# Tridentate Ligands with Platinum Group Metals 

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#### Abstract

In this thesis, a series of symmetrical and unsymmetrical pincer ligands are synthesised and explored as supports for platinum group metals, such as palladium, platinum and ruthenium. In Chapters 2 and 3, the synthesis and characterisation of novel pyridine-based dianionic aryl-containing [ $C, N_{P y}, O$ ] and phenol-containing [ $O, N_{P y}, O$ ] pincer pro-ligands and their reactivity towards palladium(II) and ruthenium(II) metal precursors is described. [ $C, N_{P y}, O$ ]-type pincer pro-ligands have been shown to promote $\mathrm{sp}^{2} \mathrm{C}-\mathrm{H}$ activations upon reaction with palladium(II) and ruthenium(II) metal salts. Phenolcontaining [ $O, N_{P_{y},}, O$ ] pincer pro-ligands demonstrated deprotonation of the phenolic oxygen, resulting in a tridentate coordination upon binding to palladium(II) and ruthenium(III) metal centres. In Chapter 4, six novel paramagnetic ruthenium(III) pincer complexes developed from aryl-containing [ $C, N_{P_{y},}, O$ ] and phenol-containing [ $O, N_{P y}, O$ ] pincer pro-ligands, have been employed as efficient catalysts for the transfer hydrogenation of ketones. Chapter 5 describes the synthesis of mono(imino)pyridyl [ $N, N_{P y}, O$ ] pincer pro-ligands incorporating an ethyl ester group at 6-position and their ability to undergo hydrolysis to a carboxylic acid upon coordination to palladium. Use of platinum(II) metal precursor, on the contrary, did not promote hydrolysis resulting in a bidentate coordination mode in the corresponding complexes. Chapter 6 explores the reactivity of two dien $[N, N, N]$ pincer pro-ligands towards palladium(II) salts. Preliminary investigations demonstrated the ability of the amine- NH donor moieties to promote $\mathrm{NH} \cdots \mathrm{A}$ (acceptor) hydrogen bond interactions with the acceptor atoms on their corresponding anions in the solid state.


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| Abbreviations |  |
| :---: | :---: |
| - | degrees |
| $\AA$ | angstrom ( 0.1 nm ) |
| Ar | aryl |
| AMLA | Ambiphilic Metal Ligand Activation |
| ASAP | Atmospheric Solids Analysis Probe |
| ca. | circa |
| d | doublet |
| DCM | dichloromethane |
| dd | doublet of doublets |
| dipp | diisopropylphenyl |
| eq. | equivalents |
| ESI | Electrospray Ionisation |
| ESIMS | Electrospray Ionisation Mass Spectrometry |
| FAB | Fast Atom Bombardment |
| FT | Fourier Transform |
| g | grams |
| h | hours |
| Hz | hertz |
| HOAc | acetic acid |
| HR | high resolution |
| $i$ | iso |
| IR | Infra Red |
| M | molar concentration |


| m | multiplet |
| :---: | :---: |
| $m / z$ | mass/charge ratio |
| MAO | methylalumooxane |
| Me | methyl fragment |
| MeCN | acetonitrile |
| MHz | mega hertz |
| Mp | melting point |
| MS | Mass Spectrometry |
| NHC | $N$-heterocyclic carbene |
| NMR | Nuclear Magnetic Resonance |
| OAc | acetate fragment |
| OTf | triflate fragment |
| $p$ | para |
| ppm | parts per million |
| $\operatorname{Pr}$ | propyl fragment |
| Py | pyridyl fragment |
| R | alkyl fragment |
| S | singlet |
| sept. | septet |
| $t \mathrm{Bu}$ | $t$-butyl fragment |
| td | triplet of doublets |
| THF | tetrahydrofuran |
| $\delta$ | chemical shift |

## 1. Introduction

### 1.1 Tridentate Pincer Ligands

In recent years, a pincer-ligand platform has received considerable attention and developed into a multifunctional building block that is incorporated into a wide variety of metal complexes. Pincer ligands play an important role in the development of organometallic and coordination chemistry, homogeneous catalysis and metal-mediated and catalysed organic synthesis. A pincer ligand is a tridentate, bis-chelating ligand which co-ordinates to the metal centre in three adjacent, co-planar sites. ${ }^{1}$ Generally, pincer ligands have $\mathrm{C}_{2 \mathrm{v}}$ symmetry and a planar framework has large, bulky substituents attached to cover as much of the surrounding coordination sphere around the metal centre. This gives control over the remaining co-ordination sites, as well as increasing the thermal stability of the complex due to chelation. ${ }^{1}$ The ligand framework can be modified in order to alter the electronic and structural properties, as well as impart suitable functionality. The first report of a pincer-type ligand was made by C. J. Moulton and B. L. Shaw in 1976, when they designed a PCP bis-chelating ligand 1,3-bis[(di- $t$-butylphosphino)methyl]benzene (Figure 1.1). ${ }^{2}$

(a)

(b)

Figure 1.1-PCP pincer ligand designed by Moulton and Shaw

Analytical studies of the properties of these compounds showed remarkable thermal stability. High melting points and sublimation without decomposition indicated a potential use of these complexes in homogeneous catalysis.

Recently, a number of pincer ligands with non-symmetric backbones has also been reported. The lack of symmetry can be beneficial as it allows the use of a single weakly coordinating group which can create a vacant coordination site following dissociation and, therefore, increase the catalytic activity. Moreover, it also opens up the possibility to develop chiral compounds for asymmetric induction.

The exceptional stability of pincer complexes is thought to come from the $\sigma$ metalcarbon bond. This bond is responsible for keeping the metal bound to the ligand and thus, avoiding the decomposition of the complex, while fine-tuning of the steric and electronic properties is possible through the donor atoms. Furthermore, changing these donor substituents also allow incorporation of stereocenters which can induce chirality during a specific process.

### 1.2 Pyridine-Based Pincer Ligands

Pyridine based ligands are prominent in the literature, both as spectator and functionalised ligands. ${ }^{3}$ They are capable of acting as both $\sigma$ donors and $\pi$-acceptors, as well as being inexpensive and easy to handle. The lone pair of electrons on nitrogen is easily accessible for donation to a metal centre and typically, electron rich metals are favoured due to synergic $\pi$-backbonding. ${ }^{4}$

Since the pioneering work by Moulton and Shaw ${ }^{2}$, a vast variety of ligands containing pyridine have been synthesised, with a tridentate PNP framework being the most common amongst them. ${ }^{5,6}$ Milstein et al. reported the formation of esters from alcohols using a $\mathrm{Ru}(\mathrm{II})$ PNN complex (Figure 1.2). ${ }^{7}$


Figure 1.2-Ester and dihydrogen formation from alcohol, where $R=$ alkyl, aryl

The pincer ligand employed in this ruthenium catalyst was prepared from a 2,6 disubstituted pyridine (Figure 1.3). In addition to the already reactive methylene group, the complex comprised of a hemi-labile amine arm which facilitated the ligand to generate a vacant coordination site on the metal centre if required. When 1-hexanol was heated with catalyst $\mathbf{1 . 1}$ and KOH , the esterification was seen to achieve $\mathbf{9 5 \%}$ yield after 24 h . This was further improved by deprotonating the complex with $\mathrm{KO}^{t} \mathrm{Bu}$ to form complex 1.2 (Figure 1.3). Interestingly, dearomatisation of the pyridine ring occurred as a result of deprotonation at the phosphine methylene arm rather than expected loss of hydride ligand. This catalyst required no base in the reaction and produced a yield of $99 \%$ and a TON of $>900 \mathrm{~h}^{-1}$ after 6 h under identical conditions.


Figure 1.3-Dehydrogenation of complex 1.1 to afford complex 1.2

This catalyst illustrated the effectiveness of the pincer ligand employed, while a comparative reaction with the $\mathrm{Ru}(\mathrm{II})$ metal precursor, $\left[\mathrm{RuH}_{2}\left(\mathrm{PPh}_{3}\right)_{4}\right]$, only gave a yield of just $2 \%$ of the aldehyde and no ester product.

In 2010, Milstein et al. developed a novel reactive PNN pincer ligand containing a bipyridine moiety. In combination with $\mathrm{Ru}(\mathrm{II})$, the complex showed great efficiency in catalysing selective hydrogenation of amides to form amines and alcohols under mild pressure and neutral, homogeneous conditions. ${ }^{8}$ Distinctive catalytic activity exhibited by both complexes $\mathbf{1 . 3}$ and $\mathbf{1 . 4}$ has been explored in a variety of hydrogenation reactions, such as the hydrogenation of urea derivatives into amines and methanol ${ }^{9}$, the hydrogenation of carbamates, carbonates and formates into methanol ${ }^{10}$, and the hydrogenation of biomass-derived cyclic diesters into 1,2-diols (Figure 1.4). ${ }^{11}$

1.3

1.4

Figure $1.4-R u(I I) P N N$ pincer complexes containing a bipyridine moiety

Moreover, the range of reactions where these $\mathrm{Ru}(\mathrm{II})-\mathrm{PNN}$ complexes can be used goes beyond hydrogenation to, for instance, dehydrogenative cross-coupling between primary and secondary alcohols. ${ }^{12}$ Complex $\mathbf{1 . 4}$ has also been shown to be an efficient catalyst in the formation of carboxylates from primary alcohols with only $0.2 \mathrm{~mol} \%$ catalyst loading and water being the oxygen source. ${ }^{13}$

With respect to the ligand potential to take part in substrate activation reactions, it has been noted that protons are not the only species that can be attached to the methylene arm of the ligand. When boranes are added to complex 1.2, the Lewis acidic boron atom ends up binding to the ligand, while the hydride coordinates to the ruthenium metal centre. ${ }^{14}$ The Sanford group has looked into the cooperative activation of $\mathrm{CO}_{2}$ using $\mathbf{1 . 2}$ through C-C coupling with the ligand and also the formation of a Ru-O bond. ${ }^{15,16}$ It has been observed that the C-C bond formation occurring at the phosphine arm is reversible at room temperature, and the one occurring at the nitrogen arm is irreversible, corresponding to the kinetic and thermodynamic products, respectively (Figure 1.5). Both isomers were investigated in the hydrogenation of carbon dioxide to formate in the presence of a base with TOF's reaching up to $2200 \mathrm{~h}^{-1} .{ }^{17}$


Figure $1.5-\mathrm{CO}_{2}$ activation by complex 1.2 leading to formation of both the kinetic and thermodynamic products

In 2009 van der Vlugt et al. reported the first example of reactive PNP ligands when used in combination with palladium. ${ }^{18}$ The ligand was coordinated to different palladium precursors via a transmetallation step of cationic AgPNP which resulted in cationic $\operatorname{Pd}(\mathrm{II}) \operatorname{PNP}\left({ }^{\mathrm{t}} \mathrm{Bu}\right)$ complexes. The neutral analogues of these complexes were obtained by monodeprotonation of the cationic complexes with $\mathrm{NaN}\left(\mathrm{SiMe}_{3}\right)_{2}$. The reactivity of the complexes was tested in the Suzuki-Miyaura coupling of bromoarenes and phenylboronic acid pinacol ester. In addition, double deprotonation of the cationic $\mathrm{Pd}(\mathrm{II}) \mathrm{PNP}$ species is also possible, affording an anionic complex (Figure 1.6). ${ }^{19}$


Figure 1.6 - Formation of anionic, cationic and neutral palladium hydride complexes

When an excess amount of MeLi was added to $\mathbf{1 . 5 a}$ or $\mathbf{1 . 5 b}$, methylated anionic complex 1.5 c is obtained, which can in turn undergo a straightforward and irreversible re-protonation to the neutral analogue (Figure 1.6). On the contrary, the neutral species can undergo reversible re-protonation back to the cationic complexes. Since the importance of metal hydrides as reactive intermediates and their role in various organometallic reactions, metal-hydride complexes ( $\mathbf{1 . 5 e}, \mathbf{1 . 5 f}$ and $\mathbf{1 . 5 g}$ ) were afforded via hydride-containing compounds. ${ }^{20}$

NNN pincer ligands are another common motif in pincer chemistry. These systems are known to behave as electron rich donors which can improve nucleophilicity of lowvalent late transition metals. The enhanced nucleophilicity, in its turn, can be used to influence the catalytic process occurring at the metal centre. ${ }^{21}$

Various modifications, particularly addition of a variety of nitrogen-based donor atoms to a central pyridine ring has been a common trend in pincer chemistry. There is an extensive library of ligands where one or both pyrazole molecules have been substituted, typically by various N -heterocycles. In 1.8, a benzimidazole moiety has been used instead of one of the pyrazole groups to create a non-symmetric ligand (Figure 1.7). ${ }^{22,23}$ An alternative substitution of 1-pyrazole was made using 3-pyrazole in
1.9, and an imine in 1.10. ${ }^{24,25}$ The non-symmetric ligand $\mathbf{1 . 1 1}$ can be obtained by N alkylation of 2,6-dibenzimidazole-pyridine at only one benzimidazole. ${ }^{26}$ Similar examples of N -alkylation are observed with other two ligands containing benzimidazole-substituted pyridines, $\mathbf{1 . 1 2}$ and $\mathbf{1 . 1 3}$, with oxazoline and benzotriazole moieties, respectively. ${ }^{27}$

1.8

1.11

1.9

$\mathrm{R}={ }^{\mathrm{i}} \mathrm{Pr}, \mathrm{Ph}$
1.12

1.10

Figure 1.7 - Non-symmetrical NNN pincer ligands

Except for $\mathbf{1 . 1 1}$ and 1.13, all of these neutral NNN pincer ligands have been reported to react with $\left[\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}\right]$, forming complexes of the type $\left[(\mathrm{NNN}) \mathrm{RuCl}_{2} \mathrm{PPh}_{3}\right]$. Interestingly, $\mathbf{1 . 1 1}{ }^{26}$ and $\mathbf{1 . 1 3}{ }^{27}$ formed cationic complexes of the type $\left[(\mathrm{NNN}) \mathrm{RuCl}\left(\mathrm{PPh}_{3}\right)_{2}\right][\mathrm{Cl}]$ and $\mathbf{1 . 1 0}$ did not react with the ruthenium source. ${ }^{25}$ Excluding 1.8 and 1.10, in all of these ligands the NH group provides an acidic proton and once coordinated to $\left[\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}\right]$, deprotonation of the ligands is possible. They become monoanionic with elimination of a chloride. The donor properties of only one of the ligand sides were greatly affected by this deprotonation since a neutral imine donor is replaced by an anionic amine, resulting in a non-symmetric electronic environment at the metal centre. This cooperative work between the metal and ligand is currently of great interest and is considered a powerful strategy for catalytic applications. ${ }^{28}$

Bis(imino)-pyridine ligands are another type of NNN pincer-type ligands, known for their redox-active nature. They are effective pre-catalysts for a number of important transformations. In particular, when coordinated to cobalt or iron metal centres, these
ligands show an outstanding performance in ethylene polymerisation catalysis. In 1998, Brookhart and Gibson independently reported a series of iron and cobalt complexes supported by bis(arylimino)-pyridine ligands showing very high activities towards ethylene polymerisation in the presence of methylaluminoxane (MAO) (Figure 1.8). ${ }^{29,30}$

$\mathrm{M}=\mathrm{Co}, \mathrm{Fe}$
Figure 1.8 - Cobalt and iron complexes supported by bis(imino)-pyridine ligand

It is worth mentioning that these were the first iron-based catalysts showing a significant activity in the polymerisation of ethylene. The molecular weight of polymers changes dramatically with modifications in metal, ligand and activator concentration. The design of these ligands included tuning of the steric and electronic properties associated with bulky ortho-substituted aryl imines. It was observed that bulkier substituents on the pincer ligand led to branched polymers of higher molecular weight and in greater yield than the less hindered analogues.

Redshaw and co-workers showed how 2-(N-alkylcarboxamide)-6-iminopyridine ligands display different coordination modes depending on the metal centre. ${ }^{31}$ On reaction with palladium, four-coordinate complexes are formed where the NNN ligand is monoanionic, in contrast to five-coordinate complexes formed from the reaction with nickel, in which the NNO ligand is neutral (Figure 1.9). Although in both cases the metal centres are supported by the same tridentate pincer ligand, according to HSAB theory, the harder oxygen donor in the NNX (where X can be oxygen and nitrogen), has a higher preference for the formation of the nickel-oxygen bond than the softer nitrogen donor.


Figure 1.9 - Different coordination modes of Pd and Ni with 2-(N-alkylcarboxamide)6 -iminopyridine ligands

Moreover, nickel can also adopt different types of geometries including trigonal pyramidal, square planar and tetrahedral, depending on the geometrical restrictions applied by the ligand. In contrast, $\mathrm{d}^{8}$ palladium complexes virtually always have a square planar geometry and prefer softer amido donors than the harder oxygen or chloride donors. As a consequence, the ligand is in a deprotonated form and becomes an unsymmetrical neutral NNO pincer for nickel and mono-anionic NNN pincer for palladium.

### 1.3 Carboxylic Acid Functionalised Ligands

Research on transition metal complexes with a carboxylic acid functionality has been the subject of numerous reports. ${ }^{32,33}$ In a deprotonated form, carboxylates can coordinate to a metal centre as a strong $\sigma$-donor, as well as undergo protonation/deprotonation reactions and form hydrogen bonds to the substrate. Dipicolinate (dipic) is one of the most frequently used aromatic carboxylates. This chelating ligand provides steric hindrance and weak stacking interactions. ${ }^{32}$ The reason for this interest mainly arises from the versatility of coordination modes of this ligand, namely monodentate, bidentate and tridentate. It can also initiate bridging in transition metal-dipicolinate complexes, depending on whether the ligand is in a protonated
anionic form (dipicH ${ }^{-}$), fully protonated $\left(\mathrm{dipicH}_{2}\right)$ or a divalent anionic form (pidic ${ }^{2-}$ )
(Figure 1.10). ${ }^{32,33}$












Figure 1.10 - Various coordination modes of dipicolinic acid ligand with metal

With a view to develop a new platinum(II) luminescent system which exhibits chromic behaviour in both the solid and solution states, Kobayashi and co-workers decided to combine a cyclometallated ligand and a carboxylate as a functional group that might offer a site for hydrogen bonding. ${ }^{34}$ In two cyclometallated Pt complexes, 1.16 and 1.17, the carboxylate groups of both ligands are supposed to behave as proton-donating and proton-accepting hydrogen-bonding sites, respectively (Figure 1.11).

1.16

1.17

Figure 1.11 - Cyclometalated Pt(II) complexes

Complex 1.16, which does not have an extra carboxylic acid functionality, displayed vibronic-structured green emission in both the solid state and in DMF solution as opposed to red emissions and no vibronic structure in the solid state exhibited by 1.17. The difference between the two compounds can be explained by the more stable $\pi^{*}$ orbital of 2-(p-carboxyphenyl)pyridine ligand in $\mathbf{1 . 1 7}$ due to the electron-withdrawing nature of the carboxylic acid group.

In 2014, Funaki and Sugihara reported the first examples of ruthenium(II) complexes as sensitisers in dye-sensitised solar cells (DSSCs) containing 6-phenylpyridine-2carboxylate as a donor ligand (Figure 1.12). ${ }^{35}$

1.18a: $\mathrm{R}_{1}=\mathrm{R}_{2}=\mathrm{H}$
1.18b: $\mathrm{R}_{1}=\mathrm{CF}_{3}, \mathrm{R}_{2}=\mathrm{H}$
1.18c: $\mathrm{R}_{1}=\mathrm{F}, \mathrm{R}_{2}=\mathrm{CF}_{3}$

Figure 1.12-6-phenylpyridine-2-carboxylate-based Ru(II) complexes

It was envisaged that by modifying the ligand, it would be possible to improve the photovoltaic performance of the sensitisers in the near-infrared (IR) region. Through the use of a ligand containing a low-lying $\pi^{*}$-level molecular orbital and/or by destabilising
the metal $\mathrm{t}_{2 \mathrm{~g}}$ orbital using a strong donor ligand, it was possible to expand the absorption band in ruthenium(II) complexes to longer wavelengths. Therefore, by rationally controlling the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels, the absorption properties can be adjusted. All three compounds (1.18a-1.18c) exhibited efficient sensitisations and further modifications can provide DSSCs with a better photovoltaic performance.

The presence of a carboxylate group on a substrate in C-H activation has been explored by Zhang and Yu , who demonstrated how a proton responsive carboxylate group on an arene substrate selectively oxygenates in the ortho position. ${ }^{36}$ Using $\mathrm{Pd}(\mathrm{OAc})_{2}$ as a $\mathrm{Pd}(\mathrm{II})$ source, an array of carboxylate benzene substrates was hydroxylated under 1 atmosphere of $\mathrm{O}_{2}$ to form the phenol product. The ability of the carboxylate group to accept a proton directs the Pd-mediated ortho oxidation, to selectively yield the oxidation product in $60-80 \%$ yield (Figure 1.13).


Figure 1.13-Oxidation of benzoate to 2-hydroxybenzoic acid

A recent study by Vedernikov et al. reported a series of ONO pincer ligands using a 2,6-pyridinedicarboxylate framework (Figure 1.14). ${ }^{37}$ They explored the use of the carboxylate arm in aerobic oxidation reactions towards $\mathrm{sp}^{3} \mathrm{C}-\mathrm{H}$ bonds in 8methylquinoline. It was hypothesised that the corresponding Pd pincer complexes would perform C-H activation towards the 8 -methylquinoline substrate under standard conditions similarly to $\mathrm{Pd}(\mathrm{OAc})_{2}$ (Figure 1.15).


Figure 1.14-Anionic dicarboxylate pincer ligands with varying 4-substituents

Analysis of the intermediate palladacycles led to a conclusion that the oxidation was more selective with pda-Pd complexes despite giving slightly lower yields. Hpda-Pd complexes were more efficient, but also resulted in the over-oxidation of the substrate to carboxylic acid derivatives.


$$
\mathrm{R}=\mathrm{H}, \mathrm{Me}, \mathrm{OMe}, \mathrm{~F}, \mathrm{Cl}, \mathrm{Br}, \mathrm{I}, \mathrm{NO}_{2}
$$

Figure 1.15 - Standard reaction conditions and reagents for the oxidation of substituted methylquinolines

Furthermore, Vedernikov and co-workers performed studies on the reaction mechanism of these catalysts, illustrating the proton responsive role of the carboxylate substituent in the catalytic cycle. ${ }^{38}$ In the proposed catalytic cycle starting with the Pd (II) pre-catalyst, a ligand substitution reaction exchanges the labile ligand with the substrate (Figure 1.16). The labile carboxylate group then activates the C-H bond of the coordinated substrate through a proton transfer and the methyl group coordinates to the catalyst. The substrate is then oxidised and the carboxylic acid arm re-attaches to the Pd metal centre. The oxidised substrate is exchanged with another molecule of substrate to complete the catalytic cycle. Having oxidised the $\mathrm{CH}_{3}$ group to a $\mathrm{CH}_{2} \mathrm{OH}$ group, this is readily acetylated with $\mathrm{Ac}_{2} \mathrm{O}$ to form the product.


Figure 1.16-The catalytic cycle for the oxidation of 8-methylquinoline to 8methylacetate quinolone

Another key result from the study showed that chelate ring size and ring strain of the catalysts formed from the ligand binding to the metal centre are the main factors affecting the rate of the $\mathrm{C}-\mathrm{H}$ activation. By altering the carbon chain length of one or both side arms, a trend in reactivity was observed. It was found that longer chelate arms in the anions allow the formation of more flexible chelates as different modes of coordination to the metal are possible. It was suggested that 5 -membered rings offer more thermal stability to the complex, as well as reduction in any steric hindrance the ligand may have on the substrate binding.

### 1.4 Platinum Group Chemistry

The members of the late second and third row transition series elements - ruthenium, rhodium, platinum, iridium, palladium and osmium - are known as platinum group metals as they all occur in platinum bearing ores. Platinum group metals together with their salts have been employed as catalysts and pre-catalysts for almost 200 years. Diverse chemistry of these metals arises from the high stability of different oxidation states and their tolerance of a variety of functional groups. Their common oxidation states are as follows: Pd (II, IV), Pt (II, IV), Ru (II, III), Os (IV), Rh (III) and Ir (III, IV). In addition to forming common $\sigma$-bonded complexes with typical ligands like halides, water, sulphur and nitrogen donors, these metals are also able to form various $\pi$-complexes. Platinum group metal complexes can be used to catalyse a wide variety of
reactions such as oxidations, hydrogenations, dehydrogenations, hydrosilylations, hydrogenolysis, hydroxylations, carbonylations and carbon-heteroatom and carboncarbon coupling. ${ }^{39}$ For the purpose of this work, only the chemistries of $\mathrm{Pt}, \mathrm{Pd}$ and Ru will be overviewed and discussed.

### 1.4.1 Platinum

Cis-diaminedichloroplatinum(II) or cisplatin, carboplatin and oxaliplatin are platinum(II) complexes which are effective members of platinum-containing anti-cancer drugs. ${ }^{40}$ Reactive cis-diamineplatinum cations are generated upon aquation of the leaving groups such as chloride from cisplatin and oxalate, and carboxylate from oxaliplatin and carboplatin, respectively. These cations further react with the purine nucleobases inducing structural changes in DNA which trigger cells to die. ${ }^{41,42}$ Anticancer complexes of platinum(IV), such as satraplatin, have also shown considerable effects in anti-cancer therapy. ${ }^{43}$ The high stability of these compounds can be assigned to their low spin $\mathrm{d}^{6}$ electronic configuration which allows them to survive the acidic environment of the gastrointestinal tract prior to being absorbed into the bloodstream. Another distinctive property of these complexes over platinum(II) systems is the availability of two additional coordination sites that can be changed to modify their pharmacokinetic properties. It is possible to modify lipophilicity and redox potential of the platinum(IV) compounds without affecting the DNA-binding cis-diamineplatinum part by just changing the two axial ligands. ${ }^{44}$

The majority of current research on platinum(II) is based on synthesising analogues of cisplatin with nitrogen donor ligands. It has been argued that substituting ammonia for $\mathrm{N}, \mathrm{N}$-donor ligands can be favourable due to the thermodynamic stability of the chelate systems. The $\pi$-acidity function of the azoimine group is known to stabilise low valent metal redox states which can be seen in $[\operatorname{Pt}(N, N)(O, O)]$ complexes, with $N, N-2-$ (arylazo)pyridines and $O, O$-catecholates, in a ligand-ligand charge transfer transition (Figure 1.17). ${ }^{45}$


Figure 1.17-[Pt(N,N)(O,O)] complexes

The relative inertness of organoplatinum pincer complexes provides a range of possibilities in materials science as self-assembled novel building blocks. Square planar complexes with $\mathrm{d}^{8}$ electronic configuration possess only one available coordination site trans to the M-C $\sigma$-bond which can be filled up by a range of neutral or ionic ligands. A supramolecular synthon which has shown promising results in crystal engineering, has been developed with a view to incorporating directional hydrogen bond acceptor (A) and donor (D) on the metal-pincer complex. In systems shown in Figure 1.18 hydroxyl or acetylene moieties were added to the aryl group of the NCN pincer ligand to act as hydrogen bond donors and a platinum-bound chloride ion were supposed to act as the hydrogen bond acceptor. ${ }^{46}$ The resulted construction initiated self-assembly through hydrogen bonding between $\mathrm{O}-\mathrm{H} \cdots \mathrm{Cl}-\mathrm{M}$ and $\mathrm{CC}-\mathrm{H} \cdots \mathrm{Cl}-\mathrm{M}$ moieties where the metal can be either Pd or Pt. Different types of self-assembly modes are largely dependent on the flexibility of hydrogen bond donors and acceptors. Thus, the $\mathrm{CH}_{2} \mathrm{OH}$ moiety led to the formation of a dimeric structure, whereas acetylene or hydroxyl groups promoted the formation of linear $\alpha$-type networks (Figure 1.18).

$\alpha$-type networks



Figure 1.18 - Self-assembly modes of $\mathrm{Pt}(\mathrm{NCN})$ complex through formation of $\mathrm{H} \cdots \mathrm{Cl}-\mathrm{M}$ hydrogen bonds

Additionally, the ability to bind and release $\mathrm{SO}_{2}$ by self-assembled platinum complexes of the formula shown above makes them efficient as gas-triggered molecular switches. Sensor properties of these platinum complexes, which arise through colour and IR absorption bands, can be used as signals to show the 'on' and 'off' modes of the switch. ${ }^{47}$

### 1.4.2 Palladium

Palladium metal can arguably be considered as the most versatile and predominant metal in contemporary organic synthesis. Almost every niche of synthesis has been influenced by this transition metal due to its efficient catalytic abilities in a variety of transformations and high tolerance of various functional groups. ${ }^{48}$ Palladium chemistry has been dominated by ( $0 / \mathrm{II}$ ) oxidation states, although the use of $\mathrm{Pd}(\mathrm{IV})$ has also been developing recently. High stability of these oxidation states is thought to be due to palladium having a tendency to undergo a two-electron oxidation and reduction as opposed to one-electron processes. As a result of these two-electron operations, palladium has found its use as a catalyst. $\operatorname{Pd}(0)$ is widely used to catalyse various crosscoupling reactions and alkene hydrogenations, whereas $\mathrm{Pd}(\mathrm{II})$ has shown a great deal of efficiency in oxidation of alcohols and cycloisomerisation reactions. In 2010, the Nobel
prize in chemistry was awarded to R.F. Heck, E-I Negishi and A. Suzuki for their work on $\operatorname{Pd}(0)$-catalysed cross coupling reactions in organic synthesis.

In 1995, Herrmann et al. reported that palladium systems can be efficient catalysts for Heck olefination of aryl halides. ${ }^{49}$ Since then, a range of palladium-based pincer complexes have been developed and employed in coupling reactions in search of effective catalysts for C-C bond forming processes. Oberhauser and co-workers developed $\operatorname{Pd}(\mathrm{II})$ complexes (1.19a-e) to study the coordination chemistry of pyridylimine ligands that have been successfully employed in ethylene oligomerisation in the presence of $\mathrm{CoCl}_{2}$ and MAO (Figure 1.19). ${ }^{50}$ These complexes have been tested as catalyst precursors for the Suzuki cross-coupling reaction of 4-bromo- and 4-chloroacetophenone with phenylboronic acid in the presence of $\mathrm{Cs}_{2} \mathrm{CO}_{3}$. Only the phosphanemodified complexes 1.19d and 1.19e have shown a significant activity.

1.19a, $\mathrm{X}=\mathrm{OAc}$ 1.19b, $\mathrm{X}=\mathrm{Cl}$

1.19c, $\mathrm{X}=\mathrm{CH}_{3} \mathrm{CN}$
1.19d, $\mathrm{X}=\mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{3}$
1.19e, $\mathrm{X}=\mathrm{HP}\left(o-\mathrm{MeO}\left(\mathrm{C}_{6} \mathrm{H}_{4}\right)\right)_{2}$

Figure 1.19 - Pd(II)-based pyridylamine-type complexes

Lapkin and Cavell developed a series of $\operatorname{Pd}(0)-$ NHC complexes which were tested in the telomerisation reaction of 1,3-pentadiene with various alcohols (Figure 1.20). ${ }^{51}$ Specifically, complex 1.20a showed moderate conversions and a very high selectivity towards the telomerisation products using alcohols such as 1-propanol and 1-butanol.


Pd(IMes)(dvds)
1.20a

$\operatorname{Pd}(\mathrm{IMesPr})(\mathrm{dvds})$
1.20b

$\mathrm{Pd}(\mathrm{TzPh})(\mathrm{dvds})$
1.20c

Figure 1.20 - Pd(0)-carbene catalysts

By combining the $\operatorname{Pd}(0)$ precursor, $\operatorname{Pd}\left[\mathrm{P}(o-\text { tol })_{3}\right]_{2}$, with the hindered Josiphos ligand CyPF'Bu, Hartwig and Ogatu reported a distinctive amination catalyst for the monoarylation of primary amines using challenging aryl tosylate substrates under very low Pd loadings (Figure 1.21). ${ }^{52}$ It is thought that the rigidity of the chelated ring can be one of the reasons for favouring this selectivity.



87\%


99\%


97\%


63\%


99\%


97\%

Figure 1.21 - Monoarylation of primary amines with aryl tosylates

### 1.4.3 Ruthenium

The ability of ruthenium to form compounds in a wide range of oxidation states $(0$ to +8 and -2 ) makes it a very versatile catalyst. Research into the reactivity of this metal has
been receiving a lot of attention because of the interesting energy transfer and electron transfer properties shown by ruthenium complexes. Numerous ruthenium compounds have been screened for anticancer properties and could potentially substitute wellknown platinum-based drugs. Despite the unstable nature of organometallic compounds, a few systems have indeed demonstrated high air and water stability and an intriguing range of anticancer activity. The most successful organometallic ruthenium-based antitumour complexes to date have been ruthenium(II)-arene complexes, $\left[\mathrm{Ru}\left(\eta^{6}-p\right.\right.$ arene) $\mathrm{Cl}_{2}$ (pta)] termed 'RAPTA' ${ }^{53}$ The PTA (1,3,5-triaza-7-phosphadamantane) ligand is highly water soluble, whereas the aromatic ring of the complex is relatively hydrophobic. These compounds bind strongly and highly selectively to proteins and display a relatively low tendency to DNA binding which is thought to be the main aim of a number of metal-based drugs.

Berry and co-workers developed a method to synthesise square planar $16 \mathrm{e}^{-} \mathrm{Ru}(0)$ complexes supported by NNN-type pincer ligands. ${ }^{54}$ The two perpendicular planes of $\mathrm{Ru}(N N N)$ interlock bulky aryl substituents, thus ensuring the necessary steric protection in the $16 \mathrm{e}^{-} \mathrm{Ru}(0)$ metal centres (Figure 1.22).


Figure 1.22 - Ruthenium NNN-type pincer complexes

When complexes 1.21e and 1.21 f undergo a reaction with an excess of triethylsilane, the $\mathrm{Si}-\mathrm{H}$ bond is activated resulting in the formation of complexes 1.21a and 1.21b as well as $\mathrm{Et}_{3} \mathrm{SiCl}, \mathrm{Et}_{4} \mathrm{Si}$ and ethane (Figure 1.23).


Figure 1.23 - Activation of Si-H bond

Furthermore, the same group has also demonstrated how $\mathrm{Ru}(0)$ complex 1.21d can activate $\mathrm{Si}-\mathrm{Cl}$ bonds (Figure 1.24). ${ }^{55}$ It was hypothesised that oxidative addition of the $\mathrm{Si}-\mathrm{H}$ bond is followed by 1,2 -migration of $\mathrm{Si-Cl}$ to give complex 1.21g. A substrate choice with a weak $\mathrm{Si}-\mathrm{Cl}$ bond is thought to play a major role in the activation of these two bonds.


Figure 1.24 - Activation of Si-Cl bond

With the idea of 'hydrogen economy' getting widespread attention, the search for an efficient renewable resource is a priority. Methanol consisting of $12.6 \% \mathrm{w} / \mathrm{w}$ of hydrogen is a good example of such a material, however, oxidation of methanol to liberate the hydrogen is a very challenging process. Beller and co-workers demonstrated how $\mathrm{Ru}(\mathrm{PNP})$ pincer complexes 1.22 a and $\mathbf{1 . 2 2 b}$ in basic aqueous conditions can efficiently dehydrogenate methanol to dihydrogen and carbon dioxide (in the form of sodium carbonate) (Figure 1.25). ${ }^{56}$



Figure 1.25 - Ru-based PNP type complexes

Another successful example of the use of Ru-based complexes, is the dehydrogenation of amines. In addition to the transformation being less researched into, the reported procedures typically require hydrogen acceptors, excess amount of base and the use of high temperatures. Szymczak synthesised a phthalimide-derived $\mathrm{Ru}(\mathrm{II})$ NNN complex 1.23 that shows efficient catalytic performance in the dehydrogenation of primary and secondary amines to nitriles and imines, respectively, without the use of oxidants and hydrogen acceptors (Figure 1.26). ${ }^{57}$


Figure 1.26 - Dehydrogenation of amines by complex 1.23

Ruthenium pincer complexes have shown efficient use and great catalytic performance in various transformations, including dehydrogenation of alkanes, amine-boranes, synthesis of acetals, amides, amines, a range of hydrogenation reactions and many more. Examples of ruthenium compounds in transfer hydrogenation will be further discussed in Section 1.5 of this work.

### 1.5 Ruthenium-Catalysed Transfer Hydrogenation

Transfer hydrogenation (TH) is a catalytic reaction involving reduction of various polar bonds into the corresponding saturated compounds using a hydrogen donor, ambient temperature and pressure (Figure 1.27).


$$
\begin{aligned}
& \mathrm{X}=\mathrm{O}, \mathrm{CHR}, \mathrm{NHR} \\
& \mathrm{M} \text {-catalyst, } \mathrm{R}_{1} / \mathrm{R}_{2}=\text { Phenyl, Alkyl } \\
& \mathrm{DH}=\text { hydrogen donor, } \mathrm{D}=\text { byproduct }
\end{aligned}
$$

Figure 1.27-General scheme for transfer hydrogenation

The first reports illustrating the use of transition metals to catalyse transfer hydrogenation reactions date back to 1950s. ${ }^{58}$ Transition metal pincer complexes of palladium, platinum, rhodium and ruthenium have been reported to catalyse transfer hydrogenation. ${ }^{59,60}$ However, superior performance and cost efficiency of ruthenium pincer complexes compared to other metal catalysts have turned them into a highly attractive catalyst choice for transfer hydrogenation.

Transfer hydrogenation is generally considered a safer alternative to direct hydrogenation as no high pressures of explosive hydrogen gas or moisture-sensitive hydride reagents are required. Typically, hydrogen donors used in TH are inexpensive, readily available and easy to handle. The most widely-used hydrogen donors are 2propanol, formic acid and the formic acid - trimethylamine azeotropic mixture. The formic acid with its salts (potassium, sodium and ammonium formate) are useful hydrogen sources as they are soluble in water making the process even more environmentally friendly. 2-propanol is a cheap and often the preferred promoter which can be easily disposed of and recycled. Acetone is the main by-product of this solvent and is easily distilled off from the mixture in the separation process.

A proposed general mechanism shown in Figure 1.28 is thought to proceed with initial chloride substitution in the catalyst precursor by the hydrogen donor, with subsequent $\beta$ elimination to give a metal hydride compound.


Figure 1.28 - Monohydride mechanism for transfer hydrogenation

The product is formed when the ketone substrate is inserted into the metal-hydride bond and then displaced by the hydrogen donor to complete the cycle. Typically, a base is used to accelerate the reaction and to increase the amount of alkoxide generated and, thus, speeding up the rate of pre-catalyst activation. ${ }^{61,62}$

An alternative to this mechanism is also possible and involves metal dihydride intermediate species (Figure 1.29).






Figure 1.29 - Dihydride mechanism for transfer hydrogenation

The chloride ligand is replaced by the hydrogen donor in a dichloride complex, followed by the substrate binding. Once the ketone substrate is inserted into a metalhydride bond, reductive elimination gives the alcohol product. Furthermore, the metal dihydride complex is regenerated upon the initial oxidative addition across the $\mathrm{O}-\mathrm{H}$ bond of the hydrogen donor and subsequent $\beta$-elimination.

Barrata and co-workers reported a series of ruthenium pincer complexes which showed high efficiency in TH. In the conversion of cyclohexanone to cyclohexanol, complex 1.24a achieved the highest TOF reported to date, $1.5 \times 10^{6} \mathrm{~h}^{-1}$ (Figure 1.30). ${ }^{63}$ The group also developed a number of complexes by replacing the chloride ligand in complex 1.24a with monodentate oxygen donors such as phenoxide, alkoxide, carboxylate, triflate and silanolate. These complexes have also shown excellent performance in transfer hydrogenation of ketones with 2-propanol as a hydrogen source and $\mathrm{NaO}^{i} \mathrm{Pr}$ as a base. For instance, complex 1.24c with an acetate ligand achieved TOF of $1.7 \times 10^{6} \mathrm{~h}^{-1}$ for the hydrogenation of cyclohexanone. ${ }^{64}$ Interestingly, while complexes based on 1.24 c with a dimethyl amine donor $\left(\mathrm{NMe}_{2}\right)$ demonstrated poor catalytic performance, all of the pincer complexes with $\mathrm{NH}_{2}$ groups and various
oxygen-based ligands such as triflate, silanolate and carboxylate efficiently converted ketones with TOFs ranging from $6 \times 10^{5} \mathrm{~h}^{-1}$ to $3.8 \times 10^{-6} \mathrm{~h}^{-1}$. It is thought that intramolecular hydrogen bonds ( $\mathrm{N} \cdots \mathrm{H} \cdots \mathrm{O}$ ) which have a stabilising effect and formation of catalytically active $\mathrm{Ru}-\mathrm{H} / \mathrm{Ru}-\mathrm{O}^{i} \mathrm{Pr}$ intermediates from the $\mathrm{Ru}-\mathrm{O}$ bond are responsible for the high reactivities of these complexes. The chiral complex $\mathbf{1 . 2 4 b}$ with a phosphine ligand, showed similar performance to 1.24 a but with a moderate selectivity of $71 \%$.

$1.24 a$

1.24b

1.24c

Figure 1.30 - Ru-based CNN type complexes

Extensive research has been done on ruthenium complexes supported by NNN-type ligands shown in Figure. 1.31.

1.25a

1.25c

1.25b


1.25d

Figure 1.31 - Ru-based NNN type catalysts for transfer hydrogenation

Complex 1.25a with a chiral pyridyl - pyrazolyl - oxazolinyl ligand was shown to be an effective catalyst in TH of ketones with good to excellent conversions and
enantioselectivities. ${ }^{24}$ Moreover, the performance of $\mathbf{1 . 2 5 a}$ was significantly higher compared to complexes lacking NH functionality suggesting that there is an 'NH' effect involved in the mechanism. The same effect was observed for complexes $\mathbf{1 . 2 5 b}$ and 1.25c. ${ }^{22,24}$ Szymczak and co-workers suggested that a rigid 6,6'-dihydroxy terpyridine (dhtp) ligand is involved in proton transfer direction with metal-coordinated substrates. ${ }^{65}$ Complex $\mathbf{1 . 2 5 d}$ demonstrated efficiency in TH of various carbonyls into alcohols, however the chemoselectivity was poor when tested with a few carbonylbased olefins.

### 1.6 Carbon-Hydrogen Bond (C-H) Activation and Functionalisation

In recent years, the area of $\mathrm{C}-\mathrm{H}$ activation has attracted much attention as an important source of development of low-cost and efficient methods for the conversion of chemical feedstock, such as natural gas, directly into value added chemicals, like methanol, ethylene, propylene, etc. Indeed, this area has become one of the greatest challenges of this century. ${ }^{66,67}$ The selective transformation of $\mathrm{C}-\mathrm{H}$ bonds found in alkanes and arenes leading to new more reactive functionalised molecules is a powerful strategy for the rapid increase of the complexity of molecules. ${ }^{68}$

For example, extensive research has been carried out on the development of catalysts for the direct conversion of methane into high-value added products and amongst various approaches used, the highest yield and the highest selectivity can be obtained through C-H activation chemistry. The process of C-H activation is divided into two steps in which, first, the C-H bond of an unactivated hydrocarbon tethers to an available site at a transition metal centre and then, the C-H bond cleaves to form a metal-carbon bond. Studies have distinguished three mechanistic pathways of C-H activation: oxidative addition, sigma bond metathesis and electrophilic substitution. In addition, recent studies by Davies and Macgregor identified a mechanism of C-H activation which involves an electron-deficient metal and a basic ligand acting together to result in a heterolytic fission of the C-H bond. ${ }^{69}$ This process was termed as AMLA (ambiphilic metal ligand activation) process.

The inert nature of $\mathrm{C}-\mathrm{H}$ bonds can be related to the fact that they are strong and robust (with bond dissociation energies in the range of $400-460 \mathrm{~kJ} / \mathrm{mol}$ ). ${ }^{70}$ It has been well reported that the second and third row transition metals have the ability to react with a
$\mathrm{C}-\mathrm{H}$ bond to form new metal-carbon ( $\mathrm{M}-\mathrm{C}$ ) and metal-hydrogen ( $\mathrm{M}-\mathrm{H}$ ) bonds through $\mathrm{C}-\mathrm{H}$ bond activation, the process which is also known as an oxidative addition reaction, and is illustrated in Figure 1.32. This reaction can be thermodynamically favourable due to the combination of the $\mathrm{M}-\mathrm{C}$ and $\mathrm{M}-\mathrm{H}$ bonds formed being significantly stronger than the $\mathrm{C}-\mathrm{H}$ bond that was broken. The $\mathrm{M}-\mathrm{C}$ bond is also more reactive than the $\mathrm{C}-\mathrm{H}$ bond and can, therefore, undergo further functionalisation. ${ }^{71}$


Figure 1.32-General scheme of the transition metal-catalysed oxidative addition reaction of an aryl or alkane $\mathrm{C}-\mathrm{H}$ bond

The first examples of $\mathrm{C}-\mathrm{H}$ bond activation employing late transition metals included both intramolecular oxidative addition to both $\mathrm{sp}^{2}$ and $\mathrm{sp}^{3}$ ligand $\mathrm{C}-\mathrm{H}$ bonds bound to the metal centre, and intermolecular oxidative addition to arene $\mathrm{C}-\mathrm{H}$ bonds. ${ }^{72,73,74} \mathrm{It}$ has been established that the stronger $\mathrm{C}-\mathrm{H}$ bonds of aromatic hydrocarbons are more readily activated than the weaker alkane $\mathrm{C}-\mathrm{H}$ bonds because they result in stronger $\mathrm{M}-$ C bonds. ${ }^{72,75}$ Bergman ${ }^{76}$ and Jones ${ }^{77}$ demonstrated how aromatic $\mathrm{C}-\mathrm{H}$ bonds are preferentially activated over alkane $\mathrm{C}-\mathrm{H}$ bonds using $\mathrm{C}-\mathrm{H}$ oxidative addition of cyclohexane to an iridium complex and $\mathrm{C}-\mathrm{H}$ oxidative addition of propane to a rhodium complex, as examples (Figure 1.33).

a)


b)




Figure 1.33 - a) Activation of cyclohexane by iridium catalyst; b) Activation of propane by rhodium catalyst

Among metal species, palladium has attracted considerable interest as the most versatile metal catalyst in organic synthesis. ${ }^{78}$ Palladium-based catalysts are attractive candidates for the activation and functionalisation of $\mathrm{C}-\mathrm{H}$ bonds for a number of reasons. Besides compatibility with various functional groups and participation in cyclometallation with different directing groups, they can readily promote $\mathrm{C}-\mathrm{H}$ activation at both $\mathrm{sp}^{2}$ and $\mathrm{sp}^{3}$ sites, unlike many other transition metal catalysts, and do not require harsh reaction conditions in most cases.

