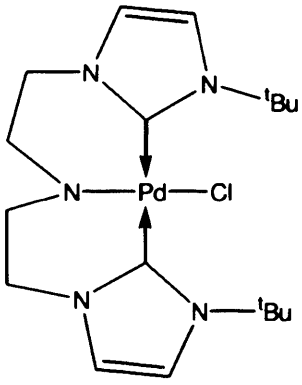
Figure 1.8.

There are examples of carbene-cyclophane and half-cyclophane type palladium complexes that have shown good activity in the coupling of aryl bromides.[61] Imino-functionalised carbene complexes of palladium have been prepared.[62,63,64] The imidazolium salt **1.20** was prepared and coordinated to palladium by a silver transfer method.[62] Other examples of catalytically active mixed donor ligands include imido(**1.21**),[65] phenolate(**1.22**)[66] and keto functionalised imidazolium salts(**1.23**).[67] Benzimidazole (**1.24**)[68] and bisoxazoline-derived NHC ligands have also been synthesised.[69]



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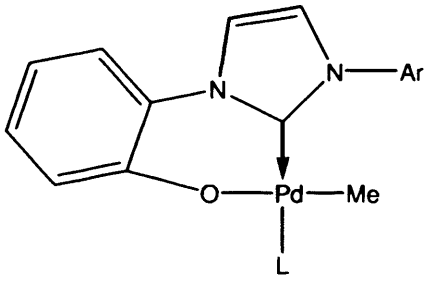

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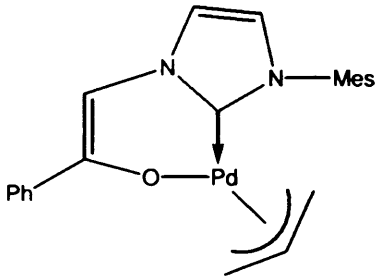

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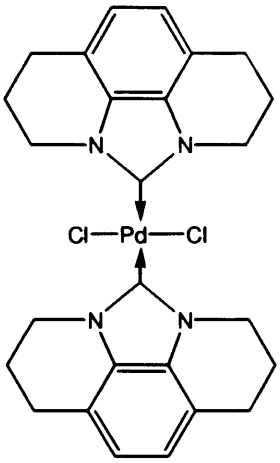

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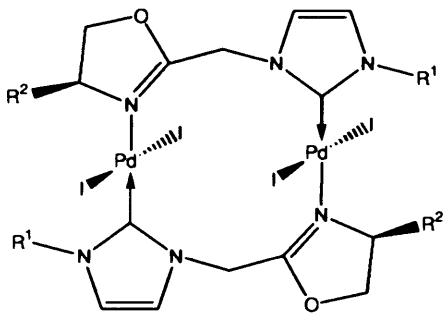
Figure 1.9

Recently there has been increased interest in chiral carbene complexes. Chiral (imidazolinylidene)- and (triazolinylylidene)palladium complexes were synthesised by reaction of the corresponding imidazolium salts with $Pd(OAc)_2$, NaI and base ($KOBu^t$).[70] Mixed oxazoline/imidazoline-2-ylidene ligands have been synthesised but only dimeric Pd complexes (**1.25**) were isolated.[71] Chiral carbenes with cyclohexanol,[72] ferrocenyl[73] and imine(**1.27**)[74,75] functional groups as well as chelating bis-carbene complexes (**1.26**) have been reported.[76,77,78]



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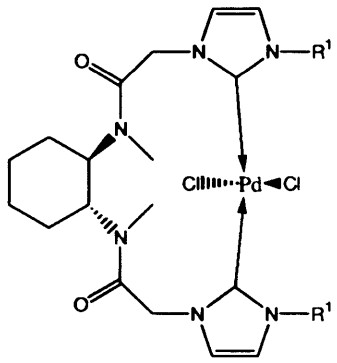

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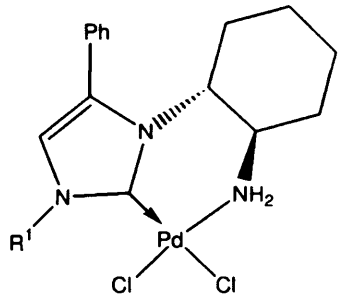

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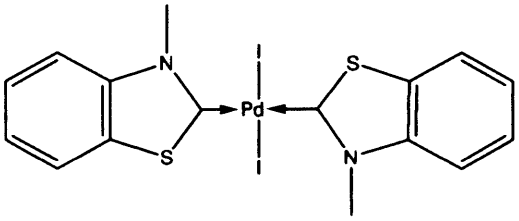
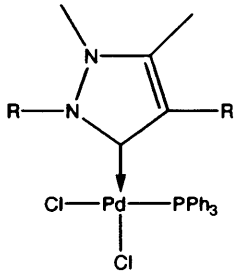
Figure 1.10.

There are also numerous examples of carbenes that are not based on the imidazole ring. Complexes of 6-membered rings based on a tetrahydropyrimidine core with sulphur[79] and selenium[80] donors have been synthesised. Triazole,[81,82,83] thiazole, benzothiazole (**1.28**)[84,85,86] and pyrazole (**1.29**)[87]-based complexes have also been reported.



1.28



R=Ph, Me

1.29

Figure 1.11

1.5. Metal Complexes of Phosphine-Carbene Ligands

The coordination chemistry of NHC's and phosphines is comparable in that both form strong σ-bonds with metals by donation of a lone pair of electrons. However, there are significant differences between the way that these ligands bond i.e. NHC's are stronger σ-donors[20,60,88] and have

negligible back-bonding from the metal centre.[89,90] Theoretical studies and photoelectron spectroscopy have shown that NHC ligands donate σ-electron density into a hybrid metal (d_z^2 + s) bonding orbital and there is negligible back-bonding from the filled metal d_{xz} and d_{yz} orbitals into the carbene p_π orbitals, even for electron-rich late-transition metals. This is thought to be due to the fact that electron density is donated to these p_π-orbitals from the neighbouring nitrogen atoms vicinal to the carbene carbon as discussed in section 1.2.

The NHC-metal bond also differs markedly from "classical" metal-carbene bonds. Fischer-type carbene complexes[1] are compounds with a donor-acceptor bond rather like the Dewar-Chatt-Duncanson model of synergistic bonding between metals and alkenes.[91] The complexes are nucleophilic with the metal usually in a low oxidation state, and at least one of the carbene substituents is a π-donor (Figure 1.12). Schrock-type carbene complexes[2] (alkylidenes) are electrophilic, have metals in high oxidation states and carbene ligands that have alkyl groups or hydrogen atoms as substituents (Figure 1.12). NHC complexes contain a carbon-metal σ-bond with no back-bonding from the metal centre (Figure 1.8).

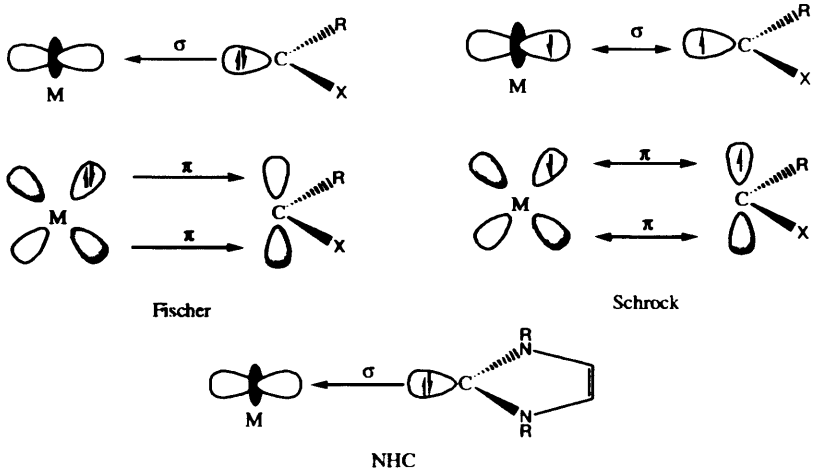
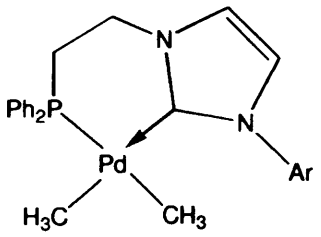
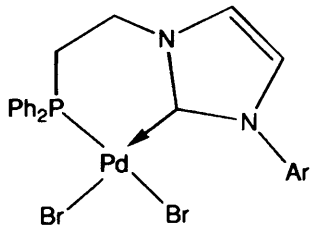


Figure 1.12. Different types of bonding in Fischer, Schrock and NHC complexes.[92]

The strong σ-donor character of NHC's and phosphines means that both ligands have a strong *trans* influence. The *trans* influence of a ligand in a metal complex is the extent to which that ligand weakens the bond *trans* to itself in the equilibrium state of that complex.[93] This is thermodynamic in nature and should not be confused with the *trans* effect, which is the effect of a coordinated ligand upon the rate of substitution of the ligand *trans* to it. The *trans* influence changes the ground state properties of a metal complex such as metal-ligand bond lengths, vibrational frequencies or force constants and NMR coupling constants.[93] The *trans* influence of a ligand depends on the σ-donor ability of the ligand and not on the π-acidity e.g. H^- and CH_3^- are not π-acidic but have a similar *trans* influence to phosphines. High *trans* influence ligands are potentially useful in metal complexes as they can labilise certain M-L bonds which may increase the rates of catalytic reactions, particularly if a migratory insertion is the rate determining step e.g. carbonylation reactions. A recent study of the Pd(II) complexes shown in Figure 1.13 has shown that there is no observed difference in the Pd-CH_3 bond lengths in complex **1.30** although the two methyls are kinetically different. The Pd-Br bond *trans* to the phosphine group is ca. 0.03Å longer than the Pd-Br bond *trans* to the NHC group in complex **1.31**. This is opposite to what is expected as NHC's are stronger σ-donors.[40]



1.30



1.31

Figure 1.13.

The hemilability of polydentate hybrid ligands when coordinated to transition metals is of growing interest because they can open coordination sites that are "masked" in the ground-state and can stabilise reactive

intermediates. Metal complexes containing hemilabile ligands have been found to be catalytically active in a range of reactions including hydrogenation, carbonylation, hydroformylation and ring-opening metathesis.[94] A ligand is hemilabile if one donor group of a polydentate ligand dissociates while another group remains firmly bound. This causes a coordination site on the metal to become available so that other reaction steps can occur. In a chelating phosphine-carbene the phosphine could dissociate while the carbene remains bound. The strong *trans* influence of the NHC could cause a weakening of bonds in the intermediate which could result in an increase in the rate of reaction. Once the catalytic cycle has proceeded the phosphine could re-coordinate to form the original species that is ready for another cycle. The substituents of both the phosphine and the NHC can be tailored to possibly alter the hemilability of the ligand and so give us some control over the reaction.

The aforementioned properties of phosphines and NHC's make them useful and attractive ligands for homogeneous catalysis, but there are certain drawbacks to using them. The concerted reaction mechanism whereby square planar Pd(II) complexes of NHC's reductively eliminate to form hydrocarbylimidazolium salts and metal(0) is a potential drawback to their use in catalysis.[95] The mechanism is thought to involve the mixing of the $C_{Carbene}$ p_z-orbital, C_{Me} orbital and Pd d-orbitals due to the fact that these orbitals are correctly oriented for overlap (Figure 1.14).

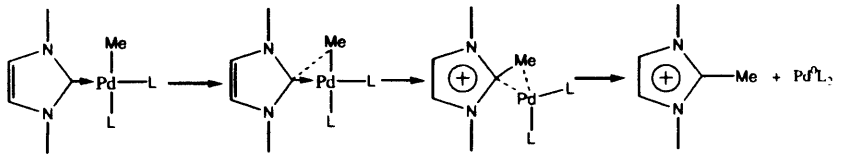


Figure 1.14. The mechanism of reductive elimination in Pd(II) complexes. Adapted from Cavell *et al.*[95]

Various strategies may be attempted in order to prevent or at least minimise reductive elimination. The electron donation from carbene to metal upon complexation is compensated by increased π-donation from the

nitrogens which results in an increase in the population of the C p_π-orbital.[92,96] During the reductive elimination mechanism there is a substantial increase in the polarisation of electron density away from the carbon nucleus towards the Pd.[95] Highly inductive groups (^{t}Bu, neopentyl) on the nitrogens could donate sufficient electron density into the p_π-orbital to prevent reductive elimination.

There is a change in the geometry around the Pd during the mechanism where the NHC-Pd-Me bond angle closes up. If the ligands L are bidentate and form a chelate then it is harder to alter this bond angle and so reductive elimination could be prevented.[95] Similarly if the NHC moiety is attached to one of the ligands L to form a chelate the NHC-Pd-Me bond angle is less favoured to close and so reductive elimination could be prevented.

1.6. Aims of this Thesis

The main aim of this thesis was the design and synthesis of a range of phosphine-carbene ligands. Changing the nature of the substituents of the carbene and phosphine groups may influence the catalytic reactivity of the ligands. Once synthesis of the ligands was achieved the coordination chemistry and catalytic activity of the ligands was tested.

The aim of chapter two was to describe the synthesis of a range of functionalized phosphine-imidazolium salts bearing different nitrogen and phosphine substituents, which were required as precursors to the respective phosphine-NHC ligands.

The aim of chapter three was to describe the synthesis and characterisation of various metal complexes. Complexes of group 10 metals in the zero and +2 oxidation state and group 9 metals in the +1 and +3 oxidation state are discussed.

The aim of chapter 4 was to describe catalytic cross-coupling reactions of the metal complexes discussed in chapter 3. The hydrosilylation of styrene and the Heck coupling of aryl bromides and chlorides are discussed.

1.7. References

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Chapter Two

Bulky N-Alkyl Substituted Imidazolium Salts

2.1. Introduction

2.1.1. Terminology

Imidazolium salts are planar, 5-membered ring systems with nitrogens at the 1 and 3 positions and substituents (H, R, Ar or X) at each position of the ring. Each atom is sp^2-hybridised and the ring bears a single positive charge that is delocalized over the ring system due to the heteroaromaticity of the ring.[1] Numbering in the ring is shown in **2.2** and is used consistently in this thesis. Imidazoles (**2.1**) are neutral species that contain 2 double bonds. The imidazol-2-ylidenes (**2.3**) formed from **2.2** have one C_4=C_5 olefinic double bond on the backbone. In this thesis R_4=R_5=H.

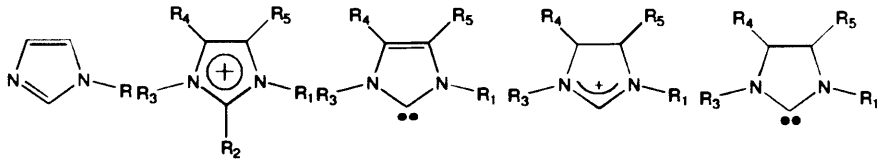


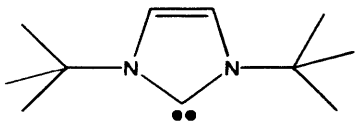
Figure 2.1.

The imidazolidinium salts **2.4** have a saturated C_4-C_5 backbone and a delocalized positive charge that is limited to the NCN region. These salts form the fully saturated imidazolidin-2-ylidenes (**2.5**). This thesis focuses exclusively on NHC's of type **2.3** and the synthesis of imidazolium salts **2.2**.

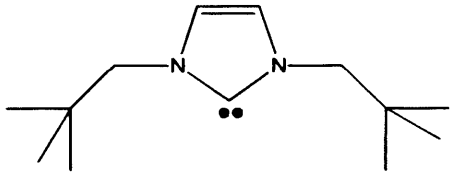
The positions of substituents on the imidazole ring are denoted by the prefix "im". For example, $_{im}C_2$ refers to the carbon atom at the 2-position and $_{im}C_2$-*H* to the hydrogen on that carbon.

2.1.2. Preparative Routes to Imidazolium Salts

As discussed in section 1.5 some Pd(II) complexes with methyl groups *cis* to the NHC group can undergo reductive elimination to form the hydrocarbylimidazolium salts.[2] A proposed method of reducing this reductive elimination is to have highly inductive groups as nitrogen substituents on the imidazole ring. These highly inductive groups could donate electron density into the carbene-metal bond and so reduce the rate of reductive elimination. One problem associated with highly inductive groups such as tertiary butyl groups (**2.6**) is that steric effects prevent easy formation of the desired metal complexes. To this end it was thought that a neopentyl-based structure (**2.7**) would provide a large enough inductive effect to prevent decomposition without being too bulky such that carbene formation is difficult (Figure 2.2).



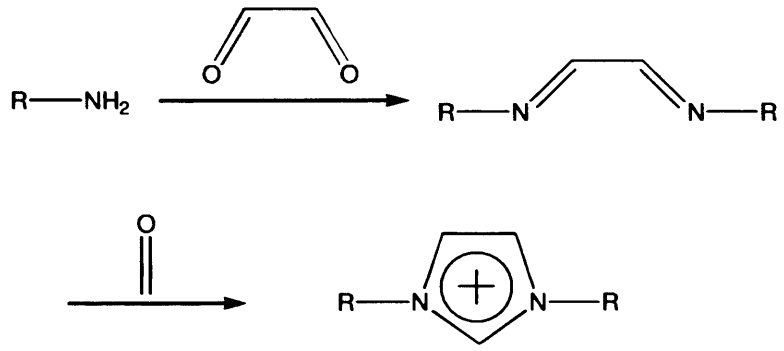
2.6



2.7

Figure 2.2

The imidazolium salts discussed in this chapter are formed from the di-imine precursors. These di-imines are formed from the primary amines (Scheme 2.1).

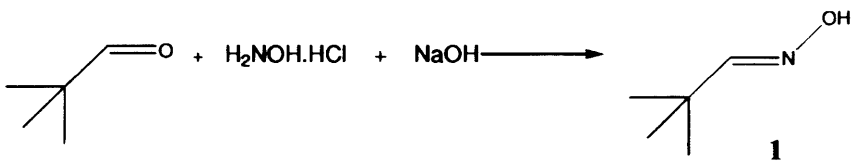


Scheme 2.1.

2.2. Results and Discussion

2.2.1. Synthesis of 1,3-bis-(2,2-dimethylpropyl)imidazolium chloride

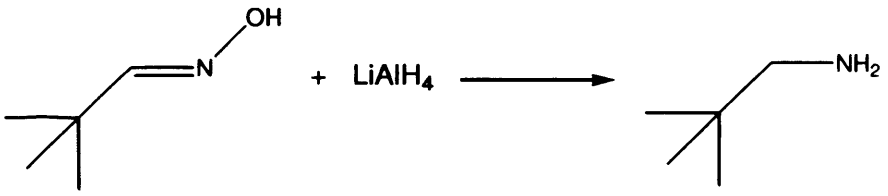
Neopentylamine (2,2-dimethylpropylamine, **2**) is not commercially available and so had to be synthesised before the imidazole could be prepared. The first step of the synthesis involved the formation of an oxime by reacting trimethylacetaldehyde with hydroxylamine hydrochloride in basic conditions. After work up the product **1** was formed as a white solid (Equation 2.1).



Equation 2.1

The ^{1}H NMR spectrum showed a singlet at 1.03ppm corresponding to the tertiary butyl group and a broad singlet at 7.30ppm corresponding to the hydroxyl proton. The proton bonded to the C=N appeared as a singlet at 7.49ppm.

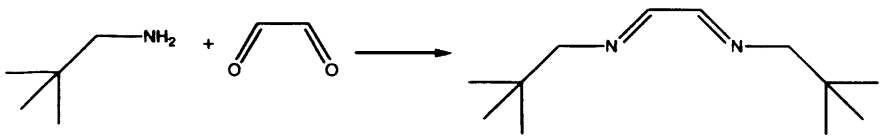
The amine was prepared by reduction of the oxime and the loss of water. Initial attempts using sodium borohydride met with limited success and yields were very low (less than 10%). The use of lithium aluminium hydride as the reducing agent gave a slight improvement of yield up to a maximum of 51%. The amine product **2** was a yellow liquid that could be stored for long periods of time at room temperature.



2

Equation 2.2.

The formation of the imidazolium salt followed a similar procedure to that of Arduengo.[3] Two equivalents of the amine were stirred with glyoxal in diethyl ether at room temperature (Equation 2.3). Removal of the solvent gave the di-imine product **3** as waxy yellow solid. The ^{1}H NMR spectrum showed the characteristic imine protons as a singlet at 7.84ppm.



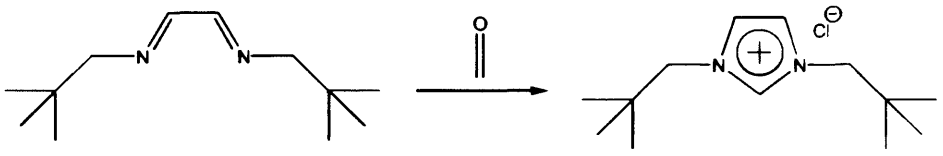
3

Equation 2.3.

The reaction of the di-imine **3** with paraformaldehyde and HCl formed a viscous brown liquid. This was triturated repeatedly with diethyl ether to give the N-alkyl substituted imidazolium salt **4** as a brown solid (Equation 2.4). The solid rapidly turned into a sticky, tar-like substance when exposed to the air but could be stored indefinitely under nitrogen.

The ^{1}H NMR spectrum shows a singlet at 9.87ppm corresponding to the $_{im}C_2$ proton. This shows that ring closure was successful. A singlet at 8.44ppm corresponds to the $C_{4,5}$ imine protons. No coupling was observed

so these protons are in chemically equivalent environments. The tertiary butyl groups appear as a singlet at 1.34ppm with no coupling observed.

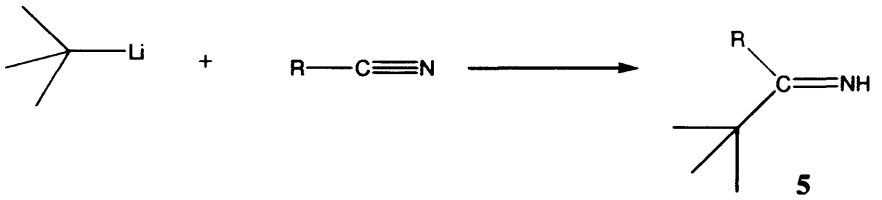


4

Equation 2.4.

2.2.2. Synthesis of Substituted Neopentyl Imidazolium Salts

The initial step in the synthesis of the more bulky imidazolium salt **8** involved the formation of an imine. The reaction was based upon the method of Mendenhall and Ingold.[4] Isobutyronitrile or trimethylacetonitrile was reacted with *tert*-butyl lithium at -78°C (Equation 2.5).



5

Equation 2.5.

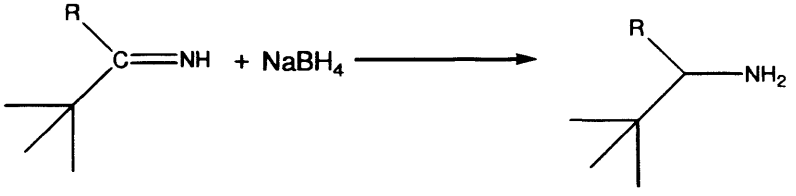
The product **5a** (R= isopropyl) was a clear liquid that could be stored in air at room temperature indefinitely. The ^{1}H NMR spectrum of **5a** shows a resonance at 9.53ppm that corresponds to the imine proton. There is a septet at 2.83ppm corresponding to the isopropyl proton that is coupling to the six equivalent protons of the isopropyl methyl groups. There is a doublet at 1.03ppm with a coupling constant of $J_{H\text{-}H}$= 7Hz corresponding to the CH_3 protons of the isopropyl group. The tertiary butyl groups appear as a singlet at 1.15ppm.

The ^{1}H NMR spectrum of **5b** (R =tertiary butyl) shows a singlet integrating to 18 protons at 1.03ppm corresponding to the tertiary butyl

groups. This singlet indicates that both tertiary butyl groups are chemically equivalent.

Reduction of the imine using sodium borohydride gave the amine product in up to 48% yield (Equation 2.6). The ^{1}H NMR spectrum of **6a** (R= isopropyl) showed an absence of a resonance at 9.53ppm showing that the C=N bond has been successfully reduced. The appearance of a singlet at 2.19ppm integrating to two protons shows that the amine product has been formed. The isopropyl proton resonances shift slightly upfield but the coupling patterns remain the same as discussed previously.