In 2016, Sanford and co-workers successfully attempted to facilitate a remote siteselective $\mathrm{C}\left(\mathrm{sp}^{3}\right)-\mathrm{H}$ arylation reaction by attaching a perfluorinated amide auxiliary onto saturated nitrogen-containing heterocycles (Figure 1.34). ${ }^{79}$ For the purpose of suppression $\alpha$-oxidation of amines, non-oxidising caesium salts were used as an effective additive to promote this transformation. A range of cyclic amines could be functionalised by using this approach, providing a quick and easy route to new aminoacid derivatives as well as analogues of pharmaceutical candidates.


Figure 1.34-Palladium(II)-catalysed C(sp3)-H arylation of cyclic amines
Shi et al. studied the palladium-catalysed direct ortho arylation of acetanilides with boronic acids as arylating reagents in the presence of stoichiometric amounts of copper and silver salts (Figure 1.35). ${ }^{80}$ It was noted that the optimised catalytic system had a good tolerance towards various important functional groups, as well as air and moisture.


Figure 1.35-Suzuki-Miyaura coupling reaction with a Pd-catalysed C-H bond activation

Davies and Macgregor reported a computational study of cyclometallation of DMBA ( $\mathrm{DMBA}-\mathrm{H}=$ dimethylbenzylamine) and $\mathrm{Pd}(\mathrm{OAc})_{2}{ }^{69}$ It was found that the most favoured pathway was a hydrogen transfer process through a six-membered transition state involving a $\mathrm{C}-\mathrm{H}$ interaction rather than a Wheland intermediate formed by electrophilic attack on the $\pi$ - system (Figure 1.36). The weak agostic interaction can polarise the $\mathrm{C}-\mathrm{H}$ bond and allow acetate to form an intermolecular hydrogen bond to the transferring hydrogen.


Figure 1.36 - Wheland intermediate and calculated agostic intermediate

Sanford's group also developed Pd catalysts with monodentate pyridinium-substituted pyridine ligands targeted for the $\mathrm{C}-\mathrm{H}$ oxygenation of benzene using potassium persulphate (Figure 1.37). ${ }^{81}$ These catalysts show a significantly improved catalytic performance compared to $\mathrm{Pd}(\mathrm{OAc})_{2}$ used on its own in this transformation. Notably, the reaction exhibits high selectivity for phenyl acetate over biphenyl. Initial investigations suggest that the cationic ligand plays a key role of serving as a phase transfer catalyst for the $\mathrm{K}_{2} \mathrm{~S}_{2} \mathrm{O}_{8}$ oxidant. Previous studies made by the group showed that this oxidant is reactive enough to promote $\mathrm{C}-\mathrm{O}$ bond formation at Pd .


Figure 1.37 - C-H oxygenation of benzene (left); Palladium catalyst containing pyridinium-substituted pyridine (right)

### 1.7 This Work

This thesis is concerned with the development of pincer and related tridentate ligands, the reaction chemistry of their corresponding complexes formed upon reactions with palladium, platinum and ruthenium metal precursors, and their application in catalysis.

Chapter 2 discusses the design and synthesis of three pyridine-based dianionic arylcontaining [ $C, N_{P_{y},}, O$ ] pincer ligands which all promote $\mathrm{sp}^{2} \mathrm{C}-\mathrm{H}$ activations upon reaction with palladium(II) and ruthenium(II) metal salts.

In Chapter 3, the chemistry of another three pyridine-based dianionic phenolcontaining [ $O, N_{P y}, O$ ] pincer ligands is explored. Similar to Chapter 2, the effect of
different substituents on the ligand backbone and the influence of the oxygen donor from the phenol group on the reaction chemistry of the synthesised organometallic complexes will be investigated.

In Chapter 4, the application of complexes formed in Chapters 2 and $\mathbf{3}$ as catalysts in transfer hydrogenation of ketones will be explored.

Chapter 5 describes the synthesis and reactivity of mono(imino)pyridyl-containing [ $N, N_{P y}, O$ ] pincer ligands towards palladium(II) and platinum(II) salts. The effect of steric hindrance around the axial positions of a metal centre will be examined by direct comparison of otherwise identical ligand frameworks.

In Chapter 6, the synthesis and reactivity of dien $[N, N, N]$ pincer ligands towards palladium(II) salts will be explored. Additionally, preliminary investigations into the ability of the NHAr donors in all the synthesised Pd (II) dien complexes to promote $\mathrm{NH} \cdots \mathrm{A}$ (acceptor) hydrogen bond interactions in the solid state will be discussed.

## 2. Design, synthesis and reactivity of palladium(II) and ruthenium(III) complexes supported by novel arylsubstituted $\left[C, N_{P y}, O\right]$-type pincer ligands

### 2.1 Introduction

In the area of homogeneous catalysis, choosing an appropriate ligand is critical for adjusting catalytic performance and stereoselectivities of metal complexes. Features of the reactive species and the course of reactions can be affected by the steric and electronic factors. In this sense, pincer metal complexes can provide both the necessary stability and reactivity through systematic modifications to either ligand and/or metal centre. Thus, developing new tridentate pincer ligands is one of the most effective approaches for making distinct metal-ligand bonds. To this day, a great variety of pincer compounds have been designed with different transition metals and ancillary ligands. ${ }^{3}$ Pyridine-based complexes with a pyridine group being the central donor atom have occupied an important niche in organic and inorganic synthesis. The possibility to finetune the electronic and steric properties of the exterior donor arms of the pincer frame has certainly advanced them in this area of research.

Numerous examples of pyridine-based ligands with a wide variety of external donor groups, such as NNN, CNC, NNC, ONO and many more, have been reported in the literature. ${ }^{3}$ Typically, these ligand systems consist of a 2,6 -disubstituted pyridine as a central moiety and either an amino, imino, aryl group or an oxygen-containing unit placed on one or both ligand arms. An example of such a ligand framework derives from CNN pro-ligand which promotes C-H activation of the aryl group upon binding to metal centres, hence providing a valuable insight into investigations related to pyridinebased pincer ligands. ${ }^{82}$ The terdentate pincer ligand a presented in Figure 2.1, was synthesised by Baratta and co-workers and was subsequently modified by adding a tertbutyl/methyl group (b) to the methylene arm and/or methylating the amine (c).

a

b

c

Figure 2.1-Terdentate pincer ligand $\boldsymbol{a}$ and its derivatives

The derivatives of a CNN ligand framework - CNO pincer pro-ligands are relatively rare examples of pyridine-based pincer ligands and have received much less attention in the research community. A novel Pd (II) CNO pincer complex was synthesised via the $\mathrm{C}-\mathrm{H}$ activation of methyl red $(\mathrm{MR}=2-\{[4-($ dimethylamino $)$ phenyl $]$ diazenyl $\}$ benzoic acid) with $\mathrm{Pd}(\mathrm{OAc})_{2}\left(\right.$ Figure 2.2). ${ }^{83}$


Figure 2.2 - Synthesis of Pd(II) CNO pincer complex

This cyclometallated CNO pincer complex was obtained under mild conditions and in good yield. Metallation occurred at the ortho-position of the (dimethylamino)phenyl group in methyl red. The complex was used to study interactions with human serum albumin (HSA). ${ }^{83}$

Employment of an unsymmetrical ligand leads to a variety of reaction chemistry upon complex formation. For instance, the pyridine-based complex with a 2-naphthyl-6alcohol framework (complex $\mathbf{e}$ ) is an interesting example to show how adjustments made to the ligand backbone can significantly affect the reactivity of the resulting metal complex (Figure 2.3). ${ }^{84}$

d

e

Figure 2.3-Peri/ortho palladation of naphthalene rings

Synthetic and computational studies demonstrated that exclusively peri C-H activation takes place when the 2-naphthyl-6-aminopyridine (complex d) binds to palladium. This is the result of using a strong bidentate $N, N$ ligand as the directing group for initial metal coordination. On the contrary, when 2-naphthyl-6-alcoholpyridine is employed, only ortho C-H activation is observed due to the absence of initial bidentate binding. Thus, by using chelate control to direct the rotation of the pendant naphthyl group, cyclopalladation can regioselectively take place at the peri-position over the ortho.
S. Pal and co-workers have synthesised cyclometallated $\mathrm{Pd}(\mathrm{II})$ complexes with tridentate $C, N, O$ Schiff base ligands. ${ }^{85}$ The complexes consist of planar acid hydrazone, 4-R-1-naphthaldehyde benzoylhydrazone $\left(\mathrm{H}_{2} \mathrm{~L}_{\mathrm{n}}\right.$ where $\mathrm{n}=1$ and $\left.2, \mathrm{R}=\mathrm{H}, \mathrm{OCH}_{3}\right)$ that has tridentate aryl-carbon, amide/amidate-oxygen and azomethane-nitrogen donors and result in six and five-membered chelate rings (Figure 2.4). In each complex, the preferred position for the metallation of 1-naphthalenyl unit of the ligands is the peri position rather than the ortho position.


Figure 2.4 - Palladation of 4-R-1-naphthaldehyde benzoylhydrazones

There are also reports in the literature where tridentate palladium(II) complexes with CNO donors feature N -heterocyclic carbenes, amidate and phenoxide groups (Figure 2.5). ${ }^{86}$ The complexes are found to be efficient catalysts for direct $\mathrm{C}-\mathrm{H}$ functionalisation of heterocycles and aryl halides with low catalyst loadings.

$\mathrm{R}=\mathrm{CH}_{2} \mathrm{Ph}, \mathrm{CH}_{3}$

$\mathrm{R}=\mathrm{CH}_{2} \mathrm{Ph}$

Figure 2.5-Tridentate CNO-donor Pd(II) complexes featuring $N$-heterocyclic carbenes

In 2017, Simayi et al. developed a $C, N_{P y}, O$ palladium(II) pincer complex where the alcohol donor unit has been shown to act as a hydrogen bond donor with the ability to direct the self-assembly of dimeric $\mathrm{Pd}(\mathrm{II})$ complexes (Figure 2.6). ${ }^{87}$ On the contrary, only monomeric palladium species are accessible using the amine/imine-based $C, N_{P y}, N$ pincer framework.


Figure 2.6-Self-assembly of dimeric Pd(II) complexes through hydrogen bonding

The range of metals utilised to form complexes containing CNN or CNO donor ligands is not just limited to palladium but also extends to another platinum group member such as ruthenium. In fact, it is of great significance to activate the CH bond of the aromatic ring with ruthenium precursor salts in order to synthesise pincer complexes that incorporate a strong Ru-C bond. Another example of a new CNN ligand framework was presented by Baratta et al. which describes a synthesis of ruthenium-based pincer complexes comprised of cyclometallated phenyl or benzoquinolinyl units, typically
through the substitution of triphenylphosphine group. ${ }^{88,89}$ Heating the CNN pincer ligand with $\left[\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}(\mathrm{dppb})\right]$ in isopropanol at reflux with a catalytic amount of triethylamine afforded CNN pincer complexes through CH activation, the substitution of triphenylphosphine and the elimination of hydrochloric acid (Figure 2.7).


Figure 2.7 - CNN-Ru(II) pincer complex synthesis

### 2.2 Aims and Objectives

In this chapter three pyridine-based dianionic $C, N_{P y}, O$ pincer pro-ligands have been developed that give an insight into the influence of the electronic and steric properties of the different substituents located on the exterior of the ligand framework (e.g $\mathrm{R}=\mathrm{H}$, ${ }^{t} \mathrm{Bu}, \mathrm{CF}_{3}$ ) (Figure 2.8).


$$
\begin{aligned}
& \mathrm{HL}_{\mathbf{1}}, \mathrm{R}=\mathrm{H} \\
& \mathrm{HL}_{\mathbf{2}}, \mathrm{R}={ }^{\mathrm{t}} \mathrm{Bu} \\
& \mathrm{HL}_{\mathbf{3}}, \mathrm{R}=\mathrm{CF}_{3}
\end{aligned}
$$

Figure 2.8-Pyridine-based C, $N_{P y}, O$ pincer pro-ligands

In addition, the reactions of aryl-containing $C, N_{P y}, O$ pincer ligands with palladium(II) and ruthenium(II) salts will be discussed. C-H activation of the aryl ring in these ligands is targeted on complexation with salts of both metal. All the products have been characterised by a combination of ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectroscopies, Mass Spectrometry and IR spectroscopy. In addition, single crystal X-Ray molecular structures have been obtained for some of the complexes.

### 2.3 Results and Discussion

### 2.3.1 Synthesis of target pro-ligands

The target pro-ligands, $\mathrm{H}_{1}, \mathrm{H}_{2}$ and $\mathrm{HL}_{3}$ shown in Figure 2.9 were readily synthesised in three steps from commercially available starting materials. Pro-ligand $\mathrm{H}_{2}$ is a novel compound and has been fully characterised by ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectroscopies, high resolution mass spectrometry and solid-state IR spectroscopy. Proligands $\mathrm{HL}_{1}$ and $\mathrm{HL}_{3}$ have been previously reported in the literature and their use in near-IR sensitisers for dye-sensitised solar cells (DSSCs) have been disclosed in Chapter 1.

$\mathrm{HL}_{1}$

$\mathrm{HL}_{2}$

$\mathrm{HL}_{3}$

Figure 2.9-Target pro-ligands $\mathrm{H}_{\mathbf{1}}, \mathrm{HL}_{2}$ and $\mathrm{HL}_{3}$

The synthesis of boronic acids, required for the subsequent preparation of $\mathrm{HL}_{2}$ and $\mathrm{HL}_{3}$, was carried out according to a protocol refined by our group and based on a literature preparation (Figure 2.10). ${ }^{90}$


Figure 2.10-Synthesis of boronic acids

The synthesised materials were used in the next step without any further purification. Phenylboronic acid, employed in the synthesis of $\mathrm{HL}_{1}$, was readily available and used without further purification. A palladium-catalysed Suzuki coupling of commercially
available ethyl-6-bromopicolinate with the corresponding boronic acids as the coupling partners yielded the picolinate ligand precursors in high yields.

### 2.3.1.1 Synthesis of 2-phenyl-6-ethylpicolinate

Phenylboronic acid and ethyl-6-bromopicolinate were employed in a Suzuki coupling reaction to give 2-phenyl-6-ethylpicolinate (Figure 2.11). The pure product was isolated in $97 \%$ yield using flash column chromatography. Characterisation data are consistent with those reported in the literature. ${ }^{35}$


Figure 2.11 - Synthesis of 2-phenyl-6-ethylpicolinate

### 2.3.1.2 Synthesis of 2-phenyl-6-carboxylatopyridine (HL1)

Synthesis of the target pro-ligand HL1 occurs smoothly by employment of an ester hydrolysis reaction of 2-phenyl-6-ethylpicolinate (Figure 2.12). The pure product can be achieved in $93 \%$ yield and data are consistent with those reported in the literature. ${ }^{35}$


Figure 2.12-Synthesis of $\mathrm{HL}_{1}$

### 2.3.1.3 Synthesis of 4-t-butylphenyl boronic acid

4 - $t$-butylphenyl boronic acid was prepared from 2-bromo-4-t-Bu-benzene, based on a literature preparation (Figure 2.13). Spectroscopic data for the product are consistent with those reported in the literature. ${ }^{90}$


Figure 2.13 - Synthesis of 4-t-butylphenyl boronic acid

### 2.3.1.4 Synthesis of 2-(4-t-butyl-)-6-ethylpicolinate

Synthesis of 2-(4-t-butyl-)-6-ethylpicolinate was based on the same synthetic procedure as that used in the synthesis of 2-phenyl-6-ethylpicolinate (Figure 2.14). The compound was obtained in high yield and purity and has been fully characterised by several analytical techniques. The infrared spectrum of the product shows peaks at $1226 \mathrm{~cm}^{-1}$, $1591 \mathrm{~cm}^{-1}$ and $1727 \mathrm{~cm}^{-1}$, which correspond to vibrations of the $(\mathrm{C}-\mathrm{O})_{\text {ester }},(\mathrm{C}=\mathrm{N})_{\text {pyridine }}$ and $(\mathrm{C}=\mathrm{O})_{\text {ester }}$ bonds, respectively. The ${ }^{1} \mathrm{H}$ NMR spectrum of the product shows a triplet and a quartet at 1.39 ppm and 4.41 ppm , respectively, assigned to the ethyl ester protons. The singlet at 1.28 ppm corresponding to 9 H protons is assigned to the tertiary butyl group on the aryl ring. The ${ }^{13} \mathrm{C}$ NMR spectrum also showed two signals at 14.3 and 62.0 ppm corresponding to the ester carbon resonances. 2-(4-t-butyl-)-6ethylpicolinate also exhibits a protonated molecular ion peak by mass spectrometry at $284[\mathrm{M}+\mathrm{H}]^{+}$. High resolution mass spectrometry revealed a peak at 284.1648, whereas the calculated molecular mass for $\mathrm{C}_{18} \mathrm{H}_{22} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}$is 284.1651.




Figure 2.14-Synthesis of 2-(4-t-butyl-)-6-ethylpicolinate

### 2.3.1.5 Synthesis of 2-(4-t-buty)-6-carboxylatopyridine (HL2)

The synthesis of $\mathrm{HL}_{2}$ was achieved via the same synthetic approach as that used for the synthesis of HL1. The product was obtained in $96 \%$ yield and in high purity (Figure 2.15). The characterisation data for $\mathrm{HL}_{2}$ are consistent with the proposed structure. Analysis of the compound by ${ }^{1} \mathrm{H}$ NMR spectroscopy confirms the absence of the ethyl ester group as no triplet and quartet signals at 1.39 ppm and 4.41 ppm , seen in the
spectrum of the ligand pre-cursor, are observed in this case. The singlet corresponding to 9 H of the tert-butyl group is seen at 1.31 ppm . The structure is also confirmed through ${ }^{13} \mathrm{C}\{\mathrm{H}\}$ NMR as no carbon resonances corresponding to the ester group are observed. Mass spectrometry reveals a protonated molecular ion peak $[\mathrm{M}+\mathrm{H}]^{+}$at $\mathrm{m} / \mathrm{z}$ 256. This is also confirmed by a strong protonated molecular peak found upon analysis by HRMS (ASAP). The infrared spectrum of $\mathrm{HL}_{2}$ also confirms the product formation as no vibrations seen in the spectrum of the ester derivative are observed. Furthermore, there is a broad peak observed at $2958 \mathrm{~cm}^{-1}$ indicating the presence of a carboxylic acid O-H stretch.


Figure 2.15-Synthesis of $\mathrm{HL}_{2}$

### 2.3.1.6 Synthesis of 4-(trifluoromethyl)phenyl boronic acid

Using the same method as for the preparation of 4-t-butylphenyl boronic acid, 4(trifluoromethyl)phenyl boronic acid was obtained in high yield and high purity upon recrystallisation from hexane (Figure 2.16). The data are consistent with those reported in the literature ${ }^{90}$.


Figure 2.16 - Synthesis of 4-(trifluoromethyl)phenyl boronic acid

### 2.3.1.7 Synthesis of 2-(4-trifluoromethyl)-6-ethylpicolinate

The synthesis of 2-(4-trifluoromethyl)-6-ethylpicolinate was achieved via the same synthetic approach as that used for 2-phenyl-6-ethylpicolinate and 2-(4-t-butyl-)-6ethylpicolinate. Suzuki coupling reaction between ethyl-6-bromopicolinate and 4(trifluoromethyl)phenyl boronic acid gave the picolinate product in $80 \%$ yield (Figure 2.17). The data are consistent with those reported in the literature ${ }^{35}$.


Figure 2.17 - Synthesis of 2-(4-trifluoromethyl)-6-ethylpicolinate

### 2.3.1.8 Synthesis of 2-(4-trifluoromethyl)-6-carboxylatopyridine (HL3)

2-(4-trifluoromethyl)-6-carboxylatopyridine was obtained in high yield and with high purity using a similar ester hydrolysis-based synthetic approach to that described for the synthesis of $\mathrm{HL}_{1}$ and $\mathrm{HL}_{2}$ (Figure 2.18). The data are also consistent with those reported in the literature ${ }^{35}$.


Figure 2.18-Synthesis of $\mathrm{HL}_{3}$

### 2.3.2 Complexation of pro-ligands $\mathrm{HL}_{1}, \mathrm{HL}_{2}$ and $\mathrm{HL}_{3}$ to Palladium(II)

Acetonitrile complexes of palladium, supported by [ $C, N_{P y}, O$ ] pincer ligands, can be obtained in good yield by direct reaction of pro-ligands $\mathrm{HL}_{1}, \mathrm{HL}_{2}$ and $\mathrm{HL}_{3}$ with $\operatorname{Pd}(\mathrm{OAc})_{2}$ in acetonitrile. The complexes have been characterised by a combination of ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ NMR and IR spectroscopies, HRMS (FAB, ASAP, TOF) and elemental analysis. In addition, single crystal X-Ray structures have been obtained for some compounds.

## Synthesis of 2a

The synthesis of $\mathbf{2 a}$ from $\mathrm{HL}_{1}$ in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}$ and acetonitrile, occurs smoothly at room temperature (Figure 2.19).


Figure 2.19-Synthesis of 2a

Analysis of 2a by ${ }^{1} \mathrm{H}$ NMR spectroscopy reveals only 7 aromatic proton environments which are in a different splitting pattern compared to the parent pro-ligand HL1. This clearly indicates that one aryl CH bond has been activated upon binding to palladium. In addition, there is a 3 H singlet peak observed at 1.97 ppm ascribed to be the methyl protons of the coordinated acetonitrile ligand. Moreover, the OH peak corresponding to the free carboxylic acid of the parent pro-ligand is no longer observed as a result of deprotonation and coordination to palladium. In addition, the ESI mass spectrometry of this solvento complex reveals a molecular ion peak corresponding to the complex at $\mathrm{m} / \mathrm{z}$ $345[\mathrm{M}+\mathrm{H}]^{+}$. It was also possible to obtain single crystals of 2a suitable for analysis by X-Ray diffraction by slow evaporation of a solution of $\mathbf{2 a}$ in acetonitrile. The crystal structure confirmed a dianionic pincer ligand and an auxiliary acetonitrile ligand coordinated to a palladium(II) metal centre (Figure 2.20).


Figure 2.20-Molecular structure of $2 a$

There are three molecules in the unit cell. Whilst two molecules align parallel to each other, the third one is slightly displaced in space, with Pd $\cdots$ Pd separations being $3.646 \AA$ and $3.370 \AA$ (Figure 2.21). There is an intra-molecular hydrogen bonding interaction visible between the two molecules initiated by a water molecule present within the cell and $\mathrm{C}=\mathrm{O}$ donor unit. Table 2.1 shows the selected bond lengths and angles for one molecule. The shortest pincer to palladium bond in 2a is formed between $\mathrm{N}(1)-\operatorname{Pd}(1)$ $[1.937(7) \AA$ A and the longest formed between $\operatorname{Pd}(1)-\mathrm{O}(1)[2.137(6) \AA$. The $\mathrm{Pd}-\mathrm{O}$ bond distance of $2.137(6) \AA$ is representative of this functional group, with the average being $2.0 \AA$. The $\mathrm{N}(1)-\mathrm{Pd}(1)-\mathrm{C}(12)$ and $\mathrm{N}(1)-\mathrm{Pd}(1)-\mathrm{O}(1)$ angles of $82.0(3)^{\circ}$ and $79.5(3)^{\circ}$, respectively, are indicative of a slightly distorted square planar geometry.


Figure 2.21 - Unusual packing behaviour in the unit cell of $2 a$
Table 2.1-Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for one molecule of $2 \boldsymbol{a}$
BOND LENGTHS (A)

| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $1.937(7)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{C}(\mathbf{1 2})$ | $82.0(3)$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{P d}(\mathbf{1})-\mathbf{C}(\mathbf{1 2})$ | $1.967(9)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $79.5(3)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $2.020(8)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{C}(\mathbf{1 2})$ | $96.6(4)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $2.137(6)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $102.1(3)$ |
| $\mathbf{O}(\mathbf{1})-\mathbf{C}(\mathbf{1})$ | $1.290(10)$ | $\mathbf{O}(\mathbf{2})-\mathbf{C}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $125.9(9)$ |
| $\mathbf{O}(\mathbf{2})-\mathbf{C}(\mathbf{1})$ | $1.240(11)$ | $\mathbf{N}(\mathbf{1})-\mathbf{C}(\mathbf{2})-\mathbf{C}(\mathbf{1})$ | $112.7(8)$ |

## Synthesis of 2b

Similarly, a reaction between $\mathrm{HL}_{2}$ and $\mathrm{Pd}(\mathrm{OAc})_{2}$ in an anhydrous acetonitrile medium has been successfully employed to synthesise 2b (Figure 2.22). The reaction is complete within 2 hours at ambient temperature, affording the target acetonitrilecontaining complex in $92 \%$ yield.


Figure 2.22-Synthesis of 2b

Upon analysis by ${ }^{1} \mathrm{H}$ NMR spectroscopy, 2b displays only 6 H environments in the aromatic region of the spectrum as opposed to 7 protons for the pro-ligand and a subsequent loss of the characteristic AB splitting pattern. The ligand coordinates to palladium in a tridentate fashion through activation of one of the aromatic C-H bonds. In addition, a singlet 9H peak attributable to the tertiary butyl group has shifted slightly downfield to 1.35 ppm . Analysis of $\mathbf{2 b}$ by ${ }^{13} \mathrm{C}$ NMR spectroscopy further confirms the proposed structure by the presence of 15 unique carbon environments with a characteristic Pd-bound acetonitrile carbon environment at 0.6 ppm . 2b displays a protonated molecular ion peak at $\mathrm{m} / \mathrm{z} 401$ upon analysis by mass spectrometry. Furthermore, a strong fragmentation peak is detected by FABMS at $\mathrm{m} / \mathrm{z} 359$ corresponding to the loss of acetonitrile $[\mathrm{M}-\mathrm{MeCN}]^{+}$, whilst TOFMS also revealed a peak at $\mathrm{m} / \mathrm{z} 423$ accounting for the presence of Na adduct in the complex $[\mathrm{M}+\mathrm{Na}]^{+}$. The IR spectrum of the complex shows peaks at $1635 \mathrm{~cm}^{-1}$ and $1582 \mathrm{~cm}^{-1}$ which is in line with the pyridyl $(\mathrm{C}=\mathrm{N})$ and carboxylate $(\mathrm{C}=\mathrm{O})$ stretching frequencies.

## Synthesis of 2c

Similar to 2a and 2b, CH activation of pro-ligand $\mathrm{HL}_{3}$ was achieved by reaction with $\mathrm{Pd}(\mathrm{OAc})_{2}$ at room temperature, affording 2c in excellent yield and purity (Figure 2.23).


Figure 2.23-Synthesis of 2c

The ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 c}$ shows the loss of the AB pattern for the phenyl protons and integrates for only 6 aromatic protons. There is also no evidence for the free carboxylic acid OH environment, indicating deprotonation upon binding to palladium. The ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{2 c}$ reveals 14 unique carbon environments, 7 of which are quarternary carbon environments, consistent with the proposed structure. Upon analysis by ESI (electrospray ionisation), 2c reveals a protonated molecular peak at $\mathrm{m} / \mathrm{z} 413$ $[\mathrm{M}+\mathrm{H}]^{+}$. The high resolution mass spectrometry (TOF) and (FAB) showed peaks whose patterns are in agreement with $[\mathrm{M}+\mathrm{Na}]^{+}$and $[\mathrm{M}-\mathrm{MeCN}]^{+}$, at $m / z 435$ and 371 , respectively.

Single crystals of $\mathbf{2 c}$ suitable for analysis by X-ray diffraction were obtained by slow evaporation of a solution of 2c in acetonitrile (Figure 2.24). Selected bond lengths and bond angles are given in Table 2.2. The solid-state structure further confirmed the C-H activated product. The palladium complex adopts a square planar geometry with two 5membered palladacycles on each side.


Figure 2.24 - Molecular structure of 2 c

Table 2.2-Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for one molecule of 2 c
BOND LENGTHS (i)

| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $1.944(3)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{C}(\mathbf{1 2})$ | $82.02(16)$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{P d}(\mathbf{1})-\mathbf{C}(\mathbf{1 2})$ | $1.965(4)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $79.60(13)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $2.009(4)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{C}(\mathbf{1 2})$ | $82.02(16)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $2.132(3)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $101.32(14)$ |
| $\mathbf{C}(\mathbf{1 0})-\mathbf{C}(\mathbf{1 3})$ | $1.494(6)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $177.99(15)$ |

The X-Ray crystallographic results reveal two unique molecules in the unit cell. The palladium(II) acetonitrile core supported by the $C, N_{P y}, O$ pincer ligand is mostly planar. In analogy with 2a discussed previously, the shortest tridentate ligand to palladium bond is the pyridyl $\operatorname{Pd}(1)-\mathrm{N}(1)$ bond $(1.944(3) \AA$ ) and the longest being $\operatorname{Pd}(1)-\mathrm{O}(1)$ (2.009(4) $\AA)$. The smallest bite angle exhibited by the two five-membered palladacycles, belongs to $\mathrm{N}(1)-\mathrm{Pd}(1)-\mathrm{O}(1)$ with $79.60^{\circ}$. This is again similar to the bite angle pattern observed in 2a.

### 2.3.3 Reaction Chemistry of $\left[\left(C, N_{P y}, O\right) \mathbf{P d}(\mathrm{MeCN})\right]$ Complexes towards Pyridines

The formation of palladium(II) pyridine complexes $\left[\left(C, N_{P y}, O\right) \operatorname{Pd}(\mathrm{X})\right]$ from the acetonitrile precursors ( $\mathbf{2 a}, \mathbf{2 b}$ and $\mathbf{2 c}$ ) is a facile transformation. All reactions were performed in chloroform at room temperature overnight to afford products in good to excellent yield. All compounds have been thoroughly characterised and are air- and moisture- stable and are amenable to structural characterisation.

Analytical results acquired for all the complexes are consistent with the proposed structures. Indeed, the ${ }^{1} \mathrm{H}$ NMR spectrum of 2.1a contains 12 aromatic proton environments as opposed to the acetonitrile precursor with only 7 protons in the aromatic region. The methyl signal for the acetonitrile moiety has also not been observed (Figure 2.25). In addition, upon analysis by the high resolution mass spectrometry (TOF), a strong protonated molecular ion is displayed at $\mathrm{m} / \mathrm{z} 382.9432$ $[\mathrm{M}+\mathrm{H}]^{+}$, whereas the calculated value is $\mathrm{m} / \mathrm{z} 382.9431$.


Figure 2.25-Synthesis of 2.1a

The same reactivity is observed when $\mathbf{2 a}$ is treated with 3,5-dimethylpyridine in chloroform to form 2.2a (Figure 2.26). The facile substitution of the acetonitrile ligand with 3,5-dimethylpyridine is evidenced by the loss of the methyl singlet peak corresponding to the acetonitrile group and the presence of three more proton environments in the aromatic region and a 6 H singlet of the methyl group in its ${ }^{1} \mathrm{H}$ NMR spectrum.


$2 a$

2.2a

Figure 2.26-Synthesis of 2.2a

Further confirmation for the formation of the complex 2.2a can be observed in the ${ }^{13} \mathrm{C}$ NMR spectrum, where a new $\mathrm{CH}_{3}$ carbon environment at 18.3 ppm corresponding to the methyl group of the 3,5-dimethylpyridine unit, has emerged. The ESI spectrum displays a strong protonated molecular peak at $m / z 411[\mathrm{M}+\mathrm{H}]^{+}$. Furthermore, TOFMS shows a range of fragmentation peaks such as, $[(\mathrm{M}-\mathrm{Py})+\mathrm{H}]^{+}$and $[\mathrm{M}+\mathrm{Na}]^{+}$, at $\mathrm{m} / \mathrm{z} 303$ and 433, respectively. Interestingly, a reaction of $\mathbf{2 a}$ with 3,5 -dichloropyridine under similar conditions proved unsuccessful. The ${ }^{1} \mathrm{H}$ NMR spectrum produced messy overlapping signal sets which were not suitable for assignment. Further attempts at recrystallisation of the sample also proved unsuccessful.

The substitution reaction to form $\mathbf{2 . 2 b}$ from its acetonitrile precursor $\mathbf{2 b}$, was also performed successfully at room temperature (Figure 2.27).


2b


Figure 2.27-Synthesis of 2.2b

The compound displays three new aromatic proton environments and a 6 H singlet at 2.40 ppm in its ${ }^{1} \mathrm{H}$ NMR spectrum, in agreement with the proposed structure. Further evidence for the formation of $\mathbf{2 . 2 b}$ is provided by FAB mass spectrometry, whereupon a
strong protonated molecular peak is observed at $m / z 467.09418[\mathrm{M}+\mathrm{H}]^{+}$, with the calculated value being $m / z 467.08726$.

The same experimental procedure was applied to synthesise $\mathbf{2 . 3 b}$, substituting the NCMe ligand with 3,5-dichloropyridine (Figure 2.28).


2b


2.3b

Figure 2.28-Synthesis of 2.3b

The complex formation is evidenced by the disappearance of the methyl singlet of the bound acetonitrile and the appearance of three new proton peaks in the aromatic region of its ${ }^{1} \mathrm{H}$ NMR spectrum. The FAB mass spectrum of $\mathbf{2 . 3} \mathbf{3}$ displays a protonated molecular peak at $m / z 507[\mathrm{M}+\mathrm{H}]^{+}$and fragmentation peak corresponding to the loss of 3,5-dichloropyridine moiety at $\mathrm{m} / \mathrm{z} 360[\mathrm{M}+\mathrm{H}-3,5 \text {-dichloropyridine }]^{+}$.

With successful results obtained from the ligand exchange reactions thus far, attempts to facilitate $\mathrm{sp}^{2} \mathrm{CH}$ activation at the ancillary ligand through the coordinated carboxylate arm have been made. Phenylpyridine was selected as the appropriate substrate for this reaction. It was hypothesised that when the acetonitrile-containing $\mathrm{Pd}(\mathrm{II})$ complex 2b reacts with phenylpyridine, $\mathrm{C}\left(\mathrm{sp}^{2}\right)$ - H bond cleavage, resulting from the liberation of the carboxylate arm, will lead to the formation of the palladocyclic complex shown in Figure 2.29.


Figure 2.29 - Palladocycle expected upon reaction with $2 \boldsymbol{b}$ and phenylpyridine

However, experimental data demonstrated that C-H activation was unsuccessful, and as opposed to the expected palladocycle shown above, complex 2.4b was formed instead (Figure 2.30). The ${ }^{1} \mathrm{H}$ NMR spectrum accounts for 15 aromatic proton resonances by integration as opposed to 6 aromatic protons for $\mathbf{2 b}$. In addition, analysis of $\mathbf{2 . 4 b}$ by ${ }^{13} \mathrm{C}$ NMR spectroscopy reveals the expected 24 distinct carbon resonances.


2b

$\mathrm{CHCl}_{3}, \mathrm{RT}, 18 \mathrm{~h}$

2.4b

Figure 2.30-Synthesis of 2.4b

Further confirmation of the molecular structure of the complex was provided by an Xray diffraction analysis (Figure 2.31). The crystals suitable for the study were grown by slow diffusion of petroleum ether (40-60) into a chloroform solution of $\mathbf{2 . 4 b}$. Selected bond lengths and angles for 2.4b are given in Table 2.3.


Figure 2.31-Molecular structure of 2.4b. Hydrogen atoms have been omitted for clarity

Table 2.3-Selected bond lengths ( $(\AA)$ and angles $\left(^{\circ}\right)$ for 2.4b

## BOND LENGTHS (Å)

| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $1.947(4)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{C}(\mathbf{1 2})$ | $81.96(19)$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{P d}(\mathbf{1})-\mathbf{C}(\mathbf{1 2})$ | $1.981(5)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $79.30(16)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $2.054(4)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{C}(\mathbf{1 2})$ | $97.03(18)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $2.155(4)$ | $\mathbf{N}(\mathbf{2})-\mathbf{C}(\mathbf{1 7})-\mathbf{C}(\mathbf{1 9})$ | $120.7(4)$ |
| $\mathbf{O}(\mathbf{1})-\mathbf{C}(\mathbf{1})$ | $1.288(6)$ | $\mathbf{C}(\mathbf{1 7})-\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})$ | $123.0(3)$ |
| $\mathbf{O}(\mathbf{2})-\mathbf{C}(\mathbf{1})$ | $1.228(6)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $177.31(16)$ |

The X-ray structural analysis of 2.4b exhibits the typical slightly distorted square planar configuration around the metal centre. All the angles around the palladium are close to $90^{\circ}$. The central $\mathrm{Pd}(\mathrm{II})$ ion is coordinated by a tridentate $\left[C, N_{P y}, O\right]$ pincer ligand and a phenylpyridine ligand. The phenylpyridine unit is not planar and the phenyl ring is not parallel to its respective carrier pyridine ring, showing a dihedral angle of $53.6(7)^{\circ}$ [ $\mathrm{N}(2)-\mathrm{C}(17)-\mathrm{C}(19)-\mathrm{C}(20)]$. The newly introduced pyridine unit is tilted with respect to the pyridyl plane of the pincer ligand, presumably as a result of steric hindrance. Again,
the shortest tridentate ligand to palladium bond is formed between the pyridyl nitrogen donor $\operatorname{Pd}(1)-\mathrm{N}(1)$ [1.947(4) $\AA$ ], and the longest one is between the carboxylic acid oxygen donor $\mathrm{Pd}(1)-\mathrm{O}(1)[2.155(4) \AA$.

Application of the same conditions proved successful when applied to $2 \mathbf{c}$ in order to form pyridine-containing complexes 2.1c and 2.2c (Figure 2.32). The ${ }^{1} \mathrm{H}$ NMR spectrum of 2.1 c displayed 11 aromatic proton environments which are in agreement with the proposed structure. The structure was also confirmed by the high resolution TOFMS analysis, whereupon a strong protonated molecular peak $[\mathrm{M}+\mathrm{H}]^{+}$at $\mathrm{m} / \mathrm{z} 451$ is observed.


Figure 2.32-Synthesis of 2.1c and 2.2c

Upon close analysis of the ${ }^{1} \mathrm{H}$ NMR data of $\mathbf{2 . 2} \mathbf{c}$, three new proton environments are observed in the aromatic region of the spectrum. In addition, a newly emerged singlet at 2.33 ppm accounting for 6 protons and corresponding to the methyl groups of 3,5dimethylpyridine is observed. It was possible to grow crystals suitable for X-ray diffraction analysis (Figure 2.33). The molecular structure is in agreement with other characterisation data acquired. Selected bond lengths and bond angles are given in Table 2.4.


Figure 2.33-Molecular structure of 2.2c

Table 2.4-Selected bond lengths ( $\AA$ ) and angles $\left(^{\circ}\right.$ ) for 2.2c

## BOND LENGTHS (Å)

BOND ANGLES $\left({ }^{\circ}{ }^{\circ}\right)$

| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $1.950(3)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{C}(\mathbf{1 2})$ | $82.20(12)$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{P d}(\mathbf{1})-\mathbf{C}(\mathbf{1 2})$ | $1.977(3)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $79.44(10)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $2.041(3)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{C}(\mathbf{1 2})$ | $98.17(12)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $2.151(2)$ | $\mathbf{C}(7)-\mathbf{C}(\mathbf{1 2})-\mathbf{P d}(\mathbf{1})$ | $112.3(2)$ |
| $\mathbf{O}(\mathbf{1})-\mathbf{C}(\mathbf{1})$ | $1.286(4)$ | $\mathbf{C}(\mathbf{1 7})-\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})$ | $119.9(2)$ |
| $\mathbf{O}(\mathbf{2})-\mathbf{C}(\mathbf{1})$ | $1.220(4)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $179.8(11)$ |

The X-ray structural analysis of 2.2c exhibits the typical square planar configuration around the palladium. The geometry is slightly distorted with the angles formed around the metal centre being close to $90^{\circ}$. The bond lengths and angles for the complex is similar to its acetonitrile precursor complex 2c. The introduced 3,5-dimethylpyridine unit is slightly tilted with respect to the pyridyl plane, possibly a result of steric bulk provided by the two methyl groups. The central pyridyl nitrogen donor forms the
shortest tridentate ligand to metal bond $[\operatorname{Pd}(1)-\mathrm{N}(1) 1.950(3) \AA]$. The complex forms a longer bond with 3,5-dimethylpyridine than with the acetonitrile ligand in complex $\mathbf{2 c}$.

### 2.3.4 Reaction Chemistry of $\left[\left(C, N_{P y}, O\right) \mathbf{P d}(\mathrm{MeCN})\right]$ Complexes towards Triphenylphosphine (PPh3)

In light of the results obtained for the reactions with pyridines, the reactivity of $\left[\left(C, N_{P y}, O\right) \operatorname{Pd}(\mathrm{MeCN})\right]$ complexes towards the triphenylphosphine ligand was probed. It is a neutral and strong binding ligand that typically binds to transition metal centres through the lone pair of its two-electron donor. Phosphine ligands are generally considered excellent ligands for transition metals as they are easily synthesised. The steric factors associated with phosphines are easily controlled and hence, it is possible to tune the reactivity of metal complexes. Similar to carbonyls, there are two important factors related to the bonding in phosphine ligands. Sigma donation from the phosphine lone pair into an empty metal orbital is considered to be the first factor. The second factor is associated with the backdonation from a filled orbital on the metal to an empty phosphine orbital (Figure 2.34). Electronegative groups on the P atom typically decrease the donating ability of the $\mathrm{PR}_{3}$. This also lowers the energy of the pi-acceptor on P atom, thus increasing the back-bonding ability. For these reasons, $\mathrm{PR}_{3}$ ligands can possess a variety of pi-acceptor and sigma donor properties, and the electronic effects of a metal centre can be tuned by using different phosphines.


Figure 2.34-Bonding in phosphine ligands

Complexes 2.5a, 2.5b and 2.5c have been prepared from the corresponding palladium(II) acetonitrile precursors 2a, 2b and 2c, respectively, by treatment with triphenylphosphine $\left(\mathrm{PPh}_{3}\right)$ (Figure 2.35). The synthesis occurs smoothly at room temperature and affords all three complexes in good yield.


2a, $\mathrm{R}=\mathrm{H}$
2.5a, $\mathrm{R}=\mathrm{H}$
$\mathbf{2 b}, \mathrm{R}={ }^{\mathrm{t}} \mathrm{Bu}$
$2 \mathbf{c}, \mathrm{R}=\mathrm{CF}_{3}$
$\mathbf{2 . 5 b}, \mathrm{R}={ }^{\mathrm{t}} \mathrm{Bu}$
$\mathbf{2 . 5} \mathbf{c}, \mathrm{R}=\mathrm{CF}_{3}$

Figure 2.35-Synthesis of 2.5a, 2.5b and 2.5c

Analysis of 2.5a by ${ }^{1} \mathrm{H}$ NMR reveals a subtle shift of all the proton environments from its precursor and the presence of additional 15 aromatic protons corresponding to the triphenylphosphine ligand. The ${ }^{31} \mathrm{P}$ NMR exhibited a singlet at 35.1 ppm suggesting one coordinated triphenylphosphine. Furthermore, upon analysis by IR spectroscopy, the complex showed strong bands near $642-1432 \mathrm{~cm}^{-1}$ indicating the coordination of $\mathrm{PPh}_{3}$ ligands to palladium. In addition, high resolution TOFMS displays a protonated molecular peak $[\mathrm{M}+\mathrm{H}]^{+}$at $\mathrm{m} / \mathrm{z} 566.0513$, with the calculated value being $\mathrm{m} / \mathrm{z} 566.0501$. In the ${ }^{31} \mathrm{P}$ NMR spectra the phosphorus resonance in the complexes is significantly shifted downfield compared to free triphenylphosphine. A downfield shift in ${ }^{31} \mathrm{P}$ resonance of the complexes is thought to be related to the donation of electron pair on P atom to the metal that reduces the shielding at phosphorus nucleus.

It was possible to obtain crystals of $\mathbf{2 . 5 a}$ suitable for X-ray diffraction studies by slow diffusion of petroleum ether (40-60) into a chloroform solution of 2.5a. The structure of 2.5a is shown in Figure 2.36. And the selected bond distances and bond angles are listed in Table 2.5.


Figure 2.36-Molecular structure of 2.5a

Table 2.5-Selected bond lengths ( $\AA$ ) and angles $\left({ }^{\circ}\right)$ for one molecule of 2.5a
BOND LENGTHS (Å)
BOND ANGLES $\left({ }^{\circ}\right)$

| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $2.001(3)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{C}(\mathbf{1 2})$ | $81.10(17)$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{P d}(\mathbf{1})-\mathbf{C}(\mathbf{1 2})$ | $2.020(4)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $77.62(13)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $2.156(3)$ | $\mathbf{C}(\mathbf{1 2})-\mathbf{P d}(\mathbf{1})-\mathbf{P}(\mathbf{1})$ | $97.83(13)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{P}(\mathbf{1})$ | $2.268(12)$ | $\mathbf{O}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{P}(\mathbf{1})$ | $103.45(8)$ |

Compound 2.3a is monoclinic and crystallises in the space group $\mathrm{C} 2 / \mathrm{c}$ with $\mathrm{Z}=8$. The palladium ion is coordinated by the tridentate pincer ligand [ $C, N_{P y}, O$ ], producing two five-membered chelate rings with the $\mathrm{C}, \mathrm{N}$ and O donor atoms. The fourth coordination site of palladium is occupied by the phosphorus atom of $\mathrm{PPh}_{3}$ ligand. The angles between the adjacent donor atoms in the coordination sphere of Pd are relatively close to $90^{\circ}$. The structure adopts a distorted square planar geometry, with the bond angles around the metal centre being in the range of $81.10(17)-103.45(8)^{\circ}$. Of the palladium bond lengths, $\operatorname{Pd}(1)-\mathrm{P}(1)$ is the longest in the structure [2.268(12) $\AA$ ], whilst the
distance of $\operatorname{Pd}(1)-\mathrm{N}(1)$ is the shortest [2.001(3) $\AA$ ]. Interestingly, the $\operatorname{Pd}(1)-\mathrm{N}(1)$ bond length of 2.5a is longer than that in the acetonitrile precursor complex $\mathbf{2 a}[1.937(7) \AA$.

Similarly, the synthesis of tert-butyl and trifluoromethyl substituent containing 2.5b and 2.5c generates palladium(II) complexes with a bound triphenylphosphine ligand. Analysis of the ${ }^{1} \mathrm{H}$ NMR spectra of the two compounds also displays the presence of additional 15 aromatic protons. Further confirmation of the proposed structure is obtained through ${ }^{31} \mathrm{P}$ NMR spectra, whereupon a singlet peak corresponding to the bound $\mathrm{PPh}_{3}$ unit is observed in both complexes. In addition, both $\mathbf{2 . 5 b}$ and $\mathbf{2 . 5 c}$ display strong protonated molecular peaks in their high-resolution mass spectra.

### 2.3.5 Complexation of pro-ligands $\mathrm{HL}_{1}, \mathrm{HL}_{2}$ and $\mathrm{HL}_{3}$ to Ruthenium(II)

Complexes 2.6a, 2.6b and 2.6c have been synthesised in good yields by reacting tris(triphenylphosphine)ruthenium(II) dichloride $\left[\mathrm{Ru}\left(\mathrm{PPh}_{3}\right)_{3} \mathrm{Cl}_{2}\right]$ with the corresponding pro-ligands $\mathrm{HL}_{1}, \mathrm{HL}_{2}$ and $\mathrm{HL}_{3}$ in methanol at elevated temperature (Figure 2.37).


Figure 2.37-Synthesis of Ru(III) complexes 2.6a, 2.6b and 2.6c

The effective magnetic moments ( $\mu_{\text {eff }}$ ) of 2.6a, 2.6b and 2.6c have been measured using a combination of Evans NMR and Gouy magnetic susceptibility balance (powder phase, $298 \mathrm{~K})$. The $\mu_{\text {eff }}$ values lie in the range $1.89-1.93 \mathrm{BM}$ which is consistent with a single unpaired electron paramagnetic character and a low spin state configuration of ruthenium in 2.6a, 2.6b and 2.6c. This confirms that ruthenium is in +3 oxidation state in all synthesised complexes. It is assumed that oxygen in the air plays a role of an oxidant during the reaction with the divalent $\left[\mathrm{Ru}\left(\mathrm{PPh}_{3}\right)_{3} \mathrm{Cl}_{2}\right]$ starting metal precursor. The complexes are highly soluble in chloroform and dichloromethane and produce
orange to red solutions. The infrared spectra display strong bands observed at $\sim 742$ and $\sim 693 \mathrm{~cm}^{-1}$ indicating the metal bound triphenylphosphine in all of the complexes. High resolution mass spectra of all three complexes 2.6a, 2.6b and 2.6c display a molecular peak with a sodium ion adduct $[\mathrm{M}+\mathrm{Na}]^{+}$present. Interestingly, complex $\mathbf{2 . 6 b}$ can be crystallised out of the reaction mixture where methanol is a solvent but it was also possible to grow crystals of $\mathbf{2 . 6} \mathbf{b}$ through a slow diffusion of petroleum ether into a solution of $\mathbf{2 . 6 b}$ in chloroform. This crystallisation behaviour could be a result of tertbutyl group adding extra solubility and hence, improved crystallinity in comparison with other substituents on 2.6a and $\mathbf{2 . 6 c}$.

The crystals suitable for X-ray diffraction studies have been analysed (Figure 2.38) and the selected bond distances and bond angles are listed in Table 2.6.


Figure 2.38-Molecular structure of 2.6b. Hydrogen atoms have been omitted for clarity

Table 2.6-Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for one molecule of 2.6b

| BOND LENGTHS ( $\AA$ ) |  |  | BOND ANGLES $\left({ }^{\circ}\right.$ ) |
| :---: | :---: | :---: | :---: |
| $\mathbf{R u}(1)-\mathbf{N}(1)$ | 2.039(6) | $\mathrm{N}(1)-\mathrm{Ru}(1)-\mathbf{C}(8)$ | 77.9(3) |
| $\mathbf{R u}(1)-\mathbf{C}(8)$ | 2.054(7) | $\mathrm{N}(1)-\mathrm{Ru}(1)-\mathrm{O}(1)$ | 75.4(2) |
| $\mathrm{Ru}(1)-\mathrm{O}(1)$ | 2.163(5) | $\mathrm{C}(8)-\mathrm{Ru}(1)-\mathrm{Cl}(1)$ | 104.7(2) |
| $\mathbf{R u}(1)-\mathbf{C l}(1)$ | 2.338(19) | $\mathrm{O}(1)-\mathrm{Ru}(1)-\mathrm{Cl}(1)$ | 102.03(13) |
| $\mathbf{R u}(1)-\mathbf{P}(\mathbf{1})$ | 2.388(2) | $\mathrm{N}(1)-\mathrm{Ru}(1)-\mathbf{P}(\mathbf{1})$ | 91.29(17) |
| $\mathbf{R u}(1)-\mathbf{P}(2)$ | 2.393(2) | $\mathbf{N}(1)-\mathrm{Ru}(1)-\mathbf{P}(2)$ | 92.14(17) |

Upon close analysis of the crystal structure of $\mathbf{2 . 6 b}$, the ruthenium atom in the complex is in a slightly distorted octahedral coordination sphere. The crystal system of $\mathbf{2 . 6 \mathbf { b }}$ is monoclinic and crystallises in space group $\mathrm{P} 2(1) / \mathrm{n}$ where $\mathrm{Z}=4$. There is an intermolecular hydrogen bond between the molecule of methanol present in the unit cell and the $\mathrm{C}=\mathrm{O}$ group. The phosphorus atoms of the two triphenylphosphine ligands occupy the two axial positions and hence are trans to each other. The chloride ligand and the tridentate pincer ligand form a square plane around the ruthenium centre. The chelate bite angles observed in $\mathrm{N}(1)-\mathrm{Ru}(1)-\mathrm{C}(8)$ and $\mathrm{N}(1)-\mathrm{Ru}(1)-\mathrm{O}(1)$ are $77.9(3)^{\circ}$ and $75.4(2)^{\circ}$, respectively, and are similar to those observed in ruthenium(III) metal complexes with -CNO donor pincer ligands ${ }^{91}$. The longest bonds are formed between the two phosphorus atoms and ruthenium $[\mathrm{Ru}(1)-\mathrm{P}(1) 2.388(2) \AA$ and $\mathrm{Ru}(1)-\mathrm{P}(2)$ $2.393(2) \AA$. The $\operatorname{Ru}(1)-\mathrm{C}(8)$ bond length is $2.054(7) \AA$ suggesting the presence of a metal-carbon $\sigma$-bond in $\mathbf{2 . 6 b}$.

It was also possible to grow crystals of $\mathbf{2 . 6 c}$ and to ascertain the similarity of the same coordination mode of ruthenium as that observed in 2.6b (Figure 2.39). Selected bond lengths and angles are listed in Table 2.7.


Figure 2.39-Crystal structure of 2.6c. Hydrogen atoms have been omitted for clarity

Table 2.7-Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 2.6 c BOND LENGTHS (Å)

BOND ANGLES $\left({ }^{\circ}{ }^{\circ}\right)$

| $\mathbf{R u}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $2.026(3)$ | $\mathbf{N}(\mathbf{1})-\mathbf{R u}(\mathbf{1})-\mathbf{C}(\mathbf{1 2})$ | $77.58(15)$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{R u}(\mathbf{1})-\mathbf{C}(\mathbf{1 2})$ | $2.031(4)$ | $\mathbf{N}(\mathbf{1})-\mathbf{R u}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $75.96(12)$ |
| $\mathbf{R u}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $2.139(3)$ | $\mathbf{C}(\mathbf{1 2})-\mathbf{R u}(\mathbf{1})-\mathbf{C l}(\mathbf{1})$ | $106.47(12)$ |
| $\mathbf{R u}(\mathbf{1})-\mathbf{C l}(\mathbf{1})$ | $2.3408(11)$ | $\mathbf{O}(\mathbf{1})-\mathbf{R u}(\mathbf{1})-\mathbf{C l}(\mathbf{1})$ | $100.03(7)$ |
| $\mathbf{R u}(\mathbf{1})-\mathbf{P}(\mathbf{1})$ | $2.3920(12)$ | $\mathbf{N}(\mathbf{1})-\mathbf{R u}(\mathbf{1})-\mathbf{P}(\mathbf{1})$ | $91.29(11)$ |
| $\mathbf{R u}(\mathbf{1})-\mathbf{P}(\mathbf{2})$ | $2.4129(12)$ | $\mathbf{N}(\mathbf{1})-\mathbf{R u}(\mathbf{1})-\mathbf{P}(\mathbf{2})$ | $89.84(9)$ |

The crystal system of $\mathbf{2 . 6} \mathbf{c}$ is also monoclinic, crystallising in space group $\mathrm{P}(2) 1 / \mathrm{c}$ with $\mathrm{Z}=4$. The ruthenium(III) centre is positioned in octahedral geometry and is supported by the $C, N_{P y}, O$ pincer ligand. In analogy to $\mathbf{2 . 6 b}$, the two $\mathrm{PPh}_{3}$ molecules are trans to each other with the chloride ligand forming a plane with the $C, N_{P y}, O$ core. The chelate bite angles observed in $\mathrm{N}(1)-\mathrm{Ru}(1)-\mathrm{C}(12)$ and $\mathrm{N}(1)-\mathrm{Ru}(1)-\mathrm{O}(1)$ are $77.58(15)^{\circ}$ and $75.96(12)^{\circ}$, respectively.

Another example to show the reactivity of pincer ligands with [CNO] donors towards ruthenium metal was performed through a facile reaction between $\mathrm{HL}_{2}$ and $\mathrm{Ru}(p-$ cymene) $\mathrm{Cl}_{2}$ precursor. The reaction was carried out in methanol at elevated temperatures overnight to form 2.7b (Figure 2.40).


Figure 2.40-Synthesis of 2.7b

Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of 2.7b solution in methanol (Figure 2.41). Selected bond lengths and angles are presented in Table 2.8.


Figure 2.41-Molecular structure of 2.7b. Hydrogen atoms have been omitted for clarity

Table 2.8 -Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $2.7 \boldsymbol{b}$

|  | BOND LENGTHS |  | BOND ANGLES $\left({ }^{\mathbf{o}}\right)$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{( \AA )}$ |  |  |  |
| $\mathbf{R u}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $2.145(8)$ | $\mathbf{N}(\mathbf{1})-\mathbf{R u}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $77.5(3)$ |
| $\mathbf{R u}(\mathbf{1})-\mathbf{C l}(\mathbf{1})$ | $2.394(3)$ | $\mathbf{N}(\mathbf{1})-\mathbf{R u}(\mathbf{1})-\mathbf{C l}(\mathbf{1})$ | $86.6(2)$ |
| $\mathbf{R u}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $2.077(6)$ | $\mathbf{O}(\mathbf{1})-\mathbf{R u}(\mathbf{1})-\mathbf{C l}(\mathbf{1})$ | $84.58(19)$ |
| $\mathbf{R u}(\mathbf{1})-\mathbf{C e n t r o i d}$ | $2.185(9)$ | $\mathbf{C e n t r o i d - R u ( 1 ) - \mathbf { C l } ( \mathbf { 1 } )}$ | $121.9(3)$ |
|  |  | Centroid-Ru(1)-N(1) | $126.7(3)$ |
|  |  | Centroid-Ru(1)-O(1) | $122.5(3)$ |

The molecular structure of $\mathbf{2 . 7 b}$ crystallises in a trigonal system. The ruthenium(II) centre of $\mathbf{2 . 7} \mathbf{b}$ displays a half-sandwich geometry (piano-stool) consisting of one $\eta^{6}$ bonded $p$-cymene ligand, one chloride and a $N, O$-bidentate ligand. X-ray analysis confirmed that the pincer ligand had not undergone a CH activation of the aryl carbon as opposed to the reaction performed with $\mathrm{Ru}\left(\mathrm{PPh}_{3}\right)_{3} \mathrm{Cl}_{2}$. A bidentate coordination to ruthenium through pyridine nitrogen and O atom resulted in the formation of just one five-membered ring. Upon detailed analysis of the structure, the distance between the ruthenium and the $p$-cymene ring centroid is $2.185 \AA$ and the $\mathrm{Ru}(1)-\mathrm{Cl}(1)$ distance is 3.394(3) A. These values are similar to those reported for other related complexes in the literature ${ }^{91}$. The bite angle for $\mathrm{N}(1)-\mathrm{Ru}(1)-\mathrm{O}(1)$ is $77.5(3)^{\circ}$, whereas the angles for $\mathrm{N}(1)$ -$\mathrm{Ru}(1)-\mathrm{Cl}(1)$ and $\mathrm{O}(1)-\mathrm{Ru}(1)-\mathrm{Cl}(1)$ are $86.6(2)^{\circ}$ and $84.58(19)^{\circ}$, respectively. The angles for ring centroid- $\mathrm{Ru}(1)-\mathrm{N}(1)$, centroid $-\mathrm{Ru}(1)-\mathrm{Cl}(1)$ and centroid $-\mathrm{Ru}(1)-\mathrm{O}(1)$ are $126.7(3)^{\circ}, 121.9(3)^{\circ}$ and $122.5(3)^{\circ}$, respectively. There is inter-molecular hydrogen bonding between a molecule of methanol present in the unit cell and a $\mathrm{C}=\mathrm{O}$ unit.

### 2.4 Conclusions

A range of novel palladium(II) and ruthenium(III) complexes supported by arylcontaining $C, N_{P y}, O$ pincer ligands have been prepared. All compounds have been thoroughly characterised by proton/carbon NMR, IR, ESMS/HRMS and, in some cases, by X-Ray diffraction analysis. The synthesised complexes of the formula $\left[\left(C, N_{P y}, O\right) \operatorname{Pd}(\mathrm{MeCN})\right]$ and $\left[\left(C, N_{P y}, O\right) \mathrm{Ru}(\mathrm{Cl})\left(\mathrm{PPh}_{3}\right)_{2}\right]$, are supported by a dianionic tridentate ligand framework, where the aryl-C is consistently activated upon coordination of pro-ligands to $\mathrm{Pd}(\mathrm{OAc})_{2}$ or $\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}$ metal precursors. The
formation of new palladium(II) pyridine and phosphine- containing complexes $\left[\left(C, N_{P y}, O\right) \operatorname{Pd}(\mathrm{X})\right]$ from the acetonitrile precursors (2a, 2b and 2c) through exchange of the labile MeCN moiety have proved to be a facile transformation under mild conditions. The results obtained in this work highlight the stability of this $C, N_{P y}, O$ ligand framework in the given palladium and ruthenium pincer complexes, therefore demonstrating them as potentially efficient candidates for catalytic transformations.

## 3. Design, synthesis and reactivity of palladium(II) and ruthenium(III) complexes supported by novel phenolsubstituted $\left[O, N_{P y}, O\right]$ pincer ligands

### 3.1 Introduction

As discussed in the previous chapters, pincer ligands bearing three coordination sites have proven to be supreme tools for producing metal complexes that have found a great number of applications in modern inorganic chemistry and catalysis. ${ }^{92}$ In spite of the extensive number of pyridine-based pincer ligands synthesised and reported in the literature, pincer ligands with oxygen donor fragments have been much less developed. In this context, Chapter 2 has covered some examples of $C, N_{P y}, O$ donor-based ligands and their use as transition metal catalysts. Another rare candidate amongst the vast and interesting array of pyridine-based pincers is the $O, N_{P y}, O$ pincer framework. Oxygen is considered a hard donor atom and based on the HSAB concept, where hard-hard/softsoft interactions are favoured, palladium-oxygen bonds are expected to be less stable. Hence, complexes incorporating pincer ligands with O as an exterior donor atom and pyridine nitrogen as a central donor are relatively scarce in the literature. Nevertheless, the exterior oxygen donor on the pincer complex can provide an attractive potential for tuning both electronic and steric properties; for example, by employing various functional groups on the carbon adjacent to the oxygen.

Amongst the different oxygen-containing groups, the hydroxy group is thought to be an important donor in a ligand framework due to its attractive properties. When the OH is involved in a non-covalent interaction, such as hydrogen bonding, it can stabilise structures and dictate orientation due to a directionality of hydrogen bonding, improve water solubility. In addition, the hydroxy group in its deprotonated form is a strong donor to a metal centre.

The capacity of the ONO class of ligands to support high oxidation state metal complexes with vacant coordination sites and their use in a range of catalytic transformations have been reported. ${ }^{93,94,95}$ The importance of pincer ligands containing ONO donor atoms and their corresponding ruthenium, iridium, molybdenum, tantalum, rhenium, iron, titanium, hafnium and zirconium complexes as catalysts in various transformations have been notably highlighted in the literature. ${ }^{96,97,98,99}$ Complexes
shown in Figure 3.1 are all active catalysts in co-polymerisations of ethylene/1-butene in the presence of $\mathrm{MAO}\left[\mathrm{Ph}_{3} \mathrm{C}\right]\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{4}\right]$ as a co-catalyst. ${ }^{98}$



$$
\mathrm{M}=\mathrm{Zr}, \mathrm{Hf}
$$

Figure 3.1-Titanium, zirconium and hafnium ONO pincer complexes

The ability of the rigid and stable ligand framework with strongly electron donating hard oxygen atoms to facilitate access to higher oxidation states of the metal, can sequentially promote the oxidative addition of the $\mathrm{C}-\mathrm{H}$ bond under mild conditions. Recently, Oro et al. reported the synthesis of $\operatorname{Ir(III)}$ complexes supported by a pyridinedicarboxylate pincer ligand and their ability to efficiently catalyse the borylation of arenes with C-H bond activation under thermal conditions (Figure 3.2). ${ }^{100}$




Figure 3.2-Ir(III) pincer complexes

2,6-pyridinedicarboxylate ligand was selected for these systems due to its dianionic nature with hard, electronegative coordination atoms and tridentate structure with available coordination sites.

It is important to note that amongst various reported iridium and rhodium complexes supported by pyridine-2,6-dicarboxylate ligands, not all complexes demonstrate catalytic activity. ${ }^{101}$

Nallasamy et al. developed new palladium(II) complexes bearing ONO hydrazone pincer type ligands which showed excellent catalytic activity towards the SuzukiMiyaura cross coupling between 2-chloroquinoline derivatives and aryl boronic acids (Figure 3.3). ${ }^{102}$ Mild conditions and low catalyst loadings offer an efficient route to biologically important 2-arylquinolines in excellent yields.


Figure 3.3-Synthetic route to ONO hydrazine-containing Pd(II) complexes

Espinet et al. reported $\mathrm{Pd}(\mathrm{II})$ complexes supported by pyridine-2,6-dicarboxylato pincer ligands and explored their coordination behaviour towards palladium metal and thermal stability properties. ${ }^{103}$ The complexes displayed high thermal stability and a rigid tridentate framework formation upon binding to palladium. Comparison of the stability of the pincer ligand was made with pyridine-2,6-bis(thiocarboxylato) SNS framework (Figure 3.4).



$\mathrm{R}=\mathrm{O}, \mathrm{S}$

Figure 3.4-Pd(II) isocyanide complexes supported by pyridine-2,6-dicarboxylato and pyridine-2,6-bis(thiocarboxylato)

It was suggested that the difference in stability between the two pincer ligands arises when the isocyanide auxiliary ligand is coordinated to Pd. The palladium core has a harder nature in ONO complexes due to $\pi$-back donation stabilising the Pd-isocyanide bond. There is also a high trans effect of the isocyanide ligand which elongates the PdN bond. This further destabilises the strained ONO complexes with short C-O distances. On the contrary, the elongation is much less pronounced with the less strained SNS
complexes which have longer Pd-S bond distances. Thus, the substitution of oxygen for the less electronegative sulfur atom leads to the reduction of the intramolecular interactions and lower melting points.

### 3.2 Aims and Objectives

As activation of phenylpyridine in the previous chapter failed to proceed as a result of the carboxylate arm not coming off and hence, failing to activate the C-H bond, it was thought that change of the ligand could solve this problem. It was assumed that the reactivity could be influenced by changing the ligand trans to the carboxylate from carbon (Chapter 2) to oxygen. Therefore, in this chapter, novel pincer compounds, 2-(3-R-phenol)-6-ethylpicolinate $\left[R=\mathrm{H}\left(\mathrm{HL}_{4}\right),{ }^{t} \mathrm{Bu}\left(\mathrm{HL}_{5}\right), \mathrm{Cl}\left(\mathrm{HL}_{7}\right)\right]$ are targeted (Figure 3.5).


$$
\begin{aligned}
& \mathrm{HL}_{\mathbf{4}}, \mathrm{R}=\mathrm{H} \\
& \mathrm{HL}_{\mathbf{5}}, \mathrm{R}={ }^{t} \mathrm{Bu} \\
& \mathrm{HL}_{\mathbf{6}}, \mathrm{R}=\mathrm{Cl}
\end{aligned}
$$

Figure $3.5-O, N_{P y}, O$ donor-based target pro-ligands

Moreover, the scope to systematically vary the $R$ group will offer a convenient way to modify the steric and electronic properties of the ligand framework and influence the solubility characteristics of the corresponding complexes. The reactivity of phenolcontaining $O, N_{P y}, O$ pincer ligands towards palladium(II) and ruthenium(II) salts will be explored. In addition, subsequent exchange of the coordinating acetonitrile ligand in the resulting palladium(II) pincer complexes for pyridines and triphenylphosphine will be probed. The influence of the oxygen donor from the phenol group on the reaction chemistry of the synthesised coordination complexes will be examined. All compounds have been thoroughly characterised by a combination of ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectroscopies, mass spectrometry and IR spectroscopy. In addition, single crystal XRay molecular structures have been obtained for some of the complexes.

### 3.3 Results and Discussion

### 3.3.1 Synthesis of target pro-ligands

Novel tridentate ligands of the type 2-(3-R-phenol)-6-ethylpicolinate $\left[R=\mathrm{H}\left(\mathrm{HL}_{4}\right),{ }^{\text {t }} \mathrm{Bu}\right.$ $\left.\left(\mathrm{H}_{5}\right), \mathrm{Cl}\left(\mathrm{H}_{7}\right)\right]$ have been prepared following a stepwise synthesis. The general synthesis of the ligands is illustrated in Figure 3.6.


Figure 3.6-Synthetic route to ${H L_{3}}_{3}, \mathrm{HL}_{4}$ and $H \boldsymbol{L}_{5}$. Steps include: (i): nBuli, triisopropyl borate, $-90^{\circ} \mathrm{C}, 2 \mathrm{M} \mathrm{HCl}$; (ii): $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}, \mathrm{THF}, 1 \mathrm{M} \mathrm{Na}_{2} \mathrm{CO}_{3}$; (iii): $\mathrm{EtOH} / \mathrm{H}_{2} \mathrm{O}, \mathrm{NaOH}$;

The first step involved the synthesis of functionalised boronic acids with $n$-butyllithium ( $n$ - BuLi ) and triisopropyl borate. The next step involved the incorporation of a nitrogen donor via a Suzuki coupling with a bromo-substituted pyridine using palladium (0) tetrakis(triphenylphosphine) $\left[\mathrm{Pd}_{( }\left(\mathrm{PPh}_{3}\right)_{4}\right]$ as a catalyst. Subsequent hydrolysis of the esters using base yielded the tridentate carboxylic acid containing ligands HLn. All three ligands have been accessed and the novel compounds HL4, HL5 and HL6 have been fully characterised by a combination of ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectroscopy, Infra Red (IR) spectroscopy and high resolution mass spectrometry.

### 3.3.1.1 Synthesis of boronic acid derivatives

2-hydroxyphenylboronic acid $[\mathrm{R}=\mathrm{H}]$ was readily available and was used without further purification. The boronic acid derivatives (1-OH-2-(B(OH) 2 ) $\left.-4-R \mathrm{C}_{6} \mathrm{H}_{3}\right)\left[R={ }^{\mathrm{t}} \mathrm{Bu}\right.$, $\mathrm{Cl}]$ were synthesised using $n$-butyllithium under an atmosphere of nitrogen (Figure 3.7). All three compounds were obtained as white solids in good yield and used without
further purification. Spectroscopic data for the products are consistent with those reported in the literature ${ }^{90}$.


Figure 3.7-Synthesis of boronic acids

### 3.3.1.2 Synthesis of ester derivatives

Synthesis of ester-containing compounds occurs by employment of a Suzuki coupling reaction between the boronic acid derivatives and commercially available ethyl-6bromopicolinate. Column chromatography has been used to remove catalyst residues. All three compounds have been fully characterised by several analytical methods.

### 3.3.1.3 Synthesis of 2-phenol-6-ethylpicolinate

The title compound was obtained in high yield and purity (Figure 3.8).


Figure 3.8 - Synthesis of 2-phenol-6-ethylpicolinate

The characterisation data for 2-phenol-6-ethylpicolinate are consistent with the proposed structure. Analysis of the ${ }^{1} \mathrm{H}$ NMR spectrum reveals the presence of a triplet and a quartet at 1.40 and 4.41 ppm , respectively, corresponding to the ester group protons. Similarly, the ${ }^{13} \mathrm{C}$ NMR spectrum also showed two signals at 14.2 and 62.1 ppm corresponding to the ester carbon resonances. In addition, the compound exhibits a protonated molecular ion peak by mass spectrometry at $m / z 244[\mathrm{M}+\mathrm{H}]^{+}$. High resolution mass spectrometry revealed a peak at $m / z$ 244.0986; the calculated molecular mass for $\mathrm{C}_{14} \mathrm{H}_{14} \mathrm{NO}_{3}[\mathrm{M}+\mathrm{H}]^{+}$is 244.0974 .

### 3.3.1.4 Synthesis of 2-(3'-t-butyl-phenol)-6-ethylpicolinate

Synthesis of 2-(3'-t-butyl-phenol)-6-ethylpicolinate was based on the same synthetic procedure as that used for 2-phenol-6-ethylpicolinate. Analysis by ${ }^{1} \mathrm{H}$ NMR spectroscopy for the product reveals a quartet at 4.47 ppm and a triplet at 1.43 ppm , assigned to the ethyl ester protons. Furthermore, a 9 H singlet observed at 1.35 ppm corresponds to the tert-butyl group while a 1 H singlet at 13.87 ppm belongs to the OH proton resonance. In addition, the ${ }^{13} \mathrm{C}$ NMR spectrum reveals a quaternary carbon resonance at 164.1 ppm which has been ascribed to the ester $\mathrm{C}=\mathrm{O}$ unit. The infrared spectrum of the compound shows peaks at 1724 and $1261 \mathrm{~cm}^{-1}$, corresponding to vibrations of the ester bond. The characteristic absorptions for $(\mathrm{O}-\mathrm{H})$ and $(\mathrm{C}-\mathrm{N})_{\text {pyridine }}$ bonds are observed at $3733 \mathrm{~cm}^{-1}$ and $1589 \mathrm{~cm}^{-1}$, respectively. 2-(3'-t-butyl-phenol)-6ethylpicolinate also exhibits a protonated molecular ion peak by mass spectrometry (300 $m / z$ ).

### 3.3.1.5 Synthesis of 2-(3'-chlorophenol)-6-ethylpicolinate

Synthesis of 2-(3'-chlorophenol)-6-ethylpicolinate was also prepared via the same synthetic route (Figure 3.9).


Figure 3.9-Synthesis of 2-(3'-chlorophenol)-6-ethylpicolinate

In analogy to other two ethylpicolinates, the ${ }^{1} \mathrm{H}$ NMR spectrum of the product reveals peaks at 1.33 and 4.35 ppm , assigned to the ethyl ester protons. The structure is also confirmed through the ethyl ester carbon resonances at 14.5 and 63.2 ppm observed in the ${ }^{13} \mathrm{C}$ NMR spectrum. ASAP mass spectrometry reveals a protonated molecular peak at $\mathrm{m} / \mathrm{z} 278.0577[\mathrm{M}+\mathrm{H}]^{+}$; calculated for $\mathrm{C}_{14} \mathrm{H}_{13} \mathrm{ClO}_{3}[\mathrm{M}+\mathrm{H}]^{+}$is 278.0506 .

### 3.3.1.6 Synthesis of 2-phenol-6-carboxylatopyridine

The target pro-ligand 2-phenol-6-carboxylatopyridine (HL4) was obtained upon ester hydrolysis of 2-phenol-6-ethylpicolinate (Figure 3.10). The synthetic procedure is
based on the literature preparation employed and described in Chapter 2. The pure product can be achieved in moderate yield and high purity.

$\mathrm{HL}_{4}$

Figure 3.10-Synthesis of the target pro-ligand HL4

The characterisation data are consistent with the proposed structure. The ${ }^{1} \mathrm{H}$ NMR spectrum confirms the absence of the ethyl ester group as no triplet and quartet signals at 1.40 ppm and 4.41 ppm , seen in the spectrum of the precursor 2-phenol-6ethylpicolinate, are observed. Furthermore, the aromatic proton signals have shifted downfield in comparison with the signals of the precursor. In addition, ethyl ester carbon resonances at 14.2 and 62.1 ppm corresponding to the parent ester disappeared in the ${ }^{13} \mathrm{C}$ NMR spectrum. The ESMS showed a protonated molecular peak at $\mathrm{m} / \mathrm{z} 216$ $[\mathrm{M}+\mathrm{H}]^{+}$, further confirming the product to be the desired carboxylic acid product HL4.

Similar to the synthesis of HL4, 2-(4'-t-butyl-phenol)-6-carboxylatopyridine (HL5) and 2-(4'-chlorophenol)-6-ethylpicolinate (HL6) were also obtained via hydrolysis of the ester precursor compounds (Figure 3.11).


Figure 3.11-Synthesis of the target pro-ligands $\mathrm{HL}_{5}$ and $\mathrm{HL}_{6}$

The ${ }^{1} \mathrm{H}$ NMR spectra of $\mathrm{HL}_{5}$ and $\mathrm{HL}_{6}$ are consistent with the proposed structures for the target pro-ligands. The absence of proton and carbon resonances corresponding to the ethyl ester moiety confirms the successful hydrolysis of the ester group. This is further
confirmed upon analysis by high resolution mass spectrometry, whereupon a protonated molecular peak is observed for both $\mathrm{HL}_{5}$ and $\mathrm{HL}_{6}$ at $\mathrm{m} / \mathrm{z} 272$ and 250, respectively.

### 3.3.2 Complexation of pro-ligands HL4, $\mathrm{HL}_{5}$ and HL6 to Palladium(II)

Reactions of pro-ligands $\mathrm{HL}_{4}$ and $\mathrm{HL}_{5}$ with $\mathrm{Pd}(\mathrm{OAc})_{2}$ in acetonitrile affords palladiumcontaining complexes with auxiliary acetonitrile ligands $\left[\left(O, N_{P y}, O\right) \operatorname{Pd}(\mathrm{MeCN})\right]$ (Figure 3.12). These palladium(II) acetonitrile complexes were obtained in good yield and purity.



$$
\begin{aligned}
& \mathrm{HL}_{4}, \mathrm{R}=\mathrm{H} \\
& \mathrm{HL}_{5}, \mathrm{R}={ }^{t} \mathrm{Bu}
\end{aligned}
$$



3a, $\mathrm{R}=\mathrm{H}$
3b, $\mathrm{R}={ }^{t} \mathrm{Bu}$

Figure 3.12-Synthesis of Pd(II)-acetonitrile containing complexes $\mathbf{3 a}$ and $\mathbf{3 b}$

The synthesis of 3a from the pro-ligand $\mathrm{HL}_{4}$ in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}$ and acetonitrile occurs at $70^{\circ} \mathrm{C}$ overnight, whereas 3b is obtained straightforwardly after 3 hours of stirring at room temperature. The complexes have been characterised by a combination of ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ NMR and IR spectroscopies, HRMS (FAB, ASAP, TOF) and elemental analysis. In addition, single crystal X-Ray structures have been obtained for some of the compounds.

Analysis of 3a and 3b by ${ }^{1} \mathrm{H}$ NMR spectroscopy reveals proton environments shifted from the parent pro-ligand $\mathrm{HL}_{4}$ and HL5. In addition, there is a 3 H singlet peak observed at 1.99 ppm and 1.97 ppm in both spectra ascribed to be the methyl protons of the coordinated acetonitrile ligand. Further confirmation of the structures of these solvento complexes was afforded by HRMS (TOF) and (FAB). Complex 3a displays a molecular peak with a bound sodium ion adduct in TOFMS at $\mathrm{m} / \mathrm{z} 383[\mathrm{M}+\mathrm{Na}]^{+}$, whereas complex 3b displays a strong fragmentation peak at $\mathrm{m} / \mathrm{z} 375$ corresponding to the loss of the acetonitrile ligand $[\mathrm{M}-\mathrm{MeCN}]^{+}$. It was also possible to grow crystals of 3b suitable for single crystal X-ray diffraction analysis by slow evaporation of a
solution of $\mathbf{3 b}$ in acetonitrile. The solid state structure confirms the product to be the acetonitrile-containing palladium(II) complex 3b. The structure reveals a palladium(II) complex in a distorted square planar geometry supported by an unsymmetrical dianionic $\left[O, N_{P y}, O\right]$ pincer ligand (Figure 3.13). Selected bond lengths and bond angles are presented in Table 3.1.


Figure 3.13-Molecular structure of 3b. Hydrogen atoms have been omitted for clarity

Table 3.1-Selected bond lengths $\left({ }^{( }\right)$) and angles $\left({ }^{\circ}\right)$ for $\mathbf{3 b}$
BOND LENGTHS (Å)

| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $1.954(4)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{3})$ | $94.26(17)$ |
| :--- | :---: | :---: | :---: |
| $\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $2.006(4)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $84.06(18)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{3})$ | $1.961(4)$ | $\mathbf{O}(\mathbf{3})-\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $177.91(16)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $2.022(5)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $172.29(18)$ |
| $\mathbf{O}(\mathbf{3})-\mathbf{C}(\mathbf{1 2})$ | $1.315(7)$ | $\mathbf{O}(\mathbf{3})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $90.35(17)$ |
| $\mathbf{O}(\mathbf{1})-\mathbf{C}(\mathbf{1})$ | $1.296(7)$ | $\mathbf{O}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $91.18(17)$ |

Upon detailed analysis, crystals of $\mathbf{3 b}$ are monoclinic and crystallise in the space group $\mathrm{P} 2(1) / \mathrm{c}$ with $\mathrm{Z}=4$. The longest bond from the tridentate ligand to palladium metal in $\mathbf{3 b}$
is $\operatorname{Pd}(1)-\mathrm{O}(1)[2.006(4) \AA$ ] and the shortest bond from the ligand to palladium is $\mathrm{Pd}(1)-$ $\mathrm{N}(1)$ [1.954(4) $\AA]$. The $\operatorname{Pd}(1)-\mathrm{O}(3)$ bond length is typical of an anionic phenolate tether to a palladium(II) centre [1.961(4) $\AA$ ]. The 6-membered metallacyclic ring has an angle of $94.26(17)^{\circ}[\mathrm{N}(1)-\mathrm{Pd}(1)-\mathrm{O}(3)]$, whereas that in the 5 -memberd ring size is $84.06(18)^{\circ}$ $[\mathrm{N}(1)-\mathrm{Pd}(1)-\mathrm{O}(1)]$.

On the contrary to the observed reactivity of $\mathbf{3 a}$ and $\mathbf{3 b}$ with $\mathrm{Pd}(\mathrm{OAc})_{2}$, it was not possible to obtain the palladium(II) acetonitrile complex from the reaction of pro-ligand $\mathrm{HL}_{6}$ with $\mathrm{Pd}(\mathrm{OAc})_{2}$ as the pro-ligand was not soluble in acetonitrile. The use of methanol as a reaction medium was not viable, as methanol is a stronger coordinating solvent than acetonitrile and could lead to the undesired outcomes. Instead, it was decided to develop a synthetic route to palladium(II) - pyridine and -triphenylphosphine-based complexes due to them being stronger binding ligands even in such a coordinating solvent as methanol. This will be further discussed in Section 3.3.3.

### 3.3.3 Reaction Chemistry of 3a and 3b $\left[\left(O, N_{P_{y},} O\right) \mathbf{P d}(\mathrm{MeCN})\right]$ Complexes and proligand HL6 towards Pyridines

Using a similar methodology to that used in Chapter 2, the palladium(II) acetonitrile complexes $\left[\left(O, N_{P y}, O\right) \operatorname{Pd}(\mathrm{MeCN})\right]$ are readily converted into the pyridine-containing analogues by reaction with corresponding pyridine compounds in chloroform under mild conditions (Figure 3.14). This method only applies to the exchange reactions of 3a and 3b. The reactions occur smoothly to afford the desired complexes in good yield and purity.


3a, $\mathrm{R}=\mathrm{H}$
3b, $\mathrm{R}={ }^{t} \mathrm{Bu}$


3.2a, $\mathrm{R}_{1}=\mathrm{H}, \mathrm{R}_{2}=\mathrm{Me}$
3.2b, $\mathrm{R}_{1}={ }^{t} \mathrm{Bu}, \mathrm{R}_{2}=\mathrm{Me}$
3.3a, $\mathrm{R}_{1}=\mathrm{H}, \mathrm{R}_{2}=\mathrm{Cl}$
3.3b, $\mathrm{R}_{1}={ }^{t} \mathrm{Bu}, \mathrm{R}_{2}=\mathrm{Cl}$

Figure 3.14-Synthesis of pyridine-containing Pd(II) complexes

Analytical data obtained for all the complexes are consistent with the proposed target structures. ${ }^{1} \mathrm{H}$ NMR spectroscopic analysis of 3.2a confirms 10 aromatic proton environments by integration. The absence of the characteristic 3 H singlet peak corresponding to the bound acetonitrile moiety provides further proof for the formation of 3.2a. Analysis by ${ }^{13} \mathrm{C}$ NMR spectroscopy reveals the predicted 9 aromatic CH carbons and 6 quaternary carbon resonances. In addition, the FAB mass spectrum displays a molecular ion peak at $m / z 426[\mathrm{M}]^{+}$, whereas ASAP data shows a strong protonated molecular peak at $m / z 427[\mathrm{M}+\mathrm{H}]^{+}$further confirming a successful binding of 3,5-dimethylpyridine to palladium(II) pincer complex.

The same reactivity was observed upon reaction of 3a with 3,5-dichloropyridine at room temperature. An additional set of aromatic signals corresponding to 3,5dichloropyridine was displayed in the ${ }^{1} \mathrm{H}$ NMR spectrum of 3.3a. The proposed target structure was further confirmed by FAB mass spectrometry whereupon a strong molecular ion peak $[\mathrm{M}]^{+}$is observed at $m / z 466.90980[\mathrm{M}]^{+}$, whilst the calculated value for $\mathrm{C}_{17} \mathrm{H}_{10} \mathrm{ClN}_{2} \mathrm{O}_{3} \mathrm{Pd}[\mathrm{M}]^{+}$is $m / z 466.91033$.

The exchange of the acetonitrile ligand with 3,5-dimethylpyridine, 3,5-dichloropyridine and phenylpyridine was also probed with the tert-butyl-based complex 3b. Using the same synthetic approach, all three complexes ( $\mathbf{3 . 2 b}, \mathbf{3 . 3 b}$ and $\mathbf{3 . 4 b}$ ) were obtained in quantitative yields and good purities. Full characterisation was carried out using ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ NMR and IR spectroscopies, ESIMS and high resolution TOF and FAB spectrometries.

Noticeably, the 3 H singlet peak at 1.97 ppm , assigned to the methyl group on the acetonitrile moiety in the ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{3 b}$, had disappeared in the proton NMR of all three complexes $\mathbf{3 . 2 b}, \mathbf{3 . 3 b}$ and 3.4b. Furthermore, there are additional aromatic signals detected in the ${ }^{1} \mathrm{H}$ NMR spectrum of all three compounds, each spectrum accounting for the proposed target number of resonances. The high-resolution mass spectrometry data further provided proof for the expected structures. FAB mass spectrum of 3.1b displays a molecular ion peak $[M]^{+}$at $m / z$ 482. The peak corresponding to the molecular ion peak with the loss of 3,5-dichloropyridine moiety [M-3,5-dichloropyridine $]^{+}$is displayed in the FAB spectrum of $\mathbf{3 . 3 b}[\mathrm{m} / \mathrm{z} 375]$.

Similar to the result obtained in Chapter 2 with phenylpyridine, changing the carbon donor in the ligand framework to a hydroxy group did not lead to $\mathrm{C}\left(\mathrm{sp}^{2}\right)$ - H activation of the phenylpyridine, and instead resulted in complex 3.4b (Figure 3.15).


3.4b

Figure 3.15-Formation of complex 3.4b

As mentioned previously in Section 3.3.2, employment of similar conditions to those used for the preparation of acetonitrile-containing complexes $\mathbf{3 a}$ and $\mathbf{3 b}$, to pro-ligand HL6 could not produce the desired compound due to insolubility of the pro-ligand in acetonitrile. Instead, it was suggested to probe the reactivity of the pro-ligand HL6 directly with pyridines in an effort to generate a route to palladium(II) complexes. Four electronically and sterically different pyridines were chosen as the coordinating ligands: pyridine, 4-tertbutylpyridine, 3,5-dimethylpyridine and 3-bromopyridine. In terms of electronic effects, the alkyl groups such as tert-butyl and methyl, are known to be electron donating, whereas the halide substituents are considered to be electron withdrawing. As for the steric hindrance, 3,5-dimethylpyridine is the most sterically strained amongst the four.

The synthesis of the pyridine-containing complexes $\mathbf{3 . 1} \mathbf{c}, \mathbf{3 . 2 c}, \mathbf{3 . 2}-\mathrm{Bu}$ and $\mathbf{3 . 2 c}-\mathrm{Br}$ was carried out between the pro-ligand $\mathrm{HL}_{6}, \mathrm{Pd}(\mathrm{OAc})_{2}$ and the corresponding pyridines at elevated temperatures in dry methanol overnight (Figure 3.16). All four complexes were accessed in good yields. All the compounds have been characterised by a range of analytical techniques such as ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ NMR and IR spectroscopies, ESIMS and HRMS (ASAP).


Figure 3.16-Synthesis of pyridine-containing complexes from $H_{6}$

Analysis of 3.1c, 3.2c, 3.2-EBu and 3.2c-Br by ${ }^{1} \mathrm{H}$ NMR spectroscopy reveals aromatic proton environments moderately shifted from the parent pro-ligand HL6 downfield. The presence of an additional set of aromatic proton signals corresponding to the employed pyridines suggests successful complexation to palladium. All four complexes display a strong protonated molecular ion peak $[\mathrm{M}+\mathrm{H}]^{+}$in HR (ASAP) mass spectra, further confirming the expected target structures.

### 3.3.4 Reaction Chemistry of $\left[\left(O, N_{P y}, O\right) \operatorname{Pd}(\mathrm{MeCN})\right]$ Complexes and pro-ligand HL4, $\mathrm{HL}_{5}$ and $\mathrm{HL}_{6}$ towards Triphenylphosphine ( $\mathbf{P P h}_{3}$ )

Complexes 3.5a and 3.5b have been prepared from the corresponding palladium(II) acetonitrile precursors $\mathbf{3 a}$ and $\mathbf{3 b}$, respectively, by treatment with triphenylphosphine ( $\mathrm{PPh}_{3}$ ) (Figure 3.17). The syntheses occur smoothly at room temperature and afford both complexes in good yields.


Figure 3.17-Synthesis of triphenylphosphine-containing complexes of $\mathrm{HL}_{4}$ and $\mathrm{HL}_{5}$

On the contrary, complex 3.5 c was obtained via the route used to access the pyridinecontaining complexes and discussed in Section 3.3.3. Methanol was employed as the solvent of choice in this transformation. The template reaction between $\mathrm{HL}_{6}, \mathrm{PPh}_{3}$ and $\mathrm{Pd}(\mathrm{OAc})_{2}$ has been used to synthesise 3.5 c with great success (Figure 3.18).


Figure 3.18-Synthesis of triphenylphosphine-containing Pd(II) complex 3.5c

Analysis of $\mathbf{3 . 5 a}$ by ${ }^{1} \mathrm{H}$ NMR spectroscopy displays a subtle shift of all proton environments from its precursor 3a and the presence of an additional 15 aromatic protons corresponding to the triphenylphosphine ligand. The ${ }^{31} \mathrm{P}$ NMR spectrum reveals a singlet peak at 23.7 ppm indicating one coordinated triphenylphosphine unit. Moreover, upon analysis by IR spectroscopy, the complex showed strong bands near $692-1433 \mathrm{~cm}^{-1}$ typical of the coordination of $\mathrm{PPh}_{3}$ ligands to palladium. Additionally, high resolution FAB mass spectrum displays a strong molecular ion peak $[\mathrm{M}]^{+}$at $\mathrm{m} / \mathrm{z}$ 581, while ASAP mass spectrum exhibits a protonated molecular ion peak $[\mathrm{M}+\mathrm{H}]^{+}$at $m / z 582$.

It was possible to obtain crystals of $\mathbf{3 . 5 a}$ suitable for X-ray diffraction studies by slow diffusion of petroleum ether (40-60) into a chloroform solution of 3.5a (Figure 3.19). Selected bond distances and bond angles are listed in Table 3.2.


Figure 3.19-Molecular structure of 3.5a

Table 3.2 - Selected bond lengths ( $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 3.5 a
BOND LENGTHS (Å)

| $\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $1.942(3)$ | $\mathbf{O}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{2})$ | $176.91(12)$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{2})$ | $2.007(3)$ | $\mathbf{O}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $93.53(13)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $2.017(3)$ | $\mathbf{O}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $83.64(13)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{P}(\mathbf{1})$ | $2.2727(11)$ | $\mathbf{O}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{P}(\mathbf{1})$ | $91.74(9)$ |
| $\mathbf{O}(\mathbf{1})-\mathbf{C}(\mathbf{1})$ | $1.317(5)$ | $\mathbf{O}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{P}(\mathbf{1})$ | $91.08(9)$ |
| $\mathbf{O}(\mathbf{2})-\mathbf{C}(\mathbf{1 2})$ | $1.305(5)$ | $\mathbf{C}(\mathbf{1})-\mathbf{O}(\mathbf{1})-\mathbf{P d}(\mathbf{1})$ | $124.5(3)$ |

The complex crystallises in a primitive monoclinic system with space group $\mathrm{P} 2_{1} / \mathrm{n}$, where $\mathrm{Z}=4$. The molecular structure reveals that the pincer ligand is coordinated to the palladium ion in a tridentate fashion via the deprotonated phenolic oxygen, pyridyl
nitrogen and the deprotonated carboxylic acid, each forming six membered and five membered chelate rings. The palladium(II) ion adopts a distorted square planar geometry satisfied by the pincer ligand as a dianionic tridentate $O, N_{P y}, O$ donor and the fourth site is occupied by a triphenylphosphine ligand. The bond lengths and bite angles are typical of those observed for other palladium(II) complexes discussed in this work and elsewhere ${ }^{85}$. The bite angles around the palladium in $\mathbf{3 . 5 a}$ are all very close to $90^{\circ}$. The longest bond in the structure is $\operatorname{Pd}(1)-\mathrm{P}(1)[2.2727(11) \AA$, similar to that observed for the triphenylphosphine complex 2.5a [2.2689(12) $\AA$ ] in Chapter 2.

In analogy to $\mathbf{3 . 5 a}$, the synthesis of tert-butyl- and chloro- substituent-containing 3.5b and 3.5 c generates palladium(II) complexes with a bound triphenylphosphine ligand. Analysis of the ${ }^{1} \mathrm{H}$ NMR spectra of the two compounds also reveals the presence of additional 15 aromatic protons corresponding to the $\mathrm{PPh}_{3}$ unit. Further confirmation of the expected structures is obtained through ${ }^{31} \mathrm{P}$ NMR, whereupon a singlet peak corresponding to the bound $\mathrm{PPh}_{3}$ ligand is observed in both complexes at 23.8 and 23.8 ppm.

The solid state structure of $\mathbf{3 . 5} \mathbf{c}$ has also been determined and found to contain the expected palladium(II) triphenylphosphine core supported by the $O, N_{P y}, O$ pincer ligand (Figure 3.20) and further supports spectroscopic data. Selected bond distances and bond angles are listed in Table 3.3.