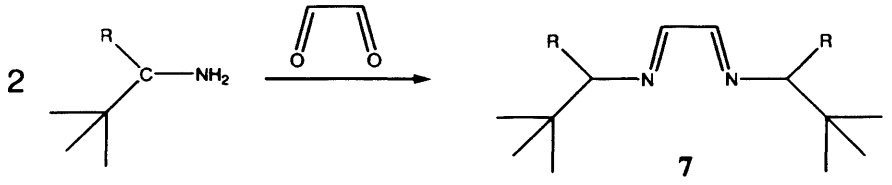
The resonance corresponding to the tertiary butyl groups in **6b** (R= tertiary butyl) appears as a singlet at 1.12ppm and the amino protons as a singlet at 2.15ppm.



6

Equation 2.6.

The formation of the di-imine **7** by reaction of two equivalents of the amine with glyoxal in diethyl ether proceeded well in good yields of up to 80% (Equation 2.7). The two equivalent imine protons appear as a singlet at 7.89ppm for imine **7a** (R= isopropyl) and 7.55ppm for imine **7b** (R= tertiary butyl).

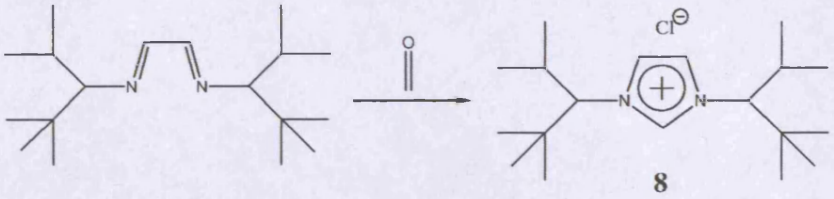


7

Equation 2.7.

The ring closing step to make the isopropyl substituted neopentyl imidazolium salt **8** proceeded well using paraformaldehyde in acidic

conditions (Equation 2.8). The imidazolium salt was formed in good yields of up to 83%. The characteristic $_{im}C_2$ proton appeared as a singlet at 9.62ppm in the ^{1}H NMR spectrum. The isopropyl methyl groups appeared as a doublet with a coupling constant of J_{H-H}=7Hz and there is a septet at 2.66ppm corresponding to the isopropyl proton coupling to the six equivalent methyl protons. The salt **8** was very moisture sensitive and had to be stored under nitrogen otherwise it formed a very sticky "tar-like" substance. The ^{1}H NMR spectrum of the "tar-like" substance was identical to the solid except that a large resonance corresponding to water appeared.



8

Equation 2.8.

The imidazolium salt **8** is potentially very interesting because it contains a chiral centre (Figure 2.3). Metal complexes of these proligands could be useful in enantioselective metal-catalysed reactions, for example asymmetric hydrogenation of unsaturated esters.[5]

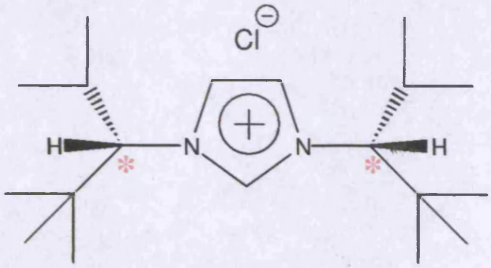
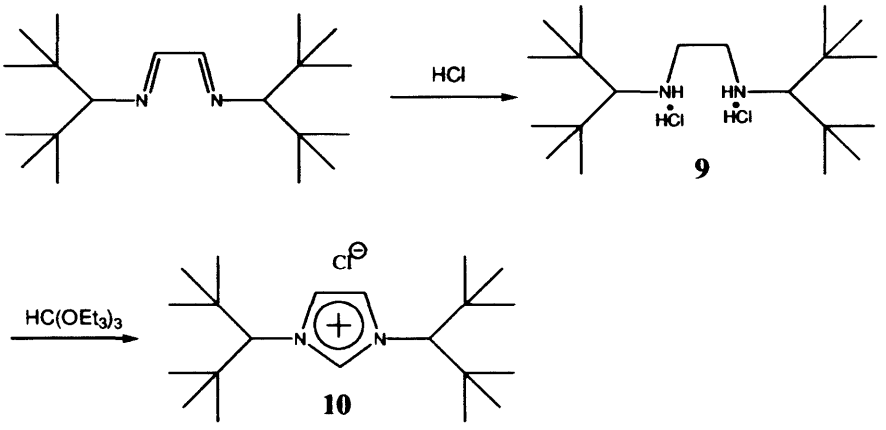


Figure 2.3. Substituted imidazolium salt **8** with chiral centers identified.

Initial attempts at the ring closure of the imine **7b** (R= tertiary butyl) proved unsuccessful. Even prolonged heating with paraformaldehyde did not result in ring closure. The imidazolium salt should precipitate immediately upon addition of HCl but analysis using ^{1}H NMR

spectroscopy after addition of HCl showed that the imine-salt had been formed as there was no resonance at around 10ppm that would correspond to the $_{im}C_2$ proton.

Small yields or no ring closure has been noted before when the N-aryl substituents had bulky groups in the *ortho* position.[6,7] Arduengo showed that treatment of the imine salt with triethyl orthoformate ($HC(OEt_3)_3$) at elevated temperatures resulted in ring closure of for more bulky N-substituents.[3] The imine **7b** was treated with sodium borohydride to reduce the C=N bond followed by concentrated HCl to form the imine salt **9**. The imine salt was treated with triethyl orthoformate to give the imidazolium salt **10** as a brown solid (Scheme 2.2).



Scheme 2.2.

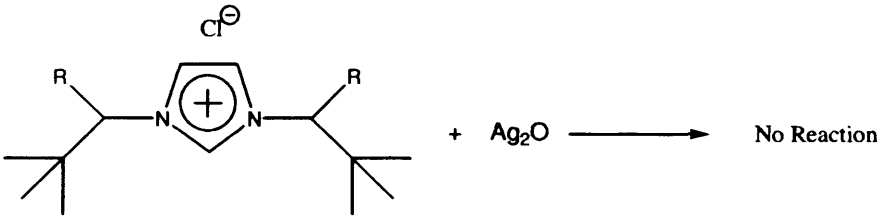
The ^1H NMR spectrum of the imidazolium salt **10** showed a singlet at 9.51ppm corresponding to the $_{im}C_2$ proton. This resonance showed that ring closure was successful. The $_{im}C_{4,5}$ protons appeared in the spectrum as a singlet at 8.01ppm. This resonance is shifted slightly upfield compared to the imine **7b**.

2.2.3. Metal Complex Formation

2.2.3.1. Silver Transfer Method

To form carbene complexes the $_{im}C_2$ proton must be removed using a suitable base. Wang and Lin showed that silver(I) oxide can be used as a base to form a silver-NHC complex.[8] This complex can then be used to transfer the NHC to a suitable metal, for example Pd(II).

Stirring the imidazolium salts **8** and **10** with silver(I) oxide in DCM for 24 hours resulted in no complex being formed. In both cases the ^{1}H NMR spectra showed exclusively the imidazolium salt starting materials. In both spectra there was a resonance at around 10ppm corresponding to the $_{im}C_2$ proton. This shows that silver oxide is not a strong enough base to deprotonate the imidazolium salts. More inductive N-substituent groups result in an increase in pK_a. For example, the pK_a of **2.5** ($R_{1,3}$=Me, $R_{4,5}$=H) is 28.5[9,10] so adding neopentyl-based N-substituents would cause an increase in the pK_a. This will make them more basic and so need stronger bases to deprotonate them.



R= iso-propyl
tert-butyl

Equation 2.9

2.2.3.2. Formation of Metal Complexes *via* Free Carbene

The free carbenes can be formed and then further reacted without being isolated to form metal complexes. The imidazolium salt **8** was stirred with potassium bistrimethylsilyl amide at low temperatures (-15°C) in THF and

this was filtered onto a solution of $PdCl_2COD$. The solvent was removed to give a tan solid. The ^1H NMR spectrum of this solid showed a small amount of starting material (**8**) and peaks corresponding to COD. This shows that complex formation was unsuccessful. This was because the imidazolium salt **8** is only sparingly soluble in THF and at low temperatures not enough would have been in solution for deprotonation to occur. When the reaction was carried out in DCM the imidazolium salt **8** dissolved fully. However, upon addition of the imidazolium salt/base solution to a THF solution of $PdCl_2COD$ a black precipitate formed immediately. The ^1H NMR spectrum of this solid was difficult to record because the black solid was insoluble in all deuterated solvents that were tried. After filtering of the deuterated mixture the spectrum showed some $_{im}C_2$ proton resonances at around 10ppm. Any complex that may have formed decomposed immediately. It should be noted that decomposition of Pd(II)-NHC complexes in chlorinated solvents has been observed before.[11] No other solvent systems were investigated due to time constraints.

2.3. Experimental

2.3.1. General Comments.

Reactions to synthesise compounds **8**, **10** and metal-carbene complexes were carried out under an atmosphere of argon or dinitrogen using standard Schlenk techniques. All ^{1}H NMR spectra were run on a Bruker 400MHz DPX Advance spectrometer. Mass spectra were obtained on a VG Fisons Platform II. Tetrahydrofuran, diethyl ether and hexane were dried over sodium benzophenone and freshly distilled under N_2 prior to use. Toluene was dried over potassium and distilled under N_2 before use. Methanol and dichloromethane were dried over calcium hydride and freshly distilled under N_2 before use. $CDCl_3$, d_6-DMSO, d_6-acetone, CD_2Cl_2 and C_6D_6 were purchased from Goss Scientific and dried over 3Å molecular sieves. All chemicals were purchased from Aldrich or Acros and used without further purification.

2.3.2. Bulky N-Alkyl Substituted Imidazolium Salts

Synthesis of 2,2-dimethylpropionaldehyde (1).

To a solution of trimethylacetaldehyde (15ml, 138mmol) and hydroxylamine hydrochloride (10.56g, 152mmol) in 1/1 EtOH/Water (100ml) was added with stirring NaOH (13.80g, 345mmol) as a 50% solution in water. The mixture was stirred for 2 hours and extracted with diethyl ether (100ml). The aqueous layer was cooled in ice and neutralised with conc.HCl and extracted with diethyl ether (2x100ml). The organic layers were combined and dried over $MgSO_4$. The solvent was removed under reduced pressure to give the product as a white solid (11.62g, 83%). ^{1}H NMR (400MHz, $CDCl_3$) δ 7.49 (s, 1H, *H*-C=N), 7.30(s, 1H, O*H*), 1.03(s, 9H, ^{t}Bu-*H*).

Synthesis of 2,2-dimethylpropylamine (2).

$LiAlH_4$ (3.75g, 98.75mmol) was added slowly to a solution of 2,2-dimethylpropionaldehyde (4.00g, 39.5mmol) in diethyl ether (100ml) at such a rate to cause a reflux. The mixture was refluxed for 18hours. The mixture was hydrolysed with diethyl ether (20ml) and water (10ml). This was filtered and the organic layer separated. The solid was extracted with DCM (100ml) and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure to give the product as a yellow liquid (1.75g, 51%). ^{1}H NMR (400MHz, $CDCl_3$) δ 2.07 (s, 2H, NH_2), 1.44 (s, 2H, CH_2), 1.05 (s, 9H, ^{t}Bu-H).

Synthesis of glyoxal-bis-(2,2-dimethylpropyl)imine (3).

2,2-dimethylpropylamine (3.0g, 34.42mmol) was dissolved in diethyl ether (100ml) and glyoxal (1.97ml, 17.21mmol, 40% solution in water) was added with vigorous stirring. This was stirred for 2 hours over which time the organic layer changed to a yellow colour. The layers were separated and the water layer washed with diethyl ether (2x25ml). The organic layers were dried over $MgSO_4$ and the solvent removed to give a yellow oil. ^{1}H NMR (400MHz, d_6-DMSO) δ 7.84 (s, 2H, N=C-*H*), 1.53 (s, 2H, C*H*$_2$), 1.11 (s, 9H, ^{t}Bu-*H*).

Synthesis of 1,3-bis-(2,2-dimethylpropyl)imidazolium chloride (4).

Paraformaldehyde (0.77g, 25.5mmol) was added to a solution of glyoxal-bis-(2,2-dimethylpropyl)imine (5.0g, 25.5mmol) in dry toluene (100ml) under nitrogen and heated to 100°C until the paraformaldehyde had dissolved. The mixture was cooled to below 40°C and HCl (6.4ml, 25.5mmol, 4M in 1,4-dioxane) was syringed in. The mixture turned a dark brown and was stirred for 18 hours. A dark brown sticky solid formed. The toluene was decanted and the solid was triturated with dry diethyl ether (5x25 ml) to give a brown solid (5.12g, 82%). ^{1}H NMR (400MHz, d_6-DMSO) δ 9.87 (s, 1H, $_{im}C_2$-*H*), 8.44 (s, 2H, $_{im}C_{4,5}$-*H*), 1.66 (s, 2H, C*H*$_2$), 1.34 (s, 9H, ^{t}Bu-*H*).

Synthesis of 1-isopropyl-2,2-dimethylpropylimine (5a).

Isobutyronitrile (17.48ml. 195mmol) was added dropwise with stirring to ^{t}BuLi (130ml, 195mmol, 1.5M in pentane) at –78°C. This mixture was allowed to come to room temp and was stirred for 2 hours to afford a yellow solution. This was cooled in ice and water (50ml) was added dropwise with stirring until the layers were both clear. The layers were separated and the aqueous layer extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$ and the solvent removed under reduced pressure to give the product as a colourless liquid (22.83g, 92%). ^{1}H NMR (400MHz, d_6-DMSO) δ 9.53 (s, 1H, C=N-*H*), 2.83 (septet, 1H, $CH(CH_3)_2$), 1.15 (s, 9H, ^{t}Bu-*H*), 1.03(d, $J_{H\text{-}H}$= 7Hz, 6H, $CH(CH_3)_2$).

Synthesis of 1-*tert*-butyl-2,2-dimethylpropylimine (5b).

Trimethylacetonitrile (16.6ml, 155mmol) was added dropwise with stirring to ^{t}BuLi (100ml, 155mmol, 1.5M in pentane) at –78°C. This mixture was allowed to come to room temp and was stirred for 2 hours to afford a yellow solution. This was cooled in ice and water (50ml) was added dropwise with stirring until the layers were both clear. The layers were separated and the aqueous layer extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$ and the solvent removed under reduced pressure to give the product as a colourless liquid (19.70g, 90%). ^{1}H NMR (400MHz, d_6-DMSO) δ 9.44 (s, 1H, C=N-*H*), 1.05 (s, 18H, ^{t}Bu-*H*).

Synthesis of 1-isopropyl-2,2-dimethylpropylamine (6a).

$NaBH_4$ (6.0g, 158mmol) was added to a solution of 1-isopropyl-2,2-dimethylpropylimine (5.0g, 39mmol) in methanol (50ml) and the mixture refluxed for 24 hours. The mixture was allowed to cool to room temperature and *c*.HCl was added dropwise with stirring until the mixture was pH1. This was filtered and the solvent removed from the filtrate under reduced pressure to give a white solid. The combined solids were stirred with $NaHCO_3$ for 1 hour and then extracted with DCM (3x50ml). The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure to give the product as a yellow liquid

(2.42g, 48%). ^{1}H NMR (400MHz, $CDCl_3$) δ 2.76 (septet, 1H, C*H*$(CH_3)_2$), 2.19(s, 2H, N*H*$_2$), 1.89 (s, 1H, *H*C-NH$_2$) 1.10 (s, 9H, ^{t}Bu-*H*), 1.03 (d, J_{H-H}=7Hz, 6H, CH(C*H*$_3$)$_2$).

Synthesis of 1-*tert*-butyl-2,2-dimethylpropylamine (6b).

$NaBH_4$ (15.0g, 400mmol) was added to a solution of 1-*tert*-butyl-2,2-dimethylpropylimine (18.81g, 133mmol) in methanol (50ml) and the mixture refluxed for 24 hours. The mixture was allowed to cool to room temperature and *c*.HCl was added dropwise with stirring until the mixture was pH1. This was filtered and the solvent removed from the filtrate under reduced pressure to give a white solid. The combined solids were stirred with $NaHCO_3$ for 1 hour and then extracted with DCM (3x50ml). The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure to give the product as a yellow liquid (5.32g, 28%). ^{1}H NMR (400MHZ, $CDCl_3$) δ 2.15(s, 2H, N*H*$_2$), 1.76 (s, 1H, *H*C-NH$_2$), 1.12 (s, 18H, ^{t}Bu-*H*).

Synthesis of glyoxal-bis-(1-isopropyl-2,2-dimethylpropyl)imine (7a).

1-isopropyl-2,2-dimethylpropylamine (5.25g, 41mmol) was dissolved in diethyl ether (50ml) and glyoxal (3.2ml, 27mmol, 40% in water) was added with vigorous stirring. This was stirred for 24 hours and the organic layer changed to a yellow colour. The layers were separated and the water layer washed with diethyl ether (2x25ml). The combined organic layers were dried over $MgSO_4$ and the solvent removed under reduced pressure to give a yellow oil (9.20g, 80%). ^{1}H NMR (400MHz, d_6-DMSO) δ 7.89 (s, 2H, *H*-C=N), 2.76 (septet, 1H, C*H*$(CH_3)_2$), 2.09 (s, 1H, *H*-C-N), 1.20 (s, 9H, ^{t}Bu-*H*), 1.15 (d, J_{H-H}=7Hz, 6H, CH(C*H*$_3$)$_2$).

Synthesis of glyoxal-bis-(1-*tert*-butyl-2,2-dimethylpropyl)imine (7b).

1-*tert*-butyl-2,2-dimethylpropylamine (5.25g, 41mmol) was dissolved in diethyl ether (50ml) and glyoxal (3.2ml, 27mmol, 40% in water) was added with vigorous stirring. This was stirred for 24 hours and the organic layer changed to a yellow colour. The layers were separated and the water layer washed with diethyl ether (2x25ml). The combined organic layers were

dried over $MgSO_4$ and the solvent removed under reduced pressure to give a yellow oil (9.20g, 80%). ^{1}H NMR (400MHz, d_6-DMSO) δ 7.55 (s, 2H, *H*-C=N), 1.82 (s, 1H, *H*-C-N), 1.36 (s, 18H, ^{t}Bu-*H*).

Synthesis of 1,3-bis-(1-isopropyl-2,2-dimethylpropyl) imidazolium chloride (8).

Paraformaldehyde (0.76g, 25.3mmol) was added to a solution glyoxal-bis-(1-isopropyl-2,2-dimethylpropyl)imine (5.28g, 25.3mmol) in dry toluene (100ml) under nitrogen and heated to 100°C until the paraformaldehyde had dissolved. The mixture was cooled to below 40°C and HCl(6.33ml, 25.3mmol, 4M in 1,4-dioxane) was syringed in. The mixture turned a dark brown and was stirred for 18 hours. A dark brown sticky solid formed. The toluene was decanted and this was triturated with dry diethyl ether (5x25 ml) to give the product as a brown solid (6.90g, 83%). ^{1}H NMR (400MHz, d_6-DMSO) δ 9.62 (s, 1H, $_{im}C_2$-*H*), 8.09 (s, 2H, $_{im}C_{4,5}$-*H*), 2.66 (septet, 1H, C*H*$(CH_3)_2$), 2.11 (s, 1H, *H*-C-N), 1.15 (s, 9H, ^{t}Bu-*H*), 1.04 (d, $J_{H\text{-}H}$=7Hz, 6H, CH(C*H*$_3)_2$).

Synthesis of N,N'-bis-(1-*tert*-butyl-2,2-dimethylpropylamino)ethane dihydrochloride (9).

Sodium borohydride (8.0g, 211mmol) was added slowly to a solution of glyoxal-bis-(1-*tert*-butyl-2,2-dimethylpropyl)imine (15.42g, 50mmol) in THF (200ml). The mixture was stirred at room temperature for 24 hours then refluxed for 2 hours. Water (200ml) and hydrochloric acid (3M, 200ml) was added cautiously over a period of 1 hour. The mixture was filtered and dried *in vacuo* to give the product as a colourless solid (16.39g, 85%). ^{1}H NMR (400MHz, d_6-DMSO) δ 3.72 (s, 4H, NC*H*$_2$), 1.96 (s, 1H, *H*-C-N), 1.44 (s, 18H, ^{t}Bu-*H*).

Synthesis of 1,3-bis-(1-*tert*-buty-2,2-dimethylpropyl)imidazolium chloride (10).

N,N'-bis-(1-*tert*-butyl-2,2-dimethylpropylamino)ethane dihydrochloride (11.68g, 30.3mmol), triethylorthoformate (100ml) and two drops of 96% formic acid were heated in distillation apparatus until the ethanol

distillation ceased. The mixture was cooled to 0°C and the solvent decanted to leave a dark brown oil. This was triturated with diethyl ether (3x100ml) to form a dark brown solid. This was dried *in vacuo* to give the product as a dark brown solid (8.73g, 80%). ^{1}H NMR (400MHz, d_6-DMSO) δ 9.51 (s, 1H, $_{im}C_2$-*H*), 8.01 (s, 2H, $_{im}C_{4,5}$-*H*), 1.62 (s, 1H, *H*-C-N), 1.01 (s, 18H, ^{t}Bu-*H*).

2.3.3. General Procedure for Synthesis of NHC-Metal Complexes.

Synthesis of Silver(I) Complexes.

Silver(I) oxide is added to a DCM solution of the imidazolium salt and stirred at room temperature in darkness for 24 hours over 4Å molecular sieves. The mixture is filtered and the solvent removed under reduced pressure to give the NHC-Silver complex.

Synthesis of Palladium(II) Complexes.

Potassium bistrimethyl silyl amide was added to a suspension of the imidazolium salt in THF at -15°C. The mixture was allowed to warm to room temperature and filtered onto a THF solution of $PdCl_2COD$. The mixture was stirred for 1 hour and the solvent removed under reduced pressure to give the product.

2.4. References

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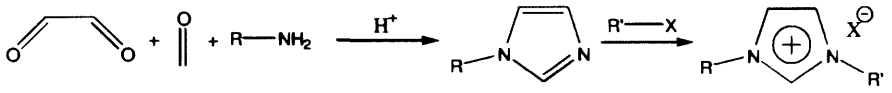
Chapter Three

Functionalised Phosphine-Imidazolium Salts

3.1. Introduction

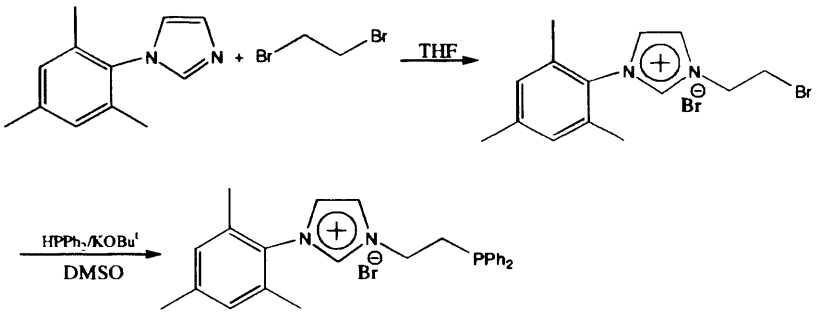
3.1.1. Preparative Routes to Phosphine-Imidazolium Salts

All the imidazolium salts in this chapter are derived from N-substituted imidazoles. The substituted imidazoles are prepared by the reaction of primary amines, glyoxal and formaldehyde in acidic conditions (Scheme 3.1). The unsymmetrical imidazolium salt is formed by reaction of the imidazole with an alky halide. This reaction follows an S_N2 mechanism and so it is difficult to achieve with a nucleophile any less reactive than a secondary alkyl bromide. This limits the number of different nitrogen substituents that can be attached to the imidazole ring.



Scheme 3.1. Synthesis of N-Substituted imidazoles and imidazolium salts.

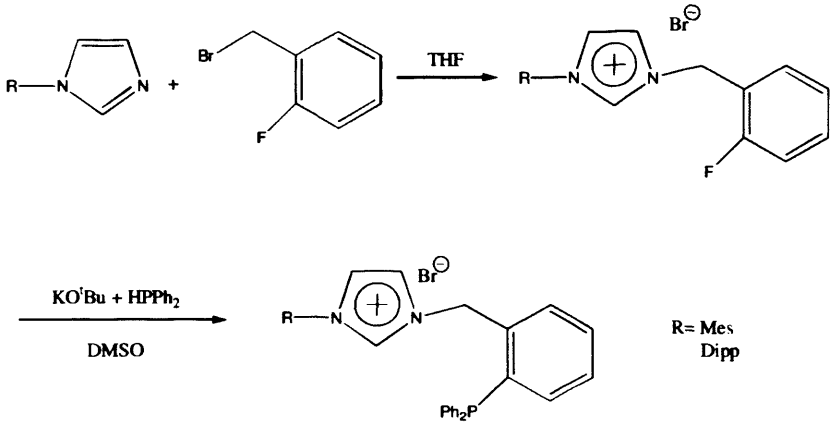
At the start of this project mixed phosphine-imidazolium salts with alkyl linkers were known. Substituted imidazoles were reacted with 1,2-dibromoethane in THF to give the imidazolium salts. These were then reacted with a mixture of diphenyl phosphine and KO^{t}Bu in DMSO to give the phosphine-imidazolium salt, **3.1** (Scheme 3.2).[4]



3.1

Scheme 3.2.