Figure 3.20-Molecular structure of 3.5c. Hydrogen atoms have been omitted for clarity

Table 3.3-Selected bond lengths ( $\AA$ ) and angles $\left(^{\circ}\right)$ for 3.5 c
BOND LENGTHS (Å)

| $\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{3})$ | $1.960(8)$ | $\mathbf{O}(\mathbf{3})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $93.5(4)$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $1.989(10)$ | $\mathbf{O}(\mathbf{3})-\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $117.5(4)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $1.991(8)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $84.0(4)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{P}(\mathbf{1})$ | $2.267(3)$ | $\mathbf{O}(\mathbf{3})-\mathbf{P d}(\mathbf{1})-\mathbf{P}(\mathbf{1})$ | $92.7(2)$ |
| $\mathbf{O}(\mathbf{1})-\mathbf{C}(\mathbf{1})$ | $1.299(12)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{P}(\mathbf{1})$ | $173.1(3)$ |
| $\mathbf{O ( 3 )} \mathbf{- C ( 1 2 )}$ | $1.309(13)$ | $\mathbf{C}(\mathbf{1 2})-\mathbf{O}(\mathbf{3})-\mathbf{P d}(\mathbf{1})$ | $124.9(7)$ |
| $\mathbf{C l}(\mathbf{1})-\mathbf{C}(\mathbf{9})$ | $1.733(12)$ | $\mathbf{O}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{P}(\mathbf{1})$ | $89.8(2)$ |

The $\mathrm{O}(1)-\mathrm{Pd}(1)-\mathrm{N}(1)$ and $\mathrm{O}(3)-\mathrm{Pd}(1)-\mathrm{N}(1)$ angles are indicative of a slightly distorted square planar geometry [84.0(4) ${ }^{\circ}$ and $93.5(4)^{\circ}$, respectively]. In analogy to $\mathbf{3 . 5 a}$, the larger six-membered metallacycle $\mathrm{O}(3)-\mathrm{Pd}(1)-\mathrm{N}(1)$ exhibits the larger bite angle. Again, the longest bond is from the coordinated phosphorus atom of the $\mathrm{PPh}_{3}$ unit $[\mathrm{Pd}(1)-\mathrm{P}(1)$
$2.267(3) \AA$ ] , whilst the shortest ligand to metal bond is formed by the phenolic oxygen donor $[\mathrm{Pd}(1)-\mathrm{O}(3) 1.960(8) \AA$. .

### 3.3.5 Complexation of pro-ligands $\mathrm{HL}_{4}, \mathrm{HL}_{5}$ and HL6 to Ruthenium(II)

Ruthenium-based complexes 3.6a, 3.6b and 3.6c have been synthesised according to the procedure described in Chapter 2. The direct reaction between tris(triphenylphosphine)ruthenium(II) dichloride $\left[\mathrm{Ru}\left(\mathrm{PPh}_{3}\right)_{3} \mathrm{Cl}_{2}\right]$ and the corresponding pro-ligands HL4, HL5 and HL6occurs smoothly in methanol under reflux (Figure 3.21).


Figure 3.21-Synthesis of Ru(III) complexes 3.6a, 3.6b and 3.6c

Room temperature magnetic susceptibility measurements showed that the effective magnetic moment ( $\mu_{\text {eff }}$ ) values for these complexes lie in the range 1.91-1.96 BM. All three compounds have one unpaired electron and are, therefore, paramagnetic, which supports the trivalent state of the ruthenium ion with an octahedral geometry.

To appreciate the coordination mode of the $O, N_{P y}, O$ pincer ligands and the stereochemistry of the ruthenium(III)-based complexes, the X-Ray crystal structure of the complex 3.6b was determined (Figure 3.22). Selected bond lengths and angles are presented in Table 3.4.


Figure 3.22-Molecular structure of 3.6b. Hydrogen atoms have been omitted for clarity

Table 3.4 - Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for $3.6 \boldsymbol{b}$

## BOND LENGTHS (Å)

| $\mathrm{Ru}(1)-\mathrm{O}(3)$ | 1.974(4) | $\mathrm{O}(3)-\mathrm{Ru}(1)-\mathrm{N}(1)$ | 90.95(18) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Ru}(1)-\mathrm{O}(1)$ | 2.034(4) | $\mathrm{O}(1)-\mathrm{Ru}(1)-\mathrm{N}(1)$ | 81.38(18) |
| $\mathrm{Ru}(1)-\mathrm{N}(1)$ | 2.053(5) | $\mathrm{O}(3)-\mathrm{Ru}(1)-\mathrm{Cl}(1)$ | 91.12(13) |
| $\mathbf{R u}(1)-\mathbf{C l}(1)$ | 2.367(17) | $\mathrm{O}(3)-\mathrm{Ru}(1)-\mathrm{P}(1)$ | 95.36(12) |
| $\mathbf{R u}(1)-\mathbf{P}(1)$ | 2.373(18) | $\mathrm{O}(3)-\mathrm{Ru}(1)-\mathrm{P}(2)$ | 81.74(13) |
| $\mathbf{R u}(1)-\mathbf{P}(2)$ | 2.411(17) | $\mathrm{O}(1)-\mathrm{Ru}(1)-\mathrm{P}(1)$ | 93.05(13) |
| O(3)-C(12) | $1.346(7)$ | $\mathrm{O}(1)-\mathrm{Ru}(1)-\mathrm{P}(2)$ | 91.83(12) |
| $\mathrm{O}(1)-\mathrm{C}(1)$ | 1.304(7) | $\mathbf{C l}(1)-\mathrm{Ru}(1)-\mathrm{P}(1)$ | 88.90(6) |

The pincer ligand is coordinated to the ruthenium(III) ion in a tridentate manner binding the metal via $\mathrm{O}(1), \mathrm{O}(3)$ and $\mathrm{N}(1)$, thus resulting in the formation of six and five membered chelate rings with bite angles of $81.38(18)^{\circ}$ and $90.95(18)^{\circ}$ for $\mathrm{O}(3)-\mathrm{Ru}(1)-$ $\mathrm{N}(1)$ and $\mathrm{O}(1)-\mathrm{Ru}(1)-\mathrm{N}(1)$, respectively. The longest tridentate ligand to metal distance
is from the pyridyl nitrogen donor $\mathrm{N}(1)-\mathrm{Ru}(1)$ [2.053(5) $\AA$ ], whereas the shortest bond length from the tridentate ligand to ruthenium is formed from the phenolic oxygen. Interestingly, two $\mathrm{PPh}_{3}$ ligands are positioned cis to each other, with the chloride being trans to one of the $\mathrm{PPh}_{3}$ units and cis to the pyridyl core of the tridentate ligand. This is opposite to the stereochemistry observed in Chapter 2 with the ruthenium(III) complex 2.6b, where the $\mathrm{PPh}_{3}$ ligands occupy the two axial positions, with the two $\mathrm{PPh}_{3}$ molecules being mutually trans to each other. The overall coordination geometry around the ruthenium(III) ion is distorted octahedral, which is reflected through all the bond parameters around the metal centre.

### 3.4 Conclusions

The synthesis and characterisation of three novel pincer ligands and their corresponding palladium(II) and ruthenium(III) complexes is described in detail in this chapter. The reactions of $\mathrm{HL}_{4}$ and HL 5 with $\mathrm{Pd}(\mathrm{OAc})_{2}$ in acetonitrile gave the tridentate palladium acetonitrile complexes of the type $\left[\left(O, N_{P y}, O\right) \operatorname{Pd}(\mathrm{MeCN})\right]$. The subsequent exchange of the labile MeCN ligand with a range of pyridines and triphenylphosphine resulted in a series of novel palladium(II) pyridine and triphenylphosphine-containing analogues of the starting complexes. In contrast, chlorine-containing HL6 pincer pro-ligand could not yield the acetonitrile complex due to the lack of solubility in acetonitrile. Instead, the pro-ligand was directly reacted with pyridines, triphenylphosphine and $\mathrm{Pd}(\mathrm{OAc})_{2}$ to yield complexes of the formula $\left[\left(O, N_{P y}, O\right) \operatorname{Pd}(\mathrm{X})\right]$ (where $\left.\mathrm{X}=\mathrm{Py}, \mathrm{PPh}_{3}\right)$. In addition, the reactivity of the pro-ligands towards $\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}$ was explored and three novel ruthenium(III) pincer complexes have been successfully synthesised. In analogy to palladium(II) pincer complexes, ruthenium(III) complexes of the type $\left[\left(O, N_{P y}, O\right) \mathrm{Ru}(\mathrm{Cl})\left(\mathrm{PPh}_{3}\right)_{2}\right]$ are supported by the tridentate ligand framework and accommodate three auxiliary ligands. In all three ligands, the phenol oxygen becomes deprotonated, resulting in a tridentate mode of binding and further stabilisation of the metal centres. It would appear that the ligands ( $\mathrm{H}_{4}$, $\mathrm{HL}_{5}$ and $\mathrm{HL}_{6}$ ) developed in this work, have an effective design to meet the geometrical requirements of palladium(II) and ruthenium(III), leading to discreet pincer complexes. The structures of all the synthesised compounds have been confirmed by the means of several analytical techniques and in some cases by single crystal X-Ray diffraction analysis.

## 4. Catalytic Performance of Ru(III) Pincer Complexes 2.6a, 2.6b, 2.6c, 3.6a, 3.6b, 3.6c in Transfer Hydrogenation of Ketones

### 4.1 Introduction

Transition metal complexes supported by pincer ligands have been extensively studied as catalysts in transfer hydrogenation of ketones to secondary alcohols. ${ }^{104,105}$ Thus, the development of new pincer ligands and their corresponding complexes, along with their catalytic applications, represents one of the popular and fast developing areas in organometallic chemistry.

The main reason for the success of these pincer complexes is the particular involvement of the ligand in several of the catalytic steps. For instance, nitrogen-based pincer ligands accelerate the heterolytic cleavage or reductive elimination of hydrogen. Therefore, even when non-noble metals are employed, hydrogenation and dehydrogenation reactions can be successfully achieved. Beller and co-workers designed two manganese catalysts, based on NNN aminopincer ligands that demonstrated a better catalytic performance in transfer hydrogenation than its phosphine-based analogues, requiring a lower catalyst loading and a lower concentration of $\mathrm{KO}^{t} \mathrm{Bu}$ base (Figure 4.1). ${ }^{106}$ Furthermore, Fu et al. reported a cobalt-based pincer catalyst for transfer hydrogenation of alkynes. The system showed great selectivity and efficiency using only $0.2 \mathrm{~mol} \%$ catalyst loadings (Figure 4.1). ${ }^{107}$



> Mn1, $\mathrm{R}=\mathrm{H}$
> Mn2, $\mathrm{R}=\mathrm{Me}$

Figure 4.1-Manganese and cobalt pincer catalysts

Amongst the exhaustive list of various transition metal catalysts, ruthenium-based catalysts are by far the most widely used ones in transfer hydrogenation. Hu et al. developed a penta-coordinated ruthenium pincer complex that has been efficiently applied in transfer hydrogenation of ketones (Figure. 4.2). ${ }^{108}$


4

Figure 4.2-Transfer hydrogenation of ketones catalysed by complex 4

At $0.2 \mathrm{~mol} \%$ catalyst loading, $5 \mathrm{~mol} \%$ of KOH in isopropanol as a reducing agent, complex 4 reduced a number of aliphatic and aromatic ketones with electronwithdrawing and electron-donating groups at ortho-, meta- and para-positions within 2 h. In addition, TOFs (at $50 \%$ conversion) of $361-3750 \mathrm{~h}^{-1}$ were achieved.

Ramesh and Venkatachalam synthesised $\mathrm{Ru}($ III ) 2-arylazo phenolate complexes incorporating $C, N$ and $O$ donors and triphenylarsine ( $\mathrm{AsPh}_{3}$ ) (Figure. 4.3). ${ }^{91}$ Complex 4.1d of the type $\left[\operatorname{RuBr}\left(\mathrm{AsPh}_{3}\right)_{2}(\mathrm{azo}-\mathrm{OMe})\right]$, was found to be an active catalyst for the transfer hydrogenation of ketones with excellent conversions to the corresponding alcohols. The reaction was carried out in 2-propanol at $80^{\circ} \mathrm{C}$ and performed well for both aromatic and aliphatic ketones.


$$
\begin{aligned}
\text { 4.1a } \mathrm{R} & =\mathrm{H}: \text { azo- } \mathrm{H} \\
\text { 4.1b } \mathrm{R} & =\mathrm{Cl}: \text { azo-Cl } \\
\text { 4.1c } \mathrm{R} & =\text { Me: azo-Me } \\
\text { 4.1d } \mathrm{R} & =\mathrm{OMe}: \text { azo-OMe } \\
\text { 4.1e } \mathrm{R} & =\mathrm{OEt}: \text { azo-OEt } \\
\mathrm{X} & =\mathrm{Cl} \text { or } \mathrm{Br}
\end{aligned}
$$

Figure 4.3-Orthometalated Ru(III) 2-arylazo phenolate complexes

Tiel and co-workers described novel ruthenium complexes supported by tridentate $N, N, N$ dipyrazolylpyridine ligands (Figure 4.4). ${ }^{109}$ The complexes showed excellent performance in the presence of 2-propanol at room temperature.


Figure 4.4-Ru(II) dipyrazolylpyridine-supported complexes

Optimisation experiments found that high concentrations of base and 2-propanol reduce the reaction rate. Additionally, the reaction rate increases greatly with higher temperatures. The results also demonstrated that the incorporation of $n$-butyl groups in the 5-position of the pyrazole rings significantly increased the catalytic activity.

A halogenated ruthenium $P, S i, P$ pincer complex developed by Li et al. demonstrated good activity in TH of various ketones when used in combination with 2-propanol and $\mathrm{KO}^{t} \mathrm{Bu}$ base at $80^{\circ} \mathrm{C}$ (Figure 4.5). ${ }^{110}$

4.3

Figure 4.5-Ruthenium P,Si,P donor-based pincer complex

The studies suggested that the high catalytic activity was linked to the stability imparted by the pincer ligand and the prospect of coordinative and electronic unsaturation.

Yu and co-workers reported a ruthenium complex supported by an unsymmetrical $N, N, C$ pincer ligand that exhibited good catalytic performance in the transfer
hydrogenation of ketones (Figure 4.6). ${ }^{88}$ It was suggested that the unsymmetrical nature of the ligand is responsible for the high catalytic activity of the complex 4.4a.


Figure 4.6-Generation of Ru-H active complex 4.4b from 4.4a

Mechanistic studies proposed that the Ru-H complex 4.4b, generated in situ, is the active species in the catalytic cycle. This was verified by treating $4.4 \mathbf{a}$ with $\mathrm{K}_{2} \mathrm{CO}_{3}$ and 2-propanol at reflux to prepare 4.4b (Figure 4.6).

Van Koten and co-workers investigated the effects of electronic factors of pincer ligands by changing the substituents on the phosphine donor arms (Figure 4.7). ${ }^{111}$ Amongst the different complexes studied complex 4.5, that is supported by a pincer ligand with electron-withdrawing substituents such as $p$-trifluoromethylphenyl group, showed a superior catalytic activity in terms of yield and TOF.


$$
\begin{aligned}
& 4.5 \mathrm{R}=p-\mathrm{CF}_{3} \mathrm{C}_{6} \mathrm{H}_{4} \\
& 4.6 \mathrm{R}=\mathrm{Cy}
\end{aligned}
$$

Figure 4.7 - Ruthenium pincer complexes employed in transfer hydrogenation

Similarly, electron-rich PCP ruthenium complex 4.6 developed by Fogg and coworkers, and containing cyclohexyl substituents on the phosphine donor atoms, exhibited high TOF in the hydrogenation of acetophenone (Figure 4.7). ${ }^{112}$

Despite the catalysts developed so far demonstrating excellent efficiency for the transfer hydrogenation reactions, it was imperative to use basic conditions for all these catalytic systems that employ 2-20 $\mathrm{mol} \%$ of various bases.

In an attempt to achieve neutral conditions, Chen and co-workers synthesised a PNNcontaining dearomatised complex 4.7, which successfully catalysed transfer hydrogenation reactions without the use of base under neutral reaction conditions at 40 ${ }^{\circ} \mathrm{C}$ (Figure 4.8). ${ }^{113}$

4.7

Figure 4.8 - PNN-containing ruthenium pincer complex 4.7

However, the reaction took a long time for completion and a good yield was only achieved after 16 h . Therefore, the development of efficient catalysts that result in higher reaction rates together with good conversions and yields under neutral conditions is still an attractive goal.

This literature survey is not intended to demonstrate an exhaustive list of all the reported ruthenium complexes, however, it is evident that ruthenium pincer complexes play a very important role as catalysts in transfer hydrogenation reactions.

### 4.2 Aims and Objectives

The transfer hydrogenation reaction is an attractive process notably for small scale synthesis of a variety of chemicals as it avoids the use of hazardous molecular hydrogen gas. As seen from the literature survey, extensive work has been undertaken in the development of transfer hydrogenation catalysts. Considering the literature results discussed above, this chapter is focused on investigating the catalytic performance of six tridentate ruthenium(III) complexes synthesised in Chapters 2 and 3, in transfer hydrogenation reactions of a range of ketones. Optimisation studies have been carried out in order to find the most suitable conditions for this transformation. In specific
examples, the results will be compared to the performance of catalysts reported in the literature.

### 4.3 Results and Discussion

To probe the catalytic capacity of $\mathrm{Ru}(\mathrm{III})$ pincer complexes $\mathbf{2 . 6 a}, \mathbf{2 . 6 b}, \mathbf{2 . 6}, \mathbf{3 . 6 a}, \mathbf{3 . 6}$, 3.6c, shown in Figure. 4.9, in transfer hydrogenation (TH) reaction of ketones, acetophenone was chosen as a model substrate.

2.6a, $R=H$
2.6b, $\mathrm{R}={ }^{t} \mathrm{Bu}$
2.6c, $\mathrm{R}=\mathrm{CF}_{3}$

3.6a, $\mathrm{R}=\mathrm{H}$
3.6b, $\mathrm{R}={ }^{t} \mathrm{Bu}$
3.6c, $\mathrm{R}=\mathrm{Cl}$

Figure 4.9-Ru(III) pincer complexes

To find the most suitable reaction conditions, catalysis with $\mathbf{2 . 6 a}$ was initially explored. The experimental procedure was carried out as follows; a mixture containing the substrate, ruthenium catalyst and base was heated at reflux in 2-propanol at $80^{\circ} \mathrm{C}$ for the appropriate period of time. The reaction was carried out under solvent-free conditions using 2-propanol as the hydrogen source. 2-propanol is the preferred choice as it is a safe, inexpensive, easy to handle solvent and reductant that is transformed into volatile acetone which is easily removed in the separation process. Some other solvents/hydrogen sources such as methanol (MeOH), ethanol (EtOH) and tert-butanol ( ${ }^{\text {' } \mathrm{BuOH} \text { ) were also examined under similar conditions but these all proved ineffective. }}$ The general reaction conditions for a ruthenium-catalysed TH are shown in Figure 4.10 .


Figure 4.10-Ru-catalysed transfer hydrogenation of acetophenone

The conversion of acetophenone to 1-phenylethanol was calculated using ${ }^{1} \mathrm{H}$ NMR spectroscopy. A blank experiment, carried out in the absence of 2.6a, gave no hydrogenation of acetophenone. For comparison, $\left[\mathrm{Ru}\left(\mathrm{PPh}_{3}\right)_{3} \mathrm{Cl}_{2}\right]$ and $\mathrm{RuCl}_{3} .3 \mathrm{H}_{2} \mathrm{O}$ were also tested as catalysts. The use of $\left[\mathrm{Ru}\left(\mathrm{PPh}_{3}\right)_{3} \mathrm{Cl}_{2}\right]$ gave $67 \%$ conversion; albeit at higher catalyst loading, whilst $\mathrm{RuCl}_{3} .3 \mathrm{H}_{2} \mathrm{O}$ did not exhibit any catalytic activity in the absence of phosphane ligation. These observations highlight the role that the ligand plays in influencing catalytic activity. Additionally, steric and electronic factors present within the ligand framework further affect the catalytic performance.

The effect of catalyst loading/concentration on conversion was investigated. The catalyst loadings were varied from $0.03 \mathrm{~mol} \%$ to $0.5 \mathrm{~mol} \%$. The results obtained are shown in Table 4.1. in terms of conversions. As predicted, the conversion of acetophenone to 1-phenylethanol increased with increasing catalyst loadings. For lower catalyst loadings (entry 1 and 2), the reactions were relatively slow and only $67 \%$ and $68 \%$ conversions were obtained for entries 1 and 2 in 18 h , respectively. As the conversion reached $99 \%$ at $0.3 \mathrm{~mol} \%$ (entry 4) and no change was observed on increasing the loading to $0.5 \mathrm{~mol} \%$ (entry 5), catalyst loading from entry 4 was selected for all further reactions.

Table 4.1-Transfer hydrogenation of acetophenone with different concentrations of 2.6a

| ENTRY | CATALYST <br> LOADING <br> $($ mol $\%)$ | TIME (h) | TEMPERATURE <br> $\left({ }^{\circ} \mathrm{C}\right)$ | CONVERSION (\%) |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 0.03 | 18 | 80 | 50 |
| 2 | 0.05 | 18 | 80 | 62 |
| 3 | 0.1 | 18 | 80 | 70 |
| 4 | 0.3 | 18 | 80 | 99 |
| 5 | 0.5 | 18 | 80 | 99 |

Alkaline conditions were promoted by using base. A range of different bases, such as $\mathrm{KOH}, \mathrm{NaOH}, \mathrm{Na}_{2} \mathrm{CO}_{3}, \mathrm{NaO}^{t} \mathrm{Bu}$ were screened in the reaction. The results are presented in Table 4.2. The best result was achieved using $\mathrm{NaO}^{t} \mathrm{Bu}$ (entry 3) and thus, it was chosen as the optimum base for further experiments. In addition, NaOH and $\mathrm{Na}_{2} \mathrm{CO}_{3}$ showed similar reactivities with $64 \%$ and $65 \%$ conversions, respectively. It was observed that in the absence of a base, transfer hydrogenation was not initiated.

Table 4.2-Transfer hydrogenation of acetophenone catalysed by 2.6a with different bases

| ENTRY | BASE | CATALYST <br> LOADING <br> $($ mol\% $)$ | TIME <br> $(\mathrm{h})$ | TEMPERATURE <br> $\left({ }^{\circ} \mathrm{C}\right)$ | CONVERSION <br> $(\%)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | KOH | 0.3 | 18 | 80 | 38 |
| 2 | NaOH | 0.3 | 18 | 80 | 64 |
| 3 | $\mathrm{NaO}^{t} \mathrm{Bu}^{2}$ | 0.3 | 18 | 80 | 99 |
| 4 | $\mathrm{Na}_{2} \mathrm{CO}_{3}$ | 0.3 | 18 | 80 | 65 |

The effect of concentration of base (base to substrate ratio) was also studied at constant catalyst and substrate concentrations. Conversion to the product increases with the increase in base concentration (Table 4.3). The highest conversion was obtained with $12 \mathrm{~mol} \%$ of $\mathrm{NaO}^{t} \mathrm{Bu}$. Further increase in concentration did not affect the conversion as seen from entry 4. Chowdhury and Backvall have reported in their work that the use of base is essential in ruthenium-catalysed TH reactions carried out in 2-propanol, as the reaction occurs faster with an increase in base concentration ${ }^{114}$. This led to various TH protocols being developed where the use of base is notably underlined ${ }^{115,116}$.

Table 4.3-Transfer hydrogenation of acetophenone catalysed by 2.6a with different concentrations of $\mathrm{NaO}^{t} \mathrm{Bu}$

| ENTRY | BASE <br> LOADING <br> $($ mol $\%)$ | CATALYST <br> LOADING <br> $($ mol $\%)$ | TIME <br> $(\mathrm{h})$ | TEMPERATURE <br> $\left({ }^{\circ} \mathrm{C}\right)$ | CONVERSION <br> $(\%)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 1 | 0.3 | 18 | 80 | 3 |
| 2 | 5 | 0.3 | 18 | 80 | 58 |
| 3 | 12 | 0.3 | 18 | 80 | 99 |
| 4 | 15 | 0.3 | 18 | 80 | 99 |

It is assumed that in this reaction base facilitates the formation of the ruthenium alkoxide by abstracting the alcohol proton and subsequently, $\beta$-elimination of the alkoxide generates a ruthenium hydride, which is considered to be the active species in the transformation. Although mechanistic studies were not performed, it is most likely that this catalytic reaction follows the ruthenium hydride intermediate pathway described in the literature. ${ }^{105}$

Furthermore, an investigation was undertaken to study the effect of temperature and time on catalytic activity of 2.6a catalyst in TH of acetophenone. The reactions were conducted at $40^{\circ} \mathrm{C}$ and $60^{\circ} \mathrm{C}$, besides the initial set temperature of $80^{\circ} \mathrm{C}$. Carrying out reactions at lower temperatures is always favourable in terms of efficiency and cost.

Table 4.4-Transfer hydrogenation of acetophenone catalysed by 2.6a at different temperatures

| ENTRY | CATALYST <br> LOADING (mol\%) | TIME <br> (h) | TEMPERATURE <br> $\left({ }^{\circ} \mathrm{C}\right)$ | CONVERSION (\%) |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 0.3 | 6 | 40 | 4 |
| 2 | 0.3 | 6 | 60 | 25 |
| 3 | 0.3 | 6 | 80 | 99 |

The data presented in Table 4.4 shows that the reactivity decreased significantly on decreasing the temperature and the best conversion was obtained at $80^{\circ} \mathrm{C}$. In addition,
the effect of time on catalyst activity was also investigated. Initially, the reaction was left for 18 hours to achieve full completion. However, further screenings, showed that $99 \%$ conversion to 1 -phenylethanol is reached after 6 hours in refluxing 2-propanol (entry 3). As seen from Table 4.5, $97 \%$ conversion is obtained within 2 h . When the time is increased further, the conversion increases as well (entry 2 ). The timescale of 6 hours was applied in further studies.

Table 4.5 - The reaction rate of transfer hydrogenation of acetophenone catalysed by 2.6a

| ENTRY | CATALYST | TIME | TEMPERATURE | CONVERSION (\%) |
| :---: | :---: | :---: | :---: | :---: |
| LOADING (mol\%) |  | $(\mathrm{h})$ | $\left({ }^{\circ} \mathrm{C}\right)$ |  |$]$

To investigate the role of electronic and steric effects on the catalytic efficiency, 2.6b, 2.6c, 3.6a, 3.6b and 3.6c were also evaluated under the optimised reaction conditions established earlier for 2.6a. The results are presented in Table 4.6.

Table 4.6-Transfer hydrogenation of acetophenone catalysed by Ru(III) pincer complexes

ENTRY CATALYST TIME (h) CONVERSION (\%)

| 1 | $2.6 \mathbf{a}$ | 6 | 99 |
| :---: | :---: | :---: | :---: |
| 2 | $2.6 \mathbf{b}$ | 6 | 93 |
| 3 | $2.6 \mathbf{c}$ | 6 | 98 |
| 4 | $3.6 \mathbf{a}$ | 6 | 95 |
| 6 | $3.6 b$ | 6 | 87 |

As seen from the results compiled in Table 4.6, 2.6a and $\mathbf{2 . 6 c}$ (entries 1 and 3, respectively) gave the highest conversions to 1-phenylethanol compared to the other catalysts. In addition, phenol-containing complexes 3.6a, 3.6b and 3.6c showed a lower catalytic performance in general, compared with their aryl-containing counterparts. As a general observation, lower conversions to the product could be the result of electronic effects.

Finally, to examine the general applicability of $\mathbf{2 . 6 a}$ as a catalyst in transfer hydrogenation, a few different ketones with varied electronic and steric effects were studied under the established conditions (Table 4.7).

Table 4.7 - Transfer hydrogenation of substituted acetophenone derivatives by 2.6a
ENTRY

From Table 4.6 it is evident that complex 2.6a is a potent catalyst that efficiently catalyses the reduction of acetophenone and its $p$-substituted derivatives to their corresponding alcohols. The complex reduces acetophenone into 1-phenyethanol in $98 \%$ isolated yield and with TON and TOF numbers which are higher than many reported in the literature. ${ }^{117,91}$ For 4-bromoacetophenone the activity decreases significantly compared to other substrates, possibly as a result of higher mesomeric effects of bromine, as reported in the literature. ${ }^{118,119}$ Despite the decreased activity, the conversion obtained for this substrate is still higher than that found in the literature. ${ }^{116,118}$ Furthermore, diphenylmethanol was generated from a greatly sterically hindered benzophenone in $94 \%$ yield after 6 h (entry 5). Transfer hydrogenation of sterically bulky ketones is often associated with poor reaction rates. The conversion of $98 \%$ and TON number of 312 are significantly higher than those reported in the literature for this substrate at higher catalyst loading and higher temperature. ${ }^{91}$ The presence of electron-donating substituents (entry 3 and 4) resulted in moderate activity
in the hydrogenation reactions; the conversions of 4-methylacetophenone and 4methoxyacetophenone to their corresponding alcohols were $92 \%$ and $94 \%$, respectively.

### 4.4 Conclusions

Although numerous examples of catalytic systems that efficiently catalyse transfer hydrogenation of ketones have been reported in the literature, a catalyst described in this work is novel for its specific $C, N_{P y}, O$ ligand framework. In addition, compared to $\mathrm{Ru}(\mathrm{II})$ analogues, there are relatively few examples of paramagnetic Ru (III) complexes and their use as transfer hydrogenation catalysts reported in the literature. In this work, six novel ruthenium(III) pincer complexes have been employed as efficient catalyst precursors for the transfer hydrogenation of ketones. Complex 2.4a was found to be superior to all the other six catalysts tested in terms of yield and TON/TOF values. Optimisation studies identified that the best results can be achieved at $0.3 \mathrm{~mol} \%$ of catalyst loading in combination with $\mathrm{NaO}^{t} \mathrm{Bu}$ in 2-propanol at reflux. The reactions reach completion and achieve excellent yields within 6 h . To probe the general applicability of $\mathbf{2 . 4 a}$ as a catalyst, a range of aromatic ketones with different electronic and steric properties was investigated. All the substrates were converted to their corresponding alcohols in excellent yields (68-98\%).

## 5. Design, synthesis and reactivity of palladium(II) and platinum(II) complexes supported by 2-ethylcarboxylate-6iminopyridyl [ $\left.N, N_{P y}, O\right]$-type pincer ligands

### 5.1 Introduction

Bis(arylimino)pyridine-based ligands first came into the spotlight in 1998 when Brookhart and Gibson and co-workers independently described the synthesis of iron and cobalt complexes incorporating these ligands and their use as highly active catalysts in olefin polymerisation. ${ }^{120,121}$ Since then, numerous reports have appeared in the literature focusing on designing analogous ligands by varying the backbone and substitution pattern of this particular ligand set. Modifications made on these robust iminopyridyl ligands have mainly been based on substitution of the imino-aryl rings and very little work has been done on asymmetric mono(imino)pyridyl ligands stabilised by substituents in the 6-position of the pyridine ring.

Bianchini et al. developed a new family of 6-substituted-2-mono(arylimino)pyridine ligands by introducing aryl or heterocyclic ring substituents such as 2-thienyl, 2-furanyl and 2-pyridyl groups into the 6-position. ${ }^{122}$ Figure $\mathbf{5 . 1}$ shows a series of mono(imino)pyridine-based $\mathrm{Co}(\mathrm{II})$ complexes with a thienyl substituent incorporated into the 6-position of the pyridine developed by Bianchini and co-workers. ${ }^{123}$


$\mathrm{R}_{1}=\mathrm{H}, \mathrm{Et}$



Figure 5.1 - Thienyl-based Co(II) complexes

It was observed that the position of the sulfur atom in the thienyl moiety greatly affected the catalytic reactivity of the corresponding Co (II) complexes in the oligomerisation of ethylene to $\alpha$-olefins in the presence of methylaluminoxane (MAO). Studies showed that complexes where the metal atom is in the 3-position of the thienyl ring catalyse the selective conversion of ethylene to 1-butene, whereas catalysts containing thien-2-yl groups give $\mathrm{C}_{4}-\mathrm{C}_{14} \alpha$-olefins. In addition, aromatic group in the 6-position of the central pyridine ring is necessary for ethylene oligomerisation, a (imino)pyridine ligands without substituents in this position are not catalytically active.

Sun et al. ${ }^{124,125}$ and Su and Zhao ${ }^{126}$ synthesised a series of novel mono(imino)pyridyl complexes supported by 2-(iminopyridine)-6-ethyl ester framework (Figure 5.2) and extended the metal centre from cobalt to metals such as iron and nickel.


Figure 5.2 - 2-(iminopyridine)-6-ethyl ester based complexes with Co, Fe and Ni metal centres

It has been found that the ester group incorporated into the ligand backbone can affect the coordination environment around the metal centre. In addition, when the steric bulk of the ligand substituent on the imine was decreased, systems showed higher catalytic activity towards olefin polymerisation.

Another analogue of the mono(imino)pyridyl ligand family was synthesised by Su and co-workers, and incorporated an acetyl group in the 6 -position. ${ }^{127}$ Their Co (II) and $\mathrm{Ni}($ II $)$ complexes bearing auxiliary chloride ligands demonstrated that the presence of a bulkier group in the ortho-position or a methyl group in the para-position of the iminoaryl ring leads to superior catalytic activities for both $\mathrm{Co}(\mathrm{II})$ and $\mathrm{Ni}(\mathrm{II})$-based complexes (Figure 5.3).

$\mathrm{M}=\mathrm{Co}, \mathrm{Ni}$
$\mathrm{R}=\mathrm{H}, \mathrm{Me}, \mathrm{Et}$

Figure 5.3 - Acetyl-based Co(II) and Ni(II) complexes

Jie and co-workers developed a series of nickel and cationic palladium complexes incorporating an alcohol in the 6-position of the tridentate (imino)pyridyl framework. ${ }^{128}$ The effects of anion, metal centre and ligand environment on the catalytic activity for norbornene polymerisation were evaluated (Figure 5.4).

a) $\mathrm{R}={ }^{i} \mathrm{Pr}$
b) $R=E t$

c)

d) $\mathrm{R}_{1}={ }^{i} \mathrm{Pr}, \mathrm{R}_{2}=\mathrm{H}, \mathrm{R}=\mathrm{Me}, \mathrm{X}=\mathrm{Cl}$
e) $\mathrm{R}_{1}={ }^{i} \mathrm{Pr}, \mathrm{R}_{2}=\mathrm{H}, \mathrm{R}=\mathrm{H}, \mathrm{X}=\mathrm{Cl}$

Figure 5.4 - Ni and Pd complexes supported by imino(pyridyl) alcohol ligands

Both Pd-based and Ni-based metal complexes demonstrated high conversions upon activation with MAO, $85.4 \%$ and $100 \%$, for Ni and Pd complexes, respectively. It was found that the substituents on the alcohol arm (R-C-OH) can affect the catalytic performance. Changing two methyl groups to two hydrogen atoms led to higher conversions and activities.

### 5.2 Aims and Objectives

This chapter describes and discusses the synthesis and characterisation of three pyridine-based monoanionic [ $N, N_{P y}, O$ ] pincer ligands that give insight into the influence of the 2 -substituted nitrogen donors and 6 -substituted oxygen donors on metal binding. The effect of steric hindrance imparted by this type of pincer ligand around the axial positions of a metal centre will be examined by direct comparison with otherwise identical ligand frameworks. In addition, the ability of these ligands to support
palladium(II) and platinum(II) metal centres will be explored through synthesising a series of complexes of the type $[(\mathrm{NNO}) \mathrm{PdX}](\mathrm{X}=\mathrm{OAc}, \mathrm{Cl}),[(\mathrm{NNO}) \operatorname{Pd}(\mathrm{MeCN})]\left[\mathrm{PF}_{6}\right]$, $[(\mathrm{NNO}) \mathrm{Pd}(\mathrm{Py})]\left[\mathrm{PF}_{6}\right]$ and $\left[(\mathrm{NNO}) \mathrm{Pt}(\mathrm{Cl})_{2}\right]$. Moreover, the reactivity of $[(\mathrm{NNO}) \operatorname{Pd}(\mathrm{MeCN})]\left[\mathrm{PF}_{6}\right]$ type complexes towards acetoxylation of 8 -methylquinoline is disclosed.

### 5.3 Results and Discussion

### 5.3.1 Synthesis of target pro-ligands

This section will focus on the synthesis of the target pincer pro-ligands EtL7, EtLs and EtL9 (Figure 5.5). The pro-ligands EtLs and EtL9 are novel compounds and have been fully characterised by ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectroscopy, high resolution mass spectrometry and solid-state IR spectroscopy. Compound EtL7 has been reported previously and its use in ethylene polymerisation has been disclosed. ${ }^{124}$




Figure 5.5 - Structure of target pro-ligands

Illustrated in Figure 5.6 is the retrosynthetic analysis for the preparation of the iminecontaining picolinic acid ethyl ester pro-ligands.


Figure 5.6-Retrosynthetic analysis of $E t \boldsymbol{L}_{7}, E t \boldsymbol{L}_{8}$ and $E t \boldsymbol{L}_{9}$ from starting materials

### 5.3.2 Synthesis of intermediates

### 5.3.2.1 Synthesis of diethyl pyridine-2,6-dicarboxylate

The synthesis of diethyl pyridine-2,6-dicarboxylate was carried out according to a literature protocol (Figure 5.7). ${ }^{124}$ The pure product was obtained in good yield and the spectroscopic data are consistent with those reported in the literature.


Figure 5.7 - Synthesis of diethyl pyridine-2,6-dicarboxylate

### 5.3.2.2 Synthesis of ethyl 6-acetyl-2-pyridinecarboxylate

The synthesis of ethyl 6-acetyl-2-pyridinecarboxylate was based on the literature procedure and involves a Claisen condensation of diethyl pyridine-2,6-dicarboxylate with ethyl acetate, followed by a hydrolysis of the formed $\beta$-carbonyl ester and finally by a decarboxylation (Figure 5.8). ${ }^{124}$


Figure 5.8 - Mechanism to show synthesis of ethyl-6-acetyl-2-pyridinecarboxylate

The reaction shown in Figure 5.9 required a strong base such as sodium ethoxide ( NaOEt ) to be formed in situ, therefore dry reagents were used to prevent the base degrading to ethanol. It is important to note that as stoichiometric amounts of base are required, any loss due to air moisture or wet solvent will directly affect the yield of the reaction, thus potentially explaining the low yield obtained in this work ( $27 \%$ ) and that reported in the literature $(40 \%)$. The characterisation data are consistent with those reported in the literature.


Figure 5.9-Synthesis of ethyl 6-acetyl-2-pyridinecarboxylate

### 5.3.2.3 Synthesis of ethyl (E)-6-(1-((2,6-diisopropylphenyl)imino)ethyl)picolinate (EtL7)

The synthesis of EtL 7 was based on the protocol described in the literature and was achieved in $84 \%$ yield by the condensation reaction of ethyl 6-acetyl-2pyridinecarboxylate with 2,6-diisopropylaniline (Figure 5.10). ${ }^{124}$


Figure 5.10-Condensation reaction of ethyl 6-acetyl-2-pyridinecarboxylate to form $E t L_{7}$

In order to maintain dry reaction conditions and aid in driving synthesis, a catalytic amount of $p$-toluene sulfonic acid ( $p$ - TsOH ) was used instead of aqueous acid reported in the literature. The pure product was isolated using flash column chromatography and the aniline starting material remained on the column. The characterisation data are consistent with those reported in the literature. Upon analysis by ${ }^{1} \mathrm{H}$ NMR spectroscopy, a singlet at $\delta 2.2 \mathrm{ppm}$ confirms the presence of the imine functionality, corresponding to the $\mathrm{CH}_{3} \mathrm{C}=\mathrm{N}$ proton environment. The relative integration of this peak shows a 3 H environment, thus showing that the isolated compound contains no bis-imine byproducts. Mass spectrometry reveals a protonated molecular peak ion at $353 \mathrm{~m} / \mathrm{z}$. It is assumed that a by-product isolated from the reaction arises from the nucleophilic attack of the amine on the ester group to form an amide compound shown in Figure 5.11. This is observed through a molecular ion peak ( $483 \mathrm{~m} / \mathrm{z}$ ) seen in ESIMS data corresponding to the above-mentioned amine compound.


Figure 5.11 - Major by-product of the condensation reaction to form EtL $\boldsymbol{L}_{7}$

### 5.3.2.4 Synthesis of 2,4,6-triisopropylaniline

In order to form target pro-ligand EtLs, commercially unavailable 2,4,6triisopropylaniline was synthesised from 1,3,5-triisopropylbenzene following a previously reported literature method. ${ }^{129}$ The two-step synthesis started off with the
nitration of 1,3,5-triisopropylbenzene to 2,4,6-triisopropyl-1-nitrobenzene (Figure 5.12).


Figure 5.12-Nitration of 1,3,5-triisopropylbenzene to form 2,4,6-triisopropyl-1nitrobenzene

The pure product was isolated in $96 \%$ yield upon recrystallisation in methanol at $0{ }^{\circ} \mathrm{C}$. The second step of the reaction involved reduction of the nitro group to an amine via catalytic hydrogenation over 5\% Pd/C using hydrazine as a powerful reducing agent (Figure 5.13).


Figure 5.13 - Synthesis of 2,4,6-triisopropylaniline from 2,4,6-triisopropyl-1nitrobenzene

The final product was isolated once the catalyst was removed by vacuum filtration in $93 \%$ yield which compares well to the literature value of $100 \%$ yield.

### 5.3.2.5 Synthesis of ethyl (E)-6-(1-((2,4,6-triisopropylphenyl)imino)ethyl)picolinate (EtL8)

EtLs pro-ligand was obtained in high yield and excellent purity using a similar synthetic approach to that described for the synthesis of EtL7, using the previously prepared 2,4,6-triisopropylaniline as the nucleophile. This compound has not been reported in the literature, and thus, has been fully characterised by several analytical methods. Analysis of the compound by ${ }^{1} \mathrm{H}$ NMR spectroscopy reveals the presence of two doublet peaks of 6 H and 12 H , respectively, coupling to two septet peaks ( $\delta 1.27 \mathrm{ppm}$ and $\delta 1.13 \mathrm{ppm}$ ), which correspond to three isopropyl groups and the presence of a 3 H singlet peak at $\delta$
2.29 ppm corresponds to the methyl imine functionality. Mass spectrometry reveals a protonated molecular ion peak at $395 \mathrm{~m} / z$. This agrees with the high-resolution mass spectrometry (HRMS TOF), where the calculated molecular mass for the compound is $395.2699 \mathrm{~m} / \mathrm{z}$. IR data of the pro-ligand shows peaks at $1585 \mathrm{~cm}^{-1}, 1670 \mathrm{~cm}^{-1}$ and 1751 $\mathrm{cm}^{-1}$ which are indicative of the $\mathrm{C}-\mathrm{N}$ pyridine, $\mathrm{C}=\mathrm{N}$ imine and $\mathrm{C}=\mathrm{O}$ ester bonds, respectively.

Furthermore, crystals suitable for X-ray diffraction studies of EtLs were obtained by slow evaporation of a saturated solution in chloroform. The solid-state structure further supports the conclusions from the other characterisation data (Figure 5.14). Selected bond lengths and bond angles for EtLs are given in Table 5.1.


Figure 5.14-Molecular structure of EtLs. Hydrogen atoms have been omitted for clarity

Table 5.1 - Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for one molecule of EtLs

BOND LENGTH (Å)

| N(2)-C(6) | 1.282(2) | $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(23)$ | 118.80(18) |
| :---: | :---: | :---: | :---: |
| N(2)-C(8) | 1.430(2) | N(2)-C(6)-C(5) | 116.21(18) |
| $\mathrm{C}(23)-\mathrm{O}(1)$ | 1.327(2) | $\mathrm{O}(1)-\mathrm{C}(23)-\mathrm{C}(1)$ | 113.11(18) |
| $\mathrm{C}(23)-\mathrm{O}(2)$ | 1.197(2) | $\mathrm{O}(2)-\mathrm{C}(23)-\mathrm{C}(1)$ | 122.5(2) |

The molecular structure of EtLs consists of a central pyridine unit substituted at its 6position by the ethyl ester fragment and at its 2-position by the aryl-imine-containing unit. The imine $\mathrm{C}=\mathrm{N}$ is coplanar with the pyridine backbone. The triisopropylsubstituted imino-aryl ring is oriented almost perpendicular to the pyridine ring, with a dihedral angle of $97.7^{\circ}$. The carbonyl linkage $\mathrm{O}(2)-\mathrm{C}(23)$ and the imine linkage $\mathrm{N}(2)$ $\mathrm{C}(6)$ have distinctive double-bond characters displaying distances of 1.282(2) and $1.197(2) \AA$, respectively. It is noteworthy that $\mathrm{N}(2)-\mathrm{C}(8)$ bond adjacent to the $\mathrm{N}(2)-\mathrm{C}(6)$ imine double bond is slightly shorter than a normal C-N single bond. The ester group on the ligand is flexible and disordered due to its free rotation. In addition, the X-ray diffraction data reveals that there are two crystallographically independent albeit relatively similar molecules in one asymmetric unit cell.

### 5.3.2.6 Synthesis of ethyl (E)-6-(1-((2,6-diisopropyl-4-bromophenyl)imino) ethylpicolinate (EtL9)

As with the synthesis of EtL7 and EtLs, pro-ligand EtL9 was prepared via a condensation reaction of ethyl 6 -acetylpicolinate and commercially available 2,6diisopropylbromoaniline (Figure 5.15). Identical reaction conditions were employed and the product was obtained as a brown solid in excellent purity and excellent yield. Purification of the crude compound by flash column chromatography was not necessary and the pure product was isolated upon recrystallisation from hot methanol.


Figure 5.15-Synthesis of EtL, 9

A 3 H singlet at $\delta 2.21 \mathrm{ppm}$ in ${ }^{1} \mathrm{H}$ NMR spectrum of the ligand was assigned to the methyl-imine unit and the 12 H doublet at $\delta 1.06 \mathrm{ppm}$ corresponds to two isopropyl groups. IR data of the pro-ligand shows characteristic peaks at $1583 \mathrm{~cm}^{-1}, 1670 \mathrm{~cm}^{-1}$ and $1746 \mathrm{~cm}^{-1}$ which are indicative of the $\mathrm{C}=\mathrm{N}$ pyridine, $\mathrm{C}=\mathrm{N}$ imine and $\mathrm{C}=\mathrm{O}$ ester bonds, respectively. A protonated molecular ion peak of $m / z 431$ was found in ESIMS further confirming the formation of the desired compound. The TOF analysis of the
product revealed a molecular ion peak at 431.1318, while the calculated value for $\mathrm{C}_{22} \mathrm{H}_{28} \mathrm{~N}_{2} \mathrm{O}_{2}{ }^{79} \mathrm{Br}(\mathrm{M}+\mathrm{H})^{+}$is 431.1334 .