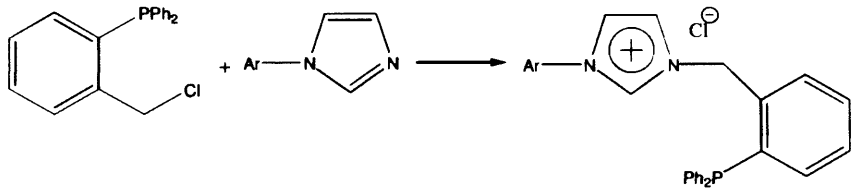
Work on the synthesis of phosphine-imidazolium salts with an aryl linker that form a 7-membered chelate ring has been previously carried out in the group. Substituted imidazoles were reacted with 2-fluorobenzyl bromide to give the imidazolium salt. These were reacted with the diphenyl phosphide salt in DMSO to give the mixed phosphine-imidazolium salt, **3.2** (Scheme 3.3).[4]



3.2.

Scheme 3.3.

Zhou *et al* used a different method to synthesise aryl linked phosphine-imidazolium salts (Equation 3.1).[5,6] Reaction of *o*-(diphenylphosphino)benzyl chloride with a substituted imidazole gave the desired product, **3.3** (Ar=Ph, Mes, Dipp), in up to 60% yields. These phosphine-imidazolium salts form a 7-membered chelate ring when complexed to a metal.

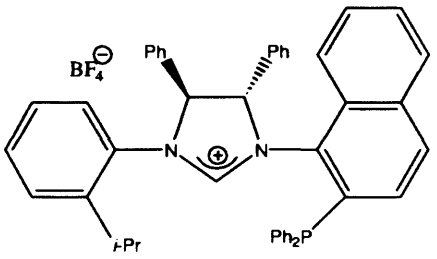


3.3

Equation 3.1.

The alkyl linked phosphine-imidazolium salts have been shown to generate active catalysts in the Heck coupling of aryl bromides when used *in situ*.[4] Palladium complexes of the alkyl linked ligands were shown to be moderately effective catalysts in the Heck coupling of aryl bromides, but seemed to decompose during the reactions to form palladium colloids.[7] This could be due to reductive elimination. The aryl linked ligands have been shown to be active in catalysis for Heck and Suzuki coupling reactions using palladium complexes that are formed *in situ*.[8,9]

Bappert and Helmchen synthesised imidazolium salts with a naphthyl linker between the saturated imidazolidinium ring and the phosphine, **3.4**.[10] These were coordinated to silver (I) and rhodium (I) and showed good activity in the asymmetric hydrogenation of α, β unsaturated esters.[10]



3.4

Figure 3.2.

3.1.2. Ligand Design

It has been shown that Pd(II) complexes of imidazol-2-ylidenes with methyl groups *cis* to the carbene can decompose. Reductive elimination occurs because orbitals of the carbene-carbon and methyl-carbon can overlap due to a "squeezing" of the bond angles.[11] This reductive elimination could be prevented by using a chelating bidentate ligand or a highly inductive substituent. Previous work has reported ligands with alkyl linkers[4,7] (**3.1**) and ligands with aryl linkers joined by one alkyl linker[5,6,10] (**3.3, 3.4**). These have shown moderate activity in C-C coupling reactions and some asymmetric hydrogenation although some decomposition has been observed in chlorinated solvents.[7]

The alkyl linker ligands, **3.1**, form a 6-membered chelate ring with a metal while the aryl linker ligands, **3.3**, form a 7-membered ring. The more rigid aryl rings may impart more stability by limiting the amount of movement of the linker around the metal centre caused by conformational changes of the alkyl chains.

To this end this thesis concentrated on synthesising a ligand that has a rigid aryl linker and forms a 6-membered chelate ring with a metal.

Attaching an aryl ring directly to the imidazole ring would form a 6-membered chelate ring upon coordination to a metal centre. This should prevent any "squeezing" of the ligand and so stop or slow down any reductive elimination. The potential for the phosphine group to be hemilabile could also prove to be interesting. Hemilability has been discussed in more detail in section 1.5.

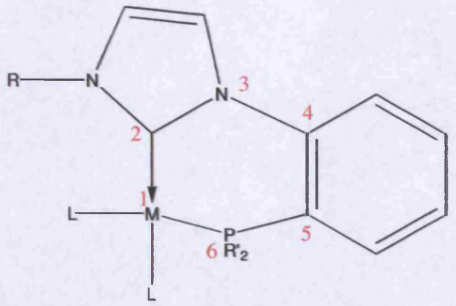
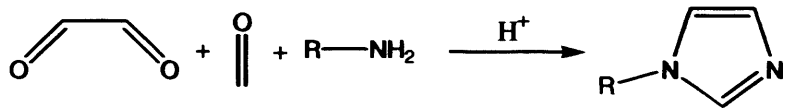


Figure 3.3.

3.2. Results and Discussion

3.2.1. Synthesis and characterisation of functionalised aryl phosphine-imidazolium salts.

A variation of the method discussed in section 3.1.2 and shown in scheme 3.1 was used to synthesise aryl phosphine-imidazolium salts that will form a 6-membered chelate ring when coordinated to a metal centre. The substituted imidazole, **11**, with fluorine in the ortho position on the aromatic ring was synthesised in moderate yields by the acid catalysed reaction of 2-fluoroaniline, glyoxal, formaldehyde and ammonium acetate (Equation 3.2).



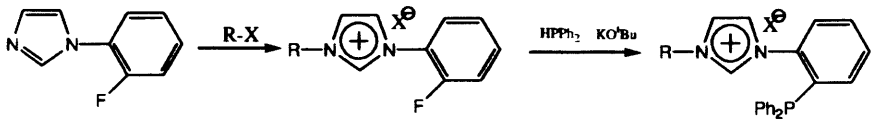
11

Equation 3.2.

The imidazole **11** was reacted with methyl iodide and benzyl bromide to give the corresponding imidazolium salts (1-fluorophenyl-3-methyl)imidazolium iodide, **12a**, and (1-fluorophenyl-3-benzyl)imidazolium bromide, **12b**, in almost quantitative yields. The imidazolium salts were purified by repeated washing with diethyl ether. The ^{1}H NMR spectra of the imidazolium salts showed a characteristic resonance for the $_{im}C_2$ protons at 10.19ppm and 10.31ppm for the methyl and benzyl substituted imidazolium salts respectively. The protons of the methyl group bonded to the imidazolium ring appear as a singlet at 4.25ppm. The protons of the CH_2 of the benzyl substituent appear as a singlet at 5.75ppm. The formation of the imidazolium salt follows an S_N2 pathway so only unhindered, primary alkyl halides such as methyl iodide can be used. The rate of the reaction falls dramatically as secondary and tertiary alkyl halides are used although isopropyl halides can be used under more forcing conditions.

The fluorophenyl salts were then reacted with a mixture of potassium tertiary butoxide and diphenyl phosphine at room temperature to give the phophine-imidazolium salts **13**. Initial attempts following the literature procedure[12] met with limited success, thought to be due to the forcing conditions needed to remove the DMSO solvent. The yields and purity of the product using this solvent were not very good. Large quantities of phosphine oxide and other unknown impurities were made so a different approach was attempted.

A DMF solution of potassium diphenyl phosphide (made from the reaction of diphenyl phosphine and potassium *tert*-butoxide) was added to a DMF solution of the fluorinated imidazolium salt and stirred at room temperature for 24 hours. More forcing conditions were not required for the nucleophilic aromatic substitution as these types of reaction require an electron withdrawing group at the ortho position. The imidazolium ring withdraws electron density and so helps stabilise the carbanion intermediate. After removal of the DMF solvent and quenching any unreacted potassium diphenyl phosphide with methanol the pure phosphine-imidazolium salts, **13** were made by repeated recrystalisation from DCM/diethyl ether.



11 **12** **13**

Scheme 3.4.

The phosphine-imidazolium salts, **13**, were isolated as orange solids and were fully characterised by ^{1}H, $^{31}P\{^{1}H\}$, ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis.

For salt **13a** (R=Me) the ^{1}H NMR spectrum showed a singlet at 9.12ppm corresponding to the $_{im}C_2$-*H* proton and a singlet at 4.0ppm for the three equivalent methyl protons. For spin ½ nuclei such as phosphorus we expect a singlet if there is no coupling. The resonance at -17.32ppm in the $^{31}P\{^{1}H\}$ NMR spectrum shows that free phosphine is present. No resonance further

upfield indicates that phosphine oxide was not formed. The $_{im}C_2$ carbon appeared as a singlet at 133.83ppm in the ^{13}C NMR spectrum. The mass spectrum showed a peak corresponding to the molecular ion at 343.1.

For salt **13b** (R=Benzyl) the ^1H NMR spectrum showed a singlet at 10.10ppm corresponding to the $_{im}C_2$-*H* proton. This is further downfield compared to the methyl substituted imidazolium salt and could be due to the fact that the benzyl group is withdrawing more electron density from the imidazolium ring. The CH_2 benzyl protons appeared as a singlet at 5.60ppm indicating that the protons were in an equivalent chemical environment. The singlet at -17.38ppm in the $^{31}P\{^1H\}$ NMR spectrum corresponds to the free phosphine and agrees closely with these and similar types of phosphine-imidazolium salts synthesised previously.[4-8] The $_{im}C_2$ carbon appeared as a singlet at 138.33ppm in the ^{13}C NMR spectrum. There was no evidence of phosphine oxide formation for either of the two imidazolium salts. The mass spectrum showed a peak corresponding to the molecular ion at 419.2. The elemental analysis for salts **13a** and **13b** were both in good agreement with calculated values. The NMR values for the $_{im}C_2$-*H* proton and the phosphine are very useful as these resonances will disappear (or shift in the case of the phosphine) upon successful coordination to a metal centre.

Diffusion of hexane into a DCM solution of **13a** yielded crystals suitable for single crystal X-ray crystallographic determination.

Figure 3.4 shows the view through the plane of the benzene ring to which both the phosphine and imidazolium salt are attached. The lone pair on the phosphine is oriented away from the imidazolium C_2 proton in order to minimize the electrostatic repulsion. The $_{im}C_2$ proton does not interact with any other atom or the iodide ion. The dihedral angle between the plane of the imidazolium ring and the plane of the central benzene ring is approximately 63.2°. 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)°).[13]

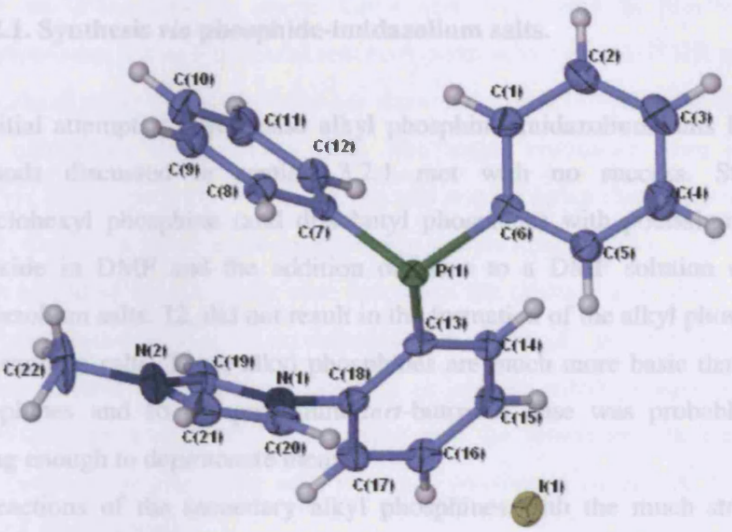


Figure 3.4. ORTEP diagram of N-substituted phosphine-imidazolium salt **13a** (R=Me) showing 50% probability ellipsoids. Hydrogens and two dichloromethane molecules omitted for clarity.

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)

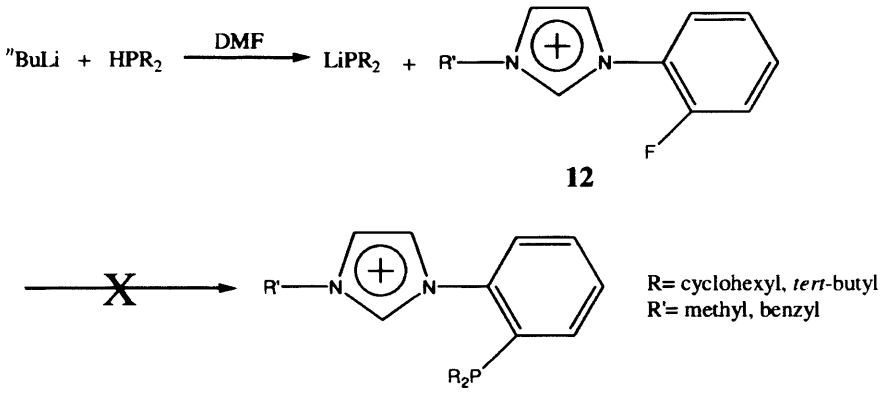
Table 3.1: Selected bond lengths (Å) and angles (degrees) for imidazolium salt **13a**.

3.2.2. Synthesis and characterisation of functionalised alkyl phosphine-imidazolium salts.

3.2.2.1. Synthesis *via* phosphide-imidazolium salts.

Initial attempts to synthesise alkyl phosphine-imidazolium salts by the methods discussed in section 3.2.1 met with no success. Stirring dicyclohexyl phosphine (and diisobutyl phosphine) with potassium *tert*-butoxide in DMF and the addition of these to a DMF solution of the imidazolium salts, **12**, did not result in the formation of the alkyl phosphine imidazolium salts. These alkyl phosphines are much more basic than aryl phosphines and so the potassium *tert*-butoxide base was probably not strong enough to deprotonate them.

Reactions of the secondary alkyl phosphines with the much stronger base *n*-butyl lithium resulted in successful deprotonation as shown by a colour change from colourless to a pale yellow. Addition of the alkyl phosphide salt solution to a solution of the fluorinated imidazolium salt, **12**, resulted in immediate precipitation of the fluorinated salt. This happened because the alkyl phosphide salt was dissolved in a mixture of DMF and hexane. The non-polar hexane solvent caused the highly polar fluorinated imidazolium salts to precipitate out before the nucleophilic substitution reaction could happen.



Scheme 3.5.

Removal of the solvent after formation of the alkyl phosphide salt gave a pale yellow solid. This solid was extremely reactive and seemed to decompose immediately if the stopper was taken off the Schlenk tube even under an atmosphere of argon. Great care was taken to prevent any decomposition but no successful reactions were achieved. All NMR spectra of products using this method did not show successful formation of the free alkyl phosphine imidazolium salts. The major resonance seen in the $^{31}P\{^{1}H\}$ NMR spectrum was at 23ppm and was probably due to phosphine oxide. Care was taken when synthesising the phosphide salt to use a very slight excess of base to make sure that when the mixture was added to the fluorinated imidazolium salt no deprotonation at the $_{im}C_2$ position occurred.

This method did not show whether or not the alkyl phosphide salts would undergo nucleophilic substitution with the fluorinated imidazolium salts because the phosphide salts were too reactive to isolate. A different method was attempted.

3.2.2.2. Synthesis *via* borane protected secondary phosphines.

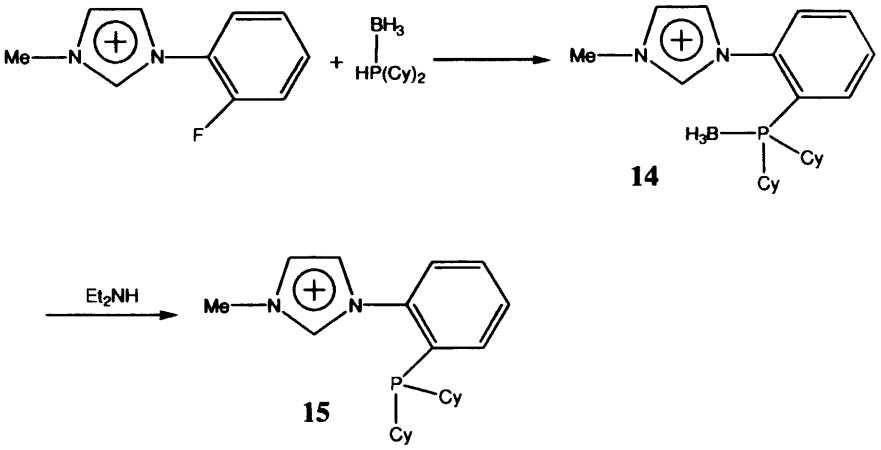
Secondary phosphines can be protected with borane groups. The phosphine-borane adducts are air stable and a wide variety of different secondary phosphines can be used, including both aryl and alkyl species. These borane protecting groups aid deprotonation, and hence the formation of the phosphide salts, as electron density is inductively removed from the phosphorous making the P-H proton more acidic. The borane protected phosphide-salt can be reacted with the fluorinated imidazolium salt to give the borane protected phosphine-imidazolium salt. The phosphine can be deprotected by using either a basic or acidic method. The most common method of deprotection is exchange of the phosphine-borane to an alternative Lewis base such as an amine (Equation 3.3).

Equation 3.3.

The equilibrium can be moved by heating with strongly basic amines such as morpholine, pyridine, diethylamine.[14,15,16] This forms the free phosphine and the borane-amine adduct.

Another method of deprotecting the phosphine is to use strongly acidic conditions to form the phosphonium salts. The free phosphine can be liberated by the addition of excess base.[17,18]

The borane protected secondary alkyl phosphines were synthesised according to literature procedure.[16] Borane THF solution was added to a solution of dicyclohexylphosphine in THF and the solvent removed to give the protected phosphine as a colourless air stable solid. The $^{31}P\{^{1}H\}$ NMR spectrum gave a quartet at 17.88ppm with a B-P coupling constant of 65.52Hz which is consistent with literature values.[16] A quartet is observed because the spin 1/2 phosphorus nucleus couples with the spin 3/2 boron nucleus. This was then deprotonated with ^{n}BuLi to give the phosphide salt which was added to a DMF solution of the fluorinated imidazolium salts, **12**. Filtration and removal of the solvent gave the borane protected alkyl-phosphine imidazolium salt, **14**, as an air stable, hygroscopic orange solid in up to 80% yield (Scheme 3.6.).



Scheme 3.6.

The $^{31}P\{^{1}H\}$ NMR spectrum gave a doublet at 14.57ppm which is upfield compared to the free borane protected phosphine. The coupling constant of 62.53Hz is consistent with literature values.[16] The $^{11}B\{^{1}H\}$ NMR gave a resonance at -44.36ppm which is consistent with literature values.[16] The proton at the C_2 position of the imidazolium ring appears at 9.48ppm in the ^{1}H NMR spectrum.

Deprotection of the phosphine was attempted by stirring **14** with a large excess of diethyl amine in DCM at 35°C for 7 days. The mixture was filtered to remove the amine-borane adduct and the solvent removed to give the free phosphine as an orange solid. However, analysis of the ^{1}H NMR spectrum showed that large amounts of the amine-borane adduct were still present. The $^{31}P\{^{1}H\}$ NMR spectrum showed that some free phosphine was present (resonance at-14.61ppm) but the major product was a resonance at 14.57ppm corresponding to the protected borane phosphine. There was also a resonance at 59.84ppm which was phosphine oxide. The orange solid was extracted with cold (0°C) THF (3x5ml) and the solvent removed to give a very small amount of orange solid. The $^{31}P\{^{1}H\}$ NMR spectrum showed a resonance at -14.61ppm corresponding to the free phosphine and a small amount of phosphine oxide (resonance at 59.84ppm). However, the yield was only 8%. The protected borane phosphine was stirred for extended periods (2weeks) but the yield was not improved. The phosphine-borane adduct was insoluble in other higher

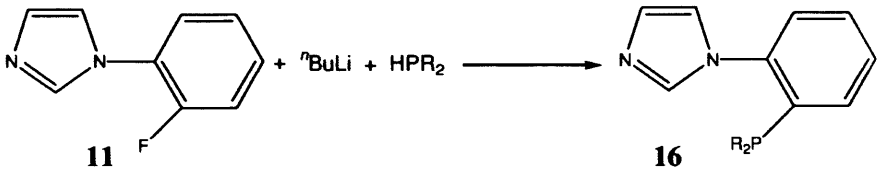
boiling solvents such as THF so no heating was possible as suggested by literature.[14,15,16] Use of dichloroethane as a solvent and subsequent heating did not increase the yield of the reaction.

A possible method that could have been used is to use a "sacrificial" phosphine or carbene to remove the borane from the dicyclohexylphosphine. The formation of the more stable adducts may have moved the equilibrium of the reaction (Figure 3.9) to the right and so increased the yield.

3.2.2.3. Synthesis *via* phosphine-imidazoles.

The strategies discussed in Sections 3.2.2.1 and 3.2.2.2 above involved the nucleophilic aromatic substitution of a phosphide salt with an imidazolium salt. The insolubility and hydroscopic nature of these imidazolium salts caused difficulties in the isolation of the free alkyl phosphine rather than the phosphine oxide. Danopuolos and co-workers showed that phosphine oxide-imidazolium salts with alkyl linkers, **3.6**, can be reduced using trichlorosilane in refluxing chlorobenzene.[7] However, Zhou and co-workers showed that the phosphine oxide with an aryl linker, **3.7**, could not be reduced.[6] To avoid having to reduce the phosphine oxide it was decided to synthesise the phosphine-substituted imidazole in a similar manner to that of Bappert and Helmchen.[10]

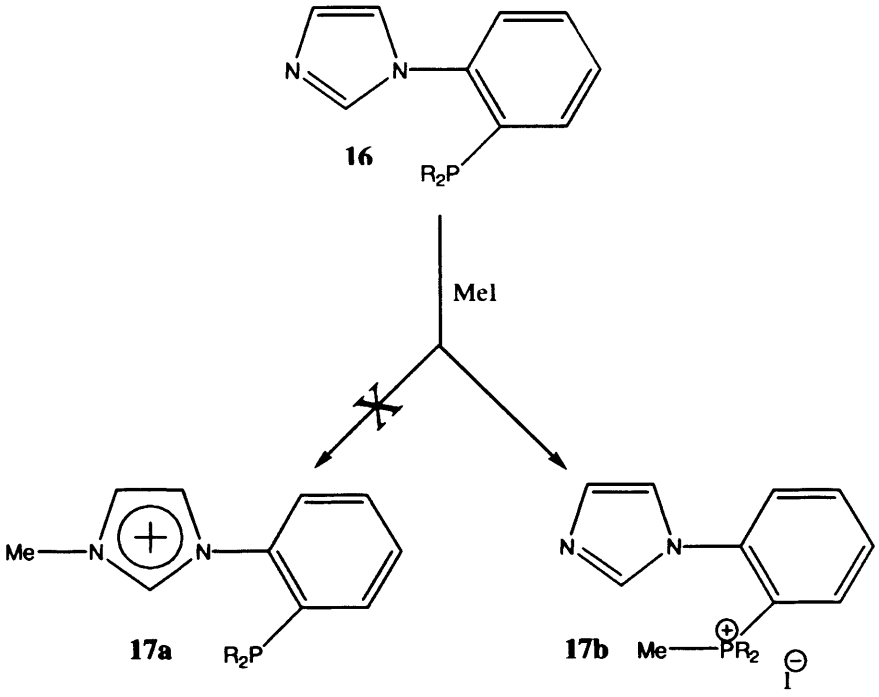
The secondary alkyl phosphine was reacted with ^{n}BuLi in THF at -78°C to form the phosphide salt. This was then added to a solution of **11** in THF at -30°C to form the phosphine-imidazole, **16**, as a brown oil. The $^{31}P\{^{1}H\}$ NMR spectrum showed a resonance at -15.88ppm corresponding to the desired free alkyl phosphine. There was also a very small amount of the starting secondary phosphine at -27.90ppm.



11 **16**

Equation 3.4. Synthesis of alkyl-phosphine imidazole where R= cyclohexyl, ^{i}Bu.

Reaction of **16** with methyl iodide in THF at -30°C did not form the desired product, **17a**. Rather than the desired S_N2 substitution reaction at the nitrogen occurring, the nucleophile reacted with the phosphine to form a phosphonium salt, **7b**. The $^{31}P\{^{1}H\}$ NMR spectrum of the product shows a resonance at δ 36.35ppm that corresponds to a methyl phosphonium salt. In the $^{31}P\{^{1}H\}$ NMR spectrum there is a very small resonance at -15.47ppm that might be the free phosphine imidazolium salt. A resonance at 9.72ppm in the ^{1}H NMR spectrum shows that some of the free phosphine imidazolium salt, **17a**, was formed but the major product was the phosphonium imidazole, **17b**.



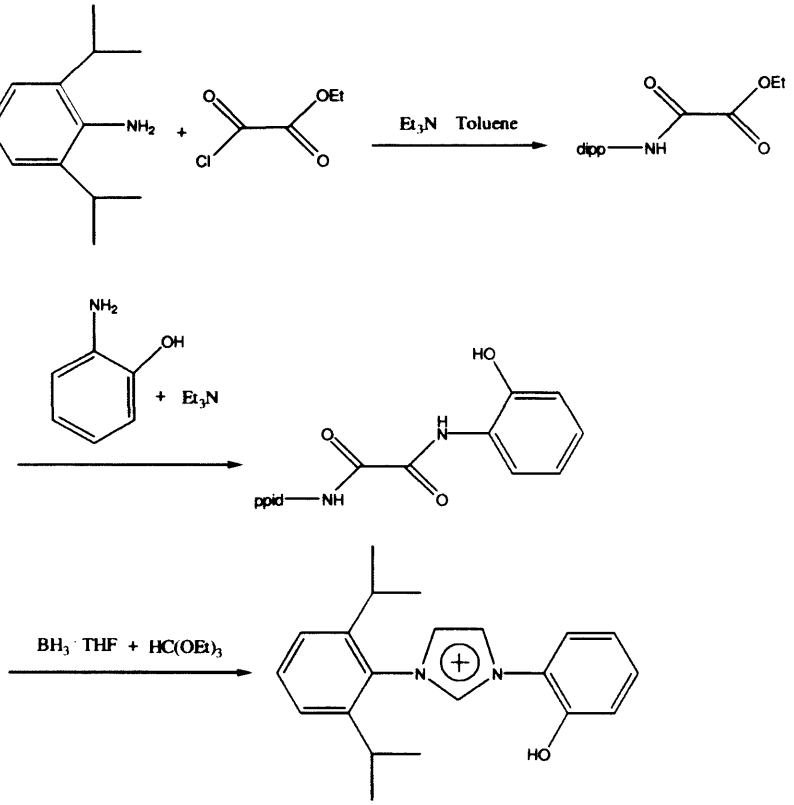
Scheme 3.7. Synthesis of alkyl-phosphine imidazolium salts where R= cycolhexyl, ^{t}Bu.

Reacting the phosphonium salt **17b** with methyl iodide may have resulted in the formation of the phosphonium-imidazolium salt being formed. Methods to form the free phosphine or complexation of this proligand to Pd(II) or Pd(0) were not attempted due to time constraints.

3.2.3. Synthesis of Imidazolium salts with aryl N-substituents.

The methods discussed above involve the synthesis of imidazolium salts with alkyl substituents in the 3 position of the ring. This is achieved by nucleophilic substitution and so only primary alkyl halides can be used although some secondary alkyl halides can be used under forcing conditions. Other methods were investigated to try to synthesise imidazolium salts bearing alkyl substituents at the 3 position of the ring.

Grubbs *et al* synthesised imidazolium salts with different aryl substituents at the 1 and 3 positions (**3.10**, Scheme 3.8) and successfully complexed these to palladium(II).[19] This reaction used aryl amines as starting materials and so a wide range of different imidazolium salts could be formed.

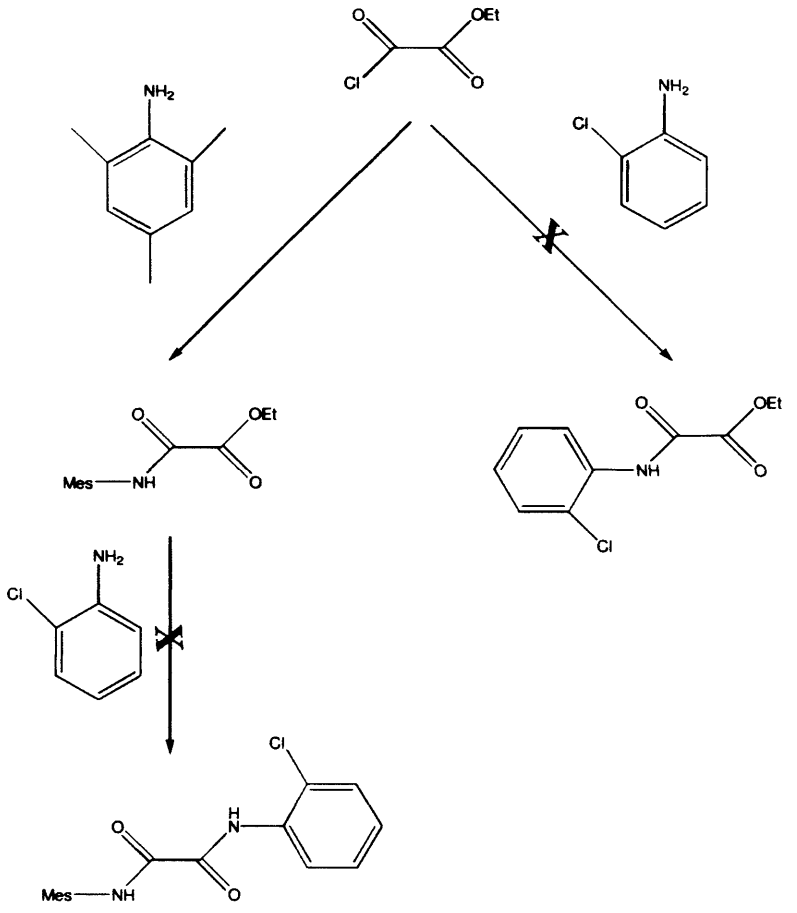


3.10

Scheme 3.8. Synthesis of unsymmetrical imidazolium salts. Adapted from Grubbs *et al.*[19]

Grubbs' method used 2-hydroxyaniline in the second step. When 2-chloroaniline was used then no reaction was observed. This is because the hydroxyl group activates the aryl amine functional group by donating electron density from its lone pair to the delocalised aromatic ring and so increases reactivity. If there is a halo group at this position then it deactivates the group as it withdraws electron density from the aromatic ring and so destabilises the intermediate. However, the reaction was

attempted in refluxing toluene for seven days but still no reaction occurred (Scheme 3.9).



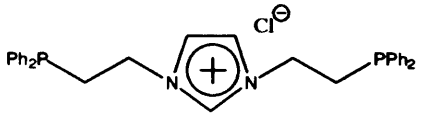
Scheme 3.9.

3.2.4. Synthesis of tridentate phosphine-imidazolium salts.

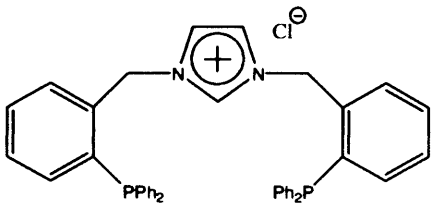
There are numerous examples of tridentate ligands with alkoxide,[20] pyridyl,[21,22] and picolyl[23,24,25] donors. These ligands have been successfully complexed to metal centres and their catalytic applications studied. Tridentate phosphine-carbene ligands have also been synthesised. The group of Lee synthesised PCP ligands containing alkyl linkers of the type **3.11** (Figure 3.4).[26] The method was similar to that discussed above for bidentate phosphine-carbene ligands in that a phosphide salt was reacted

with a halogen substituted imidazolium salt to give the phosphine-imidazolium salt.

Tridentate PCP ligands with an aryl linker were synthesised by Wang *et al.* The reaction of *o*-(diphenylphosphino)benzyl chloride with 1*H*-imidazole with K_2CO_3 as a base gave the desired product **2.12** in up to 32% yields.[5, 9]



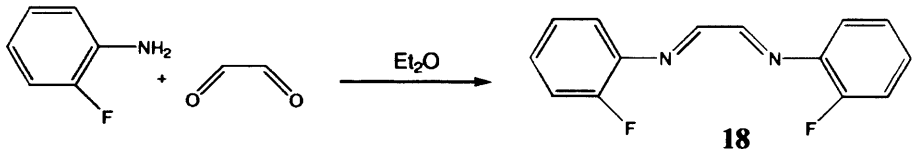
3.11



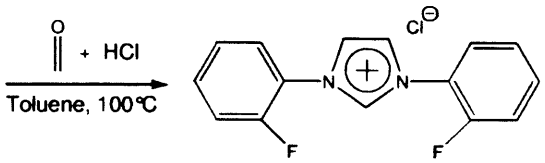
3.12

Figure 3.4.

The method used to synthesise ligands where the aryl linker is directly attached to the imidazolium ring followed the method of Arduengo *et al.*[26] Reaction of two equivalents of 2-fluoroaniline with glyoxal in diethyl ether at room temperature gave the diimine **18**. The diimine was reacted with paraformaledehyde and HCl in hot toluene (100°C) to form the symmetrical fluorinated imidazolium salt **19**.



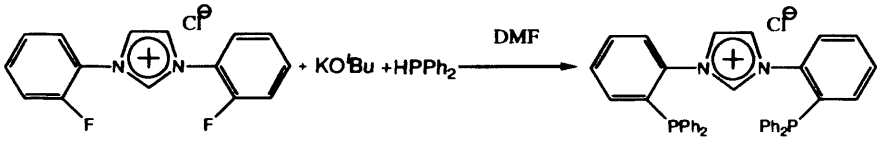
18



19

Scheme 3.10.

The fluorinated imidazolium salt **19** was a hygroscopic light brown solid. The ^{1}H NMR spectrum showed a singlet at 10.36ppm corresponding to the $_{im}C_2$ proton. Two equivalents of diphenyl phosphine was added to a DMF solution of potassium *tert*-butoxide to give a DMF solution of the potassium phosphide salt. This deep red solution was added dropwise to a DMF solution of the fluorinated imidazolium salt **19**. After stirring overnight a dark brown oily looking solution had formed. The DMF solvent was removed and methanol added to quench any unreacted diphenyl phosphine. After extraction with DCM and filtering through celite the solvent was removed to give a brown solid.



Equation 3.5. **20**

The ^{1}H NMR spectrum was very complicated and showed that there was a mixture of products. The $^{31}P\{^{1}H\}$ NMR spectrum had a major resonance at 10ppm which does not correspond to the free phosphine. There was a very small resonance at -14ppm which could have been some of the desired product **20**. This shows that the nucleophilic aromatic substitution of the fluoride group did not occur as readily as for the unsymmetrical analogue **13**. This may be because the electron withdrawing imidazolium ring is in the ortho position for both the fluoride groups and so does not activate the ring sufficiently for the reaction to happen.

All attempts to separate the mixture by extraction using different solvents failed. The mixture was insoluble in most solvents.

3.3. Experimental

3.3.1. General Comments.

All reactions to synthesise compounds **12-20** were carried out under an atmosphere of argon or dinitrogen using standard Schlenk techniques. ^{31}P (referenced to H_3PO_4 at δ_P=0) and ^{11}B (referenced to $Et_2O{\bullet}BF_3$ at δ_B=0) NMR spectra were run on a JEOL Eclipse 300MHz spectrometer. ^{1}H and ^{13}C NMR spectra were run on a Bruker 400MHz DPX Advance spectrometer. Mass spectra were obtained on a VG Fisons Platform II. Tetrahydrofuran, diethyl ether and hexane were dried over sodium benzophenone and freshly distilled under N_2 prior to use. Toluene was dried over potassium and distilled under N_2 before use. Methanol and dichloromethane were dried over calcium hydride and freshly distilled under N_2 before use. $CDCl_3$, d_6-DMSO, d_6-acetone, CD_2Cl_2 and C_6D_6 were purchased from Goss Scientific and dried over 3Å molecular sieves and freeze-thaw degassed before use. All chemicals were purchased from Aldrich or Acros and used without further purification. DMF and DMSO were freeze-thaw degassed before use.

3.3.2. Aryl phosphine-imidazolium salts.

Synthesis of 1-(2-fluorobenzene)imidazole (11).

Glyoxal (16.4ml, 0.143mmol, 40% in water) and formaldehyde (10.7ml, 0.143mmol, 37% in water) in glacial acetic acid (30ml) was heated to 70°C. To this was added over a period of three hours a mixture of NH_4OAc (11.0g, 0.143mmol) and 2-Fluoroaniline (10.4ml, 0.143mmol) in glacial acetic acid (30ml). The resulting mixture was heated at 70°C for 12 hours to give a clear red solution. This was allowed to cool to room temp and was added dropwise with stirring to a suspension of $NaHCO_3$ (151g, 1.80mol) in water (1000ml) to form an orange oil. The water layer was decanted off and extracted with DCM (3x75ml) and the organic layers combined with the oil, dried over $MgSO_4$ and the solvent removed under reduced pressure

to give the product as an orange oil (8.75g, 38%). ^{1}H NMR (400MHz, $CDCl_3$) δ 7.74 (s, 1H, $_{im}C_2$-*H*), 7.18 and 7.13 (2xs, each 1H, $_{im}C_{4,5}$-*H*), 7.33 (multiplets, 4H in total, aromatic-*H*).

Synthesis of (1-fluorobenzene-3-methyl)imidazolium iodide (12a).

Methyl iodide (19.16g, 135mmol) and 1-(*o*-fluorobenzene)imidazole (7.29g, 45mmol) was dissolved in THF (40ml) and heated to reflux for 12 hours. The solid formed was filtered, washed with Et_2O (3x10ml) and dried *in vacuo* to give the product as a tan solid (11.72g, 86%). ^{1}H NMR (400MHz, $CDCl_3$) δ 10.19 (s, 1H, $_{im}C_2$-*H*), 7.82 and 7.60 (2xs, each 1H, $_{im}C_{4,5}$-*H*), 7.97-7.20 (multiplets, 4H in total, aromatic-*H*), 4.25 (s, 3H, Me-*H*). ^{13}C NMR (500MHz, $CDCl_3$) δ 136.7, 132.4, 126.1, 124.8, 122.7, 122.3, 117.7, 117.4 ($_{arom}C$), 37.9 (CH_3). MS (ES): *M/z* 177.1 $[M\text{-}I]^+$

Synthesis of (1-benzene-*o*-diphenylphosphine-3-methyl)imidazolium iodide (13a).

KO^{t}Bu (0.13g, 1.17mmol) was dissolved in DMF (6ml) and $HPPh_2$ (0.20ml, 1.15mmol) added. This mixture was added to a solution of 1-methyl-3-(2-fluoraniline)imidazolium iodide (0.35g, 1.15mmol) in DMF (10ml) to give a clear orange solution. This was stirred at room temperature for 12 hours. The solvent was removed under reduced pressure to give a brown solid. MeOH (10ml) was added to quench any excess $HPPh_2$. The solvent was removed and the residue was extracted with DCM (3x10ml) and filtered through celite. The volume of the DCM was reduced and Et_2O added to give an orange precipitate. This was filtered, washed with Et_2O (3x10ml) and dried *in vacuo* to give the product as an orange solid (0.43g, 80%). ^{1}H NMR (400MHz, $CDCl_3$) δ 9.12 (s, 1H, $_{im}C_2$-*H*), 7.94 and 7.80 (s, 1H, $_{im}C_{4,5}$-*H*), 7.53-6.92 (multiplets, 14H in total, $_{arom}$C-*H*), 4.0 (s, 3H, Me-*H*). ^{13}C NMR (500MHz, d_6-DMSO) δ 133.83 ($_{im}C_2$), 133.77 and 133, 130.74-123.39 ($_{arom}$C), 35.92 (CH_3). $^{31}P\{^1H\}$ NMR (500MHz, d_6-DMSO) -17.32 (s). MS (ES): *M/z* 343.1360 $[M\text{-}I]^+$. 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.

Synthesis of (1-fluorobenzene-3-benzyl)imidazolium bromide (12b).

Methyl iodide (19.16g, 135mmol) and 1-(*o*-fluorobenzene)imidazole (7.29g, 45mmol) was dissolved in THF (40ml) and heated to reflux for 12 hours. The solid formed was filtered, washed with Et_2O (3x10ml) and dried *in vacuo* to give the product as a tan solid (11.72g, 86%). ^1H NMR (400MHz, d_6-DMSO) δ 10.31 (s, 1H, $_{im}C_2$-*H*), 7.82 and 7.60 (2xs, each 1H, $_{im}C_{4,5}$-*H*), 8.31-7.39 (multiplets, 19H in total, aromatic-*H*), 5.75 (s, 2H, C*H*$_2$). ^{13}C NMR (500MHz, $CDCl_3$) δ 156.34, 152.34, 134.52, 132.50, 137.24, 128.85, 126.62, 125.74, 123.64, 122.74, 117.25 ($_{arom}C$), 57.5 (*C*H_2). MS (ES): *M/z* 253.1 $[M-Br]^+$.

Synthesis of (1-benzene-*o*-diphenylphosphine-3-benzyl)imidazolium bromide (13b).

KO^{t}Bu (0.13g, 1.17mmol) was dissolved in DMF (6ml) and $HPPh_2$ (0.20ml, 1.15mmol) added. This mixture was added to a solution of 1-methyl-3-(2-fluoraniline)imidazolium iodide (0.35g, 1.15mmol) in DMF (10ml) to give a clear orange solution. This was stirred at room temperature for 12 hours. The solvent was removed under reduced pressure to give a brown solid. MeOH (10ml) was added to quench any excess $HPPh_2$. The solvent was removed and the residue was extracted with DCM (3x10ml) and filtered through celite. The volume of the DCM was reduced and Et_2O added to give an orange precipitate. This was filtered, washed with Et_2O (3x10ml) and dried *in vacuo* to give the product as an orange solid (0.43g, 80%). ^1H NMR (400MHz, $CDCl_3$) δ 10.10 (s, 1H, $_{im}C_2$-*H*), 7.60 and 7.49 (s, 1H, $_{im}C_{4,5}$-*H*), 7.39-6.91 (multiplets, 19H in total, $_{arom}$C-*H*), 5.60 (s, 2H, C*H*$_2$). ^{13}C NMR (500MHz, d_6-DMSO) δ 138.33 ($_{im}C_2$), 137.76, 134.71, 133.74, 133.57, 133.27, 131.23, 130.80, 129.77, 129.11, 128.94, 128.73, 128.25, 127.77, 124.69, 122.37 ($_{arom}$C), 51.90 (*C*H_2). $^{31}P\{^1H\}$ NMR (500MHz, d_6-DMSO) -17.38 (s). MS (ES): *M/z* 419.2 $[M-Br]^+$. 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.

3.3.3. Alkyl phosphine-imidazolium salts.

Synthesis of dicyclohexylphosphine borane.

BH3·THF solution (10ml, 10mmol, 1M in THF) was added to a solution of dicyclohexylphosphine (2ml, 5.57mmol) in THF (20ml) dropwise with vigorous stirring at room temperature. This was stirred at room temperature for one hour. The solvent was removed to give the product as a colourless solid (1.67g, 92%). $^{31}P\{^{1}H\}$ NMR (300MHz, $CDCl_3$) δ 17.88 (q, $^{1}J_{B\text{-}P}$= 62.52Hz).

Synthesis of (1-benzene-*o*-boranedicyclohexylphosphine-3-methyl)imidazolium iodide (14).

^{n}BuLi (2.98ml, 4.76mmol, 1.6M in hexane) was added to a solution of dicyclohexylphosphine borane (1.0g, 4.76mmol) in THF (18ml) at 0°C. The solution was allowed to warm to room temperature and stirred for one hour. The solvent was removed *in vacuo*. DMF (10ml) was added to the solid and this was added dropwise to a solution of 1-(2-fluorobenzene)-3-methyl imidazolium iodide (2.21g, 4.70mmol) in DMF (10ml). The mixture was stirred at room temperature for 8 hours. Solvent was removed and residue extracted with DCM (3 x 10ml) and filtered through celite. The volume of the solvent was reduced to approximately 2ml and Et_2O (20ml) added. The sticky solid was filtered, washed with Et_2O (3 x 10ml) and dried *in vacuo* to give the product as a sticky orange solid (2.25g, 71%). ^{1}H NMR (400MHz, d_6-DMSO) δ 9.48 (s, 1H, $_{im}C_2$-*H*), 8.02 (s, 1H, $_{im}C_5$-*H*), 7.81 (s, 1H, $_{im}C_4$-*H*), 7.62 (t, 1H, $^{1}J_{H\text{-}H}$= 7.52Hz, $_{arom}C_3$-*H*), 7.55, (multiplet, 2H, $_{arom}C_{4,5}$-*H*), 7.31 (t, 1H, $^{1}J_{H\text{-}H}$= 7.42Hz, $_{arom}C_6$-*H*), 3.82 (s, 3H, Me-*H*), 2.58 and 1.09 (multiplets, 22H in total, $_{Cy}C$-*H*). $^{31}P\{^{1}H\}$ NMR (300MHz, d_6-DMSO) δ 14.57. ^{11}B NMR (300 MHz, d_6-DMSO) δ -44.36.

Synthesis of (1-benzene-*o*-dicyclohexylphosphine-3-methyl)imidazolium iodide (15).

1-(o-dicyclohexylphosphinoboranebenzene)-3-methyl imidazolium iodide (1.0g, 1.51mmol) was dissolved in DCM (20ml) and diethylamine (4ml, 38mmol) was added. The mixture was stirred at 35°C for six days.

The solution was cooled to room temperature and filtered through celite, with the solid being extracted with DCM (3 x 5ml) and filtered. The volume of the solution was reduced to approximately 2ml and Et_2O added. The solid was filtered, washed with Et_2O and dried *in vacuo* to give the product as an orange solid (0.016g, 3%). ^1H NMR (400MHz, d_6-DMSO) δ 9.79 (s, 1H, $_{im}C_2$-*H*), 8.21 (s, 1H, $_{im}C_5$-*H*), 8.05 (s, 1H, $_{im}C_4$-*H*), 7.83 (t, $^1J_{H-H}$= 7.68Hz, $_{arom}C_3$-*H*), 7.67 (multiplets, 2H, $_{arom}C_{4,5}$-*H*), 7.50 (t, 1H, $^1J_{H-H}$= 7.24Hz, $_{arom}C_6$-*H*), 3.98 (s, 3H, Me-*H*). $^{31}P\{^1H\}$ NMR (300MHz, d_6-DMSO) δ -14.61.

Synthesis of 1-(benzene-*o*-dicyclohexylphosphine) imidazole (16).

^{n}BuLi (3.63ml, 5.81mmol) was added to a solution of diisobutylphosphine (1ml, 5.81mmol) in THF (10ml) at -78°C and allowed to warm to room temperature. This was added to a solution of 1-(*o*-fluorobenzene)imidazole (0.94g, 5.81mmol) in THF (8ml) at -30°C and allowed to warm to room temperature. This was stirred for 8 hours, filtered through celite to remove LiF and the solvent removed to give **6** as a viscous brown oil (1.85g, 36%). ^1H NMR (400MHz, C_6D_6) 7.74 (s, 1H, $_{im}C_2$-*H*), 7.18 and 7.13 (2xs, each 1H, $_{im}C_{4,5}$-*H*), 7.33 (multiplets, 14H in total, aromatic-*H*). $^{31}P\{^1H\}$ NMR (300MHz, C_6D_6) δ -15.88.

Synthesis of 1-(benzene-*o*-dicyclohexylphosphine-3-methyl)imidazolium iodide (17).

Methyl iodide (0.37ml, 6.0mmol) was added to a solution of **6** (1.68g, 5.83mmol) in THF (10ml) at room temperature and stirred for 12 hours. This was filtered, washed with Et_2O (3x10ml) and dried *in vacuo* to give **7** as a tan solid. $^{31}P\{^1H\}$ NMR (300MHz, d_6-DMSO) δ 36.35 (phosphonium salt).

Synthesis of glyoxal-bis-(*o*-fluorobenzene)imine (18).