### 5.3.2.7 Attempted synthesis of 2-carboxylic acid-6-iminopyridine pro-ligands

It is worth mentioning that the initial target pro-ligand was supposed to incorporate a carboxylic acid in the 6-position of the pyridine ring following ethyl ester hydrolysis. It was expected that there would be some loss of product as the imine group is also susceptible to hydrolysis. The reaction carried out with EtL 7 , adapted by H. Sugihara et al., yielded a pale brown solid as the product. ${ }^{35}$ The ${ }^{1} \mathrm{H}$ NMR spectra showed a singlet with integration of 3 H at 2.80 ppm , which was much higher than previous reports expected for the imine-methyl group. A broad peak seen at 10.0 ppm was predicted for the carboxylic acid proton, however the integration of this peak indicated a 4 H environment which was not consistent with the expected outcome. The ESI data showed two peaks at 178 and $164 \mathrm{~m} / z$, whereas the desired product would have a peak at 324 $m / z$. From the data obtained, it was assumed that the isolated solid was not the desired target product.

As previously predicted, it is possible for the imine to be hydrolysed back to a ketone. Upon acidification this would typically give two products (Figure 5.16).


Figure 5.16-By-products formed from the hydrolysis of the imine
The ketone group on the keto-acid is consistent with the 3 H environment seen at 2.80 ppm in the ${ }^{1} \mathrm{H}$ NMR spectrum of the product. The protonated amine would also give a broad peak in the same region as the carboxylic acid, accounting for the 4 H integration. Concentrated HCl was added to 2,6-diisopropylaniline and the ${ }^{1} \mathrm{H}$ NMR spectrum recorded, confirming that the peaks at $7.3,7.2,3.8$ and 1.3 ppm can be assigned to protonated dipp- $\mathrm{NH}_{2}$. The ${ }^{13} \mathrm{C}$ NMR spectrum further confirms the presence of a ketone peak, as a carbon centre with a peak at 197.6 ppm is seen.

One possible cause for the reaction to give none of the desired product is overacidification during the work-up, when the pH was taken to 3 . Taking this into the
account, the synthesis was attempted again using the same experimental procedure and a crude NMR sample was run before the acid work-up. The NMR of the aliquot showed an imine peak at 2.2 ppm , and no sign of a ketone peak at 2.70-2.80 ppm. A quartet and a triplet peak were observed at 3.62 and 1.15 ppm , respectively, which correlate to ethanol. Without an acid work-up, the carboxylic acid seems to be in its deprotonated carboxylate form, and hence, no peak is seen at 10-12 ppm.

In attempt to purify the product, a milder acid work-up was attempted, however this led to the same decomposition of the ligand to the keto-acid and protonated aniline. It was evident that a new approach to synthesising target palladium complexes was necessary. This new synthetic route will be discussed in Section 5.3.3 of this work.

### 5.3.3 Complexation of pro-ligands $E t L_{7}$, EtLs and EtL9 to Palladium(II)

Reactions of pro-ligands EtL7, EtLs and EtL9 with $\mathrm{Pd}(\mathrm{OAc})_{2}$ afford palladiumcontaining complexes supported by monoanionic $\left[\mathrm{N}, \mathrm{N}_{P y}, \mathrm{O}\right]$ pincer ligands in good yield. All complexes have been characterised by a combination of ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectroscopy, IR spectroscopy, ESMS and HRMS (FAB, TOF, ASAP).

As discussed in Section 5.2.2.7, the iminopyridyl carboxylic acid pro-ligand could not be isolated from hydrolysis reactions due to the sensitivity of the imine group to the acid environment. Therefore, a study involving the reaction of EtL 7 with $\mathrm{Pd}(\mathrm{OAc})_{2}$ to form 5a in a two-step process (Figure 5.17) was attempted. Protection of the imine group through coordination of the nitrogen to the Pd centre was proposed. The exposed ester group could then be selectively hydrolysed to the carboxylate, using the hydrolysis method previously attempted to form EtL7. With the imine group protected, the carboxylate can be acidified to a carboxylic acid without destroying the molecule. This will then be expected to bond with the Pd centre and acetic acid will be released, forming the target complex $\left[\mathrm{L}_{7} \mathrm{Pd}(\mathrm{OAc})\right](\mathbf{5 a})$.


Figure 5.17-Proposed two-step synthesis to form $\left[\boldsymbol{L}_{7} \mathrm{Pd}(\mathrm{OAc})\right]$ (5a) from $\mathrm{H}_{7}$

W-H. Sun and co-workers have previously reported the reaction of $\mathrm{EtL}_{7}$ with $\mathrm{PdCl}_{2}$, as well as other metal chlorides such as $\mathrm{NiCl}_{2} \mathrm{CoCl}_{2}$ and $\mathrm{FeCl}_{2}$. ${ }^{124} \mathrm{All}$ reported examples of EtL7 have formed bidentate complexes with cis chloride ligands, and therefore, the identical reactivity was predicted with $\mathrm{Pd}(\mathrm{OAc})_{2}$ to form $\mathbf{5 a}$, $\cdot{ }^{130}$

### 5.3.3.1 Synthesis of Imine-Containing $\left[\left(N, N_{P, y} O\right) P d O A c\right]$ complexes: $5 \mathrm{a}, 5 \mathrm{~b}$ and 5 c Synthesis of 5a

However, when the above method was applied, some unexpected outcomes were observed. Initially, the reaction of $\mathrm{EtL}_{7}$ and $\mathrm{Pd}(\mathrm{OAc})_{2}$ was attempted on a small scale ( 0.014 mmol ). After 20 minutes of stirring at room temperature, the ${ }^{1} \mathrm{H}$ NMR spectrum of the crude product already showed $40 \%$ conversion to a product (Figure 5.18).


Figure 5.18- ${ }^{1} H$ NMR spectrum after 20 minutes, a quartet at 3.65 ppm and a triplet at 1.15 ppm are newly formed

Further stirring for 24 h showed the reaction had gone to $100 \%$ conversion with no peaks due to $\mathrm{EtL}_{7}$ (Figure 5.19).


Figure 5.19- ${ }^{1} H$ NMR spectrum after 24 hours, reaction has gone to completion

In order to understand what has occured, purification of the crude product was necessary. The reaction mixture was passed through a Celite plug, which was washed with chloroform and the collected solid was extracted into acetonitrile. The solution was removed in vacuo overnight to form the product as a yellow solid in high yield.

The ${ }^{1} \mathrm{H}$ NMR analysis of the isolated product revealed some interesting data in relation to coordination of the ligand to palladium (Figure 5.20). Interestingly, the peaks typical for ester group for $\mathrm{Et} \mathrm{L}_{7}$ observed at $\delta 3.65 \mathrm{ppm}$ and $\delta 1.15 \mathrm{ppm}$ were no longer present. The 12 H doublet at $\delta 1.06 \mathrm{ppm}$ corresponding to two isopropyl groups had split into two 6 H doublets, indicating that the methyl substituents on the isopropyl groups are inequivalent which is typical for coordination of the imine group to a metal.


Figure 5.20- ${ }^{1} H$ NMR spectra of pure product isolated from the reaction

From these results, it can be concluded that the reaction of EtL 7 with $\mathrm{Pd}(\mathrm{OAc})_{2}$ results in cleavage of the ester group and tridentate coordination of the ligand to the metal in a single step to generate 5a in 97\% yield (Figure 5.21).


Figure 5.21- Synthesis of 5a

A protonated molecular ion peak of $m / z 488$ was found in ESIMS further confirming the formation of the desired compound. The TOF analysis of the product revealed a fragmentation ion peak at 429.0886 corresponding to $[(\mathrm{M}+\mathrm{H})-\mathrm{OAc}]^{+}$. A melting point in the range of $250-253{ }^{\circ} \mathrm{C}$ was recorded, providing further confirmation that a palladium complex had been formed. A melting point in this range is characteristic for these metal complexes due to thermal stability gained from chelation of the pincer ligand to the metal centre.

The compound was found to be soluble in acetonitrile and dichloromethane, however less polar solvents such as chloroform showed partial/no solubility of the complex.

Methanol was tested as a suitable solvent for NMR studies; however, the compound showed signs of degradation after 1 hour. After 24 hours, a black powder remained, suggesting that the complex was unstable in the highly polar solvent. Acetonitrile was, therefore, chosen as solvent of choice for all subsequent reactions.

The solid-state structure of $\mathbf{5 a}$ has been determined by a single crystal X-ray diffraction analysis and the crystals were grown upon slow evaporation of 5a in acetonitrile solution. The X-ray crystal structure of the complex strongly supported the other characterisation data and confirmed the product to be the expected acetate palladium complex of EtL7. Selected bond lengths and angles of 5a are reported in Table 5.2 while the molecular structure is presented in Figure 5.22.


Figure 5.22-Molecular structure of 5a

Table 5.2 - Selected bond lengths $(\AA)$ and bond angles $\left({ }^{\circ}\right)$ for one molecule of 5 a

BOND LENGTH (Å)

| $\mathrm{C}(7)$-N(2) | $1.315(10)$ | $\mathbf{N}(1)-\mathbf{P d}(1)-\mathbf{N}(2)$ | 80.9(3) |
| :---: | :---: | :---: | :---: |
| $\mathrm{C}(1)-\mathrm{O}(1)$ | 1.303(9) | $\mathrm{N}(1)-\mathrm{Pd}(1)-\mathrm{O}(1)$ | 80.4(3) |
| $\mathbf{P d}(1)-\mathrm{O}(1)$ | 2.048 (5) | $\mathrm{N}(2)-\mathrm{Pd}(1)-\mathrm{O}(3)$ | 97.1(2) |
| $\mathbf{P d}(1)-\mathrm{N}(1)$ | 1.897(7) | $\mathrm{O}(1)-\mathrm{Pd}(1)-\mathrm{O}(3)$ | 100.5(2) |
| $\mathbf{P d}(1)-\mathrm{N}(2)$ | 2.010(7) | $\mathrm{C}(7)-\mathrm{N}(2)-\mathrm{Pd}(1)$ | 113.7(6) |
| $\mathbf{P d}(1)-\mathrm{O}(3)$ | 2.011(6) | $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{Pd}(1)$ | 112.1(5) |

The unit cell contains two molecules of $\mathbf{5 a}$ and there is intra-molecular and intermolecular hydrogen bonding. The complex exhibits a square planar coordination geometry with a tridentate ligand binding to palladium(II) through the $N, N_{P y}, O$ donor sites. The 2,6 -(diisopropyl)aryl unit is tilted with respect to the coordination plane displaying a dihedral angle of $88.4(10)^{\circ}$ due to the apparent steric repulsion between the coordinating acetate moiety and an isopropyl group from the ligand.

The de-esterification seen in this reaction has not been previously reported in the literature. It was of particular interest to see if the observed de-esterification was repeated with the pro-ligands EtLs and EtL9.

## Synthesis of 5b

The reaction of EtLs with $\mathrm{Pd}(\mathrm{OAc})_{2}$ was performed following the same experimental approach as the reaction of $\mathbf{5 a}$ (Figure 5.23). After 18 hours of stirring, hexane was added to lower the solubility and aid precipitation. After 3 hours, solid was passed through a Celite plug, dissolved in chloroform and dried, yielding a yellow solid in high yield and of excellent purity.

$E t L_{8}$
5b

Figure 5.23-Synthesis of 5b

Upon analysis of the ${ }^{1} \mathrm{H}$ NMR spectrum, as seen for $\mathbf{5 a}$, the quartet at $\delta 4.49 \mathrm{ppm}$ and the triplet at $\delta 1.46 \mathrm{ppm}$ of the ester functionality had disappeared. The 12 H doublet at $\delta$ 1.13 ppm for the free ligand corresponding to two isopropyl groups had also split into two inequivalent 6 H doublets. The characteristic imine peak at $\delta 2.38 \mathrm{ppm}$ and the pair of septets at $\delta 3.26$ and $\delta 2.91 \mathrm{ppm}$ suggest that the ligand remains intact. No ketone peak is observed at $c a . \delta 2.7 \mathrm{ppm}$, thus indicating that the imine had not been hydrolysed before reacting with $\mathrm{Pd}(\mathrm{OAc})_{2}$. A 3 H singlet peak is observed at $\delta 1.53$ ppm , corresponding to the acetate donor group bound to palladium. Only one acetate peak is seen, providing further support that the ligand had coordinated in a tridentate fashion. This is further supported by the high melting point of $253^{\circ} \mathrm{C}$, as the complexes are thermally stable due to chelation of the ligand to the metal centre.

The complex $\mathbf{5 b}$ exhibits an increased solubility over $\mathbf{5 a}$ in organic solvents, readily dissolving in chloroform and dichloromethane. Analysis of $\mathbf{5 b}$ by ${ }^{13} \mathrm{C}$ NMR spectroscopy further confirms the inequivalence within the isopropyl-methyl environments by the presence of two distinct $\mathrm{CH}_{3}$ carbon environments for these fragments. Further evidence for the presence of imine, Pd-bound acetate and carboxylate units is provided by the presence of quaternary carbon peaks at $\delta 170.6$ $\mathrm{ppm}, \delta 177.6 \mathrm{ppm}$ and $\delta 177.2 \mathrm{ppm}$.

In addition, the TOF analysis of the product revealed a fragmentation ion peak at 471.1286 corresponding to $\left[(\mathrm{M}-\mathrm{OAc}]^{+}\right.$. The infrared spectrum showed the characteristic $\mathrm{C}=\mathrm{N}_{\text {imine }}, \mathrm{C}=\mathrm{N}_{\mathrm{Py}}$ and $\mathrm{COO}_{\text {symm }}$ absorption peaks at 1668,1595 and $1314 \mathrm{~cm}^{-1}$, respectively. In comparison with the free ligand's stretching frequency of the $\mathrm{C}=\mathrm{N}_{\mathrm{imine}}$ bond, $\mathbf{5 b}$ shows a shift in the $\mathrm{C}=\mathrm{N}_{\text {imine }}$ stretching vibration towards a lower frequency indicating an interaction between the imino nitrogen atom and the palladium centre.

The above-mentioned data would suggest that EtLs has also undergone de-esterification upon reaction with $\mathrm{Pd}(\mathrm{OAc})_{2}$.

## Synthesis of 5c

The synthesis of $[\mathbf{L g}(\mathrm{PdOAc})](\mathbf{5 c})$ from the pro-ligand EtL9 in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}$ occurs smoothly at room temperature following the same experimental conditions as those for the formation of $\mathbf{5 a}$ and $\mathbf{5 b}$ (Figure 5.24).


Figure 5.24-Synthesis of 5c

Analysis of $\mathbf{5 c}$ by ${ }^{1} \mathrm{H}$ NMR spectroscopy, similarly to those for $\mathbf{5 a}$ and $\mathbf{5 b}$, shows that the quartet at $\delta 4.42 \mathrm{ppm}$ and the triplet at $\delta 1.39 \mathrm{ppm}$ had disappeared. In addition, the 12 H doublet at $\delta 1.06 \mathrm{ppm}$ had also split into two distinct 6 H doublet peaks. This indicates that the isopropyl groups present in the molecule are inequivalent upon binding to the Pd centre. Moreover, the presence of 3 H singlet peaks at $\delta 1.63$ and $\delta$ 2.39 are representative of $\mathrm{CH}_{3} \mathrm{C}(\mathrm{O}) \mathrm{O}$ and methyl-imine proton environments, respectively. Analysis of $\mathbf{5 c}$ by ${ }^{13} \mathrm{C}$ NMR spectroscopy further confirms the inequivalence within the isopropyl-methyl environments by the presence of two distinct $\mathrm{CH}_{3}$ carbon environments for these fragments. Further evidence for the presence of imine, Pd-bound acetate and carboxylate units is provided by the presence of quaternary carbon peaks at $\delta 177.7 \mathrm{ppm}, \delta 177.3 \mathrm{ppm}$ and $\delta 153.3 \mathrm{ppm}$. Infrared spectroscopy reveals features attributable to $N, N_{P y}, O$ ligand coordination, namely a $\mathrm{C}=\mathrm{N}$ stretch at $1667 \mathrm{~cm}^{-1}$. The shift of the imine stretch to a lower wavenumber again is indicative of imine coordination, due to backbonding from the palladium. An additional $\mathrm{COO}_{\text {symm }}$ stretch at $1309 \mathrm{~cm}^{-1}$ confirms the presence of a monodentate acetate ligand. In addition, a strong fragmentation peak corresponding to $\mathbf{5 c}$ with the labile acetate unit removed was found upon analysis by mass spectrometry at $506.9 \mathrm{~m} / \mathrm{z}$ [M-OAc] ${ }^{+}$.

### 5.3.3.2 Imine-Containing $\left[\left(N, N_{P y}, O\right) P d C l\right]$ complexes 5.1a, 5.1b and 5.1c

## Synthesis of 5.1a

The palladium(II) chloride complex 5.1a was obtained by treatment of its palladium(II) acetate derivative with aqueous sodium chloride via the ligand exchange reaction (Figure 5.25). The synthesis was complete within one hour, affording the desired complex in excellent yield following purification by crystallisation.


Figure 5.25-Synthesis of 5.1a

Chloride-containing 5.1a was characterised by ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectroscopies, IR spectroscopy, HRMS (TOF) spectrometry. Upon analysis by ${ }^{1} \mathrm{H}$ NMR spectroscopy, 5.1a reveals that all proton environments are shifted from the acetate-containing precursor 5a. Furthermore, the absence of a 3 H singlet peak at $\delta 1.52 \mathrm{ppm}$ corresponding to the ancillary acetate ligand indicates a replacement by a chloride donor ligand. This is further confirmed through the absence of the ancillary acetate ligand in ${ }^{13} \mathrm{C}$ NMR spectroscopy where no quaternary carbon environment at $\delta 177.4$ ppm is detected. Moreover, the TOF analysis of the product revealed a strong molecular ion peak at $m / z 465.0424$ while the calculated value for $\mathrm{C}_{20} \mathrm{H}_{23} \mathrm{ClN}_{2} \mathrm{O}_{2} \mathrm{Pd}$ is 465.0409 . The infrared spectrum showed the characteristic $\mathrm{C}=\mathrm{N}_{\mathrm{Py}}$ and $\mathrm{C}=\mathrm{N}_{\text {imine }}$ absorption peaks at 1558 and $1663 \mathrm{~cm}^{-1}$, respectively.

In addition, single crystals suitable for X-ray diffraction analysis were grown by slow evaporation of chloroform. The molecular structure was determined and showed to contain the palladium(II) chloride core supported by meridional $N, N_{P y}, O$ pincer ligand (Figure 5.26) and further supports the spectroscopic data.


Figure 5.26-Molecular structure of 5.1a. Hydrogen atoms and a single MeCN molecule have been omitted for clarity

Table 5.3-Selected bond lengths $(\AA)$ and bond angles $\left({ }^{\circ}\right)$ of 5.1a
BOND LENGTH (Å)

| $\mathbf{C}(\mathbf{7})-\mathbf{N}(\mathbf{2})$ | $1.299(5)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $80.43(12)$ |
| :--- | :---: | :---: | :---: |
| $\mathbf{C}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $1.301(4)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $80.92(11)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $2.048(2)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{C l}(\mathbf{1})$ | $100.89(9)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $1.913(3)$ | $\mathbf{O}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{C l}(\mathbf{1})$ | $97.77(8)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $2.027(3)$ | $\mathbf{C}(\mathbf{8})-\mathbf{C}(\mathbf{7})-\mathbf{N}(\mathbf{2})$ | $125.4(3)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{C l}(\mathbf{1})$ | $2.2918(9)$ | $\mathbf{C}(\mathbf{1})-\mathbf{O}(\mathbf{1})-\mathbf{P d}(\mathbf{1})$ | $113.3(2)$ |

The complex adopts a square planar geometry typical of palladium pincer complexes with angles relatively close to $90^{\circ}$. Upon close analysis of the molecular structure of 5.1a, the shortest tridentate donor to metal bond is $\operatorname{Pd}(1)-\mathrm{N}(1)[1.913(3) \AA$. The longest palladium bond is $\operatorname{Pd}(1)-\mathrm{Cl}(1)$ [2.2918(9) $\AA$ ]. The bite angle exhibited by the $5-$ membered metallocycle $\left[\mathrm{N}(1)-\mathrm{Pd}(1)-\mathrm{N}(2) 80.43(12)^{\circ}\right]$ is similar to that exhibited by the 5-membered metallocycle $\left[\mathrm{N}(1)-\mathrm{Pd}(1)-\mathrm{O}(1) 80.92(11)^{\circ}\right]$. The tridentate $N, N_{P y}, O$ ligand core is planar and the $N$-aryl fragment is positioned perpendicular to the pyridyl plane.

## Synthesis of 5.1b

The reaction of $\mathbf{5 b}$ with saturated aqueous sodium chloride was performed under the same experimental conditions as those used for the synthesis of 5.1a (Figure 5.27). The complex was afforded in excellent yield without further purification.


Figure 5.27-Synthesis of 5.1b

Analysis of 5.1b by ${ }^{1} \mathrm{H}$ NMR spectroscopy reveals analogous behaviour to that observed for 5.1a. The absence of a 3 H singlet peak at $\delta 1.50 \mathrm{ppm}$ corresponding to the ancillary acetate ligand indicates a replacement by a chloride ligand. The methyl-imine peak at $\delta 2.26 \mathrm{ppm}$ and the pair of septets at $\delta 2.97 \mathrm{ppm}$ and $\delta 2.83 \mathrm{ppm}$ suggests the ligand remains intact. The incorporation of a chloride donor ligand was also confirmed through analysis of 5.1b by TOF, whereupon a strong molecular ion peak is observed at $\mathrm{m} / \mathrm{z} 507.1030$ while the calculated value is 507.1031 .

## Synthesis of 5.1c

The synthesis of $\mathbf{5 . 1} \mathbf{c}$ from $\mathbf{5 c}$ is complete within three hours, affording the desired complex in $71 \%$ isolated yield without any purification (Figure 5.28). Chloridecontaining 5.1c was isolated and characterised by ${ }^{1} \mathrm{H}$ NMR spectroscopy, IR spectroscopy, mass spectrometry and X-ray diffraction.


Figure 5.28-Metathesis reaction to form 5.1c

Upon analysis by ${ }^{1} \mathrm{H}$ NMR spectroscopy, 5.1c reveals that all resonances are shifted from the acetate precursor compound. Furthermore, the absence of a 3 H singlet peak at $\delta 1.63 \mathrm{ppm}$ corresponding to the ancillary acetate ligand indicates a replacement by another donor group. Further evidence for the absence of the ancillary acetate ligand is seen in ${ }^{13} \mathrm{C}$ NMR spectroscopy where no quaternary carbon environment at $\delta 177.3 \mathrm{ppm}$ is detected. In addition, the presence of two 6 H doublet peaks ( $\delta 1.07 \mathrm{ppm}$ and $\delta 1.30$ ppm ) coupling to the same 2 H septet peak ( $\delta 3.07 \mathrm{ppm}$ ) are indicative of restricted rotation around the $\mathrm{C}_{\mathrm{Ar}}-\mathrm{N}_{\mathrm{imin}}$ bend in complexes incorporating N -(2,6diisopropylphenyl) substituted pincer ligands. This characteristic, besides the presence of a 3 H singlet peak at $\delta 2.22 \mathrm{ppm}$, confirms that the $N$-(2,6-diisopropylphenyl)-imine unit remains intact upon reaction to form 5.1c. The successful incorporation of a chloride donor ligand was also confirmed through analysis of 5.1c by mass spectrometry, wherein both molecular ion peak ( $\mathrm{m} / \mathrm{z} 544[\mathrm{M}]^{+}$) and a strong fragmentation peak corresponding to the loss of chloride and a solvent adduct ( $\mathrm{m} / \mathrm{z}$ $\left.550.0167[(\mathrm{M}-\mathrm{Cl})+\mathrm{MeCN}]^{+}\right)$were detected.

Upon standing at room temperature in acetonitrile solution, single crystals of 5.1c suitable for X-ray diffraction studies were obtained (Figure 5.29). The crystal structure confirmed the product as the desired palladium chloride complex of 5.1c. Selected bond lengths and angles are given in Table 5.4.


Figure 5.29-Molecular structure of 5.1c. The hydrogen atoms have been omitted for clarity

Table 5.4-Selected bond lengths ( $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 5.1c
BOND LENGTHS (Å)

| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $2.011(5)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $80.6(2)$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $1.926(4)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $80.7(18)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{C l}(\mathbf{1})$ | $2.297(16)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{C l}(\mathbf{1})$ | $98.8(14)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $2.050(4)$ | $\mathbf{O}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{C l}(\mathbf{1})$ | $100.1(12)$ |
| $\mathbf{C}(\mathbf{7})-\mathbf{N}(\mathbf{2})$ | $1.294(7)$ | $\mathbf{C}(\mathbf{8})-\mathbf{C}(\mathbf{7})-\mathbf{N}(\mathbf{2})$ | $127.4(6)$ |
| $\mathbf{C}(\mathbf{1 4})-\mathbf{O}(\mathbf{1})$ | $1.300(7)$ | $\mathbf{C}(\mathbf{1 4})-\mathbf{O}(\mathbf{1})-\mathbf{P d}(\mathbf{1})$ | $113.7(4)$ |

Detailed analysis of the molecular structure shows that the imine unit has remained intact $\left[\mathrm{C}(7)-\mathrm{N}(2) 1.294(7) \AA\right.$ and $\left.\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{N}(2) 127.4(6)^{\circ}\right]$. Analysis of the $\mathrm{C}(7)-\mathrm{N}(2)$ bond length reveals characteristic lengths typically predicted for a coordinated methylimine fragment $[1.294(7) \AA]$. Moreover, the bond angles are in agreement with an $\mathrm{sp}^{2}$ hybridised imine functionality $\left[\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{N}(2) 127.4(6)^{\circ}\right]$. Similar to the parameters observed in 5.1a, the shortest pincer ligand donor to palladium bond in 5.1c is $\operatorname{Pd}(1)-$
$\mathrm{N}(1)[1.926(4) \AA]$ and the longest tridentate donor to metal bond is $\mathrm{Pd}(1)-\mathrm{O}(1)$ [2.050(4) $\AA$ ].

### 5.3.3.3 Imine-Containing $\left[\left(N, N_{P y}, O\right) P d(M e C N)\right]\left[P_{6}\right]$ complexes 5.2a, 5.2b and 5.2c

## Synthesis of 5.2a

Mono-cationic complex 5.2a with a labile, two-electron donor ligand was synthesised by a silver-mediated chloride abstraction from 5.1a with $\mathrm{AgPF}_{6}$ (Figure 5.30). Exchanging the chloride ligand with silver salts is facile and forms insoluble AgCl solid as the by-product which can be easily removed upon filtration. The product was isolated as a yellow solid in high yield.


Figure 5.30-Synthesis of 5.2a

Attempts at recrystallisation were not successful, as even a small addition of solvent turned the product to a viscous residue. This is likely to be due to the mono-cationic complex coordinating to water molecules in the solvent.

Analysis by ${ }^{1} \mathrm{H}$ NMR spectroscopy reveals a characteristic peak for the methyl signal of the bound acetonitrile at $\delta 2.25 \mathrm{ppm}$. All the peaks have been shifted downfield compared to what was observed for 5.1a. The presence of the acetonitrile methyl signal can be observed in 13C NMR spectrum at $\delta 1.1 \mathrm{ppm}$. Evidence for the formation of 5.2a can also be seen in the ${ }^{31} \mathrm{P}$ and ${ }^{19} \mathrm{~F}$ NMR. The ${ }^{31} \mathrm{P}$ NMR showed a septet at -144.5 ppm ( ${ }^{1} J_{\mathrm{PF}} 705.8 \mathrm{~Hz}$ ), corresponding to the central phosphorus atom splitting from the 6 spin active fluorine atoms. A doublet in the ${ }^{19} \mathrm{~F}$ NMR is also seen at -72.9 ppm with an equivalent $J$ value of 705.8 Hz . Analysis by TOF mass spectrometry reveals a molecular
ion peak of $m / z 470.1060$, corresponding to the cationic complex $\left[\mathrm{HL}_{7} \mathrm{Pd}(\mathrm{MeCN})\right]^{+}$. The anion $\mathrm{PF}_{6}{ }^{-}$is seen in the ESI mass spectrometry at a peak of $\mathrm{m} / \mathrm{z} 145$.

## Synthesis of 5.2b

The same synthetic protocol was applied for the synthesis of the cationic complex $[\mathrm{EtLsPd}(\mathrm{MeCN})]^{+}\left[\mathrm{PF}_{6}\right]^{-}$5.2b from the precursor 5.1b (Figure 5.31). The reaction requires the presence of acetonitrile to form the desired product, as it is the two-electron donor required to be exchanged with the chloride. As $\mathbf{5 . 2 b}$ is insoluble in acetonitrile, the complex was dissolved in chloroform and added to a solution of $\mathrm{AgPF}_{6}$ in acetonitrile. The pure product was isolated as a yellow solid in high yield.


Figure 5.31-Synthesis of 5.2b

Analysis of 5.2b by ${ }^{1} \mathrm{H}$ NMR spectroscopy reveals a 3 H singlet peak at $\delta 1.19 \mathrm{ppm}$ ascribed to be the coordinated MeCN proton environment. All the peaks in the spectrum have been shifted compared to what was observed for 5.1b. Additionaly, ${ }^{19} \mathrm{~F}$ NMR spectroscopy reveals a doublet at $\delta-72.9 \mathrm{ppm}$ and the ${ }^{31} \mathrm{P}$ NMR showed a septet at $144.5 \mathrm{ppm}\left({ }^{1} J_{\mathrm{PF}} 705.8 \mathrm{~Hz}\right.$ ), corresponding to the central phosphorus atom splitting from the 6 spin active fluorine atoms. Analysis of 5.2b by ESI mass spectrometry reveals a signal at $m / z 512\left[\mathrm{M}-\mathrm{PF}_{6}\right]^{+}$.

## Synthesis of 5.2c

The formation of palladium(II) acetonitrile cation 5.2c from the chloride precursor employing same reaction conditions as for 5.2a and 5.2b, interestingly showed signs of decomposition. Therefore, a different synthetic approach was employed in this case. The reaction was carried out first by treating $\mathrm{PdCl}_{2}(\mathrm{MeCN})_{2}$ with $\mathrm{AgPF}_{6}$ in anhydrous acetonitrile to form $\operatorname{Pd}(\mathrm{MeCN})_{2}\left(\mathrm{PF}_{6}\right)_{2}$ species which further reacted with EtL 9 to yield 5.2c in good yield (Figure 5.32).


Figure 5.32-Synthesis of 5.2c

Upon analysis of the ${ }^{1} \mathrm{H}$ NMR spectrum, the quartet and the triplet at $\delta 4.42$ and 1.39 ppm , respectively, belonging to the ethyl ester group, had disappeared. The 12 H doublet coming at $\delta 1.06 \mathrm{ppm}$ in the free ligand and corresponding to two isopropyl groups had also split into two 6 H doublets. In addition, a characteristic peak in the ${ }^{1} \mathrm{H}$ NMR spectrum corresponding to the methyl signal of the bound acetonitrile is observed at $\delta$ 1.85 ppm . The presence of the acetonitrile methyl signal can be observed in 13C NMR spectrum at $\delta 1.8 \mathrm{ppm}$. The formation of the palladium acetonitrile complex $\mathbf{5 . 2} \mathbf{c}$ can be seen through ${ }^{31} \mathrm{P}$ and ${ }^{19} \mathrm{~F}$ NMR spectroscopy. A septet at $-144.5 \mathrm{ppm}\left({ }^{1} J_{\text {PF }} 705.7 \mathrm{~Hz}\right)$ corresponding to the phosphous atom splitting from the six spin active fluorine atoms is observed in the ${ }^{31} \mathrm{P}$ NMR. The ${ }^{19} \mathrm{~F}$ NMR showed a doublet at -71.9 ppm with an equivalent $J$ value of 705.7 Hz .

### 5.3.3.4 Exchange of the MeCN ligand for pyridines

## Synthesis of 5.3a, 5.4a and 5.5a

With a view to synthesise complexes with potential catalytic properties, a relatively labile acetonitrile auxiliary ligand was exchanged for pyridines. The exchange of the MeCN coordinating ligand for pyridine rapidly occurred in chloroform at room temperature (Figure 5.33). The absence of the characteristic methyl signal of the MeCN moiety can be observed from the ${ }^{1} \mathrm{H}$ NMR spectrum of the reaction product. Furthermore, the presence of an additional five proton environments in the aromatic region and the upfield shift of the septet from 3.42 ppm to 3.06 ppm and doublet signals of the di-isopropyl moieties from $1.13 / 1.32 \mathrm{ppm}$ to $0.98 / 1.16 \mathrm{ppm}$, respectively, compared to the palladium(II) acetonitrile precursor complex can confirm the formation
of the proposed structure. Both ES and HR mass spectroscopies displayed a molecular ion peak at $m / z 508$ corresponding to the loss of $\mathrm{PF}_{6}{ }^{-}$counter ion $\left[\mathrm{M}-\mathrm{PF}_{6}\right]^{+}$.


Figure 5.33-Exchange of MeCN ligand with pyridines to form 5.3a, 5.4a and 5.5a

Interestingly, application of similar exchange reactions with 3,5-dichloropyridine and 3,5-dimethylpyridine proved unsuccessful as no reactivity was observed. This is thought to be due to the result of steric bulk imparted by the 2,6-diisopropyl phenyl ring. In light of these results, the exchange with less sterically demanding pyridines, such as $4-^{\text {t }} \mathrm{Bu}$ pyridine and 3-bromopyridine, was also attempted. Similarly, to the reaction with pyridine, reactions with $4-^{t} \mathrm{Bu}$ pyridine and 3-bromopyridine to form 5.4a and 5.5a, respectively, occur rapidly and smoothly at ambient temperature. Analytical data acquired for products are consistent with the proposed structures. The presence of additional proton signals in the aromatic region of the ${ }^{1} \mathrm{H}$ NMR spectra and the disappearance of the methyl signals of the MeCN ligand, indicate the formation of the palladium(II)-pyridine type complexes. HRMS spectroscopy of these two complexes also revealed peaks characteristic of $\left[\mathrm{M}-\mathrm{PF}_{6}\right]^{+}$, indicating a successful binding of the corresponding pyridines.

It was possible to grow single crystals of 5.5a suitable for analysis by X-ray diffraction by slow diffusion of petroleum ether into a solution of the complex in chloroform (Figure 5.34). Selected bond lengths and angles are shown in Table 5.6.



Figure 5.34 - Molecular structure of 5.5a. The hydrogen atoms have been omitted for clarity

Table 5.5-Selected bond lengths ( $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 5.5 a

BOND LENGTHS (Å)

| $\boldsymbol{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $1.918(9)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $79.3(4)$ |
| :--- | :---: | :---: | :---: |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $2.047(9)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $81.8(4)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $2.033(9)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $175.7(4)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $2.035(7)$ | $\mathbf{O}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $94.0(3)$ |
| $\mathbf{B r}(\mathbf{1})-\mathbf{C}(\mathbf{2 4})$ | $1.863(12)$ | $\mathbf{C}(\mathbf{1})-\mathbf{O}(\mathbf{1})-\mathbf{P d}(\mathbf{1})$ | $112.2(7)$ |

Upon detailed analysis of the data, the longest tridentate ligand to metal bond is formed by the imine donor unit $[\operatorname{Pd}(1)-\mathrm{N}(2) 2.047(9) \AA$, although statistically it is the same as $\operatorname{Pd}(1)-\mathrm{O}(1)$ with bond length being $2.035(7) \AA$. The central pyridine donor forms the shortest tridentate ligand to palladium bond $[\operatorname{Pd}(1)-\mathrm{N}(1) 1.918 \AA]$. The introduced 3bromopyridine unit is tilted with respect to the pyridyl plane, possibly as a result of steric interactions between the Pd-(3-BrPy) and bulky 2,6-diisopropylphenyl substituent on the imine arm of the ligand. In addition, the $N-\left(2,6-i-\mathrm{PrC}_{6} \mathrm{H}_{3}\right)$ unit is inclined
perpendicular to the pyridyl plane and each isopropyl group adopts a position which is close in space to the axial position of the palladium(II) core.

### 5.3.3.5 Reactions of Imine-Containing $\left[\left(N, N_{P y}, O\right)\right]$ pincer ligands with $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ Synthesis of 5.6a, 5.6b and 5.6c

In an attempt to look at the difference in reactivity of the imine-substituted [ $N, N_{P y}, O$ ] pincer ligands with another metal of the platinum group, the reactions of EtL7, EtLs and EtL9 with $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ were investigated. The pro-ligands were heated with $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ at reflux in acetic acid for 24 h to give a dark red precipitate (Figure 5.35).


Figure 5.35 - Synthesis of platinum(II) complexes 5.6a, 5.6b and 5.6c

Once filtered, the products of all three pro-ligands were each obtained as a red powder. Analysis of 5.6a, 5.6b and 5.6c by ${ }^{1} \mathrm{H}$ NMR spectroscopy reveals a set of resonances significantly shifted from the pro-ligands, indicating that the reaction had taken place. The presence of a triplet and a quartet signals in all cases indicates that the ester group has not been hydrolysed and is still intact. In addition, the 12 H doublet seen at $\delta 1.06$ ppm in 5.6a and 5.6c has split into two distinct 6 H doublet peaks. The two doublets of 12 H and 6 H in 5.6b have also split into three 6 H doublet peaks. The inequivalence of isopropyl groups upon binding to Pt and the presence of the ester moiety confirms the coordination of the ligands as bidentate. Further evidence for the bidentate binding of 5.6a, 5.6b and 5.6c is found upon analysis by ESIMS whereupon all three compounds showed a molecular ion peak corresponding to $[\mathrm{M}+\mathrm{H}]^{+}$. In addition, a fragmentation peak characteristic of $[\mathrm{M}-\mathrm{Cl}]^{+}$was detected for all compounds in HR(TOF) mass spectrometry.

It was also possible to grow single crystals of $\mathbf{5 . 6 c}$ suitable for analysis by X-ray diffraction through slow diffusion of petroleum ether into a solution of $\mathbf{5 . 6 c}$ in chloroform. The X-ray results confirmed the structure of $\mathbf{5 . 6 c}$ to be the bis-chloride Pt (II) complex with an $N, N$-bidentate ligand and a free ester arm (Figure 5.36, Table 5.6). Analysis of the $\mathrm{C}(7)-\mathrm{N}(2)$ bond length indicates a typical length expected for a coordinated methyl-imine $[\mathrm{C}(7)-\mathrm{N}(2) 1.297(12) \AA]$. Moreover, the bond angle of $[\mathrm{C}(8)-$ $\left.\mathrm{C}(7)-\mathrm{N}(2) 125.5(11)^{\circ}\right]$ is consistent with an $\mathrm{sp}^{2}$ hybridised imine functionality. Two $\mathrm{Pt}(1)-\mathrm{Cl}(1)$ and $\mathrm{Pt}(1)-\mathrm{Cl}(2)$ bonds are the longest in the structure, whereas the shortest ligand to metal bond is between the pyridyl nitrogen and platinum metal $[\operatorname{Pt}(1)-\mathrm{N}(1)$ $1.985(8) \AA$. .

Table 5.6-Selected bond lengths ( $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 5.6 c
BOND LENGTHS (Å)

| $\mathbf{P t}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $1.985(8)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P t}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $80.0(4)$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{P t}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $2.056(8)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P t}(\mathbf{1})-\mathbf{C l}(\mathbf{1})$ | $174.3(3)$ |
| $\mathbf{P t}(\mathbf{1})-\mathbf{C l}(\mathbf{1})$ | $2.289(3)$ | $\mathbf{C}(\mathbf{9})-\mathbf{P t}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $110.9(7)$ |
| $\mathbf{P t}(\mathbf{1})-\mathbf{C l}(\mathbf{2})$ | $2.295(3)$ | $\mathbf{C}(\mathbf{7})-\mathbf{P t}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $117.8(8)$ |
| $\mathbf{C}(\mathbf{7})-\mathbf{N}(\mathbf{1})$ | $1.297(12)$ | $\mathbf{C}(\mathbf{8})-\mathbf{C}(\mathbf{7})-\mathbf{N}(\mathbf{1})$ | $125.5(11)$ |



Figure 5.36-Molecular structure of 5.6c. The hydrogen atoms have been omitted for clarity

It is not quite clear why a bidentate binding is observed upon reaction with $\mathrm{K}_{2} \mathrm{PtCl}_{4}$, whereas with $\mathrm{Pd}(\mathrm{OAc})_{2}$ ester hydrolysis leads to a tridentate binding of the palladium metal. $\operatorname{Pd}(\mathrm{OAc})_{2}$ exists in two forms, molecular and polymeric, with a 1:2 stoichiometric ratio of Pd atoms and acetate ligands. Possibly, upon coordination to EtLin pro-ligands, $\mathrm{Pd}(\mathrm{OAc})_{2}$ acts as both Lewis acid and transition-metal catalyst in the subsequent ester hydrolysis. One plausible mechanism can be presented where upon binding to nitrogen atoms in the pro-ligands, an acetate, bound to coordinate palladium centre, can act as a nucleophile. This acetate nucleophile can attack at the electrophilic carbon of the ester $\mathrm{C}=\mathrm{O}$. This leads to the formation of an acid anhydride which is further attacked by the $\mathrm{EtO}^{-}$alkoxide, resulting in the loss of the leaving acetate group and a subsequent coordination of the newly formed carboxylate to the palladium centre (Figure 5.37).


Figure 5.37 - Possible mechanism for ester hydrolysis by $\mathrm{Pd}(\mathrm{OAc})_{2}$

### 5.3.3.6 Catalytic testing: acetoxylation of 8-methylquinoline

With a view to test the proton-responsiveness and catalytic activity of the cationic Pd complexes [ LPdMeCN$]\left[\mathrm{PF}_{6}\right]$ in C -H activation, acetoxylation of 8-methylquinoline has been chosen as the reference reaction (Figure 5.38). The procedure used was based on that described by A.N. Vedernikov et al. and was carried out under an oxygen atmosphere. ${ }^{38}$ Variations in solvent and temperature have been made in order to determine the optimal conditions.


Figure 5.38-CH acetoxylation of 8-methylquinoline

Initially each catalyst was tested at $80^{\circ} \mathrm{C}$ in acetic acid, so as to directly compare the conversion against the literature (Table 5.7). However, with a conversion of $0.25 \%$ for entry $1,0.63 \%$ for entry 7 and $5.8 \%$ for entry 4 , it was apparent that modification of the conditions was necessary. The temperature was increased to $100{ }^{\circ} \mathrm{C}$ to try to increase the activity, keeping the reaction medium in acetic acid. Neither catalyst produced any measurable product; therefore, acetic acid was changed to another high boiling solvent, such as toluene. After 20 hours at $100^{\circ} \mathrm{C}$, a conversion of $0.34 \%$ for entry 3 and $1.1 \%$ for entry 6 , and $0.71 \%$ for entry 8 was reported. Whilst the catalysts seem to show some activity, they do not compare well to the literature values ( $69 \%$ conversion in acetic acid at $80^{\circ} \mathrm{C}$ for 24 h$) .{ }^{38}$

Table 5.7 - Outline of the conditions and conversion percentage results of the catalytic testing; (5 mol\% catalyst used)

## ENTRY CATALYST TEMPERATURE SOLVENT CONVERSION

| $\left({ }^{\mathbf{o}} \mathbf{C}\right)$ |  |  |  |  |
| :---: | :--- | :---: | :---: | :---: |
| $\mathbf{1}$ | $\left[\mathbf{L}_{7} \mathrm{Pd}(\mathrm{MeCN})\right]^{+}\left[\mathrm{PF}_{6}\right]^{-}$ | 80 | Acetic acid | 0.25 |
| $\mathbf{2}$ | $\left[\mathbf{L}_{7} \mathrm{Pd}(\mathrm{MeCN})\right]^{+}\left[\mathrm{PF}_{6}\right]^{-}$ | 100 | Acetic acid | 0 |
| $\mathbf{3}$ | $\left[\mathbf{L}_{7} \mathrm{Pd}(\mathrm{MeCN})\right]^{+}\left[\mathrm{PF}_{6}\right]^{-}$ | 100 | Toluene | 0.34 |
| $\mathbf{4}$ | $\left[\mathbf{L}_{8} \mathrm{Pd}(\mathrm{MeCN})\right]^{+}\left[\mathrm{PF}_{6}\right]^{-}$ | 80 | Acetic acid | 5.8 |
| $\mathbf{5}$ | $\left[\mathbf{L}_{8} \mathrm{Pd}(\mathrm{MeCN})\right]^{+}\left[\mathrm{PF}_{6}\right]^{-}$ | 100 | Acetic acid | 0 |
| $\mathbf{6}$ | $\left[\mathbf{L}_{8} \mathrm{Pd}(\mathrm{MeCN})\right]^{+}\left[\mathrm{PF}_{6}\right]^{-}$ | 100 | Toluene | 1.1 |
| $\mathbf{7}$ | $\left[\mathbf{L}_{9} \mathrm{Pd}(\mathrm{MeCN})\right]^{+}\left[\mathrm{PF}_{6}\right]^{-}$ | 80 | Acetic acid | 0.63 |
| $\mathbf{8}$ | $\left[\mathbf{L}_{9} \mathrm{Pd}(\mathrm{MeCN})\right]^{+}\left[\mathrm{PF}_{6}\right]^{-}$ | 100 | Toluene | 0.71 |

It has been reported previously that the $\mathrm{C}-\mathrm{H}$ activation step is the rate limiting step in this catalytic reaction, and is most likely the reason for the reported low conversions. ${ }^{38}$ In theory, when the methyl group coordinates to the Pd centre, the chelate ring resulted from carboxylate arm must come off. If the ring strain of the chelate is large, then a small activation energy is required to ring open the carboxylate arm and accept the C-H proton. If the ring strain is small then the complex is more thermally stable and a higher activation energy is required. Whilst the precise activation energy of our complexes requires DFT calculations, the N-Pd-O bond angle was calculated as $161.35^{\circ}$ for $\left[\operatorname{L}_{7} \operatorname{Pd}(\mathrm{Cl})\right]$ by X-ray crystallography. In a square planar Pd complex, an angle of $180^{\circ}$ would indicate no ring strain, therefore the calculated value for $\left[{ }_{7}{ }_{7} \operatorname{Pd}(\mathbf{C l})\right]$ would suggest a relatively large ring strain. The literature value for Vedernikov's complex (Pd-dipic) reports the O-Pd-O bond angle as $161.5^{\circ}$, therefore our complex might be expected to give a similar reactivity (Figure 5.39). ${ }^{38}$


Figure 5.39-[ $\left.\boldsymbol{L}_{7} P d(\mathrm{MeCN})\right]\left[P F_{6}\right]$ complexes tested and $\boldsymbol{P d}$-dipic reported by A.N. Vedernikov ${ }^{38}$

However, acetoxylation of 8-methylquinoline by Pd-dipic occurs in $69 \%$, hence the low conversion observed here is not due to ring strain. Without further kinetic studies, the exact reason for the poor catalyst activity reported is unknown. One possible reason can be the substrate's inability to access the catalyst due to stearic hindrance from the dipp and tripp functional groups. If the substrate is unable to bind to Pd or dissociates too quickly from the catalyst, then the reaction will never proceed past the slow rate limiting step. Alternatively, if the MeCN ligand is too strongly bonded to palladium then a vacant co-ordination site is never formed. This could be tested by using a different two-electron donor and performing the acetoxylation under identical conditions to compare the calculated conversions.