2-Fluoroaniline (20ml, 207.16mmol) and glyoxal (11.88ml, 103.58mmol, 40% in H_2O) were dissolved in diethyl ether (200ml) and stirred at room temperature for 12 hours. The organic layer was separated

and the aqueous layer extracted with diethyl ether (3x20ml). The combined organic extracts were dried over $MgSO_4$ and the solvent removed to give the product **8** as a yellow solid (23.58g, 93%). ^{1}H NMR (400MHz, $CDCl_3$) δ 7.82 (s, 2H, NC*H*C*H*N).

Synthesis of 1,3-bis(*o*-fluorobenzene)imidazolium chloride (19).

Paraformaldehyde (1.20g, 40mmol) and Glyoxal-bis-(*o*-fluorobenzene)imine (**8**) were stirred in toluene (170ml) at 100°C until all the paraformaldehyde had dissolved. The mixture was allowed to cool to below 40°C and HCl (10ml, 40mmol, 4M in 1, 4-dioxane) was added. The mixture was stirred for 12 hours. The toluene was decanted off *via* cannula and the crude product dissolved in the minimum amount of ethanol. Diethyl ether was added to precipitate the product. This was filtered, washed with diethyl ether (3x75ml) and dried *in vacuo* to give the product as a light brown solid (8.78g, 75%). ^{1}H NMR (400MHz, d_6-DMSO) δ 10.36 (s, 1H, $_{im}C_2$-*H*), 8.51 (s, 2H, $_{im}C_{4,5}$-*H*), 8.01-7.56 (multiplets, 8H in total, $_{arom}$C-*H*).

Synthesis of 1,3-Bis(Benzene-*o*-diphenynlphosphine)imidazolium chloride (20).

Potassium *tert*-butoxide (0.67g, 6mmol) was dissolved in DMF (7ml) and diphenyl phosphine (1ml, 5.75mmol) added. This deep red solution was added dropwise to a solution of 1,3-Bis(*o*-Fluorobenzene)imidazolium chloride (0.84g, 2.875mmol) in DMF (7ml) and stirred at room temperature for 12 hours. The solvent was removed and methanol (10ml) added to quench any unreacted diphenyl phosphine and the solvent removed. The solid was extracted with DCM (3x15ml) and filtered through celite. The volume of the DCM was reduced to about 2ml and diethyl ether added. The solid was filtered, washed with diethyl ether (3x20ml) and dried in vacuo to give a mixture of products as a brown solid.

3.4. References

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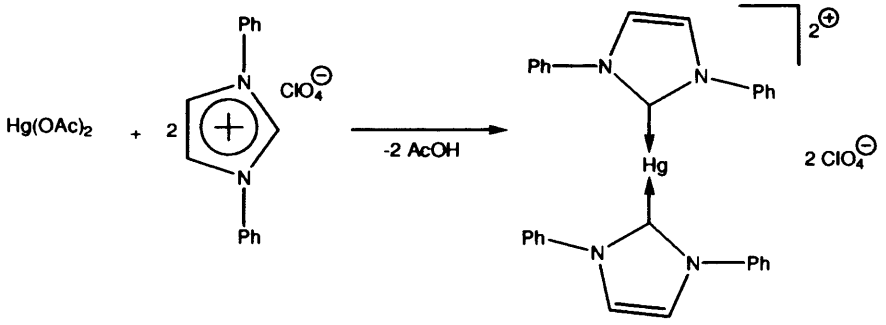
Chapter Four

Metal Complexes of Functionalised Phosphine-NHC Ligands

4.1. Introduction

4.1.1. Preparative Routes to NHC-Metal Complexes

There are various methods to prepare metal complexes of N-Heterocyclic carbenes, including cleavage of electron rich olefins, transmetallation, *in situ* deprotonation of ligand precursors and complexation of the free, pre-isolated NHC's. Öfele prepared the first example of a NHC-metal complex by deprotonation of an imidazolium salt with a basic metallate.[1] The use of acetate salts to deprotonate precursors has proved successful in the formation of complexes. Wanzlick synthesised the mercury-NHC complex **3.1** by using mercury(II) diacetate and an imidazolium salt (Equation 4.1).[2] Herrmann used a similar method to this to make a wide range of NHC-Pd complexes using palladium acetate as a starting material.[3]



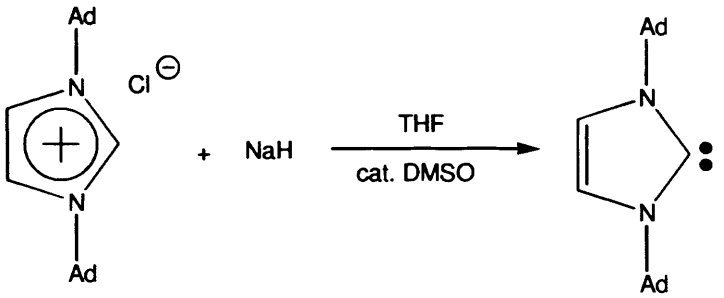
4.1

Equation 4.1.

The method of Wang and Lin uses silver(I) oxide as a base to give bis(NHC) complexes.[4] These silver complexes can be used as the NHC

source for the preparation of NHC complexes of other metals. This method has recently been used in the preparation of phosphine-NHC metal complexes of palladium, rhodium and ruthenium.[5]

More "traditional" bases such as NaH or KO^{t}Bu can be used to pre-form the NHC's. This method was used by Ardeungo to synthesise the first stable crystalline carbene.[6] 1,3-diadamantylimidazolium chloride was deprotonated using NaH with a catalytic amount of the DMSO anion in THF to give the stable free carbene **4.2** (Equation 4.2).



4.2

Equation 4.2.

These pre-formed NHC's can be reacted directly with a metal to give new NHC-metal complexes. Not all imidazolium salts will form isolable carbenes but the method of using a base to form the NHC *in situ* and then reacting with a metal is applicable. In this chapter all phosphine-NHC complexes are formed by deprotonation using potassium bis(trimethylsilyl)amide and reacting with the appropriate metal source without isolating the free carbene.

4.1.2. Group 10 Metal Complexes

The number of Group 10-NHC complexes has grown rapidly over the past few years. Herrmann[7] and Fehlhammer[8] successfully synthesised Pd(II) complexes and showed that these were active catalysts for the Heck coupling reaction. The activity of these monodentate and chelating bis-carbenes led to the synthesis of NHC ligands with other donor groups

attached. There are examples of functionalised NHC ligands bearing one or two functionalised substituents with ether (**4.3**),[9] oxazoline (**4.4**),[10] phosphine (**4.5**),[11] picolyl (**4.6**)[12-15] and 2-pyridyl (**4.7**)[16-18] groups.

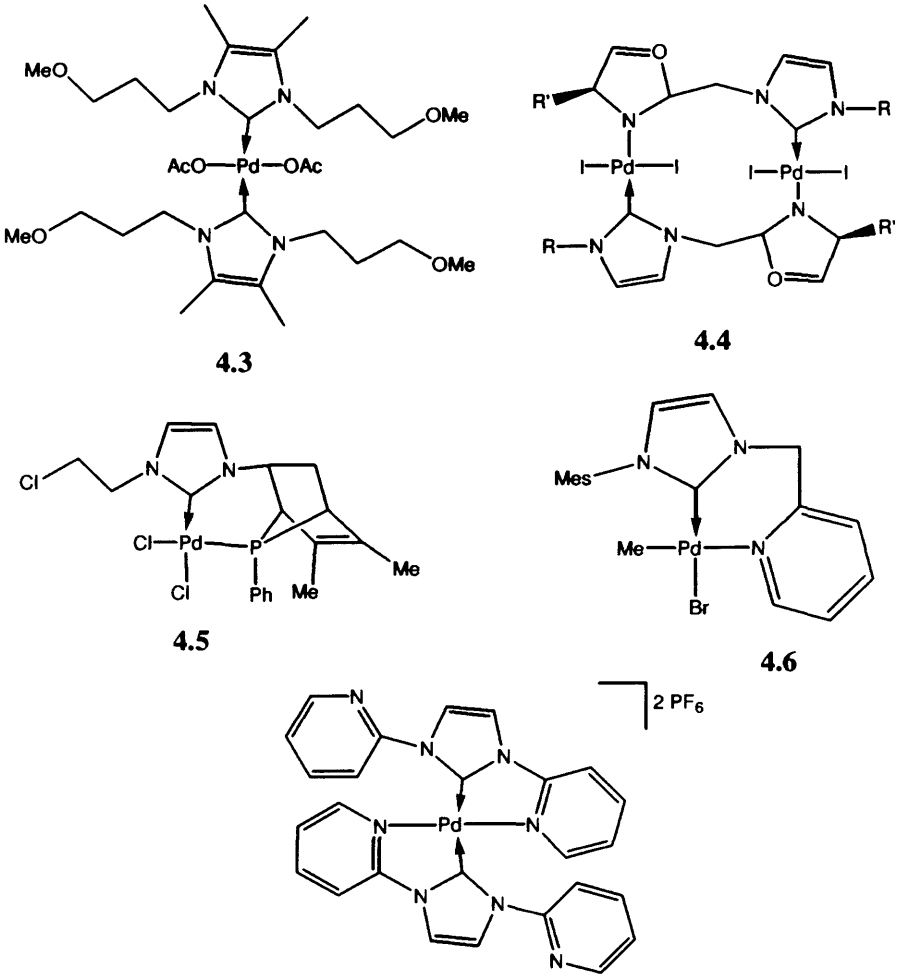
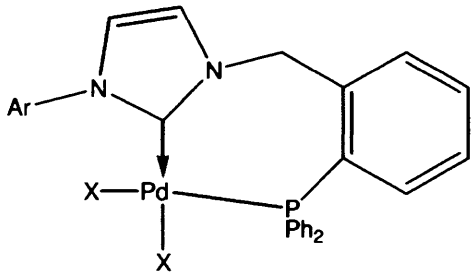


Figure 4.1.

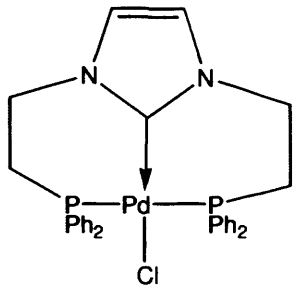
The chelating ligands may adopt a variety of geometries dependant on the steric demands of the ligands and the nature of the other donor group. Many of these types of ligands have been shown to yield active catalysts in Heck coupling reactions. Along with this high activity, NHC complexes are desirable as catalysts because they form strong metal-carbon bonds that

are more thermally stable than the more widely used phosphines.[19,20] This means that NHC's can be used in stoichiometric amounts and are generally less toxic and easier to handle than phosphines.

There are considerably fewer mixed phosphine-carbene complexes of group 10 metals. Danopoulos[21] successfully synthesised Pd(II) complexes that have an alkyl linker between the phosphine and carbene groups. These complexes were fairly active in Heck coupling reactions, although Nolan and co-workers showed higher activity for those complexes formed *in situ* than the pre-formed.[22] Bidentate (**4.8**)[23] and tridentate (**4.9**)[23,24] phosphine-carbene complexes of Pd(II) have been synthesised and are active catalysts for Heck coupling when formed *in situ*.[23]



4.8



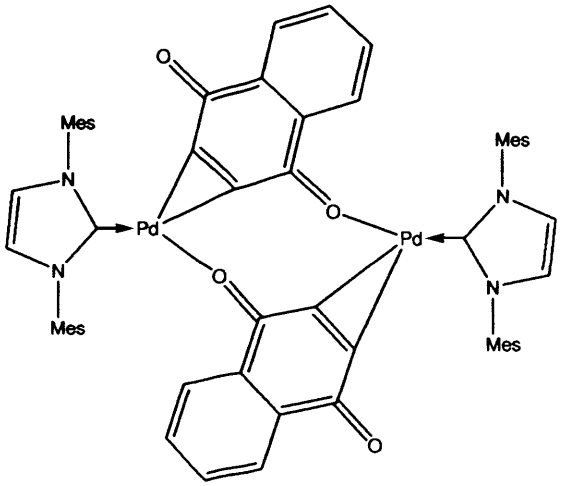
4.9

Figure 4.2.

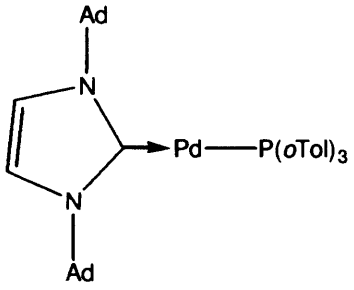
Work in our laboratory has been undertaken previously on complexing ligands of the type discussed in Chapter 3 to Ni(II), Pd(II) and Pt(II).[25] This chapter is mainly concerned with complexation of ligands of the type discussed in Chapter 3 with Ni(0), Pd(0) and Pt(0).

Pre-forming metals in the zero oxidation state is desirable as the catalytically active species in some reactions (e.g. Heck) is thought to be in the zero oxidation state. Beller demonstrated that the Pd(0) complex **4.10** shows good activity for the Heck coupling of activated and de-activated aryl chlorides with olefins in the presence of an ionic liquid ($^{n}Bu_4NBr$).[26] These complexes (**4.10**) also show good activity for the coupling of

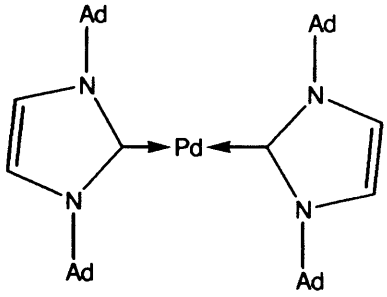
aryldiazonium salts with substituted olefins.[27] Beller also showed that Pd(0) complexes generated *in situ* were effective catalysts in telomerisation reactions.[28] Herrmann has demonstrated that Pd(0) phosphine-carbene complexes (**4.11**) show good activity for the Suzuki coupling of aryl chlorides.[29] He also demonstrated that the sterically hindered biscarbene Pd(0) complex (**4.12**) showed even better activity than the mixed phosphine-carbene analogue **4.11**, even at ambient temperatures.[29]



4.10



4.11

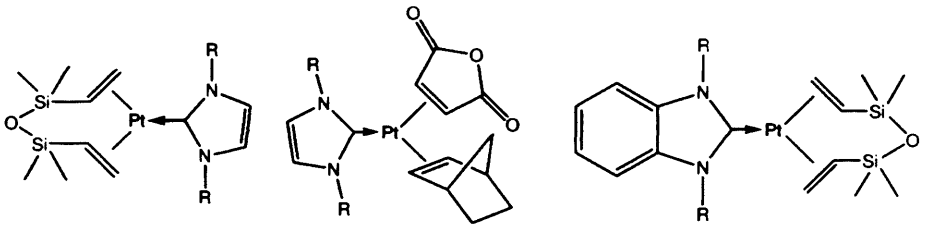


4.12

Figure 4.3.

There are examples of Pt(0)-NHC complexes that are active catalysts. Markó demonstrated that complexes of type **4.13** show good activity for the hydrosilylation of functionalised terminal alkenes.[30] Markó also showed that benzimidoazolylidene Pt(0) complexes (**4.15**) show good

activity in hydrosilylation reactions and the activity of the catalyst can be tuned by modifying their steric and electronic properties.[31] Elsevier demonstrated that Pt(0)-NHC complexes bearing olefinic ligands (**3.14**) were active catalysts for the selective hydrosilylation of alkenes, with almost no side reactions occurring.[32]



4.13 **4.14** **4.15**

Figure 4.4.

There are considerably fewer examples of Ni(0)-NHC complexes. Arduengo synthesised a bis carbene Ni(0) complex where the nickel centre has two sterically demanding NHC ligands bound to it.[33] Cavell and co-workers showed that reacting this with an imidazolium salt causes C_2-H activation and the formation of a Ni(0) (and Pd(0)) hydride complex.[34] These complexes could potentially be an atom efficient route to catalytically active species.[34]

This chapter presents results of the synthesis and characterisation of metal(0) phosphine-NHC complexes based on the structure shown in Figure 4.7, with dimethyl fumarate (DMFU) as the other coordinating ligand.

4.2. Results and Discussion

4.2.1. Synthesis and characterisation of Pd(0) complexes of substituted phosphine-imidazolium salts.

Prior to this work commencing there were no Pd(0) complexes of phosphine-imidazolium salts to be found in the literature. Pd(II) species have been synthesised by using silver as a carbene transfer agent[24] and by forming the carbene *in situ* and reacting directly with a palladium source.[21,22,23,25] It was decided that a method based on that of Elsevier and co-workers[32] to synthesise NHC-metal(0) complexes would be suitable to synthesise complexes of the structure shown in Figure 4.5.

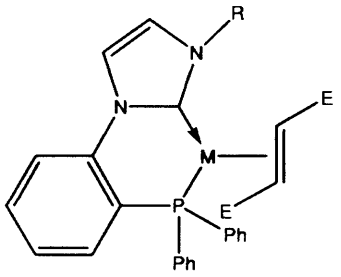


Figure 4.5.

The first efforts to synthesise these types of compounds used palladium bistetramethyldivinyldisiloxane (DVDS) as a source of Pd(0). Potassium trimethylsilylamide was added to a THF suspension of the phosphine-imidazolium salt at 0°C and allowed to warm to room temperature to give a solution of the free carbene. After stirring for 15 minutes the solution was added dropwise at 0°C to a THF solution of $Pd(DVDS)_2$ and dimethylfumarate (DMFU) and stirred for 1 hour. After filtering and removal of the solvent a light brown solid was formed.

The $^{31}P\{^{1}H\}$ NMR spectrum showed a range of resonances indicating that a mixture of products were formed. There was a resonance at 22.05ppm corresponding to a coordinated phosphine.

The ^{1}H NMR spectrum also showed that a mixture of products had formed. There was no resonance corresponding to the $_{im}C_2$ proton indicating that carbene complexes were formed. However, attempts to separate the mixture were unsuccessful. There was no evidence from the ^{1}H NMR spectrum that the DMFU had displaced the DVDS ligand. The DVDS ligand can be displaced by the carbene and phosphine moieties but not by the DMFU. There was no evidence to suggest that two phosphine-carbene ligands were bound to the Pd(0) centre.

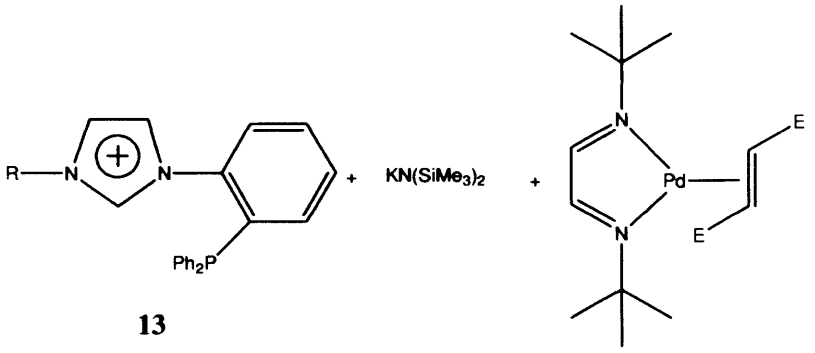
It was decided to use Pd(DAB)(DMFU) (**21**) as a Pd(0) source as $Pd(COD)_2$ was deemed too thermally unstable to be of any use. Also, work has been done in the group previously using **21** as a starting material to make monodentate NHC-Pd(0) complexes.[34,35] The carbene was formed *in situ* by reacting the phosphine-imidazolium salt **13** with $KN(SiMe_3)_2$ in THF at room temperature. This was then filtered onto a solution of **21** in THF at 0°C. After stirring at room temperature the solvent volume was reduced and Et_2O added. The solid formed was filtered to remove displaced diazabutadiene (DAB), washed with Et_2O and dried to give the product **22** as a pale tan solid in up to 80% yield (Equation 4.3). The product was air and moisture stable.

The $^{31}P\{^1H\}$ NMR spectrum showed a resonance at 24.01ppm for complex **22a** (R= methyl) and a resonance at 21.43ppm for complex **22b** (R= benzyl). Both these resonances are typical of phosphines coordinated to Pd(0).

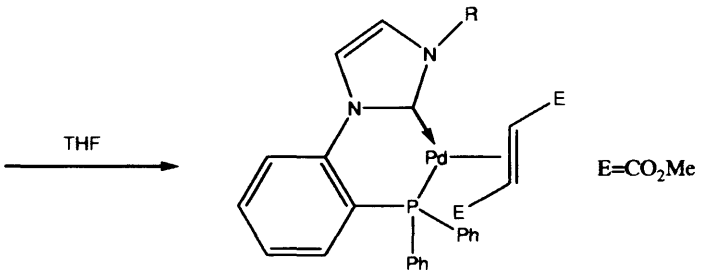
The ^{1}H NMR spectra for complexes **22a** and **22b** showed the absence of a resonance at around 10ppm which indicates the formation of a carbene (i.e. the removal of the C_2 proton). For both complexes **22a** and **22b** the DMFU proton resonances were broad singlets rather than the sharp singlets you see in the uncoordinated species. This is because the ligand is bound to the metal via the C=C double bond and is spinning rapidly in solution. This causes a broadening of the signals. The ^{1}H NMR spectrum for complex **22b** showed a pair of doublets at 5.74 and 5.15ppm corresponding to the benzyl CH_2 protons. This occurs because the protons are not in the same environments and so couple to each other with a coupling constant of $J_{H\text{-}H}$= 14.8Hz.

The resonances at 177.22 (**22a**) and 178.53ppm (**22b**) in the ^{13}C NMR spectrum are consistent with the formation of a carbene as they are both shifted downfield compared to the proligand phosphine-imidazolium salts. Elemental analysis of the complex agreed with the calculated values.

Attempts were made to grow crystals suitable for X-ray diffraction by slow diffusion of solvents and slow evaporation of solvents but all were unsuccessful.



13 **21**



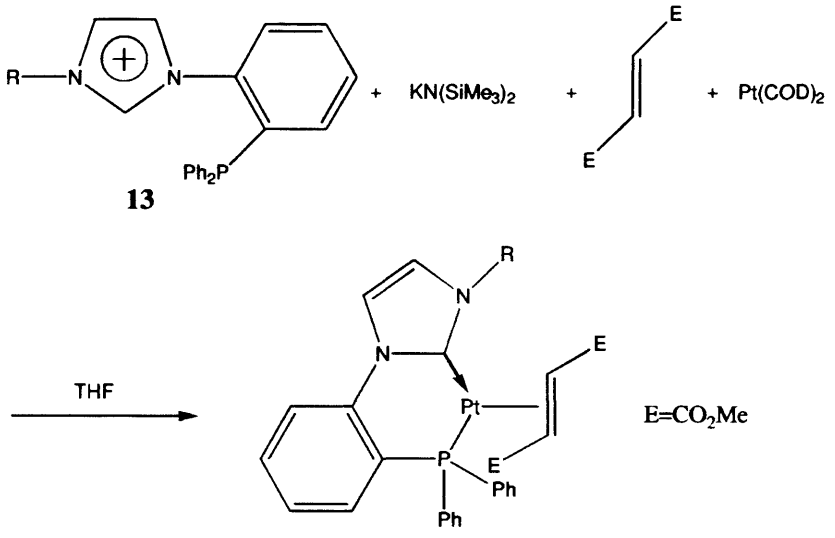
22

Equation 4.3.

4.2.2. Synthesis and Characterisation of Pt(0) complexes of phosphine-imidazolium salts.

The method discussed in section 4.2.1 can be modified and applied for the synthesis of platinum(0) complexes. Elsevier and co-workers formed Pt(0) complexes with imine and monodentate NHC ligands using $Pt(COD)_2$ as a convenient source of Pt(0).[32]

The NHC-phosphine was formed by reaction of the imidazolium salt **13** with $KN(SiMe_3)_2$ in THF at room temperature. This was then added to a solution of $Pt(COD)_2$ and DMFU in THF at 0°C (Equation 4.4). After stirring the solution was concentrated and Et_2O was added to precipitate the product as a tan solid in yields of up to 73%. Washing with Et_2O removed any impurities and the solid was dried *in vacuo* to remove any remaining COD. The reactions were carried out at -78°C and -30°C and room temperature. It was found that the reaction proceeded with the highest yield when the carbene was formed at room temperature.



Equation 4.4.

The product was an air and moisture stable tan solid that formed clear yellow solutions. The ^1H NMR spectra of complexes **23a** (R= methyl) and **23b** (R= benzyl) both showed an absence of a resonance at around 10ppm which is indicates that the imidazolium salts have been successfully deprotonated at the $_{im}C_2$ position. The resonances for all the DMFU protons in both complexes **23a** and **23b** appear as broad singlets. The reason for the broadening of these signals is discussed in section 3.2.1 above. There is no observed coupling of the protons in the ^1H NMR spectrum when R= methyl showing that the methyl protons are in the same environment. In complex **23b** (R= benzyl) the resonance for the CH_2

protons appears as two doublets at 5.84 and 5.19ppm with a coupling constant of J_{H-H}= 14.8Hz. This data agrees closely with the results for Pd(0) complexes seen in section 4.2.1. It seems that upon coordination the CH_2 protons are no longer in equivalent environments due to the rotation around the sp^3 hybridised carbon and the interaction with the metal centre causes coupling. This coupling is useful because it can provide evidence that a proligand has coordinated to the metal centre.

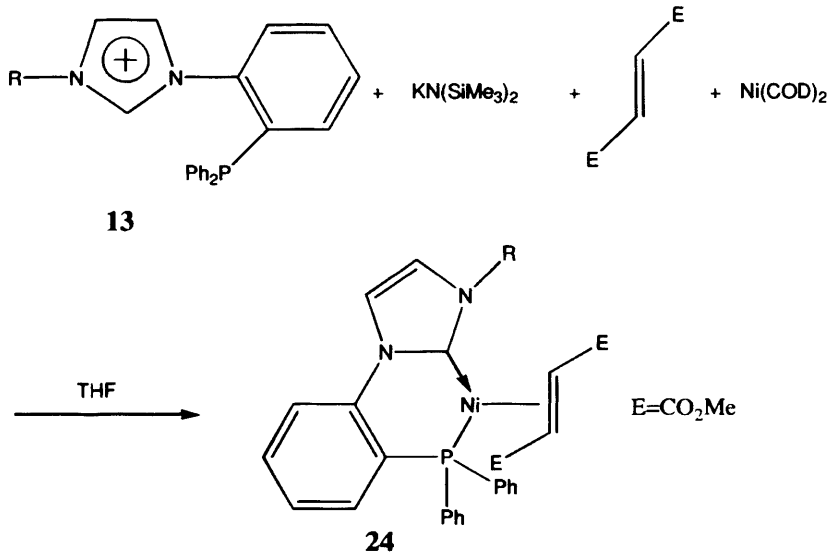
The resonances in the $^{31}P\{^1H\}$ NMR spectra show a triplet at 17.10ppm (**23a**) and 16.10ppm (**23b**). This triplet is characteristic of a phosphine coordinating to a platinum centre. The coupling constants of J_{P-Pt}=4056.39Hz for complex **23a** and J_{P-Pt}= 4093.03Hz for complex **23b** are consistent for platinum phosphine complexes. The appearance of this triplet in the $^{31}P\{^1H\}$ NMR spectra provides evidence that complexation has occurred because the phosphine peak is a singlet much further upfield for the phosphine-imidazolium salt proligand.

The resonances corresponding to the $_{im}C_2$ carbon for complexes **23a** and **23b** appeared as a singlet at 173.4ppm and 174.5ppm respectively. There was no observed coupling with the platinum centre in either of the complexes. Data from elemental analysis agrees with calculated values.

Attempts to grow crystals suitable for X-ray diffraction by slow diffusion and slow evaporation did not meet with any success.

4.2.3. Synthesis and characterisation of Ni(0) complexes of phosphine-imidazolium salts.

A similar procedure to that discussed in section 4.2.2 was used to form Ni(0) complexes. The carbene was formed by reacting the phosphine-imidazolium salt **13** with $KN(SiMe_3)_2$ in THF at -30°C. This was then added to a solution of $Ni(COD)_2$ in THF at -30°C (Equation 4.5). After stirring the solution was concentrated and Et_2O added to precipitate the solid as a tan solid in up to 54% yield. Washing with Et_2O removed any impurities and the solid was dried *in vacuo* to remove any remaining COD.



Equation 4.5.

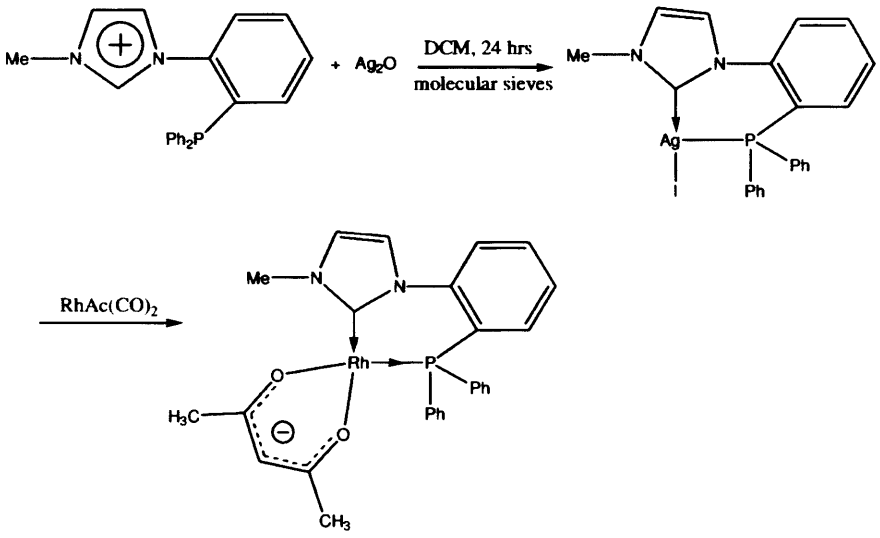
All reactions using $Ni(COD)_2$ had to be carried out at -30°C to prevent any decomposition. The complexes **24a** (R= methyl) and **24b** (R= benzyl) were both stable at room temperature and could be stored under nitrogen for long periods of time with observed decomposition.

Analysis of the ^1H NMR spectra of **24a** and **24b** shows the absence of a resonance at around 10ppm indicating deprotonation at the C_2 position of the imidazolium ring. In the ^1H NMR spectrum of complex **24a** there is a singlet at 3.8ppm corresponding to the N-substituted methyl group. Unlike with the Pt(0) complex discussed previously (**23b**) there is no observed coupling of the CH_2 benzyl protons. The DMFU methyl and olefinic resonances appear as broad singlets. The reasons for this have been discussed previously in section 4.2.1.

The $^{31}P\{^1H\}$ NMR spectra shows a singlet at 26.33ppm for complex **24a** and 25.44ppm for complex **24b**. These values are consistent with a phosphine coordinated to a nickel centre. The $_{im}C_2$ carbon appears as a singlet at 178.6ppm for complex **24a** and 178.33ppm for complex **24b** in the ^{13}C NMR spectra. Data from elemental analysis agrees with calculated values.

4.2.4. Synthesis and characterisation of Rh(I) complexes of phosphine-imidazolium salts.

The synthesis of rhodium(I) complexes was carried out in a similar manner to the group 10 metals discussed above. There are previous examples of Rh(I) complexes being formed by transmetallation from the corresponding silver(I) complexes.[25,36] Initial attempts to isolate and characterise silver complexes of the phosphine-imidazolium salts met with limited success. Formation of a silver complex and transmetallation reactions to Rh(I) have been carried out before (Scheme 4.1).[25] This thesis focuses only on the formation of free carbenes and subsequent complex formation.

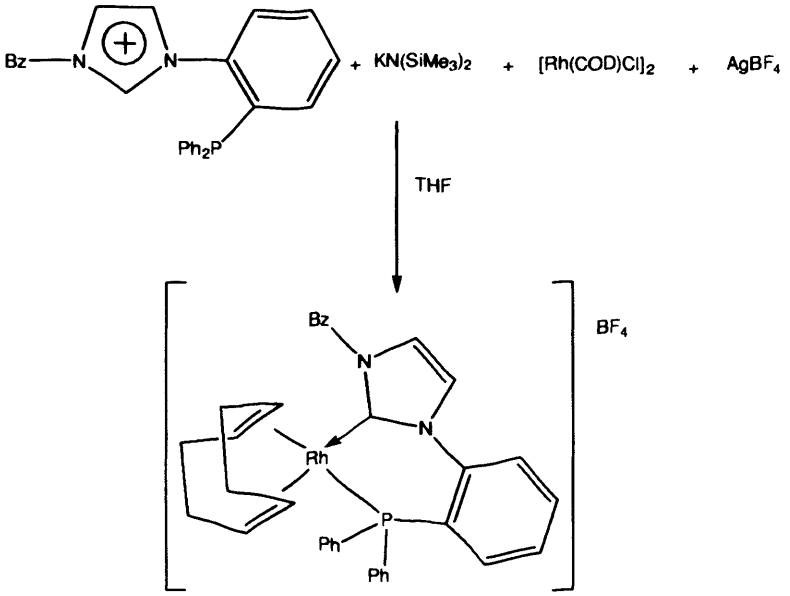


Scheme 4.1.

The method used in this thesis was a variation of that used by Herrmann in 1998 to synthesis chiral oxazoline/imidazoline-2-ylidene complexes of Rh(I).[37] A THF solution of lithium *tert*-butoxide and $[Rh(COD)Cl]_2$ was stirred at room temperature for ten minutes. A THF solution of the phosphine-imidazolium salt was added dropwise at 0°C, the mixture allowed to warm to room temperature and then stirred for 8 hours. Silver tetrafluoroborate was added and a precipitate formed immediately. After 15 minutes of stirring the mixture was filtered, the volume of the solvent

reduced and diethyl ether added to precipitate the product. The resulting solid was washed with diethyl ether and dried *in vacuo* to give the product **25** as a tan solid (Equation 4.6).

The $^{31}P\{^{1}H\}$ NMR spectrum shows a doublet at 40.26ppm with a coupling constant of $^{1}J_{Rh\text{-}P}$=127.58Hz. The resonance appears as a doublet because ^{31}P and ^{103}Rh are both spin ½ nuclei. There is no resonance corresponding to either the phosphine oxide or the free phosphine indicating successful coordination of the ligand.



25

Equation 4.6.

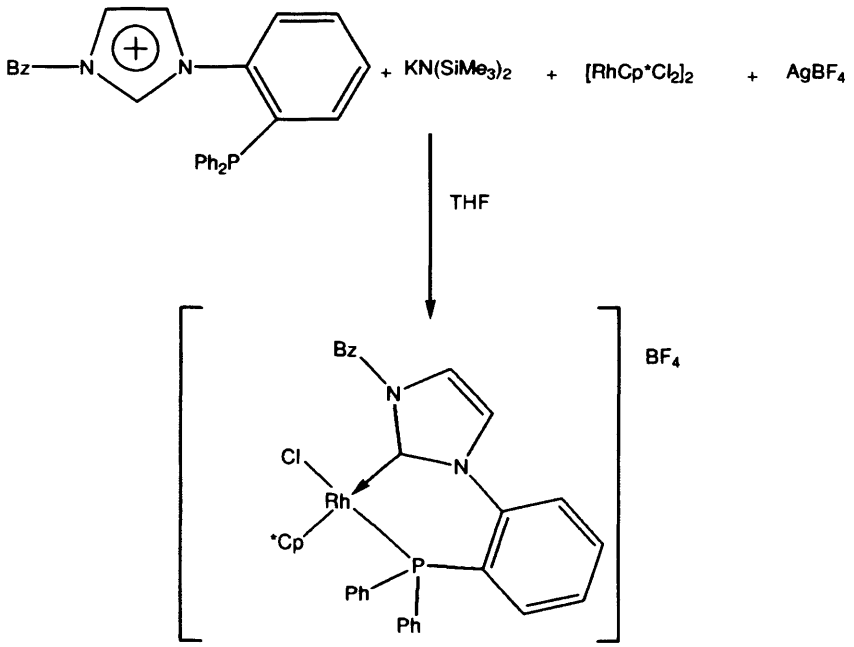
The ^{1}H NMR spectrum does not show a peak at around 9 or 10ppm indicating successful deprotonation at the $_{im}C_2$. Two doublets appear at 5.22 and 4.99ppm with a coupling constant of $^{1}J_{H\text{-}H}$=14.88Hz corresponding to the benzyl CH_2 protons. The olefinic COD protons appeared as a multiplet at 5.02ppm and the CH_2 COD protons appeared as a multiplet at 3.18ppm. The resonances did not appear as singlets because the protons are not in the same environment and so couple to each other.

The ^{13}C NMR spectrum shows a doublet at 162.9ppm corresponding to the $_{im}C_2$ carbon. The coupling constant of $J_{C\text{-}Rh}$= 51Hz is consistent with previously observed rhodium-NHC complexes.[38] A doublet is expected as

both ^{13}C and ^{103}Rh nuclei are spin ½. Data from elemental analysis agrees with calculated values.

4.2.5. Synthesis and characterisation of Rh(III) complexes of phosphine-imidazolium salts.

The preparation of rhodium(III) complexes of phosphine-carbene ligands was adapted from the procedure of Yamaguchi *et al.* They showed that monodentate NHC complexes of Ir(III) were effective catalysts in the Oppenauer-Type oxidation of alcohols.[38] The rhodium(III) source for the reactions was $[RhCp^*Cl_2]_2$. The phosphine-imidazolium salts were stirred with a base to form the free carbene at room temperature. Subsequent addition of the rhodium source followed by silver tetrafluoroborate resulted in immediate precipitation of silver chloride. Filtration and addition of diethyl ether gave the product **26** in moderate yields (Equation 4.7).



26

Equation 4.7.

The $^{31}P\{^{1}H\}$ NMR spectrum shows a doublet at 24.73ppm with a coupling constant of $^{1}J_{P\text{-}Rh}$= 122.07Hz. This is consistent with a phosphine coordinated to rhodium. No evidence of phosphine oxide or uncoordinated phosphine was observed in the spectrum.

The ^{1}H NMR spectrum showed coupling of the benzyl CH_2 protons upon coordination with a coupling constant of $J_{H\text{-}H}$= 7.50Hz. There is no $_{im}C_2$ proton resonance at around 10ppm which indicates that a carbene has been successfully formed. The cyclopentadienyl protons appear as a doublet with a splitting constant $^{1}J_{H\text{-}H}$= 3.54Hz which is consistent with Cp^* bound to Rh(III) centres.[39]

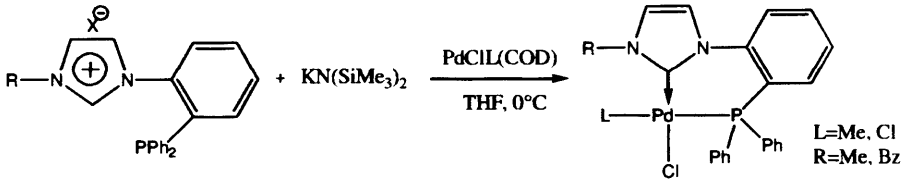
The ^{13}C NMR spectrum shows a doublet at 171.33ppm with a coupling constant of $J_{C\text{-}Rh}$= 49Hz corresponding to the $_{im}C_2$ carbon that has coupled to the Rh(III) centre. This is consistent with the results obtained for the rhodium (I) phosphine-NHC complex **25**. Data from elemental analysis agrees with calculated values.

Attempts to grow crystals for X-ray diffraction by slow diffusion and slow evaporation were not successful.

4.2.6. Synthesis and characterisation of Pd(II) complexes of phosphine-imidazolium salts.

Different palladium(II) complexes of these phosphine-imidazolium salts have been formed by other members of the group and are presented elsewhere.[25] Palladium 2+ complexes are 16 electron complexes and so readily adopt a square planar conformation. This is because all the electrons will be in bonding orbitals rather than antibonding orbitals and this helps to stabilise the complex.

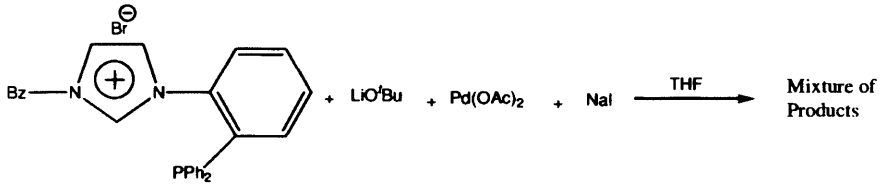
The method involved formation of the carbene using potassium bistrimethylsilyl amide and then reacting this with a source of palladium (Equation 4.8). When L= Me then a mixture of products as shown by NMR spectroscopy are formed. This is unusual because we expect the methyl group to go *trans* to the phosphine as it is a weaker σ-donor (section 1.5).



Equation 4.8.

Herrmann showed that Pd(II) dimers were formed if chiral oxazoline/imidazoline-2-ylidene ligands were used.[37] A variation of this method was used to see if phosphine-imidazolium dimers were formed under similar conditions.

Palladium acetate and sodium iodide were stirred together in THF for 30 minutes to form the intermediate sodium tetraiodopalladate, $Na_2[PdI_4]$.[37] Lithium *tert*-butoxide and the phosphine-imidazolium salt (**13b** R= benzyl) were stirred in THF for 30 minutes. This was added to the palladium solution and stirred at room temperature for 1 hour. The mixture was filtered through celite and the volume of the THF solvent reduced. The addition of diethyl ether precipitated a tan solid that was washed with diethyl ether and dried *in vacuo* (Equation 4.9).



13b

Equation 4.9.

Analysis of the tan solid showed that a mixture of products had formed. The $^{31}P\{^{1}H\}$ NMR spectrum showed three distinct peaks at 12.95, 16.27 and 19.73ppm. There was no evidence of phosphine oxide or free phosphine starting materials being present. The ^{1}H NMR spectrum shows

that no $_{im}C_2$-*H* is present indicating successful formation of carbene complexes. Both these data confirm that a mixture of coordinated phosphine-carbene complexes had been formed. When R=benzyl for other complexes (**22b**, **23b**, **24b**, **25**, **26**) we observed splitting of the CH_2 protons. However, the ^1H NMR spectrum for the tan solid formed in equation 4.9 showed no evidence of this. The spectrum was very complicated indicating the formation of a mixture of products. This agrees with the $^{31}P\{^1H\}$ NMR spectrum. The tan solid was insoluble in most solvents such as THF, diethyl ether, hexane. Extraction into DCM and the slow diffusion of diethyl ether into this solution failed to separate the mixture. There was evidence of decomposition if the DCM solution was left at room temperature for longer than 24 hours although the decomposition products were not resolved.

4.3. Experimental

4.3.1. General Comments

All reactions were carried out under an atmosphere of argon or dinitrogen using standard Schlenk techniques. ^{31}P (referenced to H_3PO_4 at δ_P=0) and ^{11}B (referenced to $Et_2O{\bullet}BF_3$ at δ_B=0) NMR spectra were run on a JEOL Eclipse 300MHz spectrometer. ^{1}H and ^{13}C NMR spectra were run on a Bruker 400MHz DPX Advance spectrometer. Mass spectra were obtained on a VG Fisons Platform II. Tetrahydrofuran, diethyl ether and hexane were dried over sodium benzophenone and freshly distilled under N_2 prior to use. Toluene was dried over potassium and distilled under N_2 before use. Methanol and dichloromethane were dried over calcium hydride and freshly distilled under N_2 before use. Dimethyl formamide was dried over 3Å molecular sieves and freeze-thaw degassed before use. $CDCl_3$, d_6-DMSO, d_6-acetone, CD_2Cl_2 and C_6D_6 were purchased from Goss Scientific and dried over 3Å molecular sieves and freeze-thaw degassed before use. All chemicals were purchased from Aldrich or Acros and used without further purification. If required, the chemicals were freeze-thaw degassed before use. Pd(DAB)(DMFU),[40] $Pt(COD)_2$[41] and $Ni(COD)_2$[41] were prepared by literature procedures.

4.3.2. Pd(0) complexes of phosphine-imidazolium salts

Synthesis of Pd(η^2-dimethylfumarate)(1-benzene-*o*-diphenylphosphine-3-methyl)imidazol-2-ylidene (22a).

(1-benzene-*o*-diphenylphosphine-3-methyl)imidazolium iodide (112mg, 0.24mmol) and potassium trimethylsilyl amide (50mg, 0.25mmol) was dissolved in THF (10ml) and stirred at room temperature for 10 minutes. This was filtered onto a solution of Pd(DMFU)(DBA) in THF (5ml) at 0°C. This was allowed to warm to room temperature and stirred for 1 hour. The volume of the solvent was reduced to approximately 2ml and Et_2O (20ml) added. The solid formed was filtered, washed with Et_2O (4x10ml)

and dried *in vacuo* to give the product as a tan solid (10mg, 72%). ^{1}H NMR (400MHz, d_6-acetone) δ 7.82-6.33 (multiplets, 16H in total, $_{arom}$C-*H* and $_{im}C_{4,5}$-*H*), 5.33 (br s, 2H, $_{DMFU}$C=C-*H*), 3.96 (s, 3H, N-CH_3), 3.42 (br s, 6H, $_{DMFU}$CH_3). ^{31}P{^{1}H} NMR (300MHz, d_6-acetone) δ 21.43 (s). ^{13}C{^{1}H} NMR (500MHz, d_6-acetone) 178.53 (s, $_{im}C_2$). Calc. for $C_{28}H_{27}N_2O_4PPd$: C, 56.72; H, 4.59; N, 4.42; found: C, 56.98; H, 4.85; N, 3.95.

Synthesis of Pd(η^2-dimethylfumarate)(1-benzene-*o*-diphenylphosphine-3-benzyl)imidazol-2-ylidene (22b).

(1-benzene-*o*-diphenylphosphine-3-benzyl)imidazolium iodide (82mg, 0.24mmol) and potassium trimethylsilyl amide (50mg, 0.25mmol) was dissolved in THF (10ml) and stirred at room temperature for 10 minutes. This was filtered onto a solution of Pd(DMFU)(DBA) in THF (5ml) at 0°C. This was allowed to warm to room temperature and stirred for 1 hour. The volume of the solvent was reduced to approximately 2ml and Et_2O (20ml) added. The solid formed was filtered, washed with Et_2O (4x10ml) and dried *in vacuo* to give the product as a tan solid (117mg, 80%). ^{1}H NMR (400MHz, d_6-acetone) δ 7.71-6.20 (multiplets, 21H in total, $_{arom}$C-*H* and $_{im}C_{4,5}$-*H*), 5.74 + 5.15 (2d, J= 14.8Hz, CH_2), 5.30 (br s, 2H, $_{DMFU}$C=C-*H*), 3.15 (br s, 6H, $_{DMFU}$CH_3). ^{31}P{^{1}H} NMR (300MHz, d_6-acetone) δ 24.01 (s). ^{13}C{^{1}H} NMR (500MHz, d_6-acetone) δ 178.53 (s, $_{im}C_2$). Calc for $C_{34}H_{31}N_2O_4PPd$: C, 61.04; H, 4.67; N, 4.19; found: C, 60.94; H, 4.62; N, 3.98.

4.3.3. Pt(0) complexes of phosphine-imidazolium salts

Synthesis of Pt(η^2-dimethylfumarate)(1-benzene-*o*-diphenylphosphine-3-methyl)imidazol-2-ylidene (23a).

THF (10ml) was added to (1-benzene-*o*-diphenylphosphine-3-methyl)imidazolium bromide (42mg, 0.122mmol) and potassium trimethylsilyl amide (30mg, 0.146mmol) and stirred at room temperature for 20 minutes. This was filtered onto a solution of $Pt(COD)_2$ (50mg, 0.122mmol) and dimethyl fumarate (19mg, 0.134mmol) in THF (10ml) at room temperature. This mixture was stirred at room temperature for one

hour. The volume of the solvent was reduced *in vacuo* to until approximately 2ml remained and Et_2O (15ml) was added to precipitate a solid. This was filtered, washed with Et_2O (3x10ml) and dried *in vacuo* to give the product as a tan solid (61mg, 73%). ^1H NMR (400MHz, $CDCl_3$) δ 7.42-6.52 (multiplets, 16H in total, $_{arom}C$-*H* and $_{im}C_{4,5}$-*H*), 5.49 (br s, 2H, $_{DMFU}C$=C-*H*), 4.11 (s, 3H, N-C*H*$_3$), 3.20 (br s, 6H, $_{DMFU}C$*H*$_3$). $^{31}P\{^1H\}$ NMR (300MHz, $CDCl_3$) δ 17.10 (t, $J_{P\text{-}Pt}$= 4056.39Hz). $^{13}C\{^1H\}$ NMR (500MHz, $CDCl_3$) δ 173.4 (s, $_{im}C_2$).Calc. for $C_{28}H_{27}N_2O_4PPt$: C, 49.34; H, 3.99; N, 4.11; found: C, 48.97; H, 3.84; N, 4.07.

Synthesis of Pt(η^2-dimethylfumarate)(1-benzene-*o*-diphenylphosphine-3-benzyl)imidazol-2-ylidene (23b).