### 5.3.3.7 Probing proton-responsiveness with $\mathbf{H C l}$

For the complexes to function as active catalysts, the carboxylate arm must be able to reversibly protonate, resulting in a bidentate complex. This offers an alternative approach of testing the proton responsive capability of the complex. The inability of the carboxylate arm to dissociate as a result of strong bonding to Pd centre would indicate the complex will not be active towards $\mathrm{C}-\mathrm{H}$ activation. This is a crucial step in the catalytic cycle proposed by Vedernikov and co-workers.

In an attempt to test the proton responsiveness of the carboxylate so as to protonate it to a carboxylic acid and form the bidentate complex $\left[\mathrm{L}_{7} \mathrm{Pd}\left(\mathrm{Cl}_{2}\right)\right]$, 5.1a was dissolved in acetonitrile and stirred in a solution of conc. HCl for 1 hour (Figure 5.40).


Figure 5.40-Predicted proton responsive reaction of 5.1a and conc. HCl

However, upon work-up of the reaction, the obtained ${ }^{1} \mathrm{H}$ NMR spectrum of the crude product showed no sign of the desired complex, or starting material. The experiment was repeated with less concentrated acid, but this also proved ineffective as no change in starting material was observed.

The lack of reactivity of the complex under weakly acidic conditions, might possibly be one of the reasons for low conversions observed when the catalysts were tested. Nonetheless, switching acetic acid to toluene as the solvent, and carrying out the reaction at room temperature did not produce any significant improvement.

The reaction was further tested with a different two electron donor such as pyridine and under the same reaction conditions, however, this also yielded no measurable results.

### 5.3 Conclusions

In this chapter, a series of palladium(II) and platinum(II) complexes supported by carboxylate containing mono(imino)pyridyl $\left[N, N_{P y}, O\right.$ ] pincer ligands have been described. All pincer complexes obtained have been thoroughly characterised by a combination of ${ }^{13} \mathrm{C},{ }^{1} \mathrm{H}$ NMR and IR spectroscopies, high resolution mass spectrometry and, in some cases, by X-Ray diffraction. It was found that the ligand framework incorporating an ethyl ester group at the 6-position hydrolyses to a carboxylic acid upon coordination to palladium. This trend does not occur upon reaction with a platinum(II) salt and a bidentate metal binding is observed with platinum(II) complexes $\left[\operatorname{LPt}\left(\mathrm{Cl}_{2}\right)\right]$ (5.6a, 5.6b and 5.6c). Reactions with $\mathrm{Pd}(\mathrm{OAc})_{2}$ with all three pro-ligands gave the palladium acetate complexes [LPdOAc] while the subsequent ligand exchange reactions with NaCl resulted in the chlorinated complexes [ $\mathbf{L P d C l}]$ (5.1a, 5.1b and 5.1c). Complexes 5.1a and 5.1b were further reacted to form mono-cationic derivatives $[\mathrm{LPdMeCN}]\left[\mathrm{PF}_{6}\right]$ with a labile acetonitrile ligand and $\mathrm{PF}_{6}$ anion. In the case of 5.1c, a
direct synthetic approach from $\mathrm{PdCl}_{2}(\mathrm{MeCN})_{2} / \mathrm{AgPF}_{6}$ and ligand EtL9 has been employed in order to produce the mono-cationic derivative of the complex. Furthermore, exchange of the labile -NCMe moiety with various pyridines readily gave a range of new palladium cationic pincer complexes with pyridines as the fourth ligand $[\mathbf{L P d X}]\left[\mathrm{PF}_{6}\right]$ (5.3a, 5.4a and 5.5a).

## 6. Synthesis and reactivity of palladium(II) complexes supported by substituted diethylenetriamine [ $N, N, N$ ]-type tridentate complexes

### 6.1 Introduction

### 6.1.1 Functionalised dien ligands

Diamido-donor ligands derived from functionalised diethylenetriamines (dien) have been the source of considerable interest in transition metal catalysis. They have shown great compatibility with both main group ${ }^{131}$ and transition metals ${ }^{132,133}$ and resulted in a generation of catalysts for a variety of chemical transformations. ${ }^{134}$ The ability to incorporate steric bulk and modify substituents on the N -aryl arm of the dien framework with regards to both their steric and electronic properties gives access to a variety of substituted dien compounds and makes them an important ligand class in organometallic chemistry. In addition, the features of the substitution on the aryl ring can affect the catalytic performance of the complex.

Bertrand et al. showed that diamidoamine ligands can successfully stabilise neutral four-coordinated gallium and aluminium complexes with various substituents (Figure 6.1). ${ }^{131}$ All complexes exhibit trigonal-monopyramidal coordination geometry due to the formation of a rigid bicyclic framework enforced by the tridentate nitrogen donors. This particular geometry makes the empty axial coordination site available for substrate binding. Initial studies have demonstrated that these Lewis acid systems can be promising catalysts for the ring-opening polymerisation of heterocycles.


$$
\begin{aligned}
& \mathrm{M}=\mathrm{Al}, \mathrm{Ga} \\
& \mathrm{R}=\mathrm{SiMe}_{3},{ }^{i} \mathrm{Pr} \\
& \mathrm{R}^{\prime}=\mathrm{SiMe}_{3}, \mathrm{Me} \\
& \mathrm{X}=\mathrm{H}, \mathrm{Cl}, \mathrm{Me}
\end{aligned}
$$

Figure 6.1 - Al and Ga complexes supported by diamidoamine ligands

Solan et al. have developed a series of iron and cobalt chloride complexes supported by the aryl-substituted N -picolylethylenediamine and diethylenetriamine ligands. ${ }^{134}$ Results indicate that the $N, N, N$ chelates can adopt both facial and meridional configurations with
the metal centre (Figure 6.2). Solution studies suggest that isomerisation between the facand mer-structures is a facile process at room temperature.

a) $\mathrm{M}=\mathrm{Co}, \mathrm{R}=\mathrm{H}(f a c, \mathrm{R} / \mathrm{S}$ and $\mathrm{S} / \mathrm{R})$
b) $\mathrm{M}=\mathrm{Co}, \mathrm{R}=\mathrm{Me}(f a c, \mathrm{R} / \mathrm{S}$ and $\mathrm{S} / \mathrm{R})$
c) $\mathrm{M}=\mathrm{Fe}, \mathrm{R}=\mathrm{H}($ mer, $\mathrm{R} / \mathrm{S}$ and $\mathrm{S} / \mathrm{R})$

Figure 6.2 - Co and Fe complexes supported by the aryl-substituted $N$ picolylethylenediamine ligands

Further studies by Solan et al. led to derivatising the central amine on the dien ligand with a methyl group and 2-pyridyl methyl in order to examine the effects on their coordination chemistry (Figure 6.3). ${ }^{135}$

d) $\mathrm{M}=\mathrm{Co}, \mathrm{R}_{1}=\mathrm{Me}, \mathrm{R}_{2}=\mathrm{H}$
e) $\mathrm{M}=\mathrm{Co}, \mathrm{R}_{1}=\mathrm{H}, \mathrm{R}_{2}=\mathrm{Me}$

f) $\mathrm{M}=\mathrm{Co}, \mathrm{R}_{1}=\mathrm{R}_{2}=\mathrm{Me}$
g) $\mathrm{M}=\mathrm{Fe}, \mathrm{R}_{1}=\mathrm{R}_{2}=\mathrm{Me}$

Figure 6.3-Co and Fe complexes supported by the functionalised dien ligands

Evidently, steric bulk plays an important role on the efficient ligand coordination. As Figure 6.4 shows, only cobalt(II) systems can coordinate in a tridentate fashion. Complexes $\mathbf{f}$ and $\mathbf{g}$ indicate a possibility of a tetradentate coordination. Solution state experiments performed on complexes $\mathbf{f}$ and $\mathbf{g}$ suggest that there is a possible interconversion occurring in solution as broad signals corresponding to only one type of aryl group environment are displayed (Figure 6.4).


Figure 6.4-Interconversion observed in solution

The dien family of ligands, besides behaving as neutral ligands, $\left(\mathrm{ArNHCH}_{2} \mathrm{CH}_{2}\right)_{2} \mathrm{NH}$, have the capacity to act as ligands in the dianionic form, $\left.\left(\mathrm{ArNCH}_{2} \mathrm{CH}_{2}\right)_{2} \mathrm{NH}\right)^{2-}$.

Feghali et al. developed several novel vanadium and vanadium-aluminium systems supported by the trimethylsilylamino(trimethylsilyldiamido) ligand (Figure 6.5). ${ }^{133}$ It was found that this ligand system is able to stabilise mono- and dinuclear trivalent vanadium alkyl derivatives and is responsible for aggregating vanadium and aluminium residues.




Figure 6.5 - Vanadium and vanadium-aluminium systems supported by substituted diamido-amine ligands

Gade and Mountford employed a range of diamido-donor ligands as supporting ligands for scandium metal. ${ }^{136}$ The complexes can be easily obtained but there is an evident relationship between the ligand backbone chain length and amino N -substituent of the diamido-amine ligands $\mathrm{RN}\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NSiMe}_{3}\right)_{2}$ (where $\mathrm{R}=\mathrm{Me}, \mathrm{SiMe}_{3}$ ) (Figure 6.6).

$\mathrm{R}=\mathrm{Me}, \mathrm{SiMe}_{3}$

Figure 6.6-Scandium complexes supported by diamido-amine ligands

Schrock et al. synthesised a zirconium complex supported by a stable diamido-donor ligand, $\left[\left(2,6-\mathrm{Cl}_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{NCH}_{2} \mathrm{CH}_{2}\right)_{2} \mathrm{NMe}\right]^{2-}$ (Figure 6.7). ${ }^{132}$ The complex was found to be an active catalyst for polymerisation of 1 -hexene. It is assumed that the 2,6dichlorophenyl group might stabilise cationic species through transiently dative coordination of the chloride group to the metal centre.


Figure 6.7 - Substituted Zr diamido complex

### 6.1.2 Self-assembly through hydrogen bonding

The self-assembly process can be described as the spontaneous arrangement of individual components into an ordered structure without human involvement. ${ }^{137}$ Nature has fully advanced this self-assembly mechanism to build highly sophisticated macromolecules. Proteins, peptides and nucleotides interact and self-organise to form well-defined structures which perform important life functions and processes. Inspired by these natural systems, the self-assembly approach can be applied to the design of homogenous catalysts. While conventional approaches involve tethering metal centres through covalent bonds, this strategy could be replaced by a non-covalent bonding interaction such as hydrogen bonding. ${ }^{138}$

Hydrogen bonding plays an important role in influencing the structural coordination and ligand binding of organometallic compounds and serves as a versatile base to control their reactivity. ${ }^{139}$ The addition of hydrogen bonding moieties to the ancillary ligands comprising metal complexes results in the stabilisation of high-energy species ${ }^{140}$, activation of chemical bonds, molecular recognition ${ }^{141}$, mediation of proton transfer and new reactivity modes as well as triggering selectivity in catalytic transformations. ${ }^{142}$

The supramolecular approach using directional hydrogen bonding is potentially very attractive as it can allow the rapid construction of multinuclear systems in solution through the self-assembly of monomeric units. Remarkably, the rate acceleration and enantioselectivity of the nitro-aldol (Henry) reaction was considerably improved when a dinuclear $\operatorname{Co}$ (II)-salen catalyst self-assembled through hydrogen bonding was employed (Figure 6.8). ${ }^{143}$ The corresponding monomeric Co-salen catalyst proved inferior under the same reaction conditions. The rate acceleration was rationalised by the facile dimer formation through hydrogen bonding mediated by two sets of remotely located $\mathrm{NR}_{2} \mathrm{H}^{\cdots} \mathrm{O}$ hydrogen bond donor/acceptor groups.




Figure 6.8 - Monomeric Co-salen complex (left); Dimeric, bimetallic Co-salen complex (right)

A careful choice of the hydrogen bond donor/acceptor pair can be considered as a tool to tune the strength of the hydrogen bonding and thus, to control the stability of the newly-emerged self-assembly. Amine functional groups, especially primary and secondary amines, besides coordinating to metal centres, are also well recognised for their capacity to act as a hydrogen bond donor, acceptor and proton source. These moieties $\left(\mathrm{R}_{2} \mathrm{NH} / \mathrm{RNH}_{2}\right)$ are stable and can be easily incorporated into the ligand skeleton with a view to establish the desired properties.

The use of the amine group with an appropriate hydrogen bond acceptor is known to initiate the formation of self-assembled dimeric species of neighbouring molecules. For instance, 2-pyridone and its tautomer 2-hydroxypyridine can readily undergo dimerisation through two hydrogen bonds based upon the tautomeric isomers involved (Figure 6.9). ${ }^{144}$


2-pyridone 2-hydroxypyridine




Figure 6.9 - 2-pyridone and its tautomeric isomer (top); possible hydrogen-bonded self-assemblies of 2-pyridone (bottom)

Breit and co-workers reported a library of chiral bidentate phosphorus donor ligands based on hydrogen-bonded self-assembly which was screened in the rhodium-catalysed asymmetric hydrogenation (Figure 6.10). ${ }^{145}$ Studies demonstrated that employment of a self-assembly approach with the matching ligand systems can lead to a generation of catalysts with excellent activity and enantioselectivity.


$$
\mathrm{Do}^{\mathrm{a}}, \mathrm{Do}^{\mathrm{b}}=\mathrm{PAr}_{1} \mathrm{Ar}_{2}, \mathrm{P}(\mathrm{OR})_{2}
$$

Figure 6.10 - Self-assembly of chiral monodentate ligands into bidentate ligands through hydrogen bonding

Solan et al. reported that sterically protected palladium pincer complexes with built-in directional hydrogen bond-donor (D) and acceptor (A) moieties, can readily undergo intermolecular dimerisation through hydrogen bonding (Figure 6.11). It is the presence of an amine donor that triggers the self-assembly of the dimeric species.


Figure 6.11-Homobimetallic palladium complex self-assembled through hydrogen bonding

Recently, asymmetric hydrogen-bonding organocatalysis has emerged as an attractive and useful branch of catalysis. The bulk of hydrogen bonding (HB) catalysts are based on the (thio)urea motif, with other HB motifs such as squaramides, sulphonamides, triamides etc. being less established in this area. ${ }^{146}$ Organocatalysts based on a thiourea motif have taken up an important place in catalysis due to their distinct feature of a double hydrogen bonding donor. ${ }^{147}$ The use of these double hydrogen bond-donor
catalysts has become an efficient strategy for electrophile activation, both in synthetic and biological catalysis. This is attributed to properties, such as increased strength and directionality, compared to a single hydrogen bond. Simultaneous hydrogen bonding defines the orientation and position of bound substrates. For example, two-point binding is a very powerful approach which can be used for asymmetric catalysis with metalcentred Lewis acids. ${ }^{148}$ A number of research groups studied the interaction of ureas with anions and neutral molecules such as benzoates, phosphates, esters and nitroarenes in the solution state. ${ }^{149,150}$

A series of novel HB phosphorus (tri)amide catalysts, including chiral $\mathrm{P}^{\mathrm{V}}$ cyclodiphosphazane, were reported by Goldfuss et al. and employed in Michael addition of 2-hydroxynaphthoquinone to $\beta$-nitrostyrene (Figure 6.12).


Figure 6.12 - Predicted bidentate HB mechanism of nitroolefin activation by ciscyclodiphosphazane

It was anticipated that cis-cyclodiphosphazane activates the nitroolefin in the nucleophilic addition step of the reaction, whereas the tertiary amine unit acts as a base deprotonating 2-hydroxy-1,4-naphthoquinone. As a result, 1,4-dioxo-1,4-dihydronaphthalen-2-olate serves as the nucleophile. Studies showed that ciscyclodiphosphazane is significantly superior to its trans-isomer. This can be associated with the inability of trans-cyclodiphosphazane to engage in bidentate hydrogen bonding. As far as yields are concerned, the efficiency of cis-isomer is attributed to the relative strength of the hydrogen bonds it forms.

### 6.2 Aims and Objectives

The aim of this chapter is to develop novel tridentate $\mathrm{Pd}(\mathrm{II})$ complexes supported by aryl-substituted dien-based $N, N, N$-chelates containing a central tertiary amine. Built-in hydrogen bond donor functionalities will offer the opportunity for these systems as potential mediators of self-assemblies or complex/substrate assemblies through hydrogen bonding.

All the prepared complexes are new and have been characterised by ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ NMR and IR spectroscopies, ESI and HMRS spectrometries as well as by single crystal X-ray diffraction.

### 6.3 Results and Discussion

### 6.3.1 Synthesis of pro-ligands $\mathrm{HL}_{10}$ and $\mathrm{HL}_{11}$

Pro-ligands $\mathrm{HL}_{10} \quad\left(\mathrm{ArNHCH}_{2} \mathrm{CH}_{2}\right)_{2} \mathrm{NH} \quad\left(\mathrm{Ar}=2,6-\mathrm{Me}_{2} \mathrm{C}_{6} \mathrm{H}_{3}\right)$ and $\mathrm{HL}_{11}$ $\left(\mathrm{ArNHCH}_{2} \mathrm{CH}_{2}\right)_{2} \mathrm{NMe}\left(\mathrm{Ar}=2,6-\mathrm{Me}_{2} \mathrm{C}_{6} \mathrm{H}_{3}\right)$ were prepared in high yield by employing a palladium catalysed $\mathrm{N}-\mathrm{C}$ (aryl) coupling reaction of diethylenetriamine or N methyldiethylenetriamine (prepared from N -methyldiethanolamine), respectively, with two equivalents of the corresponding aryl bromide following the experimental protocols established by Buchwald and Hartwig (Figure. 6.13). ${ }^{151,152,153}$ Both ligands have been thoroughly characterised by a range of analytical techniques and the data is in agreement with those in the literature. ${ }^{134,135}$



Figure 6.13-Synthesis of pro-ligands $H \boldsymbol{L}_{10}$ and $H_{11}$; Reagents and conditions:
(i) Phthalimide, heat; (ii) $\mathrm{H}^{+}$; (iii) NaOH ; (iv) $\mathrm{Ar}-\mathrm{Br}, \mathrm{Pd}_{2}(\mathrm{dba})_{3}(0.5 \mathrm{~mol} \%)$, racBINAP, NaOBu ${ }^{t}$, toluene, heat

### 6.3.2 Synthesis of acetate-containing complexes $\mathbf{6 a}$ and $\mathbf{6 b}$

The reaction of pro-ligands $\mathrm{HL}_{10}$ and $\mathrm{HL}_{11}$ with $\mathrm{Pd}(\mathrm{OAc})_{2}$ in chloroform at room temperature overnight affords acetate-containing complexes 6a of the type [(NHdien $) \operatorname{Pd}(\mathrm{OAc})][\mathrm{OAc}]$ and $\mathbf{6 b}$, $[(\mathrm{NMe}-\mathrm{dien}) \mathrm{Pd}(\mathrm{OAc})][\mathrm{OAc}]$ in good yield (Figure 6.14). Both complexes are air stable and were characterised using a combination of FAB mass spectrometry, IR, ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectroscopies.


Figure 6.14-Synthesis of acetate-containing Pd(II) complexes

The FAB mass spectra of both complexes reveal strong molecular ion peaks corresponding to the loss of acetate ligands $[\mathrm{M}-\mathrm{OAc}]^{+}$. In their IR spectra, the $v(N H)$ absorption bands seen at ca. $3257 \mathrm{~cm}^{-1}$ and $3286 \mathrm{~cm}^{-1}$ for $\mathbf{6 a}$ and $\mathbf{6 b}$, respectively, are shifted to lower wavenumbers than those in the corresponding free ligands. Analysis of $\mathbf{6 a}$ and $\mathbf{6 b}$ by ${ }^{1} \mathrm{H}$ NMR spectroscopy reveals a change in all proton environments upon
binding to palladium, compared to their parent pro-ligands. ${ }^{1} \mathrm{H}$ NMR spectra of both $\mathbf{6 a}$ and $\mathbf{6 b}$ show a singlet 1 H peak at 4.18 ppm and 4.98 ppm , respectively, corresponding to the NH resonance. Compound 6a also displays a peak corresponding to the central NH group at 8.56 ppm . In addition, the presence of two singlet peaks accounting to 3 protons each ( 0.93 and 1.23 ppm for $\mathbf{6 a} ; 1.31$ and 1.96 ppm for $\mathbf{6 b}$ ), corresponds to a coordinated acetate ligand and an acetate counterion.

Intriguingly, the room temperature ${ }^{1} \mathrm{H}$ NMR spectra of both complexes run in deuterated chloroform show signals corresponding to two diastereomers which appear in a 6:4 ratio and are attributed to the cis and trans isomers (Figure 6.15). However, on changing the solvent to deuterated methanol, only one isomer is observed. This observation might suggest that the complexes are solvent-dependent, or that the cistrans interchange occurs very fast and hence only one isomer is seen in the ${ }^{1} \mathrm{H}$ NMR spectrum run in deuterated methanol.

$R=H, M e$

Figure 6.15-Cis-trans diastereomers of $\mathbf{6 a}$ and $\mathbf{6} \boldsymbol{b}$ observed in solution

Further confirmation of the predicted structures was afforded by the single crystal X-ray analysis. Crystals of both $\mathbf{6 a}$ and $\mathbf{6 b}$ were grown by layering a chloroform solution of the corresponding complex with petroleum ether at room temperature. The structures of both complexes are essentially the same and will be discussed together. The X-ray structures of $\mathbf{6 a}$ and $\mathbf{6 b}$ are shown in Figure 6.16 and the selected bond distances and angles are collected in Tables 6.1 and 6.2.


Figure 6.16 - Molecular structures of $\mathbf{6} \boldsymbol{a}$ and $\mathbf{6}$. Hydrogen atoms have been omitted for clarity

Table 6.1-Selected bond distances and bond angles for $\mathbf{6 a}$

## BOND LENGTHS (Å)

| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $2.058(6)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $175.6(2)$ |
| :--- | :---: | :---: | :---: |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $2.000(6)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $84.8(2)$ |
| $\mathbf{P d}(\mathbf{1}) \mathbf{- O}(\mathbf{1})$ | $2.014(5)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $84.5(2)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $2.073(5)$ | $\mathbf{O}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $96.4(2)$ |
|  |  | $\mathbf{O}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $95.2(2)$ |
|  |  | $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})-\mathbf{H}(\mathbf{1})$ | 104.1 |
|  |  | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $163.80(2)$ |
|  |  |  |  |

Table 6.2 - Selected bond distances and bond angles for $\boldsymbol{6} \boldsymbol{b}$

|  | BOND LENGTHS <br> $(\AA)$ | BOND ANGLES $\left({ }^{\mathbf{o}}\right)$ |  |
| :--- | :---: | :---: | :---: |
|  | $2.072(2)$ | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $166.91(9)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $2.041(2)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $86.62(10)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $2.017(2)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $86.58(9)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{O}(\mathbf{1})$ | $2.050(2)$ | $\mathbf{O}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $95.74(8)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $1.489(4)$ | $\mathbf{O}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $90.36(9)$ |
| $\mathbf{N}(\mathbf{2})-\mathbf{C}(\mathbf{2 3})$ |  | $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})-\mathbf{C}(\mathbf{2 3})$ | $108.2(2)$ |

The X-Ray crystallographic results reveal two unique molecules in the unit cell for $\mathbf{6 a}$ and one molecule for $\mathbf{6 b}$. Both structures consist of a palladium acetate core supported by a tridentate 2,6-dimethylphenyl-substituted dien ligand. The four-coordinate geometry adopted by both complexes is best described as distorted square planar. Both dien ligands adopt a mer configuration with the $\mathrm{N}(1)-\mathrm{Pd}(1)-\mathrm{N}(3)$ angles being $163.80(2)^{\circ}$ for $\mathbf{6 a}$ and $166.91(9)^{\circ}$ for $\mathbf{6 b}$. The aryl substituents on each of the terminal nitrogen atoms of the dien ligands are mutually cis with ipso-carbon atoms $[\mathrm{C}(1)$ and $\mathrm{C}(11)$ ], positioned below the $\mathrm{N}(1)-\mathrm{N}(2)-\mathrm{N}(3)-\mathrm{Pd}(1)$ plane. In addition, both hydrogen atoms on the terminal nitrogen atoms are also cis and are pointed outwards. The $\mathrm{Pd}-\mathrm{N}$ bond lengths to the central atom of the dien ligand are relatively similar for both complexes. Both complexes have two chiral centres located on the termini of the $N, N, N-$ chelate at $\mathrm{N}(1)$ and $\mathrm{N}(3)$.

In 6a, a polymeric network arises through hydrogen bonding involving the central $\mathrm{N}-\mathrm{H}$, one of the exterior NHs , the acetate counterion and the bound acetate. In contrast, in $\mathbf{6} \mathbf{b}$, the $\mathrm{N}-\mathrm{Me}$ prevents initiation of the hydrogen bonding (Figure 6.17). There is an intramolecular hydrogen bonding interaction between the pendant O of the acetate and the exterior NH group in $\mathbf{6 b}(\mathrm{N} \cdots \mathrm{O} 2.372 \AA)$ as well as hydrogen bonding involving the other NH group and the acetate counterion and water molecules.

$6 a$


6b

Figure 6.17-ChemDraw representation showing the multiple types of $O \cdots H$ hydrogen bonding in $\boldsymbol{\sigma} \boldsymbol{a}$ and $\boldsymbol{\sigma} \boldsymbol{b}$

### 6.3.3 Synthesis of chloride-containing complexes 6.1a and 6.1b

The reaction of pro-ligands $\mathrm{H}_{10}$ and $\mathrm{HL}_{11}$ with bis(acetonitrile)palladium(II) chloride $\left(\mathrm{PdCl}_{2}(\mathrm{MeCN})_{2}\right)$ in chloroform at room temperature overnight, affords chloride-
containing complexes 6.1a of the type $[(\mathrm{NH}-\mathrm{dien}) \mathrm{Pd}(\mathrm{Cl})][\mathrm{Cl}]$ and 6.1b, [(NMedien $) \mathrm{Pd}(\mathrm{Cl})][\mathrm{Cl}]$ in good yield (Figure. 6.18). The complexes were fully characterised ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ NMR and IR spectroscopies, FAB and ESIMS spectrometries.


Figure 6.18 - Synthesis of chloride-containing complexes 6.1a and 6.1b

Analysis of 6.1a and 6.1b by ${ }^{1} \mathrm{H}$ NMR spectroscopy reveals all proton environments shifted from their parent pro-ligands upon coordination to palladium. The spectra of both complexes show 6 aromatic protons accounting for the protons on the two aryl groups. The chloride-containing complexes, unlike their acetate analogues are only soluble in methanol, thus the ${ }^{1} \mathrm{H}$ NMR spectra of 6.1a and 6.1b do not show a cis-trans diastereomeric mixture in solution. However, again as with 6a and 6b, there is a possibility that the cis-trans interchange occurs very fast and hence only one isomer can be observed. In the same way as the acetate analogues, the $\mathrm{v}(\mathrm{NH})$ absorption bands in the IR spectra for 6.1a and 6.1b are shifted to lower wavenumbers than those in the corresponding free ligands and are seen at ca. $3247 \mathrm{~cm}^{-1}$ and $3235 \mathrm{~cm}^{-1}$, respectively. The FAB mass spectra of both complexes reveal molecular ion peaks corresponding to the loss of chloride ligand $[\mathrm{M}-\mathrm{Cl}]^{+}$.

In addition, it was possible to grow crystals of 6.1a suitable for the X-ray analysis from hot methanol solution of the corresponding complex. The molecular structure is shown in Figure 6.19 and selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ are given in Table 6.3.


Figure 6.19 - Molecular structure of 6.1a. Hydrogen atoms have been omitted for clarity

Table 6.3-Selected bond distances and bond angles for 6.1a

## BOND LENGTHS (Å)

| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $2.069(18)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $84.68(7)$ |
| :---: | :---: | :---: | :--- |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $2.017(16)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $84.12(7)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{C l}(\mathbf{1})$ | $2.2960(6)$ | $\mathbf{C l}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $96.20(6)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $2.0619(16)$ | $\mathbf{C l}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $93.40(5)$ |
| $\mathbf{N}(\mathbf{2})-\mathbf{H}(\mathbf{2})$ | 0.9300 | $\mathbf{N}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $165.79(7)$ |

The molecular structure of 6.1a revealed a slightly distorted square planar geometry around the Pd centre which is coordinated to a tridentate $N, N, N$ pincer and an auxiliary chloride ligand. Similar to $\mathbf{6 a}$ and $\mathbf{6 b}$, the dien ligand adopts a mer configuration with the $\mathrm{N}(1)-\operatorname{Pd}(1)-\mathrm{N}(3)$ angle being $165.79(7)^{\circ}$. Both aryl substituents on each terminal nitrogen atom of the dien ligand are mutually cis with ipso-carbon atoms [ $\mathrm{C}(1)$ and $\mathrm{C}(11)$ ] positioned below the $\mathrm{N}(1)-\mathrm{N}(2)-\mathrm{N}(3)-\mathrm{Pd}(1)$ plane. The ortho-methyl groups of each aryl group sit above and below the $\mathrm{N}(1)-\mathrm{N}(2)-\mathrm{N}(3)-\mathrm{Pd}(1)$ plane. There is an intramolecular
hydrogen bond observed between the chloride counterion and the central NH proton as well as an intermolecular hydrogen bond that exists between the chloride anion and a molecule of methanol (Figure 6.20).


Figure 6.20-ChemDraw representation showing the types of $O^{\cdots} H$ hydrogen bonding in 6.1a

After several unsuccessful trials to grow crystals of 6.1b in methanol solution, dichloromethane was added to aid crystallisation. The complex was first dissolved in a minimum volume of the hot methanol in which it is soluble and dichloromethane was then added to the boiling solution until it turned cloudy. The slow evaporation of the solvent mixture upon prolonged standing resulted in crystals suitable for X-ray diffraction studies. The molecular structure of 6.1b is shown in Figure 6.21 and the selected bond distances and angles are given in Table 6.4.


Figure 6.21-Molecular structure of 6.1b

Table 6.4 - Selected bond distances and angles for 6.1b
BOND LENGTHS (Å)

| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $2.072(6)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $86.3(2)$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $2.051(6)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $85.4(2)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{C l}(\mathbf{1})$ | $2.302(2)$ | $\mathbf{C l}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $94.45(17)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $2.083(6)$ | $\mathbf{C l}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $93.36(17)$ |
| $\mathbf{N}(\mathbf{2})-\mathbf{C}(\mathbf{2 1})$ | $1.466(8)$ | $\mathbf{C}(\mathbf{2 1})-\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})$ | $117.4(4)$ |

From the Table 6.4 it is seen that all four Pd bond distances in 6.1b are similar to those of 6.1a. However, the bond angles of the tridentate pincer chelate in 6.1b $[\mathrm{N}(2)-\operatorname{Pd}(1)-$ $\mathrm{N}(1)$ and $\mathrm{N}(2)-\mathrm{Pd}(1)-\mathrm{N}(3), 86.3(2)^{\circ}$ and $85.4(2)^{\circ}$, respectively] are larger than those in 6.1a $\left[\mathrm{N}(2)-\mathrm{Pd}(1)-\mathrm{N}(1)\right.$ and $\mathrm{N}(2)-\mathrm{Pd}(1)-\mathrm{N}(3), 84.12(7)^{\circ}$ and $84.68(7)^{\circ}$, respectively], suggesting that the framework is less strained compared to the NH -substituted dien complex 6.1a. In addition, there is a molecule of solvent, dichloromethane, and a molecule of water present in the unit cell together with the two chloride anions being at half occupancy. There is also an interesting pattern of intra-molecular hydrogen bonding observed in the structure where both NHAr groups are involved. One of the NHAr moieties is coordinated to a chloride anion whereas the other NHAr group is
coordinated to the oxygen on the water molecule. The water molecule is further coordinated to another chloride anion in the cell. There is also a single molecule of water present in the unit cell, which is connected to both chloride anions via hydrogen bonding. This hydrogen bonded solvent network appears in the shape of a distorted rhombus. Below is a ChemDraw representation showing the $\mathrm{Cl} \cdots \mathrm{HN}$ and $\mathrm{O} \cdots \mathrm{HN}$ hydrogen bonding interactions in 6.1b, involving the cation, anions, water and an oxygen atom (Figure 6.22).


Figure 6.22-ChemDraw representation showing hydrogen bonding in 6.1b

### 6.3.4 Exploring the potential of cationic [(Me-dien-2,6-Me2 $\mathbf{P h}) \mathrm{PdCl}]^{+}$to mediate hydrogen bonding with counterions

Section 6.3.3 demonstrated the capacity of the NHAr donors in all the synthesised $\mathrm{Pd}(\mathrm{II})$ dien complexes to promote $\mathrm{NH} \cdots \mathrm{A}$ (acceptor) hydrogen bond interactions in the solid state. In complexes $\mathbf{6 a}$ and $\mathbf{6 b}$, both the bound acetate ligand and the acetate anion are involved in hydrogen bonding. In addition, in the NH -dien analogues, 6a and 6.1a, the third meridional $N H$ donor group is also engaged in hydrogen bonding interactions, thus preventing the bonding pattern where two equatorial NHAr donors with cis orientation are involved in hydrogen bonding. Notably, only in the case of the NMedien complexes, $\mathbf{6 b}$ and $\mathbf{6 . 1 b}$, in the absence of the meridional NH group, do these interactions feature both NHAr donors. Therefore, it was proposed to perform a series of counterion exchange reactions with substrates possessing two or more hydrogen bond acceptor groups in order to see if both NHAr donors in the $\mathrm{N} M e$-dien analogues can promote hydrogen bonding interactions with an appropriate host substrate.

For the purpose of abstracting the chloride anion from complex 6.1b, five different silver salts have been chosen to provide weakly coordinating anions: silver acetate ( AgOAc ), silver triflate $\left(\mathrm{AgSO}_{3} \mathrm{CF}_{3}\right)$, silver tetrafluoroborate $\left(\mathrm{AgBF}_{4}\right)$, silver
hexafluorophosphate $\left(\mathrm{AgPF}_{6}\right)$ and silver nitrate $\left(\mathrm{AgNO}_{3}\right)$. Weakly coordinating anions, also known as non-coordinating anions, typically act as counterions for cationic metal complexes with an unsaturated coordination sphere. During the chloride abstraction reaction, the silver cation $\left(\mathrm{Ag}^{+}\right)$will react with the chloride anion $\left(\mathrm{Cl}^{-}\right)$to produce the insoluble silver chloride $(\mathrm{AgCl})$ as a white precipitate (Figure 6.23).

$$
\begin{gathered}
\mathrm{Ag}_{(\mathrm{aq})}^{+}+\mathrm{X}_{(\mathrm{aq})}^{-} \longrightarrow \mathrm{AgX}_{(\mathrm{s})} \\
\mathrm{X}=\mathrm{Cl}, \mathrm{Br}, \mathrm{I}
\end{gathered}
$$

Figure 6.23-General reaction for a halide abstraction

The reactions between 6.1b and the silver salts were performed smoothly in dichloromethane at room temperature, affording the target complexes in good yield (Figure 6.24). All five complexes were analysed by a range of relevant analytical techniques, such as ${ }^{1} \mathrm{H},{ }^{31} \mathrm{P},{ }^{19} \mathrm{~F}$ NMR spectroscopies, ESI and high-resolution mass spectrometry. Upon analysis by ${ }^{1} \mathrm{H}$ NMR spectroscopy, all the synthesised complexes display a subtle shift of the aromatic protons. The acetate anion-containing complex 6.2b shows a singlet peak appearing at 0.11 ppm accounting for 3 protons, which can be attributed to the acetate anion. There is a singlet resonance observed at -77.8 ppm in the ${ }^{19} \mathrm{~F}$ NMR of $\mathbf{6 . 3 b}$, corresponding to fluorine atoms on the triflate anion. Furthermore, ${ }^{19} \mathrm{~F}$ NMR spectra of $\mathbf{6 . 4 b}$ and $\mathbf{6 . 5 b}$ display a singlet peak at $-146.7 \mathrm{ppm}\left(\mathrm{BF}_{4}^{-}\right)$and a doublet at $-71.2 \mathrm{ppm}\left(\mathrm{PF}_{6}{ }^{-}\right)$, respectively. Additionally, there is a multiplet resonance corresponding to the phosphorus atom of the $\mathrm{PF}_{6}$ anion observed in the ${ }^{31} \mathrm{P}$ NMR spectrum of $\mathbf{6 . 5 b}$.


Figure 6.24-Counterion exchange reaction between 6.1b and silver salts

Analysis of all five complexes by ESI mass spectrometry reveals signals indicating the loss of the anion $[\mathrm{M}-\mathrm{X}]^{+}$. It was also possible to obtain crystals of all five complexes suitable for X-ray diffraction studies (Figure 6.25), (Table 6.5). Yellow crystals, characteristic of the five complexes, were obtained upon slow diffusion of hexane into a mixture of the corresponding complexes in dichloromethane or chloroform solution. The crystallographic data supported the other data and further confirmed the displacement of the chloride anion and formation of the target compounds, 6.2b-6.6b . Analogous to the molecular structure of the parent complex 6.1b, the molecular structures of the new compounds shows the coordination of the dianionic dien ligand, $N, N_{M e}, N$ to palladium(II) core with the coordinating chloride ligand and the presence of a non-coordinating anionic species, $\mathrm{OAc}, \mathrm{SO}_{3} \mathrm{CF}_{3}, \mathrm{BF}_{4}, \mathrm{PF}_{6}$ and $\mathrm{NO}_{3}$. This confirms the overall cationic charge at the palladium centre.

6.2b, $X=O A c$

6.3b, $\mathrm{X}=\mathrm{SO}_{3} \mathrm{CF}_{3}$

(20)

6.5b, $X=P F_{6}$
6.4b, $\mathrm{X}=\mathrm{BF}_{4}$


Figure 6.25-Molecular structures of 6.2b-6.6b

|  | 6.2b | 6.3b | 6.4b | 6.5b | 6.6b |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{P d}(1)-\mathrm{N}(1)$ | 2.067(5) | 2.0713(17) | 2.072(3) | 2.055(4) | 2.052(5) |
| $\mathbf{P d}(1)-\mathrm{N}(2)$ | 2.054(5) | 2.0470(17) | 2.049(3) | 2.043(5) | 2.050(2) |
| $\mathbf{P d}(1)-\mathrm{N}(3)$ | 2.053(5) | $2.0689(17)$ | 2.061(5) | 2.061(5) | 2.072(5) |
| Pd(1)-Cl(1) | 2.2957(18) | 2.2990(6) | $2.3147(16)$ | 2.293(16) | 2.293(2) |
| N(2)-Pd(1)-N(1) | 85.4(2) | 85.66(7) | 85.33(13) | 85.70(19) | 86.2(2) |
| N(2)-Pd(1)-N(3) | 86.1(2) | 85.80(7) | 85.60(14) | 85.88(19) | 85.6(2) |
| C(21)-N(2)-Pd(1) | 116.5(4) | 115.13(13) | 112.9(3) | 115.1(4) | 115.5(4) |

All five cations are seen to interact with their anions through a double hydrogen bond. As in the case with $\mathbf{6 b}$ and $\mathbf{6 . 1 b}$, these interactions feature both NHAr donors promoting hydrogen bonds to acceptor groups on the corresponding substrates. ChemDraw representations below in Figure 6.26 show the dual $\mathrm{O} \cdots \mathrm{HN}$ hydrogen bonding in $\mathbf{6 . 2 b}$, 6.3b and 6.6b involving the cation and the anion.




Figure 6.26 - ChemDraw representation showing hydrogen bonding in 6.2b, 6.3b and $6.6 b$

Similarly, ChemDraw representations shown in Figure 6.27 show the dual $\mathrm{F} \cdots \mathrm{HN}$ hydrogen bonding in $\mathbf{6 . 4 b}$ and $\mathbf{6 . 5 b}$, also involving the cation and the anion. The average distance between the two acceptor groups on the substrates is $2.2746 \AA$,
whereas the average distance between the $N H A r$ donor groups is $4.262 \AA$. The shortest distance between the two acceptor groups belongs to the nitrate counterion [2.175 $\AA$ ] and the longest distance is observed in the $\mathrm{SO}_{3} \mathrm{CF}_{3}$ anion [2.431 $\AA$ ]. In addition, amongst 6.2b-6.6b, the shortest average distance between the donors and the acceptors $\mathrm{H}^{\cdots} \mathrm{O}$ belongs to $\mathbf{6 . 6 \mathrm { b }}$ with nitrate [ $2.199 \AA$ ] and the longest distance is for $\mathbf{6 . 3 \mathrm { b }}$ with hexafluorophosphate [2.199 $\AA$ ]. Furthermore, the average $\mathrm{N}-\mathrm{H} \cdots \mathrm{A}$ angle for all the complexes is $141.34^{\circ}$, with the hexafluorophosphate complex $\mathbf{6 . 5 b}$ having the smallest angle and the triflate complex 6.3b having the largest angle.



Figure 6.27 - ChemDraw representation showing hydrogen bonding in $6.4 b$ and $6.5 b$

Evidently, the presence and a particular cis orientation of the $N H A \mathrm{Ar}$ donor groups plays an important role in mediating and directing double hydrogen bonding in cationic $[(N \mathrm{Me}-\mathrm{dien}-2,6-\mathrm{Me} 2 \mathrm{Ph}) \mathrm{PdCl}]^{+}$complexes.

To explore the potential of cationic $\left[\left(N \mathrm{Me}-\mathrm{dien}-2,6-\mathrm{Me} \mathrm{e}_{2} \mathrm{Ph}\right) \mathrm{PdCl}\right]^{+}$complex to mediate hydrogen bonding interactions with other compounds based on the data obtained with the silver salts, a carboxylate framework was chosen as the potential substrate. Three benzoic acids with different substituents at the 4-position have been employed for this purpose: benzoic acid, 4-tert-butylbenzoic acid and 4-chlorobenzoic acid. If referring to the result obtained with the acetate anion, benzoic acids should technically result in the same binding pocket with the two acceptor oxygen atoms provided one of the oxygens becomes deprotonated. The reactions between 6.1b and the benzoic acids were performed in dichloromethane at room temperature overnight (Figure 6.28).


Figure 6.28 - Counterion exchange reaction between 6.1b and 4-substituted benzoic acids

The ${ }^{1} \mathrm{H}$ NMR spectrum of free benzoic acid displays a singlet at 11 ppm corresponding to the OH resonance. However, upon analysis of the newly formed complex by ${ }^{1} \mathrm{H}$ NMR, no OH resonance is observed and there is an apparent shift of all the peaks corresponding to the Pd-dien complex. In the IR spectrum of $\mathbf{6 . 7 b}$, the $v(\mathrm{NH})$ absorption band is seen at ca. $2985 \mathrm{~cm}^{-1}$, whereas the absorption band for the parent compound 6.1b comes at ca. $3235 \mathrm{~cm}^{-1}$. Further confirmation of the complex formation comes from the analysis by high resolution mass spectrometry, whereupon a fragmentation peak corresponding to loss of the chloride ion from the [(NMe-dien-2,6-Me2 Ph$) \mathrm{Pd}]^{+}$ complex with the benzoate unit being intact is observed. The signal comes at $587 \mathrm{~m} / \mathrm{z}$ $[\mathrm{M}-\mathrm{Cl}]^{+}$, where M is the palladium fragment. Figure 6.29 shows a ChemDraw representation of the fragment accounting for the peak observed in the TOF mass spectrum of $\mathbf{6 . 7} \mathbf{7}$. The so-called 'necklace' unit corresponding to the benzoate anion seems to remain intact with the complex upon ionisation.


Figure 6.29-Fragment observed in the mass spectrum of 6.7b

In addition, it was possible to grow crystals of $\mathbf{6 . 7 b}$ and they have been the subject of a single crystal X-ray diffraction study. Yellow crystals of $\mathbf{6 . 7 b}$ suitable for the X-ray determination were grown by layering a dichloromethane solution of the complex with petroleum ether at ambient temperature. A view of 6.7b is shown in Figure 6.30; selected bond distances and angles are listed in Table 6.6.


Figure 6.30 - Molecular structure of $\mathbf{6 . 7 b}$. Hydrogen atoms excluding H3A and H1 have been omitted for clarity

Table 6.6 - Selected bond lengths and bond angles for 6.7
BOND LENGTHS (Å)
BOND ANGLES $\left({ }^{\circ}{ }^{\circ}\right)$

| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $2.054(5)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $86.4(2)$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{2})$ | $2.039(6)$ | $\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $86.2(2)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{C l}(\mathbf{1})$ | $2.287(2)$ | $\mathbf{C l}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{1})$ | $92.54(15)$ |
| $\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $2.055(5)$ | $\mathbf{C l}(\mathbf{1})-\mathbf{P d}(\mathbf{1})-\mathbf{N}(\mathbf{3})$ | $93.72(16)$ |
| $\mathbf{N}(\mathbf{2})-\mathbf{C}(\mathbf{2 1})$ | $1.495(8)$ | $\mathbf{C}(\mathbf{2 1})-\mathbf{N}(\mathbf{2})-\mathbf{P d}(\mathbf{1})$ | $117.4(4)$ |

Similar to the molecular structures of $\mathbf{6 . 2 b - 6 . 6 b}$, the structure of $\mathbf{6 . 7 b}$ consists of a palladium centre supported by a tridentate $N, N, N$ bischelate, one terminal chloride ligand and a benzoic acid in its deprotonated form acting as an anion. The geometry at the palladium(II) centre can be described as distorted square planar with the equatorial plane defined by $\mathrm{N}(2)$ and $\mathrm{Cl}(1)\left[\mathrm{Cl}(1)-\mathrm{Pd}(1)-\mathrm{N}(1) 92.54(15)^{\circ}\right]$, and the axial plane by $\mathrm{N}(1)$ and $\mathrm{N}(3)\left[\mathrm{N}(3)-\operatorname{Pd}(1)-\mathrm{N}(1) 86.4(2)^{\circ}\right]$. The tridentate $N, N, N$ chelate is bound to palladium(II) in a mer configuration and forms two five-membered chelate rings with the bite angles being $86.2(2)^{\circ}$ and $86.4(2)^{\circ}$ for $\mathrm{N}(2)-\mathrm{Pd}(1)-\mathrm{N}(3)$ and $\mathrm{N}(2)-\mathrm{Pd}(1)-\mathrm{N}(1)$, respectively. The methyl groups on the $N$-aryl substituents are positioned below the plane defined by $\mathrm{N}(3)-\mathrm{Pd}(1)-\mathrm{N}(1)$. There is intramolecular and intermolecular hydrogen bonding present in the structure. As expected, the cation in 6.7b interacts with the benzoic acid counterion through a dual hydrogen bonding mediated from $\mathrm{N}(1)-\mathrm{H}(1)$ and $\mathrm{N}(3)-\mathrm{H}(3 \mathrm{~A})$ to $\mathrm{O}(1)$ and $\mathrm{O}(2)$ atoms. Results show that the benzoate moiety exhibits approximately equivalent C-O bond distances, $1.256(8) \AA$ and $1.258(8) \AA$, for $\mathrm{C}(22)-$ $\mathrm{O}(1)$ and $\mathrm{C}(22)-\mathrm{O}(2)$, respectively. The small difference in the distances of these two C $O$ bonds suggests a delocalised structure for the benzoate anion.