THF (10ml) was added to (1-benzene-*o*-diphenylphosphine-3-benzyl)imidazolium bromide (61mg, 0.122mmol) and potassium trimethylsilyl amide (30mg, 0.146mmol) and stirred at room temperature for 20 minutes. This was filtered onto a solution of $Pt(COD)_2$ (50mg, 0.122mmol) and dimethyl fumarate (19mg, 0.134mmol) in THF (10ml) at room temperature. This mixture was stirred at room temperature for one hour. The volume of the solvent was reduced *in vacuo* to until approximately 2ml remained and Et_2O (15ml) was added to precipitate a solid. This was filtered, washed with Et_2O (3x10ml) and dried *in vacuo* to give the product as a tan solid (48mg, 52%). ^1H NMR (400MHz, $CDCl_3$) δ 7.58-6.74 (multiplets, 21H in total, $_{arom}C$-*H* and $_{im}C_{4,5}$-*H*), 5.84 + 5.19 (2d, J= 14.8Hz, C*H*$_2$), 5.53 (s, 2H, $_{DMFU}C$*H*$_3$), 3.16 (s, 6H, $_{DMFU}$C=C*H*). $^{31}P\{^1H\}$ NMR (300MHz, $CDCl_3$) δ 16.10 (t, $J_{P\text{-}Pt}$= 4093.03Hz). $^{13}C\{^1H\}$ NMR (500MHz, $CDCl_3$) δ 174.5 (s, $_{im}C_2$). Calc. for $C_{34}H_{31}N_2O_4PPt$: C, 49.27; H, 4.13; N, 4.10; found: C, 52.62; H, 4.00; N, 3.92.

4.3.4. Ni(0) complexes of phosphine-imidazolium salts

Synthesis of Ni(η^2-dimethylfumarate)(1-benzene-*o*-diphenylphosphine-3-methyl)imidazol-2-ylidene (24a).

THF (10ml) was added to (1-benzene-*o*-diphenylphosphine-3-methyl)imidazolium bromide (250mg, 0.73mmol) and potassium trimethylsilyl amide (16mg, 0.80mmol) and stirred at room temperature for 20 minutes. This was filtered onto a solution of $Ni(COD)_2$ (200mg, 0.73mmol) and dimethyl fumarate (11mg, 0.75mmol) in THF (10ml) at room temperature. This mixture was stirred at room temperature for one hour. The volume of the solvent was reduced *in vacuo* to until approximately 2ml remained and Et_2O (15ml) was added to precipitate a solid. This was filtered, washed with Et_2O (3x10ml) and dried *in vacuo* to give the product as a tan solid (209mg, 51%). ^1H NMR (400MHz, d_6-DMSO) δ 7.42-6.71 (multiplets, 16H in total, $_{arom}C$-*H* and $_{im}C_{4,5}$-*H*), 6.30 (br s, 2H, $_{DMFU}C$=C-*H*), 3.80 (s, 3H, N-C*H*$_3$), 3.58 (br s, 6H, $_{DMFU}C$*H*$_3$). $^{31}P\{^1H\}$ NMR (300MHz, d_6-DMSO) δ 26.33 (s). $^{13}C\{^1H\}$ NMR (500MHz, d_6-DMSO) δ 178.6 (s, $_{im}C_2$). Calc. for $C_{28}H_{27}N_2NiO_4P$: C, 61.68; H, 4.99; N, 5.14; found: C, 61.44; H, 3.86; N, 4.82.

Synthesis of Ni(η^2-dimethylfumarate)(1-benzene-*o*-diphenylphosphine-3-benzyl)imidazol-2-ylidene (24b).

THF (10ml) was added to (1-benzene-*o*-diphenylphosphine-3-benzyl)imidazolium bromide (36mg, 0.73mmol) and potassium trimethylsilyl amide (16mg, 0.80mmol) and stirred at room temperature for 20 minutes. This was filtered onto a solution of $Ni(COD)_2$ (200mg, 0.73mmol) and dimethyl fumarate (11mg, 0.75mmol) in THF (10ml) at room temperature. This mixture was stirred at room temperature for one hour. The volume of the solvent was reduced *in vacuo* to until approximately 2ml remained and Et_2O (15ml) was added to precipitate a solid. This was filtered, washed with Et_2O (3x10ml) and dried *in vacuo* to give the product as a tan solid (45mg, 54%). ^1H NMR (400MHz, d_6-DMSO) δ 7.67-7.08 (multiplets, 21H in total, $_{im}C_{4,5}$-*H*, $_{arom}C$-*H*), 6.78 (s, 2H, $_{DMFU}C$=C-*H*), 3.63 (s, 2H, C*H*$_2$), 3.28 (br s, 6H, $_{DMFU}C$*H*$_3$). $^{31}P\{^1H\}$

NMR (300MHz, d_6-DMSO) δ 25.44 (s). ^{13}C NMR (500MHz, d_6-DMSO) δ 178.33 (s, $_{im}C_2$). Calc. for $C_{34}H_{31}N_2NiO_4P$: C, 65.73; H, 5.03; N, 4.51; found: C, 65.65; H, 4.51; N, 4.41.

4.3.5. Rh(I) complexes of phosphine-imidazolium salts

Synthesis of Rh(cycloocatadiene))(1-benzene-*o*-diphenylphosphine-3-benzyl)imidazol-2-ylidene (25).

$[Rh(COD)Cl]_2$ (200mg, 0.41mmol) and lithium *tert*-butoxide (80mg, 1.00mmol) were stirred in THF (10ml) at room temperature for 10 minutes. To this was added a solution of (1-benzene-*o*-diphenylphosphine-3-benzyl)imidazolium bromide (400mg, 0.80mmol) in THF (5ml). The mixture was stirred at room temperature for 8 hours. $AgBF_4$ (167mg, 0.86mmol) was added and the mixture stirred for 20 minutes. This was filtered, the volume of the solvent reduced and diethyl ether (80ml) added to precipitate the product. The solid was washed with diethyl ether (3x10ml) and dried *in vacuo* to give the product **6** as a tan solid (316mg, 63%). ^1H NMR (400MHz, $CDCl_3$) δ 8.0-6.3 (multiplets, 21H in total, $_{im}C_{4,5}$-*H* & $_{arom}$C-*H*), 5.22 & 4.99 (d, each 1H, $^1J_{H-H}$=14.88Hz, CH_2), 5.02 (m, 4H, $_{COD}$C=C-*H*), 3.18 (m, 4H, $_{COD}$CH_2). $^{31}P\{^1H\}$ NMR (300MHz, $CDCl_3$) δ 40.26 (d, $^1J_{P-Rh}$= 127.58Hz). $^{13}C\{^1H\}$ NMR (500MHz, $CDCl_3$) δ 162.8 (d, J_{C-Rh}= 51Hz, $_{im}C_2$). Calc. for $C_{36}H_{35}BF_4N_2PRh$: C, 60.36; H, 4.92; N, 3.99; found: C, 59.71; H, 5.21; N, 4.55.

4.3.6. Rh(III) complexes of phosphine-imidazolium salts

Synthesis of Rh(chlorocyclopentadienyl)(1-benzene-*o*-diphenylphosphine-3-benzyl)imidazol-2-ylidene (26).

$AgBF_4$ (62mg, 0.32mmol) and $[RhCp^*Cl_2]_2$ (100mg, 0.16mmol) were stirred in THF (10ml) at 0°C for 10 minutes. (1-Benzene-*o*-diphenylphosphine-3-benzyl)imidazolium bromide (160mg, 32mmol) and

potassium bistrimethylsilyl amide (80mg, 0.40mmol) were stirred in THF (10ml) at room temperature for 10 minutes and added to the rhodium solution dropwise with stirring. The mixture was stirred for 1 hour and the solvent was removed under reduced pressure. The residue was extracted with THF (3x5ml) and filtered through celite. The volume of the solvent was reduced and diethyl ether added to precipitate product. The solid was washed with diethyl ether and dried *in vacuo* to give the product as a tan solid (140mg, 56%). ^{1}H NMR (400MHz, CD_3CN) 7.94-6.96 (multiplets, 21H in total, $_{im}C_{4,5}$-*H* & $_{arom}$C-*H*), 6.38 & 6.30 (d, each 1H, $^{1}J_{H-H}$= 7.50Hz, CH_2), 1.29 (d, 15H, $^{1}J_{H-H}$= 3.54Hz, Cp*-*H*). ^{31}P{^{1}H} NMR (300MHz, CD_3CN) δ 24.75 (d, $^{1}J_{P-Rh}$= 122.07Hz). ^{13}C{^{1}H} NMR (500MHz, CD_3CN) δ 171.3 (d, J_{C-Rh}= 49Hz, $_{im}C_2$). Calc. for $C_{39}H_{37}N_2BClF_4PRh$: C, 56.27; H, 4.58; N, 3.86; found: C, 58.30; H, 5.19; N, 3.35.

4.3.7. Pd(II) complexes of phosphine-imidazolium salts

Palladium acetate (200mg, 0.89mmol) and sodium iodide (450mg, 3.00mmol) were stirred together in THF (10ml) for 30 minutes. (1-Benzene-*o*-diphenylphosphine-3-benzyl)imidazolium bromide (444mg, 0.89mmol) and lithium *tert*-butoxide (200mg, 2.5mmol) were stirred in THF (10ml) for 30 minutes. This was then added to the palladium solution and stirred at room temperature for 30 minutes. The mixture was filtered through celite and the volume of the solvent reduced to approximately 1ml. Diethyl ether was added, the solid filtered and washed with diethyl ether (3x10ml) to give a tan solid. ^{31}P{^{1}H} NMR (300MHz, d_6-DMSO) δ 19.73, 16.27, 12.95.

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Chapter Five

Catalytic Cross Coupling Reactions

5.1. Introduction

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 catalytic 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., polyethane, 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.

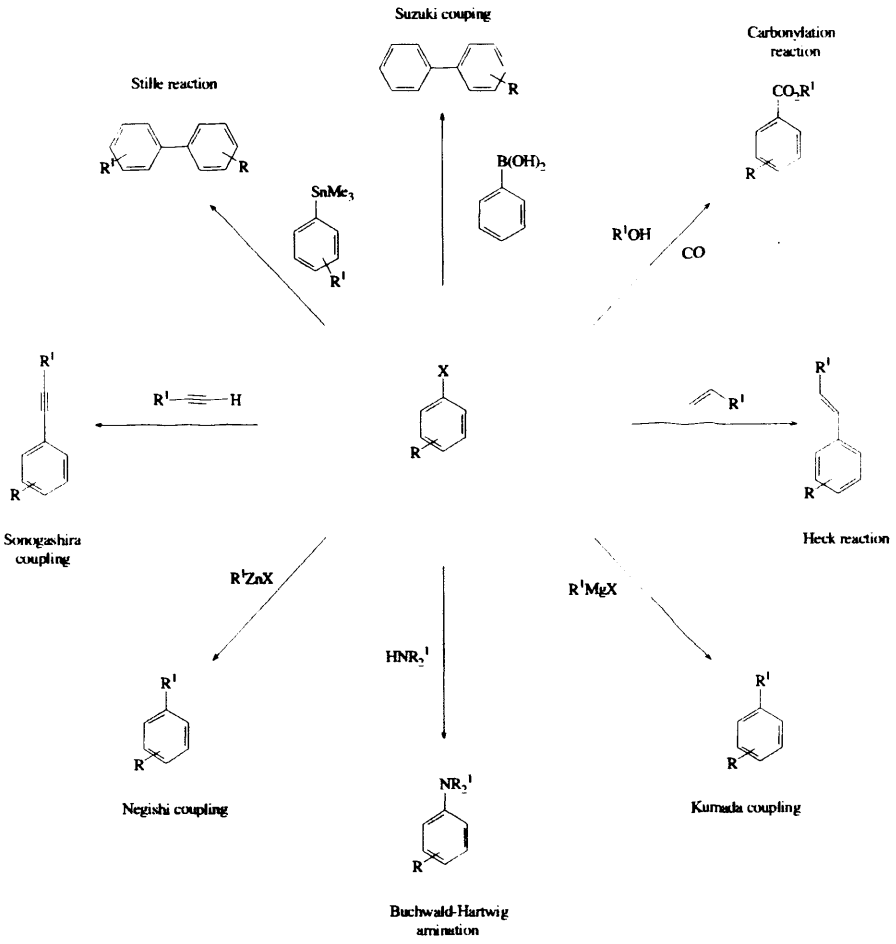
The coordination of the reacting species to a transition metal brings the species in close proximity and can even activate them, thus promoting reactivity.[3] However, the coordinating ligands which are bound to the metal centre play a vital role in promoting and controlling catalytic activity; through 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).
2) The availability of 'cheap' starting materials to generate new bonds in fundamental and novel compounds.[7]

The late 1960's and early 1970's saw a maeked increase in the number of cross-coupling reactions being studied. Metal 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-catalysed reaction.[5,7,8,15-19]



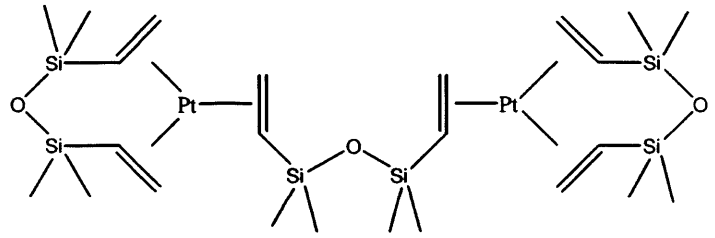
Scheme 4.1: Selected examples of palladium-catalysed coupling reactions of aryl-X derivatives. Several recent papers and reviews cover these coupling reactions in detail.[7-9,15-20]

5.2. Hydrosilylation Reactions

The hydrosilylation reaction is the addition of an Si-H unit to a carbon-carbon double or triple bond to give an alkyl or vinyl silane. This reaction is important in the production of many commodities such as resins, lubricants, pressure sensitive adhesives and liquid injection moulding products.[21] Since the first report of catalytic hydrosilylation by Sommer[22] and the first metal-catalysed hydrosilylation by Wagner[23] there have been

many efforts to develop improved catalytic systems. There are numerous examples of catalytic systems using group 8, 9, and 10 metals. Platinum systems are highly active for the hydrosilylation of unsaturated carbon-carbon bonds.

The Karstedt complex[24] (H_2PtCl_6 dissolved in tetramethyldivinylsiloxane, **4.1**) and the Spier catalyst[25] (H_2PtCl_6 dissolved in propan-2-ol) are the most commonly used industrial catalysts.



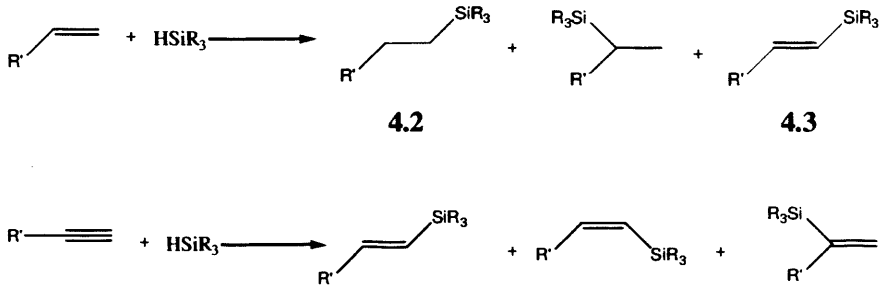
4.1

Figure 4.1. The Karstedt catalyst system.[24]

The platinum salt H_2PtCl_6 can be dissolved in alcohols, ketones, organic acids, esters and hydrocarbons to make different catalytic systems.

The platinum-catalysed hydrosilylation of alkenes generally gives the anti-Markovnikov products although small amounts of the Markovnikov products are observed. This selectivity could be due to the fact that M-C bonds to primary alkyls are less sterically hindered than to secondary alkyls. The rate of hydrosilylation is also affected by steric factors. Sterically undemanding groups on the silane favour oxidative addition. Internal double bonds and substituted double bonds show a reduced rate of reaction.[26] Hydrosilylation generally gives the *trans* alkene product (**4.3**) although other isomers are also observed.[26]

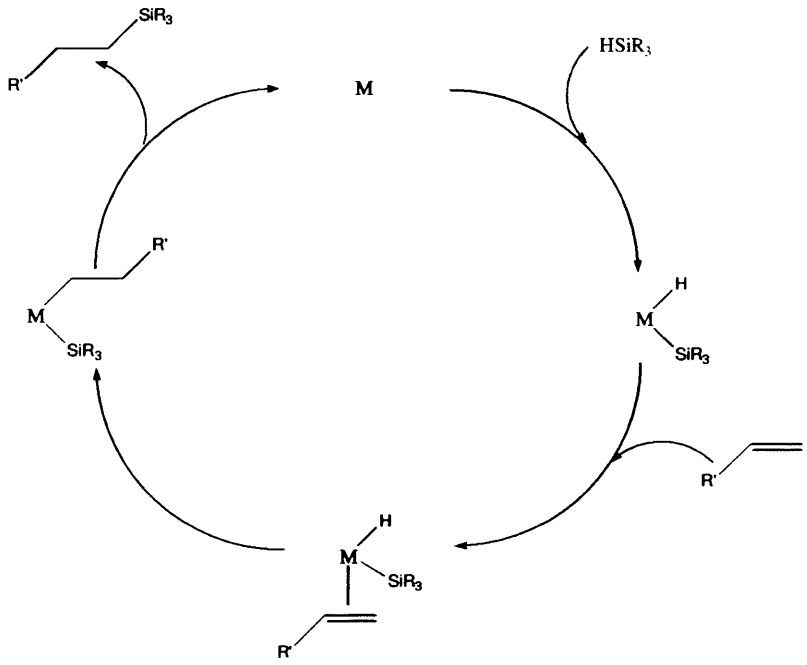
The hydrosilylation of alkenes with platinum complexes can be highly selective but there are also undesired side reactions, such as isomerisation of the terminal alkene and hydrogenation of the C-C double bond (Scheme 4.2). Platinum colloids are also formed during the reaction which can be observed by a decolouration of the reaction mixture.[27] The by-product **4.3** formed by dehydrogenative silylation is a very useful synthetic reagent.



Scheme 4.2. Products of the hydrosilylation of alkenes and alkynes.

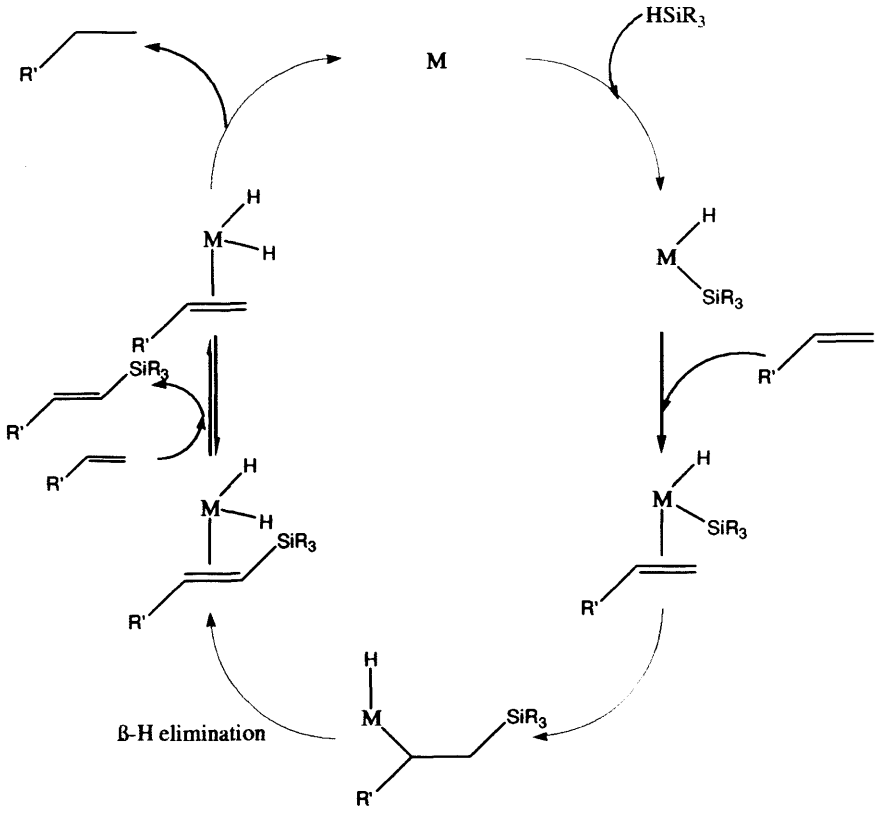
Electronegative groups bound to the silane favour the oxidative addition to transition metals because back-bonding from the metal to the silane increases with more electrophilic silanes.[28] Alkynes have a higher activity compared to alkenes due to the higher degree of nucleophilicity of the alkynes compared to alkenes. $HSiR_3$ will add to internal alkynes at a faster rate than to terminal alkenes.[29] Electron donating groups on the alkyne or alkene cause an increase in the rate of reaction. Lewis *et al.* suggested that this is because hydrosilylation proceeds via nucleophilic attack on an activated metal-silane complex.[30]

A widely accepted mechanism for the hydrosilylation of alkenes is the Chalk-Harrod mechanism.[31] The first step is the oxidative addition of the hydrosilane. The alkene is inserted into the metal-hydride bond followed by reductive elimination to yield the product (Scheme 4.3).



Scheme 4.3. The Chalk-Harrod Mechanism of hydrosilylation.[31]

However, this mechanism does not take into account the formation of vinylsilane products formed by dehydrogenative silylation. In the modified Chalk-Harrod Mechanism the alkene is inserted into the metal-silane bond. β-H elimination of the metal-hydride intermediate yields vinylsilane, which is released by dissociation, and a metal hydride. The metal hydride then hydrogenates one equivalent of alkene to form the starting metal complex (Scheme 4.4).[32]



Scheme 4.4. The Modified Chalk-Harrod Mechanism of hydrosilylation.[32]

There are numerous examples of platinum containing hydrosilylation catalysts that incorporate different co-ligands. There are examples of catalysts containing monodentate phosphines, for example $[Pt(PPh_3)_2Cl_2]$,[14] $[Pt(PPh_3)_4]$,[33] $[Pt(PPh_3)_2(C_2H_4)_2]$,[34] [Pt(*R*-benzylmethylphenylphosphine)$_2$],[35] $[Pt(SiCl_3)_2(PPh_3)_2]$,[36] $[HPt(Si(OEt)_3)(PPh_3)_2]$,[36] and *cis*-$[PtCl_2(PR_3)_2]$.[37,38] Watanabe *et al.* showed that $[Pt(PPh_3)_2Cl_2]$ and $[Pt(PPh_3)_4]$ were much less active than the Speier catalyst.[33] The formation of phosphine oxides by the addition of molecular oxygen resulted in an increase in rate probably due to the fact that phosphine oxides are weaker ligands than the corresponding phosphines. This results in more of the active platinum pre-catalyst being present.[38] There are some examples of phosphine containing catalysts being more active than Karstedt's catalyst although generally they are less active.[39-42] Complexes containing chelating phosphines were found to have

little or no activity.[43] The introduction of a carbene group may cause an increase in activity due to the high *trans* influence.

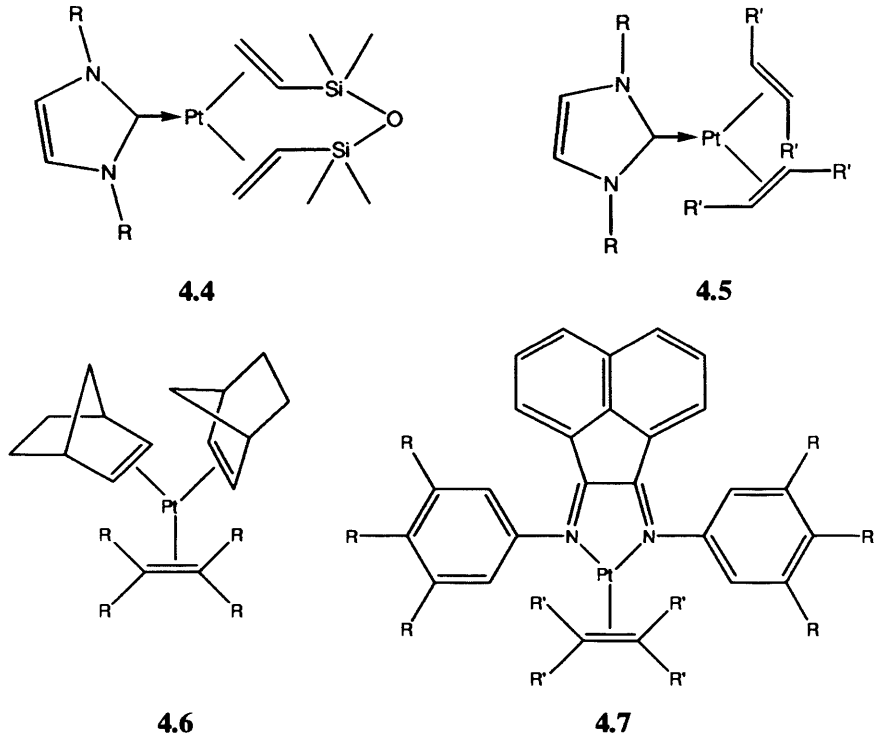


Figure 4.2. Different types of Pt(0) complexes containing different ligands. The R and R' groups can be changed to alter the properties of the catalysts.