The distance between the two hydrogen bond donors in $\mathbf{6 . 7 b}, \mathrm{H}(1)$ and $\mathrm{H}(3 \mathrm{~A})$ is 4.305 $\AA$, whereas the distance between the acceptors $\mathrm{O}(1)$ and $\mathrm{O}(2)$ is $2.234 \AA$. The average distance of the hydrogen bonding interactions between the donors and acceptors $\mathrm{H}^{\cdots} \mathrm{A}$ in 6.7 b is $2.141 \AA$. This hydrogen bonding is the shortest in comparison to the interactions observed in complexes 6.2b-6.6b, generated from reactions with silver salts and discussed previously (Table 6.7). The longest hydrogen bonding distance $\left(\mathrm{H}^{\cdots} \mathrm{A}\right)$ is displayed by $\mathbf{6 . 5 b}$ where hexafluorophosphate is the counterion. In addition, the average
$\mathrm{N}-\mathrm{H}^{\cdots} \mathrm{A}$ angle in $\mathbf{6 . 7 b}$ is $139.57^{\circ}$, which is the second shortest angle after that observed in 6.5b [138.14 ${ }^{\circ}$.

Table 6.7 - Average hydrogen bond distances for complexes 6.2b-6.7b

| COMPLEXES | BOND LENGTHS (A) $H \cdots A$ | $\begin{gathered} \text { BOND ANGLES }\left({ }^{\circ}\right) \\ \text { N-H } \cdots \mathrm{A} \end{gathered}$ | $\mathbf{U}(\mathbf{N}-\mathrm{H})$ |
| :---: | :---: | :---: | :---: |
| 6.1b | - | - | 3235 |
| 6.2b | 2.202 | 141.01 | 3199 |
| 6.3b | 2.209 | 145.39 | 3210 |
| 6.4b | 2.263 | 142.48 | 2964 |
| 6.5b | 2.373 | 138.14 | 3203 |
| 6.6b | 2.199 | 141.47 | 2964 |
| 6.7b | 2.141 | 139.57 | 2985 |
| 6.8b | - | - | 2987 |
| 6.9b | - | - | 2992 |

The reactions between 6.1b and 4 -substituted benzoic acids also occurred smoothly in dichloromethane at room temperature. Likewise, no OH resonance have been observed in the ${ }^{1} \mathrm{H}$ NMR spectrum of the newly formed complexes $\mathbf{6 . 8 b}$ and $\mathbf{6 . 9 b}$ suggesting that the deprotonated acids interact with the NH groups of the complexes. Upon analysis by high resolution mass spectrometry of both compounds, strong fragmentation peaks corresponding to $\mathbf{6 . 8 b}$ and $\mathbf{6 . 9 b}$ together with their respective acid counterions and the loss of chloride ions are observed. Similar to $\mathbf{6 . 7 b}$, the 'necklace' unit consisting of the substituted benzoates remains intact with the complexes. Compound 6.8b displays a fragmentation peak at $608.2496 \mathrm{~m} / \mathrm{z}[\mathrm{M}-\mathrm{Cl}]^{+}$, whereas $\mathbf{6 . 9 b}$ shows a peak at 586.1469 $\mathrm{m} / \mathrm{z}[\mathrm{M}-\mathrm{Cl}]^{+}$. In the IR spectra of $\mathbf{6 . 8 b}$ and $\mathbf{6 . 9 b}$, the $v(\mathrm{NH})$ absorption bands are seen at ca. $2987 \mathrm{~cm}^{-1}$ and $2992 \mathrm{~cm}^{-1}$, respectively, whereas the absorption band for the parent 6.1b comes at ca. $3235 \mathrm{~cm}^{-1}$. Table 6.7 showing $v(N H)$ absorption frequencies corresponding to the parent complex 6.1b and its analogues 6.2b-6.9b, can confirm hydrogen bonding observed in the X-ray data. Complexes 6.2b-6.9b exhibit lower $v(\mathrm{NH})$ vibrations compared to the parent 6.1b, indicating the presence of hydrogen bonding. The H -bond acceptor atoms pull on the hydrogen atoms as they move around, thus lowering the vibration frequency and increasing the dipole moment.

### 6.4 Conclusions

12 novel complexes were successfully prepared from the di-aryl-substituted diethylenetriamines, HL10 and HL11, upon treatment with $\mathrm{Pd}(\mathrm{OAc})_{2}$ and $\mathrm{PdCl}_{2}(\mathrm{NCMe})_{2}$. The X-ray analysis of the complexes revealed the dien pincer ligand to adopt mer-configuration with the exterior NHAr donors which in each case are mutually cis. Furthermore, the structures in the solid state demonstrated the capacity of these NHAr donors to promote hydrogen bonding interactions with their corresponding counterions. It was established that anions can act as counterions for the synthesised complexes. Results suggest that the position of NH protons has a favourable directional effect for the observed self-assembly through hydrogen bonding. The majority of the synthesised complexes were studied by single crystal X-ray diffraction, which confirmed the geometry and bonding in these types of complexes.

## 7. Summary and Conclusions

### 7.1 Crystallographic comparisons

The synthesis of a range of novel platinum group metal complexes supported by pincer ligands has been described in this work. All the compounds have been thoroughly characterised by a variation of spectrometric and spectroscopic techniques and a number of the structures have been further confirmed by single crystal X-ray diffraction studies.

The solid-state structures of three solvento complexes 2a, 2c and 3b have been determined and confirmed the acetonitrile coordination. Single crystals of these acetonitrile-containing palladium(II) complexes have been grown by a slow evaporation of compounds in acetonitrile solution. All three structures reveal a palladium(II) complex in a distorted square planar geometry supported by an unsymmetrical dianionic pincer ligand. In 2a and $\mathbf{2 c}$, the $\mathrm{C}\left(\mathrm{sp}^{2}\right)$ - H activation of the aryl-C is observed supporting other characterisation data. On the contrary, 3b confirms the coordination of a deprotonated phenolic oxygen to palladium, thus fulfilling the tridentate mode of binding. Table 7.1 presents some examples of selected palladium bond lengths discussed in this work.

In CH-activated complexes, 2a-2.3b, the longest Pd-C bond is observed in the triphenylphosphine-containing complex 2.3a, whereas the shortest Pd-C bond distance belongs to the acetonitrile-containing complex with a $\mathrm{CF}_{3}$ substituent in the 4-position (Table 7.1).

The Pd- $\mathrm{O}_{\text {(carboxylate) }}$ bond distance in 3b is significantly shorter [2.006(4) $\AA$ ] than those observed in 2a and 2c [2.137(6) and 2.132(3) $\AA$, respectively] (Table 7.1). The bite angle between $\mathrm{N}(1)-\mathrm{Pd}(1)-\mathrm{O}(1)_{\text {carboxylate }}$ in $\mathbf{3 b}$ is the largest with $86.06(18)^{\circ}$ compared to those in $\mathbf{2 a}$ and $\mathbf{2 c}$, with similar bite angles being $79.5^{\circ}$ and $79.6^{\circ}$, respectively. The same trend is observed with $\operatorname{Pd}-\mathrm{N}_{\text {(pyridine) }}$ distances in these structures (Table 7.1). The $\mathbf{P d}-\mathrm{O}_{\text {(phenolate) }}$ bond length in $\mathbf{3 b}, \mathbf{3 . 3}$ and $\mathbf{3 . 4} \mathbf{c}$ is typical of an anionic phenolate tether to palladium(II) centre, with the shortest belonging to the triphenylphosphine-containing compound 3.3a (Table 7.1).

Table 7.1 - Selected bond lengths ( $\AA$ )

| Entry | Pd-O ${ }_{\text {(carboxylate) }}\left(\right.$ A $^{\text {) }}$ | $\mathbf{P d - N} \mathbf{N}_{\text {centr.pyridine }}\left(\mathbf{A} \mathbf{A}^{\text {) }}\right.$ | $\mathbf{P d - C ~ ( ~} \mathbf{A}_{\text {) }}$ ) | $\mathbf{P d - O}{ }_{\text {(phenolate }}(\mathbf{( \AA )}$ |
| :---: | :---: | :---: | :---: | :---: |
| 2 a | 2.137(6) | 1.937(7) | 1.967(9) | - |
| 2 c | 2.132(3) | 1.944(3) | $1.965(4)$ | - |
| 3b | 2.006(4) | 1.954(4) | - | 1.961(4) |
| 2.2c | 2.151(2) | 1.950(3) | 1.977(3) | - |
| 2.5a | 2.156 (3) | 2.001(3) | 2.020(4) | - |
| 2.4b | $2.155(4)$ | 1.947(4) | 1.981(5) | - |
| 3.5a | 2.007(3) | 2.017(3) | - | 1.942(3) |
| 3.4c | 1.991(8) | 1.989(10) | - | 1.960 (8) |

It was also possible to determine crystal structures of two pyridine-containing palladium(II) complexes, 2.4b and 2.2c, obtained from their corresponding acetonitrile analogues. In compound $\mathbf{2 b}$, acetonitrile ligand was easily substituted with 1phenylpyridine to form $\mathbf{2 . 4 b}$, whereas in compound $\mathbf{2 c}$, the auxiliary acetonitrile was exchanged with 3,5-dimethylpyridine. Both structures exhibit the typical square planar configuration around the palladium. The geometry is slightly distorted with the angles formed around the metal centre being close to $90^{\circ}$. The central $\mathrm{Pd}(\mathrm{II})$ ion is supported by a tridentate $\left[C, N_{P y}, O\right]$ pincer ligand and the corresponding substituted-pyridine ligands. In both cases, the pyridines are slightly tilted with respect to the pyridyl plane of the pincer ligand. It is assumed that this incline is a result of steric hindrance arising either from the adjacent phenyl ring on 1-phenylpyridine or the two methyl groups of 3,5-dimethylpyridine.

Furthermore, the reactivity of pincer ligands/complexes towards triphenylphosphine was probed. Three crystal structures have been determined for this set of compounds, $\mathbf{2 . 5 a}, \mathbf{3 . 5 a}$ and 3.4c. In case of $\mathbf{3 . 4} \mathbf{c}$, direct reaction of the pro-ligand with triphenylphosphine had to be applied due to solubility issues. The solid-state structures have all been shown to contain the expected palladium(II) triphenylphosphine core supported by a tridentate pincer ligand, further supporting their spectroscopic data. The angles between the adjacent donor atoms in the coordination sphere of palladium are relatively close to $90^{\circ}$ in all three cases. In 2.5a, the $\operatorname{Pd}(1)-\mathrm{N}(1)_{\text {pyridine }}$ bond length is longer than that in the acetonitrile precursor complex 2a. It is assumed that the bond
elongates in order to accommodate the bulky triphenylphosphine ligand. In both structures 3.5a and 3.4c, the larger six-membered metallacycle $\mathrm{O}(3)-\mathrm{Pd}(1)-\mathrm{N}(1)$ exhibits the larger bite angle. In complexes $2 \mathrm{a}-2.4 \mathrm{~b}$, the longest tridentate ligand to metal bond belongs to $\mathrm{Pd}-\mathrm{O}_{\text {(carboxylate) }}$ bond. This differs for 3.5a, where the $\mathrm{Pd}-\mathrm{N}_{\text {(central }}$ pyridine) could be considered as the longest bond, although not chemically significant in this case.

Furthermore, the reactivity of the $C, N_{P y}, O$ and $O, N_{P y}, O$ pro-ligands towards $\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}$ was explored and six novel ruthenium(III) pincer complexes have been successfully synthesised. The reaction of pro-ligand $\mathrm{HL}_{2}$ and $\mathrm{Ru}(p$-cymene $) \mathrm{Cl}_{2}$ precursor was also probed and reported in this work for comparison purposes. It was possible to determine four crystal structures corresponding to ruthenium complexes, $\mathbf{2 . 6} \mathbf{b}, \mathbf{2 . 6} \mathbf{c}, \mathbf{2 . 7 b}$ and 3.6b. The overall coordination geometry around the ruthenium(III) ion in 2.6b, 2.6c and 3.6b is distorted octahedral, which is reflected through all the bond parameters around the metal centre. The pincer ligand is coordinated to the ruthenium(III) ion in a tridentate fashion. Interestingly in $\mathbf{3 . 6 b}$, two $\mathrm{PPh}_{3}$ ligands are positioned cis to each other, with the chloride being trans to one of the $\mathrm{PPh}_{3}$ units and cis to the pyridyl core of the tridentate ligand. This is the opposite to the stereochemistry observed in complexes 2.6b and 2.6c, where the $\mathrm{PPh}_{3}$ ligands occupy the two axial positions, with the two $\mathrm{PPh}_{3}$ molecules being mutually trans to each other. The longest ligand to metal bonds for the tridentate ligand in $\mathbf{2 . 6} \mathbf{b}$ and $\mathbf{2 . 6} \mathbf{c}$ are formed between the carboxylate oxygen atoms and ruthenium $[\mathrm{Ru}(1)-\mathrm{O}(1) 2.163(5) \AA$ for $\mathbf{2 . 6 b}$, and $\mathrm{Ru}(1)-\mathrm{O}(1) 2.139(3) \AA$ for $\mathbf{2 . 6 c}]$. This is contradictory to what is observed in $\mathbf{3 . 6} \mathbf{b}$, where the metal bond from the pyridyl nitrogen $[\mathrm{Ru}(1)-\mathrm{N}(1) 2.053(5) \AA$ is only slightly different from the carboxylate bond [2.034(4) Å].

To appreciate the coordination mode and the stereochemistry of the pincer ligands upon reaction with a different ruthenium precursor such as $\mathrm{Ru}(p$-cymene $) \mathrm{Cl}_{2}$, the X -ray crystal structure of the complex $\mathbf{2 . 7 b}$ was determined. The molecular structure of 2.7b crystallises in a trigonal system as opposed to monoclinic crystal systems of $\mathbf{2 . 6 b}, \mathbf{2 . 6} \mathbf{c}$ and 3.6b. Upon reaction with $\mathrm{Ru}(p$-cymene $) \mathrm{Cl}_{2}$, the pincer ligand $\mathrm{HL}_{2}$ does not undergo a CH activation of the aryl carbon as happens in $\mathbf{2 . 6} \mathbf{b}$ where the reaction is performed with $\mathrm{Ru}\left(\mathrm{PPh}_{3}\right)_{3} \mathrm{Cl}_{2}$. The ruthenium(II) centre of $\mathbf{2 . 7 b}$ displays a half-sandwich geometry (piano-stool) consisting of one $\eta^{6}$-bonded $p$-cymene ligand, one chlorido and a $\mathrm{N}, \mathrm{O}$ bidentate ligand.

Subsequently, a series of palladium(II) and platinum(II) complexes supported by carboxylate containing mono(imino)pyridyl $\left[N, N_{P y}, O\right]$ pincer ligands have been synthesised and described in Chapter 5. For this work, five crystal structures have been determined (5a, 5.1a, 5.1c, 5.5a and 5.6c) and further confirmed all the other characterisation data. All the palladium(II) complexes excluding the platinum(II) complex 5.6c, exhibit a square planar coordination geometry with a tridentate ligand binding to palladium(II) through the $N, N_{P y}, O$ donor sites. Selected examples of bond lengths found in structures synthesised in this chapter are presented in Table 7.2. Analysis of the methyl-imine bond length of all mentioned structures reveals characteristic lengths typically predicted for a coordinated methyl-imine fragment with the longest belonging to $\mathbf{5 . 5 a}$ [ $2.047(9) \AA$, although chemically not much different from 5.1a $[2.027(3) \AA$ ]. In addition, in complex 5.5a, the introduced 3-bromopyridine unit is tilted with respect to the pyridyl plane, as a possible result of steric interactions between the Pd-(3-bromopyridine fragment and bulky 2,6-diisopropylphenyl substituent on the imine arm of the ligand. In all the complexes, the $N-\left(2,6-i-\operatorname{PrC}_{6} \mathrm{H}_{3}\right)$ unit is positioned perpendicular to the pyridyl plane and each isopropyl group adopts a position which is close in space to the axial position of the palladium(II) core. As Pd complexes are tridentate, $\mathrm{Pd}-\mathrm{N}_{\text {(central pyridine) }}$ bonds are always the shortest.

Unlike palladium(II) complexes 5a, 5.1a, 5.1c and 5.5a which exhibit a tridentate binding to the metal ion, complex 5.6c is found to be the bis-chloride platinum(II) complex with an $N, N$-bidentate ligand and a free ester arm. Upon analysis of 5.6c, the longest ligand to metal bonds in the structure is between the central pyridyl nitrogen and platinum metal $[\operatorname{Pt}(1)-\mathrm{N}(1) 2.056(8) \AA$, and the imine nitrogen bond to metal is the shortest in the structure. This pattern in the bond length between the central pyridyl nitrogen and the metal is opposite to what is observed with the palladium(II) structures shown in Table 7.2, where the imine nitrogen bond to the metal is longer compared to that from the central pyridyl nitrogen.

Table 7.2-Selected bond lengths ( $\AA$ )

| Entry | $\mathbf{M - N}_{\text {(pyridine) }}(\AA)$ | $\mathbf{P d - O}(\mathbf{1})(\AA)$ | $\mathbf{M}-\mathbf{C l}(\mathbf{1})(\mathbf{\AA})$ | $\mathbf{M}-\mathbf{N}(\mathbf{i m i n e})(\AA)$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathbf{5 a}$ | $1.897(7)$ | $2.048(5)$ | - | $2.010(7)$ |
| 5.1a | $1.913(3)$ | $2.048(2)$ | $2.292(9)$ | $2.027(3)$ |
| 5.1c | $1.926(4)$ | $2.050(4)$ | $2.297(16)$ | $2.011(5)$ |
| 5.5a | $1.918(9)$ | $2.035(7)$ | - | $2.047(9)$ |
| 5.6c | $2.056(8)$ | - | $2.289(3)$ | $1.985(8)$ |

### 7.2 Concluding Remarks

In this work, a series of novel symmetrical and unsymmetrical pincer pro-ligands of the $\left[C, N_{P y}, O\right], \quad\left[O, N_{P y}, O\right], \quad\left[N, N_{P y}, O\right]$ and $[N, N, N]$ have been prepared and fully characterised. To explore their reactivity towards platinum group metals, reactions of the corresponding pro-ligands with palladium(II), platinum(II) and ruthenium(II) metal precursors have been examined leading to generation of an extensive library of novel discreet pincer complexes. Aryl-containing [ $C, N_{P y}, O$ ] pincer ligands were found to promote $\mathrm{sp}^{2} \mathrm{C}$-H activations upon reactions with palladium(II) and ruthenium(II) metal salts. In phenol-containing $\left[O, N_{P y}, O\right.$ ] pincer ligands, the phenol oxygen becomes deprotonated, resulting in a tridentate binding and providing further stabilisation of the palladium(II) and ruthenium(III) metal centres. Mono(imino)pyridyl [ $N, N_{P y}, O$ ] pincer ligands incorporating an ethyl ester group at 6-position were found to undergo a hydrolysis to a carboxylic acid upon coordination to palladium. This trend does not occur upon reaction with a platinum(II) salt resulting in a bidentate binding of the corresponding complexes. Six novel paramagnetic ruthenium(III) pincer complexes developed from aryl-containing $\left[C, N_{P y}, O\right]$ and phenol-containing [ $O, N_{P_{y},} O$ ] pincer ligands have been employed as efficient catalysts for the transfer hydrogenation of ketones. Furthermore, the reactivity of dien $[N, N, N]$ pincer ligands towards palladium(II) salts have been explored and twelve novel pincer complexes have been prepared upon reaction with two palladium(II) metal precursors. The amine-NH moieties have been found to promote $\mathrm{NH} \cdots \mathrm{A}$ (acceptor) hydrogen bond interactions with the acceptor atoms on their corresponding anions.

## 8. Experimental

### 8.1 General Experimental

All synthetic operations were performed under an inert atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from appropriate drying agents or were employed directly from a Solvent Purification System (Innovative Technology, Inc). All NMR spectra were recorded on a Bruker DPX $300\left({ }^{1} \mathrm{H}, 300 \mathrm{MHz}\right)$, a Bruker DPX $400\left({ }^{1} \mathrm{H}, 400 \mathrm{MHz} ;{ }^{13} \mathrm{C}\right.$, 100 MHz ; $\left.{ }^{19} \mathrm{~F}, 375 \mathrm{MHz}\right)$ or a Bruker Avance III $500\left({ }^{1} \mathrm{H}, 500 \mathrm{MHz} ;{ }^{13} \mathrm{C}, 125 \mathrm{MHz} ;{ }^{31} \mathrm{P}\right.$, 161 MHz ) spectrometers as indicated, with TMS used as a standard reference (excl. ${ }^{19} \mathrm{~F}$ ). All the spectra were at ambient temperature unless otherwise stated; chemical shifts ( ppm ) are referred to the residual protic solvent peaks and coupling constants are expressed in hertz (Hz). Electrospray Mass Spectrometry (ESIMS) data were collected by means of a micromass Quattra LC mass spectrometer with methanol or acetonitrile as a matrix. High resolution FAB (fast atom bombardment) mass spectra were recorded using a Kratos Concept spectrometer (xenon gas, 7 kV ) with NBA as a matrix. Elemental analyses were performed at the Science Technical Support Unit, London Metropolitan University. The infrared spectra were recorded in the solid state with Universal ATR sampling accessories on a Perkin Elmer Spectrum One FTIR instrument. All compounds, including $n-\mathrm{BuLi}(1.6 \mathrm{M}$ in hexane) and triisopropyl borate were purchased from Sigma Aldrich and rigorously maintained under a nitrogen atmosphere. $\mathrm{Na}_{2} \mathrm{PdCl}_{4}$ and $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ were purchased from Alfa-Aesar and used as obtained. $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}{ }^{154}$ and $\mathrm{PdCl}_{2}(\mathrm{NCMe})_{2}{ }^{155}$ and $\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}{ }^{156}$ were synthesized by literature routes. The palladium salts, $\mathrm{PdCl}_{2}$ and $\mathrm{Pd}(\mathrm{OAc})_{2}$ were loaned from Johnson Matthey and used as received.

### 8.2 Experimental procedures for Chapter 2

### 8.2.1 Synthesis of 2-phenyl-6-ethylpicolinate



A mixture of ethyl-6-bromopicolinate ( $0.724 \mathrm{~g}, 3.16 \mathrm{mmol}$ ), phenylboronic acid $\left(\begin{array}{l}0.462 \quad \mathrm{~g}, \quad 3.79 \mathrm{mmol}) \text {, }\end{array}\right.$ tetrakis(triphenylphosphine)palladium $(0)\left[\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}\right] \quad(0.109$ $\mathrm{g}, 0.0948 \mathrm{mmol})$ in tetrahydrofuran $(30 \mathrm{ml})$ and $1 \mathrm{M} \mathrm{Na}_{2} \mathrm{CO}_{3}$ aqueous solution $(14.5 \mathrm{ml}$, 14.5 mmol ) was stirred and heated to reflux for 24 h . After cooling to room temperature, the reaction mixture was extracted with dichloromethane ( $3 \times 20 \mathrm{ml}$ ), and dried over $\mathrm{MgSO}_{4}$. The filtrate was concentrated under reduced pressure to give 2-phenyl-6-ethylpicolinate as a brown viscous oil which was purified by column chromatography ( $\mathrm{SiO}_{2}$, dichloromethane:hexane) $(0.698 \mathrm{~g}, 97 \%) .{ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 1.39\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 4.42\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.0 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right)$, $7.37\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}\right.$, Py/Ar-H), $7.42\left(\mathrm{t}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.83(\mathrm{t}, 1 \mathrm{H}$, ${ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz}$, Py/Ar-H), $7.97\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.0 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 8.01\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.3\right.$ $\mathrm{Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 13.3\left(\mathrm{CH}_{3}\right), 60.8\left(\mathrm{CH}_{2}\right), 122.4(\mathrm{CH})$, $126.2(\mathrm{CH}), 127.8(\mathrm{CH}), 128.4(\mathrm{CH}), 134.2(\mathrm{CH}), 136.6(\mathrm{CH}), 138.2(\mathrm{C}), 148.3(\mathrm{C})$, $155.0(\mathrm{C}), 164.6(\mathrm{C})$. IR $\left(\mathrm{cm}^{-1}\right): 1715(\mathrm{C}=\mathrm{O}), 1580(\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1237$ (C-O). ESIMS (+ve, MeOH): $m / z 228[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{14} \mathrm{H}_{14} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}$ 228.1025, found 228.1034. The NMR data are consistent with those reported in the literature ${ }^{35}$.

### 8.2.2 Synthesis of 2-phenyl-6-carboxylatopyridine (HL1)



A 250 ml round bottom flask, equipped with stir bar was charged with 2-phenyl-6-ethylpicolinate ( $0.515 \mathrm{~g}, 2.27 \mathrm{mmol}$ ), bench ethanol ( 60 ml ) and $\mathrm{NaOH}(3.63 \mathrm{~g}, 90.7 \mathrm{mmol})$, pre-dissolved in water ( 30.5 ml ), and was stirred and heated to reflux for 6 hours. The reaction mixture was allowed to cool to room temperature, and then acidified with 3 M HCl to pH 3 . The mixture was poured into water $(100 \mathrm{ml})$ resulting in the formation of a white precipitate. The precipitate was filtered, washed with water, and dried to give 2-phenyl-6carboxylatopyridine as an off white solid ( $0.420 \mathrm{~g}, 93 \%$ ). Mp: 110-112 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.47$ (m, 3H, Py/Ar-H), 7.98-7.90 (m, 4H, Py/Ar-H), 8.12 (d, 1H, $\left.{ }^{3} J_{\mathrm{HH}}=7.1 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right), 11.01(\mathrm{bs}, 1 \mathrm{H}, \mathrm{OH}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 122.0$
(CH), $124.8(\mathrm{CH}), 127.0(\mathrm{CH}), 129.1(\mathrm{CH}), 130.2(\mathrm{CH}), 137.1(\mathrm{C}), 139.3(\mathrm{CH}), 145.8$ (C), 156.5 (C), 164.1 (C). ESIMS (+ve, MeOH): $m / z 200[M+H]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+}$200.0712, found 200.0712. IR ( $\mathrm{cm}^{-1}$ ): $2847(\mathrm{O}-\mathrm{H}), 1694$ $(\mathrm{C}=\mathrm{O}), 1582(\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1245(\mathrm{C}-\mathrm{O})$. The NMR data are consistent with those reported in the literature ${ }^{35}$.

### 8.2.3 Synthesis of 4-t-butylphenyl boronic acid



A three-necked round bottomed flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with 1-t-butyl-4-bromobenzene ( $1.614 \mathrm{~g}, 7.61 \mathrm{mmol}$ ) and dry diethyl ether ( 45 ml ) and the stirred solution cooled to $-90^{\circ} \mathrm{C}$. $n$-BuLi ( $10 \mathrm{ml}, 16 \mathrm{mmol}, 2.1 \mathrm{eq}$.) was added dropwise to the cooled $\left(-90^{\circ} \mathrm{C}\right)$ solution and the reaction mixture allowed to warm to room temperature and stirred under nitrogen for 2 h . The flask was cooled back to $-90^{\circ} \mathrm{C}$ and a solution of triisopropyl borate ( $3.5 \mathrm{ml}, 2.86 \mathrm{~g}, 15.2 \mathrm{mmol}, 2 \mathrm{eq}$.) was added rapidly. The mixture was stirred at $90^{\circ} \mathrm{C}$ for 30 min and then at room temperature for 15 h under nitrogen. $2 \mathrm{M} \mathrm{HCl}(6 \mathrm{ml})$ was added slowly to the ice cooled reaction mixture and then stirred for a further 30 min resulting in the milky white emulsion becoming clear. The ether layer was separated and the aqueous layer extracted with diethyl ether ( $3 \times 20 \mathrm{ml}$ ). The combined ether solutions were dried with $\mathrm{MgSO}_{4}$ and the solvent removed under reduced pressure to give a gummy solid. The solid was recrystallised from hexane and dried overnight to give 4-t-butylphenyl boronic acid as a white solid $(0.704 \mathrm{~g}, 52 \%) .{ }^{1} \mathrm{H}$ NMR $(400 \mathrm{MHz}$, $\mathrm{CDCl}_{3}$ ): $\delta 1.38\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 7.54\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}} 8.2, \mathrm{Ar}-\mathrm{H}\right), 8.17\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.1\right.$ $\mathrm{Hz}, \mathrm{Ar}-\mathrm{H})$. ESIMS (+ve, MeOH): $m / z 179[\mathrm{M}+\mathrm{H}]^{+}$. The NMR data are consistent with those reported in the literature ${ }^{90}$.

### 8.2.4 Synthesis of 2-(4'-t-butyl-)-6-ethylpicolinate



The same procedure as that described for 2-phenyl-6ethylpicolinate using ethyl-6-bromopicolinate ( 1.56 g , 6.81 mmol ), 4 - $t$-butylphenylboronic acid ( $1.33 \mathrm{~g}, 7.49$ mmol), tetrakis(triphenylphosphine)palladium(0)
$\left[\left(\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}\right](0.236 \mathrm{~g}, 0.204 \mathrm{mmol})\right.$, dry tetrahydrofuran $(63 \mathrm{ml})$ and $1 \mathrm{M} \mathrm{Na}{ }_{2} \mathrm{CO}_{3}$
aqueous solution ( $33.4 \mathrm{ml}, 33 \mathrm{mmol}$ ) gave 2-(4'-t-butyl)-6-ethylpicolinate as a yellow viscous oil which was purified by column chromatography $\left(\mathrm{SiO}_{2}\right.$, dichloromethane) $(1.77 \mathrm{~g}, 92 \%) .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.28\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 1.39\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=\right.$ $\left.7.1 \mathrm{~Hz}, \mathrm{CH}_{3}\right), 4.41\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.4 \mathrm{~Hz}, \mathrm{CH}_{2}\right), 7.43\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.3 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right)$, 7.75-7.81 (m, 2H, Py/Ar-H), 7.90-7.95 (m, 3H, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 14.3\left(\mathrm{CH}_{3}\right), 31.3\left(\mathrm{CH}_{3}\right), 34.7(\mathrm{C}), 62.0\left(\mathrm{CH}_{2}\right), 123.2(\mathrm{CH}), 125.6(\mathrm{CH}), 127.8(\mathrm{CH})$, 130.4 (CH), 135.2 (CH), 135. 8 (C), 148.4 (C), 152.7 (C), 157.7 (C), 165.6 (C). IR ( $\mathrm{cm}^{-}$ $\left.{ }^{1}\right)$ : 1727 (C=O), 1591 (C=N) pyridine, 1226 (C-O). ESIMS ( $+v e$, MeOH): m/z 284 $[\mathrm{M}+\mathrm{H}]^{+}$. ESIMS (-ve, MeOH): $m / z 283[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{18} \mathrm{H}_{22} \mathrm{NO}_{2}$ $[\mathrm{M}+\mathrm{H}]^{+}$284.1651, found 284.1648 .

### 8.2.5 Synthesis of 2-(4'-t-butyl)-6-carboxylatopyridine (HL2)



The same procedure as that described for 2-phenyl-6carboxylatopyridine using 2-(4'-t-butyl)-6-ethylpicolinate $(0.885 \mathrm{~g}, 3.12 \mathrm{mmol})$, bench ethanol ( 100 ml ) and NaOH ( 5 $\mathrm{g}, 125.1 \mathrm{mmol}$ ), pre-dissolved in water ( 50 ml ), gave 2-( 4 '-t-$\mathrm{Bu})$-6-carboxylatopyridine as a white solid ( $0.763 \mathrm{~g}, 96 \%$ ). Mp: 167-169 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.31\left(\mathrm{~s}, 9 \mathrm{H},\left(\mathrm{CH}_{3}\right)_{3}\right), 7.48\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.3 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.86$ $\left(\mathrm{d}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.66 \mathrm{~Hz}\right.$, Py/Ar-H), 7.90-7.97 (m, 2H, Py/Ar-H), $8.09\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8\right.$ $\mathrm{Hz},{ }^{4} J_{\mathrm{HH}}=1.93 \mathrm{~Hz}$, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 31.2\left(\mathrm{CH}_{3}\right), 34.8(\mathrm{C})$, $121.6(\mathrm{CH}), 124.6(\mathrm{CH}), 126.1(\mathrm{CH}), 126.8(\mathrm{CH}), 127.2(\mathrm{CH}), 139.2(\mathrm{C}), 145.8(\mathrm{C})$, 153.6 (C), 156.5 (C), 164.2 (C). IR ( $\mathrm{cm}^{-1}$ ): $2958(\mathrm{O}-\mathrm{H}), 1700(\mathrm{C}=\mathrm{O}), 1589(\mathrm{C}=\mathrm{N})_{\text {pyridine }}$, 1229 (C-O). ESIMS (+ve, MeOH): $m / z 256[\mathrm{M}+\mathrm{H}]^{+}$. ESIMS ( $-v e, \mathrm{MeOH}$ ): $m / z 254$ [M$\mathrm{H}]^{+}$. HRMS (ASAP): $m / z$ calc. for $\mathrm{C}_{16} \mathrm{H}_{18} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}]^{+} 256.1338$, found 256.1337 .

### 8.2.6 Synthesis of 4-(trifluoromethyl)phenyl boronic acid



The same procedure described as that for 4-t-butylphenylboronic acid using 1-bromo-4-(trifluoromethyl) benzene ( $2.0 \mathrm{~g}, 9.6 \mathrm{mmol}$ ), dry diethyl ether ( 45 ml ), $n$-BuLi ( $6.1 \mathrm{ml}, 9.7 \mathrm{mmol}, 2.1 \mathrm{eq}$.$) and$ triisopropyl borate ( $5.14 \mathrm{ml}, 4.18 \mathrm{~g}, 22 \mathrm{mmol}, 2.5 \mathrm{eq}$.$) to give a gummy solid which was$ recrystallised from hexane and dried overnight to afford 4-(trifluoromethyl)phenyl boronic acid as a white solid ( $1.78 \mathrm{~g}, 98 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta 7.51$ (d,
$\left.{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz}, 2 \mathrm{H}\right), 7.78\left(\mathrm{~d},{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz}, 2 \mathrm{H}\right) .{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}\right): \delta 117.7$ $\left(\mathrm{s}, C \mathrm{~B}(\mathrm{OH})_{2}\right), 124.6\left(\mathrm{q},{ }^{3} J_{\mathrm{CF}}=3.07 \mathrm{~Hz}, C \mathrm{H}\right), 125.3\left(\mathrm{q},{ }^{1} J_{\mathrm{CF}}=270.3, C \mathrm{~F}_{3}\right), 132.3\left(\mathrm{q},{ }^{2} J_{\mathrm{CF}}\right.$ $=31.7, C^{2}$ ), 134.8. ${ }^{19} \mathrm{~F}$ NMR ( $376 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta-64.1$. ESIMS ( $+v e, \mathrm{MeOH}$ ): $m / z 189[\mathrm{M}]^{+}, 361\left[2 \mathrm{M}-\mathrm{H}_{2} \mathrm{O}\right]^{+}$. The NMR data are consistent with those reported in the literature ${ }^{90}$.

### 8.2.7 Synthesis of 2-(4'-trifluoromethyl)-6-ethylpicolinate



The same procedure as that described for 2-phenyl-6ethylpicolinate using ethyl-6-bromopicolinate ( 1.86 g , 8.13 mmol ), 4-(trifluoromethyl)phenylboronic acid ( 1.85 $\mathrm{g}, 9.76 \mathrm{mmol})$, tetrakis(triphenylphosphine)palladium(0) [( $\left.\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}\right](0.281 \mathrm{~g}, 0.244$ mmol ), dry tetrahydrofuran ( 75 ml ) and $1 \mathrm{M} \mathrm{Na} \mathrm{Na}_{2} \mathrm{CO}_{3}$ aqueous solution ( $37 \mathrm{ml}, 37 \mathrm{mmol}$ ) gave 2-(4'-trifluoromethyl)-6-ethylpicolinate as a yellow viscous oil which was purified by column chromatography $\left(\mathrm{SiO}_{2}\right.$, dichloromethane) ( $1.93 \mathrm{~g}, 80 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( 500 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 1.40\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 4.43\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, $\mathrm{CH}_{2} \mathrm{CH}_{3}$ ), $7.68\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.4 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.86-7.88(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 8.02-8.06$ (m, 1H, Py/Ar-H), 8.12 (d, 2H, $\left.{ }^{3} \mathrm{JHH}_{\mathrm{HH}}=7.4 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 14.1\left(\mathrm{CH}_{3}\right), 61.2\left(\mathrm{CH}_{2}\right), 123.6(\mathrm{CH}), 124.5\left(\mathrm{q},{ }^{3} J_{\mathrm{CF}}=3.2 \mathrm{~Hz}, \mathrm{CH}\right), 125.4(\mathrm{CH}), 126.1$ $\left(\mathrm{q},{ }^{1} J_{\mathrm{CF}}=271.9, C \mathrm{~F}_{3}\right), 127.2(\mathrm{CH}), 128.3\left(\mathrm{q},{ }^{2} J_{\mathrm{CF}}=31.4, \mathrm{CCF}_{3}\right), 138.2(\mathrm{CH}), 142.6(\mathrm{C})$, 153.7 (C), 156.4 (C), 162.1 (C). ${ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 376 MHz ): $\delta$-62.8 (s, 3F, CF ${ }_{3}$ ). IR $\left(\mathrm{cm}^{-1}\right): 1737(\mathrm{C}=\mathrm{O}), 1581(\mathrm{C}=\mathrm{N})_{\text {pyridine, }} 1237(\mathrm{C}-\mathrm{O})$. ESIMS (+ve, MeOH): m/z 296 $[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{15} \mathrm{H}_{13} \mathrm{NO}_{2} \mathrm{~F}_{3}[\mathrm{M}+\mathrm{H}]^{+}$296.0898, found 296.0901. The NMR data are consistent with those reported in the literature ${ }^{35}$.

### 8.2.8 Synthesis of 2-(4'-trifluoromethyl)-6-carboxylatopyridine (HL3)



The same procedure as that described for 2-phenyl-6carboxylatopyridine using 2-(4'-trifluoromethyl)-6ethylpicolinate ( $0.465 \mathrm{~g}, 1.57 \mathrm{mmol}$ ), bench ethanol ( 54 ml ) and $\mathrm{NaOH}(2.52 \mathrm{~g}, 63 \mathrm{mmol})$, pre-dissolved in water ( 27 ml ) gave 2-(4'-trifluoromethyl)-6-carboxylatopyridine as a white solid ( $0.401 \mathrm{~g}, 96 \%$ ). M.p: 153-156 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.73\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.1 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right.$ ), $7.98(\mathrm{~d}, 1 \mathrm{H}$, ${ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}$, Py/Ar-H), $8.03(\mathrm{~m}, 3 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 8.20\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.4 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right)$,
$11.05(\mathrm{bs}, 1 \mathrm{H}, \mathrm{OH}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 122.8(\mathrm{CH}), 125.2(\mathrm{CH}), 126.1(\mathrm{q}$, $\left.{ }^{3} J_{\mathrm{CF}}=3.5 \mathrm{~Hz}, C \mathrm{H}\right), 127.4(\mathrm{CH}), 128.3\left(\mathrm{q},{ }^{1} J_{\mathrm{CF}}=272.3, C \mathrm{~F}_{3}\right), 132.1\left(\mathrm{q},{ }^{2} J_{\mathrm{CF}}=31.4\right.$, $\mathrm{CCF}_{3}$ ), 139.7 (CH), 140.3 (C), 146.2 (C), 155.1 (C), 163.7 (C). ${ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (376 $\mathrm{MHz}): \delta-62.8(\mathrm{~s}, 3 \mathrm{~F}, \mathrm{CF} 3)$. IR $\left(\mathrm{cm}^{-1}\right): 2965(\mathrm{O}-\mathrm{H}), 1701(\mathrm{C}=\mathrm{O}), 1590(\mathrm{C}=\mathrm{N})_{\text {pyridine }}$, 1229 (C-O). ESIMS (+ve, MeOH): $m / z 268[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{13} \mathrm{H}_{9} \mathrm{NO}_{2} \mathrm{~F}_{3}[\mathrm{M}+\mathrm{H}]^{+}$268.0585, found 268.0592. The NMR data are consistent with those reported in the literature ${ }^{35}$.

### 8.3 Complexes supported by aryl-substituted $\left[C, N_{P_{y},} O\right]$ pincer ligands

## Synthesis of 2a



A small dry Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with 2-phenyl-6-carboxylatopyridine ( $0.080 \mathrm{~g}, 0.402 \mathrm{mmol}$ ) and $\mathrm{Pd}(\mathrm{OAc})_{2}(0.090 \mathrm{~g}, 0.402 \mathrm{mmol})$ in dry acetonitrile $(5 \mathrm{ml})$. The reaction mixture was stirred at room temperature for 18 h in an atmosphere of nitrogen affording a yellow suspension, which was filtered through a Celite plug and extracted with acetonitrile. The solvent was removed under reduced pressure to give $2 \mathbf{2 a}$ as a yellow powder ( $0.134 \mathrm{~g}, 97 \%$ ). Single crystals suitable for Xray determination were grown by slow evaporation of a solution of $\mathbf{2 a}$ in acetonitrile. Mp: 240-242 ${ }^{\circ} \mathrm{C}$ (decomp.). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 1.95$ ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Pd}-\mathrm{NCMe}$ ), 6.62-6.86 (m, 3H, Py/Ar-H), $7.06\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.3 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.26\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=\right.$ 7.0 Hz, Py/Ar-H), $7.36\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.4 \mathrm{~Hz}\right.$, Py/Ar-H), $7.67\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 0.5$ ( $\mathrm{MeC} \equiv \mathrm{N}-$ ), $117.0(\mathrm{MeCN}), 121.8(\mathrm{CH})$, $123.6(\mathrm{CH}), 124.6(\mathrm{CH}), 129.3(\mathrm{CH}), 133.3(\mathrm{CH}), 133.6(\mathrm{CH}), 139.6(\mathrm{CH}), 145.7(\mathrm{C})$, 149.8 (C), 151.5 (C), 162.5 (C), 169.5 (C), 171.7 (C). IR ( $\mathrm{cm}^{-1}$ ): 1745 (C=O), 1567 $(\mathrm{C}=\mathrm{N})_{\text {pyridine }}$. ESIMS ( $+v e, \mathrm{MeCN}$ ): $m / z 345[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{14} \mathrm{H}_{10} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{NaPd}[\mathrm{M}+\mathrm{Na}]^{+} 366.9675$, found 366.9678 .

## Synthesis of 2.1a



A small round bottomed flask equipped with stir bar was charged with $2 \mathbf{2 a}(0.012 \mathrm{~g}, 0.0348 \mathrm{mmol})$ and pyridine $(0.00275 \mathrm{~g}, 0.0028$ $\mathrm{ml}, 0.0348 \mathrm{mmol}$ ) in chloroform ( 5 ml ). The reaction was stirred at room temperature for 18 h . The resultant filtrate was removed under reduced pressure to give 2.1a as a green-yellow solid ( 0.010 g, 77\%). Mp: 237-239 ${ }^{\circ} \mathrm{C}$ (decomp.). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 6.65$ (d, $1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=$ $7.4 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}), 7.02\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.1 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.08\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.3 \mathrm{~Hz}\right.$, Py/Ar-H), $7.41\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.4 \mathrm{~Hz}\right.$, Py/Ar-H), $7.46\left(\mathrm{t}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, Py/Ar-H), $7.55\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.4 \mathrm{~Hz}\right.$, Py/Ar-H), $7.70\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{JHH}_{\mathrm{HH}}=7.5 \mathrm{~Hz}\right.$, Py/Ar-H), 7.83-7.9 $(\mathrm{m}, 2 \mathrm{H}), 8.85\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} \mathrm{JHH}_{\mathrm{HH}}=7.1 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 119.6$ $(\mathrm{CH}), 123.1(\mathrm{CH}), 124.0(\mathrm{CH}), 125.3(\mathrm{CH}), 125.7(\mathrm{CH}), 130.1(\mathrm{CH}), 133.3(\mathrm{CH}), 138.7$ (CH), 139.5 (CH), 146.8 (C), 147.1 (C), 150.8 (C), 151.2 (C), 152.5 (CH), 162.7 (C). IR $\left(\mathrm{cm}^{-1}\right): 1738(\mathrm{C}=\mathrm{O}), 1648(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$. ESIMS ( $\left.+v e, \mathrm{MeOH}\right): m / z 383[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{17} \mathrm{H}_{12} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Pd}[\mathrm{M}+\mathrm{H}]^{+} 382.9431$, found 382.9432 .

## Synthesis of 2.2a



The same procedure as that described for 2.1a, using $2 \mathbf{a}(0.012 \mathrm{~g}$, 0.0348 mmol ) and 3,5 -dimethylpyridine $(0.00374 \mathrm{~g}, 0.00398 \mathrm{ml}$, 0.0348 mmol ) in chloroform ( 5 ml ) gave 2.2a as a green solid ( $0.0095 \mathrm{~g}, 68 \%$ ). Mp: $245-247{ }^{\circ} \mathrm{C}$ (decomp.). ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta 2.32\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right), 6.64\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{JHH}_{\mathrm{HH}}=7.5 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right)$, $7.02\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, Py/Ar-H), $7.08\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, Py/Ar-H), 7.41 (d, 1H, $\left.{ }^{3} J_{\mathrm{HH}}=7.4 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.47$ (s, 1H, Py/Ar-H), 7.55 (d, 1H, ${ }^{3} J_{\mathrm{HH}}=7.4 \mathrm{~Hz}$, Py/Ar-H), $7.70\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}\right.$, Py/Ar-H), $7.84\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.3\right.$ $\mathrm{Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 8.48$ (s, 2H, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 18.3\left(\mathrm{CH}_{3}\right), 119.5$ (CH), 122.9 (CH), 123.9 (CH), 125.2 (CH), 130.1 (CH), 133.5 (CH), 135.3 (C), 139.5 (CH), 140.0 (CH), 146.9 (C), 149.6 (CH), 151.3 (C), 152.7 (C), 162.8 (C), 170.7 (C). IR $\left(\mathrm{cm}^{-1}\right): 1699(\mathrm{C}=\mathrm{O}), 1586(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$. ESIMS ( $\left.+v e, \mathrm{MeOH}\right): \mathrm{m} / \mathrm{z} 411[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{12} \mathrm{H}_{8} \mathrm{NO}_{2} \mathrm{Pd}[(\mathrm{M}-\mathrm{Py})+\mathrm{H}]^{+} 302.9606$, found 302.9631.