Platinum containing catalysts with ligands other than phosphines are also known. The groups of Markó[44,45] (**4.4**) and Elsevier[46] (**4.5**) have both shown that platinum(0) complexes containing N-Heterocyclic carbenes (Figure 4.2) and different alkene ligands show a high selectivity. The activity does not necessarily increase but the numbers of side-products are reduced considerably.[4,47,48] Elsevier also showed that the alkene ligands bound to the metal determined the activity and stability of the catalyst.[49] There are many examples of Pt(0) complexes bearing alkene ligands that have been used as catalyst precursors. For example [Pt(cyclooctadiene)$_2$],[50,51] [Pt(η^2-norbornene)$_2$],[52,53] [Pt(η^2-ethene)$_3$[51] and "mixed" alkene complexes such as [Pt(η^4-cyclooctadiene)(η^2-dimethyl

fumarate)],[54,55] [Pt(η^2-tetrafluoroethene)(η^2-norbornene)$_2$],[56] [Pt$_2$(μ- η^4-*p*-benzoquinone)$_2$(η^2-norbornene)$_2$].[57] These types of complexes generally show high activity but have a low thermal stability.

Work by Elsevier on different bidentate nitrogen containing ligands (similar structure to **7**) showed that ligands that formed more stable complexes exhibited lower catalytic activity and more dehydrogenative silylation compared to ligands that form more stable complexes.[57] As discussed above the introduction of NHC ligands improved the selectivity.[54-58]

5.3. Heck Reactions

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 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[58] and Heck.[59]

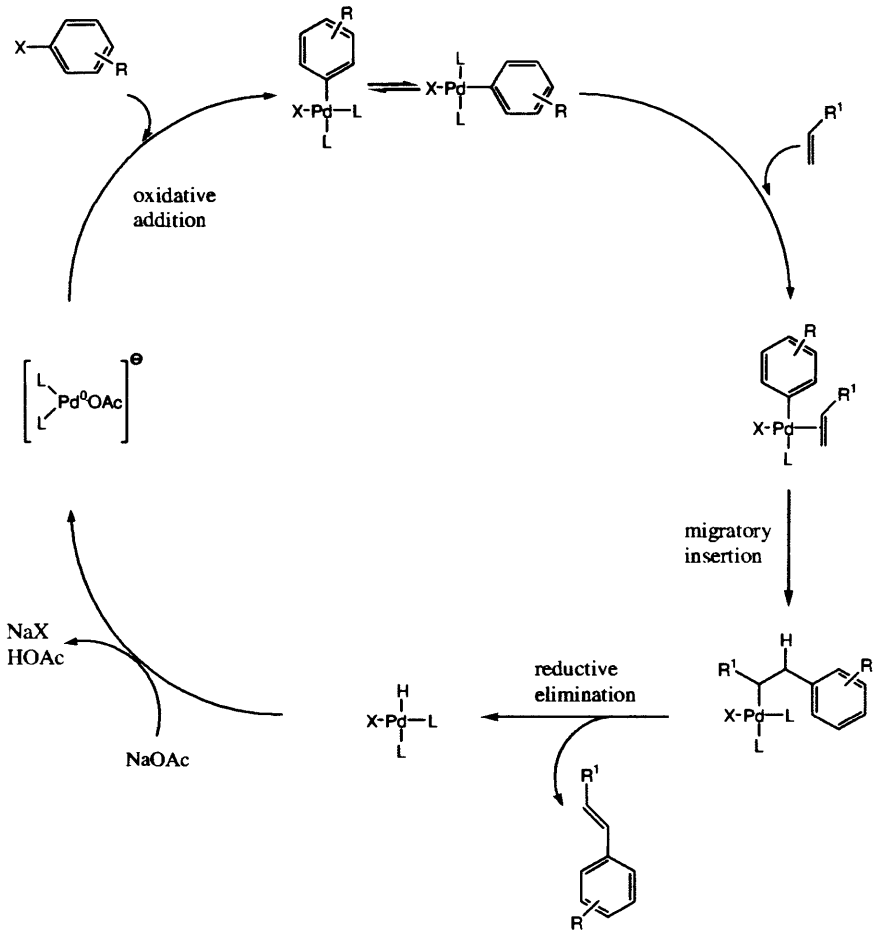
Due to the expense of aryl iodides the Heck reaction did not have a great impact until the late 1980's. However, Alwyn Spencer in the group of Hans-Ulrich Blaser investigated the effect of reaction conditions on Heck olefinations of aryl bromide and was able to report turnover number (TON) > 100000 for the first time in 1983.[60]

Phosphines have been widely used in coupling reactions due to their ability to stabilise a variety of oxidation states.[61-65] There has been much recent interest in using N-Heterocyclic carbene ligands in place of phosphines. The stronger metal-carbene bond compared to the phosphine-metal bond can result in catalysts that are active longer at elevated temperatures, often without using specially purified solvents or inert atmospheres.[8,66-69] Palladium(II) complexes with two carbene ligands were described by Herrmann *et al.* for the Heck reaction of aryl bromide and

activated aryl chlorides.[70,71] Subsequently, Herrmann,[72-74] Cavell,[75-77] Nolan,[78-80] and others[81-89] described various applications of palladium carbene catalysts for aryl-X functionalisation.

Mixed donor carbene complexes have been the topic of many papers and reviews.[66,76,86-89,90-94] The carbene ligand can bind strongly to the metal so the other ligand has the potential to be hemi-labile, 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[76,77,92,94-96] and these 'pincer' complexes are more thermally stable than bidenate non-pincer counterparts.[90]

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.[70,97-101] The classical textbook interpretation for the reaction reported by Heck[99] 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,[20,97,102] which can be generated *in-situ* from an 18-electron palladium(II) moiety. 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.[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 oxidation is I >> OTf > Br >> Cl.[20,53] Aryl chloride substrates are ultimately still preferred due to the fact that they are readily available, cost effective, and highly stable.[90]



Scheme 4.5. The Heck Mechanism.[97,104]

5.4. Results and Discussion

5.4.1. Hydrosilylation Reactions

5.4.1.1. *In situ* hydrosilylation of styrene

The *in situ* catalyst testing of functionalised phosphine-imidazolium salts focused on the coupling of triethylsilane and styrene. The ligands used (**13a** and **13b**) comprised of phosphine-imidazolium salts that varied in the nature of the ligands N-substituent. The results of the hydrosilylation reactions of styrene and triethylsilane are listed in table 4.1 with their structures shown in Figure 4.3.

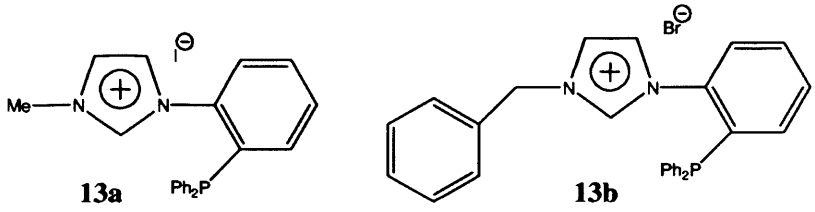
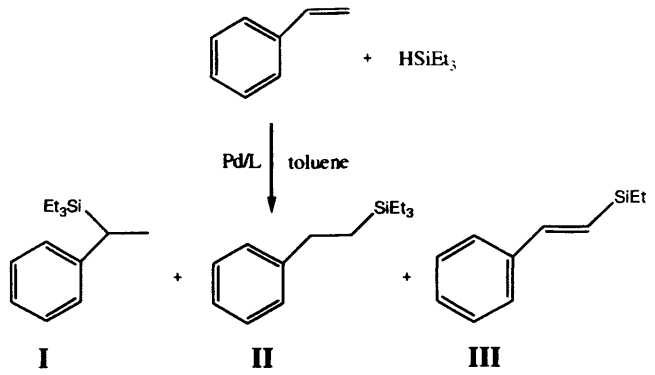


Figure 4.3. Proligands used in the *in situ* hydrosilylation of styrene with triethylsilane.

The functionalised phosphine-imidazolium salts **13a** and **13b** were used as pre-catalysts with $Pt(nbe)_3$. The imidazolium salts were stirred with 1.1 equivalents of potassium *tert*-butoxide for 20 minutes in toluene to allow formation of the NHC. $Pt(nbe)_3$ was added and the mixture stirred for one hour. Elsevier *et al* noted that yields for the hydrosilylation reaction increased if a period of one hour was used to form the metal complexes.[47] Styrene, *n*-decane and triethylsilane were added in quick succession and the mixture was heated at 100°C for 8 hours.



Equation 4.1. Hydrosilylation of styrene with triethylsilane.[a]

[a]Triethylsilane/styrene ratio 1.0, 1mol % of $Pt(nbe)_3$, 1mol % phosphine-imidazolium salt, 1.1 equivalents of KO^{t}Bu, *n*-decane, toluene, 100°C.

Entry	Imidazolium Salt	Amount of catalyst (mol %)	Time (h)	Temp (°C)	Yield[a] (%)	Selectivity (%) **I**:**II**
1	**13a**	1	8	100	3.6	25:75
2	**13b**	1	8	100	3.4	23:77
3	**13a**	1	8	110	2.2	18:82
4	**13b**	1	8	110	3.1	28:72

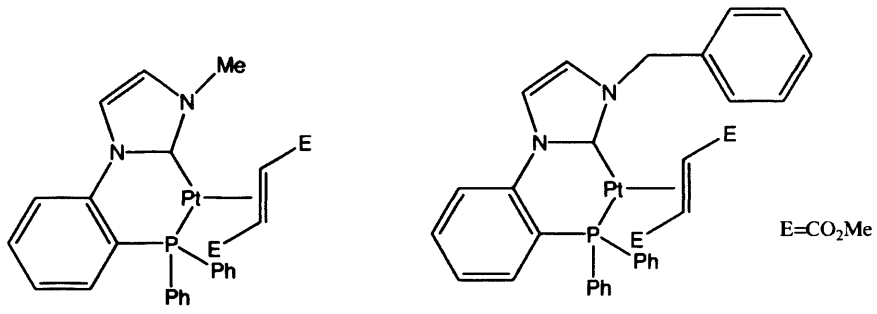
Table 4.1. Results of the *in situ* hydrosilylation of styrene with triethylsilane catalysed with functionalised phosphine-imidazolium salts.

[a]Total GC yield using *n*-decane as internal standard.

The yields for the reactions with both phosphine-imidazolium salts **13a** and **13b** were very low. These types of results have been noticed before using monodentate carbene ligands.[46,47,49] Analysis of the GC results showed that more of the linear hydrosilylation product (**I**) was formed than the branched (**II**). This pattern of selectivity has been noted before.[46] The low yields could be attributed to the fact that the NHC-phosphine complexes formed are too stable and that very few active sites are generated. Also, the alkene ligand plays an important role in hydrosilylation reactions[49] and only DMFU was used. It is possible that

changing the alkene ligand would increase yields and selectivities. During the reactions no products from dehydrogenative silylation (**III**, Equation 4.1) were observed.

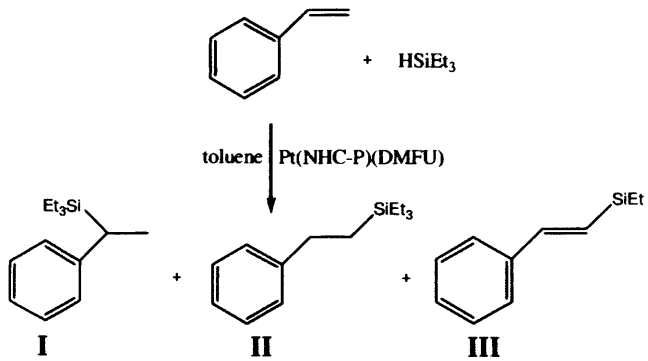
5.4.1.2. Hydrosilylation using preformed Pt(NHC-P) complexes



23a **23b**

Figure 4.4. Metal complexe4s used in the hydrosilylation of styrene with triethylsilane.

Preformed platinum-NHC complexes (**23a** and **23b**) were tested in the hydrosilylation of styrene with triethylsilane. The complexes comprised a platinum zero centre with NHC-phosphine and dimethylfumarate co-ligands. The results of the hydrosilylation reactions of styrene and triethylsilane are listed in table 4.2 with the structures of the catalysts shown in Figure 4.4.



I **II** **III**

Equation 4.2. Hydrosilylation of styrene with triethylsilane.[a]

[a]Triethylsilane/styrene ratio 1.0, 1mol % of complexes **23a** or **23b**, *n*-decane, toluene, 100°C.

Entry	Catalyst	Amount of catalyst (mol %)	Time (h)	Yield[a] (%)	Selectivity (%) I:II
1	**23a**	1	8	2.7	18:82
2	**23b**	1	8	2.5	23:77

Table 4.2. Results of the hydrosilylation of styrene with triethylsilane catalysed with preformed platinum complexes.

[a]Total GC yield using *n*-decane as internal standard.

The metal catalysts used for hydrosilylation were synthesised according to the methods discussed in chapter 4. The catalysts were dissolved in toluene and styrene, *n*-decane and triethylsilane were added sequentially. The mixture was heated at 100°C for 8 hours. There are induction periods observed for platinum (II) and platinum (IV) catalysts as it is believed that these are reduced to platinum (0) before catalysis occurs.[105] The catalysts **23a** and **23b** do not suffer from an induction period.

The yields for the preformed catalysts were very low. This could be because the metal complexes formed are very stable. One step in the catalytic cycle (Scheme 4.4) involves the coordination of an alkene to the metal centre. For this occur one of the ligands has to dissociate otherwise the metal would be five coordinate. It is unlikely that the carbene would dissociate as it forms stronger metal-carbon bonds than the metal-phosphine bond. The results indicate that there is very little dissociation of the phosphine group to make a vacant coordination site available. This would cause the rate of reaction to slow considerably.

A possible method of making the phosphine group more hemi-labile would be to use a carbene-phosphine oxide ligand. Phosphine oxides will be bound as strongly to the metal centre and so may dissociate more easily during the catalytic cycle. This would result in more vacant coordination sites being available and so increase the rate of reaction.

The hysdrosilylation reaction was carried out at 100°C and no decomposition of the preformed metal complexes was observed. This,

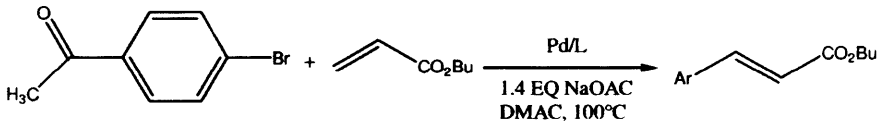
along with the low yields shown in Table 4.2 indicates that a very stable metal complex is formed. The high thermal stability of the complexes could make the ligands useful for metal extraction.

The selectivities of the preformed catalysts were very similar to that of the *in situ* catalysts. More of the linear product (**I**) was observed than the branched (**II**). Once again there were only traces of the dehydrogenative silylation product **III**.

5.4.2. Heck Reaction

5.4.2.1. Palladium catalysed *in situ* Heck reactions

The *in-situ* catalyst testing of functionalised imidazolium salts in the Heck reaction focused on the coupling of the activated aryl bromide 4-bromoactophenone (BAP) with *n*-butyl acrylate (BA) under standardised conditions (Equation 4.3). Sodium acetate was used as the base as it has been shown to be effective for the Heck reaction across a range of substrates and catalyst systems.[73,74,77,106] The proligands used (**13a** and **13b**, Figure 4.3) comprised of phosphine-imidazolium salts that varied in the nature of the ligands' N-substituent. 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 4.3.



Equation 4.3. The Heck reaction of 4-bromoacetophenone (BAP) and *n*-butyl acrylate (BA) catalysed with functionalised imidazolium salts.[a]

[a]Performed at 0.5mol % Pd/L (1:1), $Pd(OAC)_2$.

Entry	Proligand	Amount of catalyst (mol %)	Time (h)	Yield[a] (%)	TON
1	**Blank**	-	5	12	-
2	**8**	0.5	5	97	194
3	**9**	0.5	5	78	151

Table 4.3. Results of the *in situ* Heck reaction of 4-bromoacetophenone (BAP) and *n*-butyl acrylate (BA) catalysed with functionalised phosphine-imidazolium salts.

1.4 equivalents of NaOAc performed at 0.5 mol % Pd/L (1:1), $Pd(OAc)_2$.

[a]GC yield.

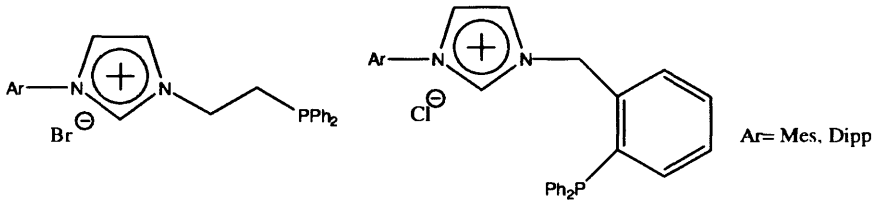
The data in table 4.3 show that there is a difference in the activity of the ligands depending on the N-substituent. The yield is significantly higher when the N-substituent is a methyl group (**13a**) compared to the more bulky benzyl group (**13b**). Work with similar phosphine-imidazolium salts by Wang *et al* have shown that activity can increase if there are bulky substituents on the nitrogen and phosphine.[86] The bulky benzene ring may be sufficiently far away from the metal centre to have less of an influence on the reaction. Having bulky mesityl and diisopropylphenyl rings directly attached to the imidazolium ring causes an increase in activity.[107] The electron donating properties of the methyl and other alkyl substituents could increase the activity by increasing the electron density at Pd which would facilitate the oxidative addition of BAP.

One disadvantage of *in situ* testing using imidazolium salts is that one can never be sure to what extent the imidazolium salts has been deprotonated to form the free carbene. Both salts **13a** and **13b** are very insoluble in most solvents. It has been shown that changing the counter ion to a BARF group increases the solubility and so increases the yield during Heck coupling reactions.[107] It could be that only a small amount of active metal catalyst is being formed. It could also be that the metal complexes that are formed are too stable and few active sites are available.

Nolan *et al* showed that phosphine-imidazolium salts with an alkyl linker between the imidazolium ring and phenyl ring (**4.8**) were efficient catalysts for the Heck coupling of aryl bromides.[108] He also showed that changing the base from NaOAc to Cs_2CO_3 resulted in an increase in activity.[108] Danopoulos showed that using triethylamine as a base when using preformed Pd(II) catalysts also increased the yield compared to using Cs_2CO_3.[89] The activity of the reaction can be changed by altering the base. This was not attempted in this thesis due to time restraints.

Wang *et al* showed that triaryl phosphine-imidazolium salts (**4.9**) were active catalysts in the coupling of a wide range of aryl bromides and iodides with acrylates using a variety of palladium catalyst precursors.[87] They also reported that having bulky substituents attached to the phosphine or the imidazolium ring can increase activity.[86]

The phosphine-imidazolium salts showed no activity for the Heck coupling of aryl chlorides such as 4-chloroacetophenone with butyl acrylate. These results are similar to work done within the research group at Cardiff University[107] but also to other groups.[86,89,108] When used as preformed Pd(II) catalysts these types of ligands with alkyl, aryl and no linker show good activity in the Heck coupling of aryl bromides and iodides but no activity in the Heck coupling of aryl chlorides.



4.8 **4.9**

Figure 4.5. Substituted phosphine-imidazolium salts used in Heck coupling reactions.[86,89,107,108]

5.5. Conclusion

A range of phosphine-imidazolium salts have been tested in the *in situ* hydrosilylation of styrene with triethylsilane and the *in situ* Heck coupling of butyl acrylate with aryl bromides. The complexes formed from salts **13a** and **13b** showed poor activity and selectivity in the hydrosilylation of styrene. Activities and selectivities may be improved by changing the alkene co-ligand and optimisation of reaction conditions. Complexes of the salt **13a** showed good activity in the Heck coupling of butyl acrylate while complexes of the salt **13b** only showed moderate activity. However, changing the base and/or counter ion may result in a significant increase in activity as noticed by others using similar salts.[86,89,107,108]

Using the preformed Pt(0) catalysts **23a** and **23b** did not show an increase in activity or selectivity compared to *in situ* reactions for the hydrosilylation of styrene with triethylsilane. However, changing the alkene co-ligand may improve the activity and selectivity of these complexes as has been demonstrated by others.[49]

5.6. Experimental

5.6.1. 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 catalytic testing was carried out at Cardiff University. 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 an Agilent Technologies 6890N Network GC/MS.

5.6.2. *In situ* hydrosilylation of styrene with triethylsilane

(1-Benzene-*o*-diphenylphosphine-3-methyl)imidazolium iodide (23.5mg, 0.05mmol) was stirred with potassium *tert*-butoxide (11mg, 0.1mmol) in toluene (12ml) at room temperature for 20 minutes. $Pt(nbe)_3$ (24mg, 0.05mmol) was added and the mixture stirred at room temperature for 1 hour. Styrene (0.58ml, 5mmol), *n*-decane (0.58ml, 3mmol) and triethylsilane was added in quick succession *via* syringes and the mixture heated at 100°C for 8 hours. The mixture was allowed to cool to room temperature and aliquots taken, filtered and injected on the GC.

5.6.3. Preformed testing of Pt(0) complexes

$Pt(\eta^2$-dimethylfumarate)(1-Benzene-*o*-diphenylphosphine-3-methyl)imidazol-2-ylidene (11mg, 0.015mmol) was dissolved in toluene (10ml). To this was added styrene (0.17ml, 1.5mmol), *n*-decane (0.17ml, 0.90mmol) and triethylsilane (0.24ml, 1.5mmol) in quick succession *via* syringes. The mixture was heated to 100°C and stirred for 8 hours. The mixture was allowed to cool to room temperature, an aliquot taken and filtered and injected on the GC.

5.6.4. Palladium catalysed *in situ* Heck Coupling Reactions

(1-Benzene-*o*-diphenylphosphine-3-methyl)imidazolium iodide (6mg, 0.01mmol), NaOAc (0.23g, 5.6mmol), stock solution A (5ml) and stock solution B (5ml) was added to a Schlenk tube and heated at 100°C for 5 hours. The tube was allowed to cool to room temperature and an aliquot taken, filtered and injected into the GC.

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

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

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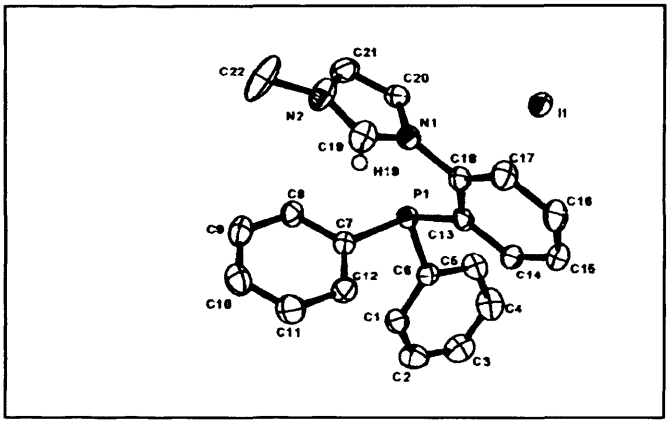
APPENDIX

Crystal data

Table 1: Crystal data and structure refinement for phosphine-imidazolium salt **13a**.



Identification code	Phosphine-imidazolium salt **13a**	
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		

Appendix

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.$Å^{-3}$

Appendix

Table 2: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for phosphine-imidazolium salt **13a**. 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)

Appendix

Table 3. Bond lengths [Å] and angles [°] for phosphine-imidazolium salt **13a**.

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

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(1B)-C(23)-Cl(2B)	103.8(7)

Appendix

Cl(1A)-C(23)-Cl(2B)	120.7(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)		

Appendix

Table 4: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for phosphine-imidazolium salt **13a**. 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)

Appendix

Table 5: Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for phosphine-imidazolium salt **13a**.

	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	8