## Synthesis of 2.5a

The same procedure as that described for 2.1a, using $2 \mathbf{2 a}(0.012 \mathrm{~g}$,
 $0.0348 \mathrm{mmol})$ and triphenylphosphine ( $0.00913 \mathrm{~g}, 0.0348 \mathrm{mmol}$ ) in chloroform ( 5 ml ) gave $\mathbf{2 . 5 a}$ as a yellow solid $(0.014 \mathrm{~g}, 71 \%)$. Single crystals suitable for X-ray determination were grown by slow diffusion of petroleum ether (40-60) into a chloroform solution of 2.5a. Mp: 227-230 ${ }^{\circ} \mathrm{C}$ (decomp.). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 6.31$ (m, $1 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 6.57\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right), 6.95\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\right.$ H), 7.33-7.38 (m, 6H, Py/Ar-H), 7.39-7.42 (m, 3H, Py/Ar-H), 7.59-7.64 (m, 8H, Py/ArH), $7.77\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.88\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.1 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 119.5(\mathrm{CH}), 122.9(\mathrm{CH}), 124.2(\mathrm{CH}), 125.1(\mathrm{CH}), 128.5$ (CH), $128.8(\mathrm{CH}), 129.5(\mathrm{C}), 129.8(\mathrm{C}), 130.5(\mathrm{CH}), 131.9(\mathrm{CH}), 132.1(\mathrm{CH}), 134.8$ (CH), 134.9 (CH), $139.0(\mathrm{CH}), 139.2(\mathrm{CH}), 140.2$ (CH), 148.1 (C), 150.2 (C), 151.9 (C), 161.6 (C), 170.1 (C). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}(161 \mathrm{MHz}): \delta 35.06\left(\mathrm{~s}, 1 \mathrm{P}, P \mathrm{Ph}_{3}\right)$. IR $\left(\mathrm{cm}^{-1}\right): 1638$ (C=O), 1596 (C=N) pyridine. ESIMS (-ve, MeOH): $m / z 564[M-H]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{30} \mathrm{H}_{23} \mathrm{NO}_{2} \mathrm{PdP}\left[(\mathrm{M}+\mathrm{H}]^{+} 566.0501\right.$, found 566.0513. HRMS (TOF): $\mathrm{m} / \mathrm{z}$ calc. for $\mathrm{C}_{30} \mathrm{H}_{22} \mathrm{NO}_{2} \mathrm{PdPNa}\left[(\mathrm{M}+\mathrm{Na}]^{+} 588.0321\right.$, found 588.0339.

## Synthesis of 2.6a



A small round bottomed flask equipped with a stir bar was charged with 2-phenyl-6-carboxylatopyridine $(0.060 \mathrm{~g}, 0.301$ mmol), methanol (15 ml) and tris(triphenylphosphine)ruthenium(II) dichloride $\left[\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}\right]$ $(0.289 \mathrm{~g}, 0.301 \mathrm{mmol})$ was stirred and heated to reflux for 24 h . On cooling to cool to room temperature, the precipitate was filtered through a Celite plug and washed thoroughly with methanol. Pure product was extracted with dichloromethane and dried under reduced pressure to afford 2.6a as an orange solid ( $0.253 \mathrm{~g}, 98 \%$ ). Mp: 255-258 ${ }^{\circ} \mathrm{C}$ (decomp.). IR ( $\mathrm{cm}^{-1}$ ): 1749 ( $\mathrm{C}=\mathrm{O}$ ), $1640(\mathrm{C}=\mathrm{N})_{\text {pyridine }}$. ESIMS (+ve, MeOH): m/z $859[\mathrm{M}+\mathrm{H}]{ }^{+} .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ ( 161 MHz ): $\delta 29.1$ (s, 2P, $\mathrm{PPh}_{3}$ ). HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{48} \mathrm{H}_{38} \mathrm{ClNO}_{2} \mathrm{P}_{2} \mathrm{Ru}\left[(\mathrm{M}+\mathrm{H}]^{+}\right.$859.1200, found 859.1234. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{48} \mathrm{H}_{37} \mathrm{ClNO}_{2} \mathrm{P}_{2} \mathrm{RuNa}\left[(\mathrm{M}+\mathrm{Na}]^{+} 881.0929\right.$, found 881.0917. $\mu_{\mathrm{eff}}=1.89 \mathrm{BM}$.

## Synthesis of 2b



A clean dry Schlenk flask equipped with a stir bar was evacuated and backfilled with nitrogen. The flask was charged with 2-(4'-tertbutyl)-6-carboxylatopyridine $(0.100 \mathrm{~g}$, $0.392 \mathrm{mmol})$ and $\mathrm{Pd}(\mathrm{OAc})_{2}(0.088 \mathrm{~g}, 0.392 \mathrm{mmol})$ in dry acetonitrile ( 5 ml ). The reaction mixture was stirred at room temperature for 2 hours affording an orange suspension, which was filtered through a Celite plug and washed thoroughly with acetonitrile. The solvent was removed under reduced pressure to give $\mathbf{2 b}$ as an orange powder ( 0.144 g , $92 \%$ ). Mp: > $260^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 1.35\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{CH}_{3}\right), 1.99(\mathrm{~s}, 3 \mathrm{H}$, Pd-NCMe), 7.16 (s, 1H, Py/Ar-H), 7.23 (dd, $1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.1 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=1.7 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-$ H), $7.43\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.4 \mathrm{~Hz}\right.$, Py/Ar-H), $7.56\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.3 \mathrm{~Hz}\right.$, Py/Ar-H), $7.68(\mathrm{~d}$, $\left.1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.4 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.96\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.4 \mathrm{~Hz}\right.$, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( 125 $\left.\mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right): \delta 0.6(\mathrm{MeC} \equiv \mathrm{N}-), 30.1\left(\mathrm{CH}_{3}\right), 34.4(\mathrm{C}), 117.0(\mathrm{MeCN}-\mathrm{C}), 119.7(\mathrm{CH})$, $121.7(\mathrm{CH}), 122.3(\mathrm{CH}), 123.6(\mathrm{CH}), 130.9(\mathrm{CH}), 140.1(\mathrm{CH}), 143.5(\mathrm{C}), 147.9(\mathrm{C})$, 149.3 (C), 153.6 (C), 169.8 (C), 171.4 (C). IR ( $\mathrm{cm}^{-1}$ ): 1635 (C=O), 1582 (C=N) pyridine. ESIMS (+ve, MeCN): $m / z 401[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{18} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{PdNa}$ $[\mathrm{M}+\mathrm{Na}]^{+} 423.0296$, found 423.0301.

## Synthesis of 2.2b



The same procedure as that described for 2.1a, using $\mathbf{2 b}$ $(0.020 \mathrm{~g}, 0.05 \mathrm{mmol})$ and 3,5 -dimethylpyridine $(0.005 \mathrm{~g}$, 0.05 mmol ) in chloroform ( 10 ml ) gave $\mathbf{2 . 2 b}$ as a yellow solid ( $0.021 \mathrm{~g}, 93 \%$ ). Mp: > $260{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta 1.25\left(\mathrm{~s}, 9 \mathrm{H},\left(\mathrm{CH}_{3}\right)_{3}\right), 2.40\left(\mathrm{~s}, 6 \mathrm{H},\left(\mathrm{CH}_{3}\right)_{2}\right), 6.78(\mathrm{~s}$, $1 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 7.18\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.6 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=1.6 \mathrm{~Hz}\right.$, Py/Ar-H), 7.42 (d, 1H, $\left.{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}, \operatorname{Py} / A r-H\right), 7.56$ (s, 1H, Py/Ar-H), 7.59 (d, 1H, ${ }^{3} J_{\mathrm{HH}}=7.4 \mathrm{~Hz}$, Py/Ar-H), $7.75\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.94\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.2\right.$ Hz, Py/Ar-H), 8.58 (s, 2H, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 18.3\left(\mathrm{CH}_{3}\right), 31.1$ $\left(\mathrm{CH}_{3}\right), 33.8(\mathrm{C}), 119.2(\mathrm{CH}), 122.3(\mathrm{CH}), 122.5(\mathrm{CH}), 123.5(\mathrm{CH}), 130.3(\mathrm{CH}), 135.1$ (C), $139.4(\mathrm{CH}), 139.9(\mathrm{CH}), 142.7(\mathrm{C}), 146.5(\mathrm{C}), 149.8(\mathrm{CH}), 151.1(\mathrm{C}), 153.6(\mathrm{C})$, 162.8 (C), $168.5(\mathrm{C})$. IR $\left(\mathrm{cm}^{-1}\right): 1641(\mathrm{C}=\mathrm{O}), 1586(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$. ESIMS (+ve, MeOH): $m / z 467[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{23} \mathrm{H}_{24} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{PdNa}[\mathrm{M}+\mathrm{Na}]^{+}$489.0770,
found 489.0775. HRMS (FAB): $m / z$ calc. for $\mathrm{C}_{23} \mathrm{H}_{25} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Pd}[\mathrm{M}+\mathrm{H}]^{+} 467.08726$, found 467.09418.

## Synthesis of 2.3b



The same procedure as that described for 2.1a, using $\mathbf{2 b}$ $(0.020 \mathrm{~g}, 0.05 \mathrm{mmol})$ and 3,5 -dichloropyridine $(0.007 \mathrm{~g}, 0.05$ mmol ) in chloroform ( 10 ml ) gave 2.3b as a yellow solid ( $0.022 \mathrm{~g}, 87 \%$ ). Mp: > $260^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.21\left(\mathrm{~s}, 9 \mathrm{H},\left(\mathrm{CH}_{3}\right)_{3}\right), 6.65(\mathrm{~s}, 1 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 7.14(\mathrm{dd}, 1 \mathrm{H}$, ${ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=1.6 \mathrm{~Hz}$, Py/Ar-H), $7.35\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=\right.$ $7.5 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}), 7.53\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.67\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}\right.$, Py/Ar-H), $7.84\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.3 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.94(\mathrm{~s}, 1 \mathrm{H}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}), 8.83(\mathrm{~s}, 2 \mathrm{H}$, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 30.1\left(\mathrm{CH}_{3}\right), 34.2(\mathrm{C}), 118.5(\mathrm{CH}), 121.7$ (CH), 122.8 (CH), $124.1(\mathrm{CH}), 128.5(\mathrm{CH}), 132.9(\mathrm{C}), 137.5(\mathrm{CH}), 138.8(\mathrm{CH}), 141.4$ (C), 143.1 (C), 148.5 (CH), 149.5 (C), 152.9 (C), 161.9 (C), 172.2 (C). IR ( $\mathrm{cm}^{-1}$ ): 1699 $(\mathrm{C}=\mathrm{O}), 1577(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$. ESIMS (+ve, MeOH): $m / z 507[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (FAB): $m / z$ calc. for $\mathrm{C}_{21} \mathrm{H}_{19} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{ClPd}[\mathrm{M}+\mathrm{H}]^{+} 506.98584$, found 506.98508. HRMS (FAB): $\mathrm{m} / \mathrm{z}$ calc. for $\mathrm{C}_{16} \mathrm{H}_{15} \mathrm{NO}_{2} \mathrm{Pd}$ [M-3,5-dichloropyridine] ${ }^{+} 360.01376$, found 360.02090 .

## Synthesis of 2.4b



The same procedure as that described for 2.1a, using $\mathbf{2 b}$ $(0.020 \mathrm{~g}, 0.05 \mathrm{mmol})$ and phenylpyridine $(0.008 \mathrm{~g}, 0.05$ mmol ) in chloroform ( 10 ml ) gave $\mathbf{2 . 4 b}$ as a brown solid ( $0.022 \mathrm{~g}, 89 \%$ ). Single crystals suitable for X-ray determination were grown by slow diffusion of petroleum ether (40-60) into a chloroform solution of $\mathbf{2 . 4 b}$. Mp : > $260{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.10\left(\mathrm{~s}, 9 \mathrm{H},\left(\mathrm{CH}_{3}\right)_{3}\right), 6.03(\mathrm{~s}, 1 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H})$, $7.02\left(\mathrm{~d},{ }^{3} J_{\mathrm{HH}}=7.4 \mathrm{~Hz}, 1 \mathrm{H}\right.$, Py/Ar-H), $7.42\left(\mathrm{~d},{ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}, 3 \mathrm{H}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.47\left(\mathrm{~d},{ }^{3} J_{\mathrm{HH}}\right.$ $=7.5 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 7.74(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 7.83\left(\mathrm{t},{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right)$, 8.01 (m, 1H, Py/Ar-H), 8.10 (d, ${ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}, 2 \mathrm{H}$, Py/Ar-H), 9.20 (s, 1H, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 31.0\left(\mathrm{CH}_{3}\right)$, $34.8(\mathrm{C}), 119.1(\mathrm{CH}), 121.8(\mathrm{CH}), 122.3(\mathrm{CH})$, $123.1(\mathrm{CH}), 123.3(\mathrm{CH}), 126.0(\mathrm{CH}), 126.9(\mathrm{CH}), 128.6(\mathrm{CH}), 128.7(\mathrm{CH}), 130.0(\mathrm{CH})$, 130.1 (CH), 132.1 (CH), 138.6 (CH), 139.2 (CH), 139.4 (C), 143.5 (C), 150.6 (C), 152.5 (C), 152.9 (CH), $153.2(\mathrm{C}), 161.9$ (C), 162.8 (C), $170.8(\mathrm{C})$. IR ( $\left.\mathrm{cm}^{-1}\right): 1674$
$(\mathrm{C}=\mathrm{O}), 1588(\mathrm{C}=\mathrm{N})_{\text {pyridine }}$. ESIMS $(+v e, \mathrm{MeOH}): m / z 515[\mathrm{M}+\mathrm{H}]^{+} . \mathrm{HRMS}(\mathrm{TOF}): m / z$ calc. for $\mathrm{C}_{27} \mathrm{H}_{24} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{PdNa}[\mathrm{M}+\mathrm{Na}]^{+} 537.0770$, found 537.0719.

## Synthesis of 2.5b



The same procedure as that described for $\mathbf{2 . 1 a}$, using $\mathbf{2 b}$ $(0.020 \mathrm{~g}, 0.05 \mathrm{mmol})$ and triphenylphosphine $(0.013 \mathrm{~g}, 0.05$ $\mathbf{m m o l}$ ) in chloroform ( 10 ml ) to give $\mathbf{2 . 5 b}$ as an orange solid (0.030 g, 97\%). Mp: > $260{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 6.57(\mathrm{~s}, 1 \mathrm{H}, \mathrm{Ar}-\mathrm{H}), 6.98\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.1 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=1.8\right.$ $\mathrm{Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 7.31-7.43$ (m, 10H, Py/Ar-H), 7.57-7.65 (m, 7H, Py/Ar-H), 7.74 (d, 1H, $\left.{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.86\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta 29.6\left(\mathrm{CH}_{3}\right), 33.6(\mathrm{C}), 118.2(\mathrm{CH}), 120.8(\mathrm{CH}), 121.4(\mathrm{CH}), 122.8(\mathrm{CH})$, $127.7(\mathrm{CH}), 127.8(\mathrm{CH}), 130.2(\mathrm{CH}), 130.9(\mathrm{C}), 133.8(\mathrm{CH}), 133.9(\mathrm{CH}), 136.8(\mathrm{CH})$, $136.9(\mathrm{CH}), 139.1(\mathrm{CH}), 144.3(\mathrm{C}), 148.8(\mathrm{C}), 150.9(\mathrm{C}), 152.3(\mathrm{C}), 160.5(\mathrm{C}), 170.7$ (C). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}(161 \mathrm{MHz}): \delta 34.18\left(\mathrm{~s}, 1 \mathrm{P}, P \mathrm{Ph}_{3}\right)$. IR $\left(\mathrm{cm}^{-1}\right): 1637(\mathrm{C}=\mathrm{O}), 1583$ $(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$ ESIMS $(+v e, \mathrm{MeOH}): m / z 622[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{34} \mathrm{H}_{30} \mathrm{NO}_{2} \mathrm{PPdNa}[\mathrm{M}+\mathrm{Na}]^{+}$644.0947, found 644.0947. HRMS (ASAP): $m / z$ calc. for $\mathrm{C}_{34} \mathrm{H}_{31} \mathrm{NO}_{2} \mathrm{PPd}[\mathrm{M}+\mathrm{H}]^{+}$622.1127, found 622.1155. HRMS (FAB): $\mathrm{m} / \mathrm{z}$ calc. for $\mathrm{C}_{34} \mathrm{H}_{31} \mathrm{NO}_{2} \mathrm{PPd}[\mathrm{M}+\mathrm{H}]^{+}$622.1127, found 622.1116 .

## Synthesis of 2.6b



The same procedure as that described for 2.6a, using 2-(4'-tertbutyl)-6-carboxylatopyridine $(0.030 \mathrm{~g}, 0.117 \mathrm{mmol})$, methanol $(10 \mathrm{ml})$ and tris(triphenylphosphine)ruthenium(II) dichloride ( $0.112 \mathrm{~g}, 0.117 \mathrm{mmol}$ ) afforded $\mathbf{2 . 6 b}$ as a brown solid $(0.099 \mathrm{~g}$, $93 \%$ ). Single crystals suitable for X-ray determination were grown by slow evaporation of a solution of $\mathbf{2 . 6 b}$ in methanol. Mp :
$>260{ }^{\circ} \mathrm{C} .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}(161 \mathrm{MHz}): \delta 29.10\left(\mathrm{~s}, 2 \mathrm{P}, P \mathrm{Ph}_{3}\right)$. IR $\left(\mathrm{cm}^{-1}\right): 1661(\mathrm{C}=\mathrm{O}), 1579$ $(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$ ESIMS $(+v e, \mathrm{MeOH}): m / z 915[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{52} \mathrm{H}_{45} \mathrm{NO}_{2} \mathrm{P}_{2} \mathrm{ClRuNa}[\mathrm{M}+\mathrm{Na}]^{+} 937.1555$, found 937.1541. $\mu_{\mathrm{eff}}=1.90 \mathrm{BM}$.

## Synthesis of 2.7b



The same procedure as that described for 2.6a, using 2-(4'-tertbutyl)-6-carboxylatopyridine ( $0.030 \mathrm{~g}, 0.117 \mathrm{mmol}$ ), methanol $(10 \mathrm{ml})$ and dichloro( $p$-cymene)ruthenium(II) dimer $(0.036 \mathrm{~g}$, 0.0585 mmol ) afforded $\mathbf{2 . 7 b}$ as red crystals $(0.023 \mathrm{~g}, 76 \%)$. Single crystals were suitable for X-ray determination analysis. $\mathrm{Mp}:>260{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{MeOD}\right): \delta 1.01\left(\mathrm{~d}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.4 \mathrm{~Hz}, \mathrm{C}\left(\mathrm{CH}_{3}\right)\right), 1.11$ $\left(\mathrm{d}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.4 \mathrm{~Hz}, \mathrm{C}\left(\mathrm{CH}_{3}\right)\right), 1.47\left(\mathrm{~s}, 9 \mathrm{H},\left(\mathrm{CH}_{3}\right)_{3}\right), 2.12\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 2.62$ (sept., 1 H , $\left.{ }^{3} J_{\mathrm{HH}}=6.9 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 3.70\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.1 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 5.04\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.3\right.$ $\mathrm{Hz}, \operatorname{Ar}-\mathrm{H}), 5.21\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.3 \mathrm{~Hz}, \operatorname{Ar}-\mathrm{H}\right), 5.46\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.1 \mathrm{~Hz}, \operatorname{Ar}-\mathrm{H}\right), 7.58$ $\left(\mathrm{d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.7 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.74\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.7 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.80\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}\right.$ $=7.7 \mathrm{~Hz}$, Py/Ar-H), $8.02\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}\right.$, Py/Ar-H), $8.17\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.2 \mathrm{~Hz}\right.$, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{MeOD}$ ): $\delta 21.6\left(\mathrm{CH}_{3}\right)$, $24.4 \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}, 27.3 \mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}$, $30.9 \mathrm{CC}\left(\mathrm{CH}_{3}\right)_{2}, 32.4 \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}, 35.2 \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}, 81.5(\mathrm{CH}), 82.5(\mathrm{CH}), 82.9(\mathrm{CH}), 87.7$ $(\mathrm{CH}), 89.1(\mathrm{C}), 126.4(\mathrm{CH}), 127.8(\mathrm{CH}), 129.1(\mathrm{CH}), 132.3(\mathrm{CH}), 141.4(\mathrm{CH}), 141.7$ $(\mathrm{CH}), 142.1(\mathrm{CH}), 162.3(\mathrm{C}), 171.4(\mathrm{C}) . \mathrm{IR}\left(\mathrm{cm}^{-1}\right): 1610(\mathrm{C}=\mathrm{O}), 1595(\mathrm{C}=\mathrm{N})_{\text {pyridine }}$. ESIMS (+ve, MeOH): $m / z 490[\mathrm{M}-\mathrm{Cl}]^{+} ; m / z 548[\mathrm{M}+\mathrm{Na}]^{+} . \mathrm{HRMS}$ (TOF): $m / z$ calc. for $\mathrm{C}_{26} \mathrm{H}_{30} \mathrm{NO}_{2} \mathrm{RuNa}[\mathrm{M}+\mathrm{Na}]^{+} 548.0906$, found 548.0909 .

## Synthesis of 2c



The same procedure as that described for 2a, using 2-(4'-
 trifluoromethyl)-6-carboxylatopyridine ( $0.080 \mathrm{~g}, 0.299 \mathrm{mmol}$ ) and $\mathrm{Pd}(\mathrm{OAc})_{2}(0.067 \mathrm{~g}, 0.299 \mathrm{mmol})$ in dry acetonitrile ( 5 ml ) gave 2c as an orange powder ( $0.118 \mathrm{~g}, 96 \%$ ). Single crystals suitable for X-ray determination were grown by slow evaporation of a solution of $\mathbf{2 c}$ in acetonitrile. $\mathrm{Mp}:>260^{\circ} \mathrm{C}$. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 1.94$ (s, 3H, Pd-NCMe), 7.20 (s, 1H, Py/Ar-H), 7.33 (d, $1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.0 \mathrm{~Hz}$, Py/Ar-H), $7.50\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}\right.$, Py/Ar-H$), 7.55\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=\right.$ $7.0 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}), 7.64\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right) 7.91\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.0 \mathrm{~Hz}\right.$, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 0.5(\mathrm{MeC} \equiv \mathrm{N}-$ ), $117.0(\mathrm{MeCN}-\mathrm{C}), 120.8$ $(\mathrm{CH}), 121.9(\mathrm{CH}), 123.3(\mathrm{CH}), 123.7\left(\mathrm{q},{ }^{3} J_{\mathrm{CF}}=3.3 \mathrm{~Hz}, C \mathrm{H}\right), 125.6\left(\mathrm{q},{ }^{1} J_{\mathrm{CF}}=270.8\right.$, $\left.C F_{3}\right), 130.0(\mathrm{CH}), 132.3\left(\mathrm{q},{ }^{2} J_{\mathrm{CF}}=31.6, C C F_{3}\right), 140.5(\mathrm{CH}), 149.5(\mathrm{C}), 150.3(\mathrm{C}), 151.5$ (C), 161.1 (C), 163.1 (C), 168.1 (C). ${ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 376 MHz ): $\delta-62.9$ (s, 3F, CF $\mathrm{F}_{3}$ ). IR $\left(\mathrm{cm}^{-1}\right): 1648(\mathrm{C}=\mathrm{O}), 1585(\mathrm{C}=\mathrm{N})_{\text {pyridine }}$. ESIMS ( $\left.+v e, \mathrm{MeCN}\right): m / z 413[\mathrm{M}+\mathrm{H}]^{+}$. HRMS
(TOF): $m / z$ calc. for $\mathrm{C}_{15} \mathrm{H}_{9} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{~F}_{3} \mathrm{PdNa}[\mathrm{M}+\mathrm{Na}]^{+}$434.9549, found 434.9556. HRMS (FAB): $m / z$ calc. for $\mathrm{C}_{15} \mathrm{H}_{9} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{~F}_{3} \mathrm{Pd}[\mathrm{M}-\mathrm{MeCN}]^{+} 370.9385$, found 370.9381.

## Synthesis of 2.1c



The same procedure as that described for 2.1a, using 2c $(0.015 \mathrm{~g}, 0.0360 \mathrm{mmol})$ and pyridine $(0.0029 \mathrm{~g}, 0.0029 \mathrm{ml}$, 0.0360 mmol ) in chloroform ( 5 ml ) gave 2.1c as a yellow solid ( $0.012 \mathrm{~g}, 76 \%$ ). Mp: > $260{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 6.86(\mathrm{~s}, 1 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 7.35\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.0 \mathrm{~Hz}\right.$, Py/Ar-H), 7.51 (t, 3H, $\left.{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.64(\mathrm{~d}, 1 \mathrm{H}$, ${ }^{3} J_{\mathrm{HH}}=7.0 \mathrm{~Hz}$, Py/Ar-H), $7.79\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.0 \mathrm{~Hz}\right.$, Py/Ar-H), $7.94\left(\mathrm{t}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.1\right.$ $\mathrm{Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 8.81\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.0 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ $120.3(\mathrm{CH}), 121.1(\mathrm{CH}), 122.2(\mathrm{CH}), 123.5(\mathrm{CH}), 124.1\left(\mathrm{q},{ }^{1} J_{\mathrm{CF}}=271.6, \mathrm{CF}_{3}\right), 126.0$ $\left(\mathrm{q},{ }^{3} J_{\mathrm{CF}}=3.1 \mathrm{~Hz}, C \mathrm{H}\right), 126.7(\mathrm{CH}), 127.2(\mathrm{CH}), 129.4(\mathrm{CH}), 130.1(\mathrm{CH}), 138.6\left(\mathrm{q},{ }^{2} J_{\mathrm{CF}}\right.$ $=30.5$, CCF $_{3}$ ), 139.1 (C), 140.0 (C), 150.6 (C), 152.2 (C), 164.9 (C). ${ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 376 MHz ): $\delta-62.9\left(\mathrm{~s}, 3 \mathrm{~F}, \mathrm{C} F_{3}\right) . \mathrm{IR}\left(\mathrm{cm}^{-1}\right): 1617(\mathrm{C}=\mathrm{O}), 1587(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$. ESIMS $(+v e, \mathrm{MeOH}): m / z 451[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{18} \mathrm{H}_{11} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{~F}_{3} \mathrm{Pd}[\mathrm{M}+\mathrm{H}]^{+}$ 450.9893, found 450.9296. Anal. calc. for $\left(\mathrm{C}_{18} \mathrm{H}_{11} \mathrm{~F}_{3} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Pd}^{\circ} \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$ : C 42.60, H 2.45, N 5.23. Found: C 42.14, 1.93, N 5.89.

## Synthesis of 2.2c



The same procedure as that described for 2.1a, using 2c $(0.015 \mathrm{~g}, 0.0360 \mathrm{mmol})$ and 3,5 -dimethylpyridine $(0.0039 \mathrm{~g}$, $0.0041 \mathrm{ml}, 0.0360 \mathrm{mmol}$ ) in chloroform ( 5 ml ) gave 2.1c as a yellow solid ( $0.010 \mathrm{~g}, 62 \%$ ). Single crystals suitable for Xray determination were grown by slow diffusion of petroleum ether (40-60) into a chloroform solution of 2.2c. Mp: > 260 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 2.33$ (s, $6 \mathrm{H}, \mathrm{CH}_{3}$ ), 6.87 ( $\mathrm{s}, 1 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}$ ), 7.33 (d, $1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.3 \mathrm{~Hz}$, Py/Ar-H), 7.49 ( $\mathrm{s}, 1 \mathrm{H}$, Py/Ar-H), 7.51 (s, 1H, Py/Ar-H), 7.63 (d, 1H, ${ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}$, Py/Ar-H), $7.78\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.3 \mathrm{~Hz}\right.$, Py/Ar-H), $7.92\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.1\right.$ $\mathrm{Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 8.44(\mathrm{~s}, 2 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 17.3\left(\mathrm{CH}_{3}\right), 119.2$ $(\mathrm{CH}), 121.0(\mathrm{CH}), 122.4(\mathrm{CH}), 122.9\left(\mathrm{q},{ }^{3} J_{\mathrm{CF}}=3.1 \mathrm{~Hz}, C H\right), 127.5\left(\mathrm{q},{ }^{1} J_{\mathrm{CF}}=271.4\right.$, $\left.C F_{3}\right), 128.6(\mathrm{CH}), 129.7\left(\mathrm{q},{ }^{2} \mathrm{~J}_{\mathrm{CF}}=30.8, \mathrm{CCF}_{3}\right), 134.6(\mathrm{C}), 138.8(\mathrm{CH}), 139.4(\mathrm{CH})$,
148.4 (CH), 149.1 (C), 150.4 (C), 152.0 (C), 160.5 (C), 169.4 (C). ${ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (376 $\mathrm{MHz}): \delta-63.0\left(\mathrm{~s}, 3 \mathrm{~F}, \mathrm{C} F_{3}\right)$. IR $\left(\mathrm{cm}^{-1}\right): 1634(\mathrm{C}=\mathrm{O}), 1594(\mathrm{C}=\mathrm{N})$ pyridine. ESIMS (+ve, MeOH ): $m / z 479[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{15} \mathrm{H}_{9} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{~F}_{3} \mathrm{PdNa}$ [M$\left.\mathrm{CF}_{3}+\mathrm{Na}\right]^{+}$433.7587, found 433.8555. Anal. calc. for $\left(\mathrm{C}_{20} \mathrm{H}_{15} \mathrm{~F}_{3} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Pd}\right)$ : $\mathrm{C} 50.17, \mathrm{H}$ 3.16, N 5.85. Found C 46.90, H 2.87, N 5.49.

## Synthesis of 2.5c



The same procedure as that described for 2.1a, using $\mathbf{2 c}$
 $(0.015 \mathrm{~g}, 0.0360 \mathrm{mmol})$ and triphenylphosphine $(0.00944 \mathrm{~g}$, 0.0360 mmol ) in chloroform ( 5 ml ) gave $\mathbf{2 . 5 c}$ as a yellow solid ( $0.016 \mathrm{~g}, 70 \%$ ). Mp: > $260{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR $(500 \mathrm{MHz}$, $\mathrm{CDCl}_{3}$ ) : $\delta 6.53$ ( $\mathrm{s}, 1 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}$ ), 7.36 (m, 7H, Py/Ar-H), 7.43 (m, 3H, Py/Ar-H), 7.52 (d, 1H, ${ }^{3} J_{\mathrm{HH}}=8.1 \mathrm{~Hz}$, Py/Ar-H), 7.57-7.62 (m, 6H, Py/ArH), $7.71\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.85\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.96(\mathrm{t}$, $\left.1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.2 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 120.2(\mathrm{CH}), 121.9(\mathrm{CH})$, $123.6(\mathrm{CH}), 123.9\left(\mathrm{q},{ }^{3} J_{\mathrm{CF}}=3.5 \mathrm{~Hz}, C \mathrm{H}\right), 127.2\left(\mathrm{q},{ }^{1} J_{\mathrm{CF}}=272.1, C \mathrm{~F}_{3}\right), 128.5(\mathrm{CH})$, $128.9(\mathrm{CH}), 129.0(\mathrm{CH}), 129.3(\mathrm{C}), 130.4\left(\mathrm{q},{ }^{2} J_{\mathrm{CF}}=30.8, \mathrm{CCF}_{3}\right), 131.4(\mathrm{CH}), 134.7$ $(\mathrm{CH}), 134.8(\mathrm{CH}), 150.0(\mathrm{C}), 151.4(\mathrm{C}), 152.1(\mathrm{C}), 160.2(\mathrm{C}), 162.1(\mathrm{C}), 171.5(\mathrm{C}) .{ }^{31} \mathrm{P}$ $\left\{{ }^{1} \mathrm{H}\right\}(161 \mathrm{MHz}): \delta 33.91\left(\mathrm{~s}, 1 \mathrm{P}, \mathrm{PPh}_{3}\right) .{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 376 MHz ): $\delta-63.2(\mathrm{~s}, 3 \mathrm{~F}$, $\mathrm{C} F_{3}$ ). IR ( $\mathrm{cm}^{-1}$ ): $1652(\mathrm{C}=\mathrm{O}), 1591(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$. ESIMS ( $+v e$, MeOH): m/z 634 $[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $\mathrm{m} / \mathrm{z}$ calc. for $\mathrm{C}_{31} \mathrm{H}_{22} \mathrm{NO}_{2} \mathrm{~F}_{3} \mathrm{PdP}[\mathrm{M}+\mathrm{H}]^{+}$634.0375, found 634.0400. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{31} \mathrm{H}_{21} \mathrm{NO}_{2} \mathrm{~F}_{3} \mathrm{PdPNa}[\mathrm{M}+\mathrm{Na}]^{+} 656.0195$, found 656.0216.

## Synthesis of 2.6c



The same procedure as that described for 2.6a, using 2-(4'-trifluoromethyl)-6-carboxylatopyridine ( $0.060 \mathrm{~g}, 0.225 \mathrm{mmol}$ ), methanol ( 15 ml ) and tris(triphenylphosphine)ruthenium(II) dichloride ( $0.215 \mathrm{~g}, 0.225 \mathrm{mmol}$ ) afforded $\mathbf{2 . 6 c}$ as an orange solid ( $0.202 \mathrm{~g}, 97 \%$ ). Single crystals suitable for X-ray determination were grown by slow evaporation of a solution of $\mathbf{2 . 6}$ c in dichloromethane. ${ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 376 MHz ): $\delta-65.3(\mathrm{~s}, 3 \mathrm{~F}, \mathrm{CF} 3) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}(161 \mathrm{MHz})$ : $\delta 30.91\left(\mathrm{~s}, 2 \mathrm{P}, \mathrm{PPh}_{3}\right)$. IR $\left(\mathrm{cm}^{-1}\right): 1659(\mathrm{C}=\mathrm{O}), 1605(\mathrm{C}=\mathrm{N})_{\text {pyridine }}$. ESIMS (+ve, MeOH):
$m / z 927[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{49} \mathrm{H}_{36} \mathrm{NO}_{2} \mathrm{~F}_{3} \mathrm{NaP}_{2} \mathrm{ClRu}[\mathrm{M}+\mathrm{Na}]^{+}$ 949.0803 , found $949.0851 . \mu_{\mathrm{eff}}=1.93 \mathrm{BM}$.

### 8.4 Experimental procedures for Chapter 3

### 8.4.1 Synthesis of 2-phenol-6-ethylpicolinate



A mixture of ethyl-6-bromopicolinate ( $2.97 \mathrm{~g}, 8 \mathrm{mmol}$ ), 2hydroxyphenylboronic acid ( $2.13 \mathrm{~g}, 15.5 \mathrm{mmol}, 1.2 \mathrm{eq}$.$) ,$ tetrakis(triphenylphosphine)palladium $(0)\left[\left(\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}\right](0.451\right.$ $\mathrm{g}, 0.39 \mathrm{mmol}, 0.03 \mathrm{eq}$.) in tetrahydrofuran $(90 \mathrm{ml})$ and $1 \mathrm{M} \mathrm{Na}_{2} \mathrm{CO}_{3}$ aqueous solution ( $60 \mathrm{ml}, 5.98 \mathrm{mmol}, 4.6 \mathrm{eq}$.) was stirred and heated to reflux for 24 h . After cooling to room temperature, the reaction mixture was extracted with dichloromethane ( $3 \times 50 \mathrm{ml}$ ), and dried over $\mathrm{MgSO}_{4}$. The filtrate was concentrated under reduced pressure to give a yellow viscous oil which was purified by column chromatography $\left(\mathrm{SiO}_{2}\right.$, petroleum ether and ethyl acetate, 80:20) to give 2-phenol-6-ethylpicolinate as a brown viscous oil $(1.47 \mathrm{~g}, 47 \%) .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.40\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.7 \mathrm{~Hz}, \mathrm{CH}_{3}\right), 4.41(\mathrm{q}$, $\left.2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}, \mathrm{CH}_{2}\right), 6.85\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.6 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right), 6.99\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.1\right.$ $\mathrm{Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 7.27\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.6 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.74\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.9 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\right.$ H), $7.89\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.2 \mathrm{~Hz}, \operatorname{Py} /\right.$ Ar-H), $7.96\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.6 \mathrm{~Hz}, \operatorname{Py} /\right.$ Ar-H), $8.01(\mathrm{~d}$, $1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.2 \mathrm{~Hz}$, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 14.2\left(\mathrm{CH}_{3}\right), 62.1\left(\mathrm{CH}_{2}\right)$, 118.2 (C), 118.9 (CH), $119.0(\mathrm{CH}), 122.1(\mathrm{CH}), 122.4(\mathrm{CH}), 126.3(\mathrm{CH}), 132.1(\mathrm{CH})$, 138.6 (CH), 144.6 (C), 157.6 (C), 160.2 (C), 164.0 (C). IR ( $\mathrm{cm}^{-1}$ ): 2986 (sharp O-H), $1714(\mathrm{C}=\mathrm{O}), 1592(\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1231(\mathrm{C}-\mathrm{O})$. ESIMS ( $\left.+v e, \mathrm{MeOH}\right): m / z 244[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{14} \mathrm{H}_{14} \mathrm{NO}_{3}[\mathrm{M}+\mathrm{H}]^{+} 244.0974$, found 244.0986.

### 8.4.2 Synthesis of 2-phenol-6-carboxylatopyridine (HL4)



A 250 ml round bottom flask, equipped with a stir bar was charged with 2-phenol-6-ethylpicolinate ( $0.895 \mathrm{~g}, 3.68 \mathrm{mmol}$ ), bench ethanol ( 104 ml ) and $\mathrm{NaOH}(5.88 \mathrm{~g}, 147.2 \mathrm{mmol})$, pre-dissolved in water ( 52 ml ), was stirred and heated to reflux for 6 hours. The reaction mixture was allowed to cool to room temperature, and acidified with conc. HCl to pH 3 . The mixture was poured into water ( 100 ml ) resulting in the formation of a precipitate. The
precipitate was filtered, washed with water, and dried to give 2-phenol-6carboxylatopyridine as a grey solid ( $0.42 \mathrm{~g}, 53 \%$ ). M.p: 143-147 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR (500 $\left.\mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}\right): \delta 6.85\left(\mathrm{t}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.2 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.23\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.6 \mathrm{~Hz}\right.$, Py/Ar-H), $7.89\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, Py/Ar-H), $7.96\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.6 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right)$, $8.02\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.6 \mathrm{~Hz}\right.$, Py/Ar-H), $8.20\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.1 \mathrm{~Hz}\right.$, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta 119.4(\mathrm{CH}), 120.3(\mathrm{CH}), 122.4(\mathrm{CH}), 123.6(\mathrm{CH}), 123.8(\mathrm{CH})$, 127.8 (CH), 133.0 (CH), 134.1 (C), 139.3 (C), 139.8 (C), 140.4 (C), 165.2 (C). IR ( $\mathrm{cm}^{-}$ ${ }^{1}$ ): 2652 (sharp O-H), 2545 (br. O-H), $1696(\mathrm{C}=\mathrm{O}), 1586(\mathrm{C}=\mathrm{N})_{\text {pyridine, }} 1230(\mathrm{C}-\mathrm{O})$. ESIMS (+ve, MeOH): m/z $216[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{NO}_{3}$ $[\mathrm{M}+\mathrm{H}]^{+}$216.0661, found 216.0662 .

### 8.4.3 Synthesis of 3-t-butyl-6-hydroxybenzene boronic acid



A three-necked round bottomed flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with $4{ }^{-}{ }^{-} \mathrm{Bu}-2$-bromophenol $(3.76 \mathrm{~g}, 16.4 \mathrm{mmol})$ and dry diethyl ether $(100 \mathrm{ml})$ and the stirred solution cooled to $-90{ }^{\circ} \mathrm{C} . n-\mathrm{BuLi}(21.5 \mathrm{ml}, 34.4$ $\mathrm{mmol}, 2.1 \mathrm{eq}$.) was added dropwise to the cooled $\left(-90^{\circ} \mathrm{C}\right)$ solution and the reaction mixture allowed to warm to room temperature and stirred under nitrogen for 2 h . The flask was cooled back to $-90{ }^{\circ} \mathrm{C}$ and a solution of triisopropyl borate $(6.3 \mathrm{ml}, 27.3$ mmol, 1.67 eq.) was added rapidly. The mixture was stirred at $-90^{\circ} \mathrm{C}$ for 30 min and then at room temperature for 15 h under nitrogen. $2 \mathrm{M} \mathrm{HCl}(13 \mathrm{ml})$ was added slowly to the ice cooled reaction mixture and then stirred for a further 30 min resulting in the milky white emulsion becoming clear. The ether layer was separated and the aqueous layer extracted with diethyl ether ( $3 \times 50 \mathrm{ml}$ ). The combined ether solutions were dried with $\mathrm{MgSO}_{4}$ and the solvent removed under reduced pressure to give a gummy solid. The solid was recrystallised from hexane and dried overnight to give 3-t-butyl-6hydroxybenzeneboronic acid as a white solid ( $3.28 \mathrm{~g}, 98 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta 1.28\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 4.69\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{B}(\mathrm{OH})_{2}\right), 6.75(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Ar}-\mathrm{H}), 7.23(\mathrm{~d}, 1 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{HH}}=6.4 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right)$. ESIMS ( $+v e, \mathrm{MeOH}$ ): $m / z 195[\mathrm{M}+\mathrm{H}]^{+}$. ESIMS ( $-v e, \mathrm{MeOH}$ ): $m / z$ $193[\mathrm{M}-\mathrm{H}]^{+}$. The NMR data are consistent with those reported in the literature ${ }^{90}$.

### 8.4.4 Synthesis of 2-(3'-t-butyl-phenol)-6-ethylpicolinate



The same procedure as that described for 2-phenol-6ethylpicolinate, using ethyl-6-bromopicolinate ( $1.83 \mathrm{~g}, 8$ mmol ), 3-t-butyl-6-hydroxybenzeneboronic acid ( 1.86 g , $9.6 \mathrm{mmol}, 1.2 \mathrm{eq}$.$) , tetrakis(triphenylphosphine)palladium (0)\left[\left(\mathrm{Pd}_{( }\left(\mathrm{PPh}_{3}\right)_{4}\right](0.277 \mathrm{~g}, 0.24\right.$ mmol, 0.03 eq.) in tetrahydrofuran ( 74 ml ) and $1 \mathrm{M} \mathrm{Na}_{2} \mathrm{CO}_{3}$ aqueous solution ( 37 ml , $36.8 \mathrm{mmol}, 4.6$ eq.) gave a yellow viscous oil which was purified by column chromatography ( $\mathrm{SiO}_{2}$, ethyl acetate and hexane, 20:80) to give 2-(4'-t-butyl-phenol)-6ethylpicolinate as a brown viscous oil ( $1.76 \mathrm{~g}, 74 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ $1.35\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 1.43\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.1 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 4.47\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}\right.$, $\left.C H_{2} \mathrm{CH}_{3}\right), 7.01\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.9 \mathrm{~Hz}\right.$, Py/Ar-H), $7.39\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.7 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=\right.$ 2.4 Hz, Py/Ar-H), 7.71-7.64 (m, 1H, Py/Ar-H), $7.79\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.4 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right)$, $8.02\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.7 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=1.2 \mathrm{~Hz}\right.$, Py/Ar-H), $8.11\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.1 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}\right.$ $=1.1 \mathrm{~Hz}$, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 14.2\left(\mathrm{CH}_{3}\right), 31.5\left(\mathrm{C}_{\left.\left(\mathrm{CH}_{3}\right)_{3}\right), 34.2}\right.$ $\left(\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 62.1\left(\mathrm{CH}_{2}\right), 117.3(\mathrm{C}), 118.5(\mathrm{CH}), 122.2(\mathrm{CH}), 123.9(\mathrm{CH}), 129.6(\mathrm{CH})$, 131.6 (C), 138.4 (CH), 139.1 (CH), 141.4 (C), 144.7 (C), 157.8 (C), 164.1 (C). IR ( $\mathrm{cm}^{-}$ ${ }^{1}$ ): 2990 (sharp O-H), $1724(\mathrm{C}=\mathrm{O}), 1589(\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1261(\mathrm{C}-\mathrm{O})$. ESIMS (+ve, MeOH ): $m / z 300[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{18} \mathrm{H}_{22} \mathrm{NO}_{3}[\mathrm{M}+\mathrm{H}]^{+}$300.1600, found 300.1601.

### 8.4.5 Synthesis of 2-(3'-t-butyl-phenol)-6-carboxylatopyridine (HL5)



The same procedure as that described for 2-phenol-6carboxylatopyridine, using 2-(4'-t-butyl-phenol)-6ethylpicolinate ( $0.085 \mathrm{~g}, 0.000284 \mathrm{~mol}$ ), bench ethanol (10 $\mathrm{ml})$ and sodium hydroxide ( $0.454 \mathrm{~g}, 0.0114 \mathrm{~mol}, 4.6$ eq. $)$, pre-dissolved in water ( 2 ml ) gave 2-(4'-t-butyl-phenol)-6-carboxylatopyridine as a white solid ( $0.055 \mathrm{~g}, 71 \%$ ). M.p: $228-230{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta 1.27\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 6.81\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=\right.$ $8.6 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}), 7.31\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.6 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=2.3 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.84(\mathrm{~s}, 1 \mathrm{H}$, Py/Ar-H), $7.95\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.6\right.$, Py/Ar-H), $8.02\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, Py/Ar-H), 8.21 $\left(\mathrm{d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.8 \mathrm{~Hz}\right.$, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $\left.125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}\right): \delta 31.9\left(\mathrm{C}_{\left.\left(\mathrm{CH}_{3}\right)_{3}\right), 35.1}\right.$ $\left(\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right)$, $119.1(\mathrm{C}), 119.5(\mathrm{CH}), 123.7(\mathrm{CH}), 124.2(\mathrm{CH}), 130.4(\mathrm{CH}), 130.7(\mathrm{CH})$, 140.5 (CH), 143.1 (C), 146.4 (C), 158.4 (C), 159.1 (C). IR ( $\mathrm{cm}^{-1}$ ): 2961 (O-H), 2604
(br. O-H), 1701 (C=O), 1595 (C=N) pyridine, 1263 (C-O). ESIMS (+ve, MeOH): m/z 272 $[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{16} \mathrm{H}_{18} \mathrm{NO}_{3}[\mathrm{M}+\mathrm{H}]^{+}$272.1287, found 272.1293.

### 8.4.6 Synthesis of 3-chloro-6-hydroxybenzene boronic acid



The same procedure as that described for 3-t-butyl-6hydroxybenzeneboronic acid, using 4-chloro-2-bromophenol (1 g, $4.82 \mathrm{mmol})$, dry diethyl ether ( 30 ml ), $n-\operatorname{BuLi}(6.33 \mathrm{ml}, 10.1 \mathrm{mmol}$, 2.1 eq.) and a solution of triisopropyl borate ( $1.86 \mathrm{ml}, 8.05 \mathrm{mmol}, 1.67 \mathrm{eq}$.$) gave 3-$ chloro-6-hydroxybenzeneboronic acid as a white solid ( $0.820 \mathrm{~g}, 98 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( 500 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 4.72\left(\mathrm{bs}, 2 \mathrm{H}, \mathrm{B}(\mathrm{OH})_{2}\right), 6.76\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{JHH}_{\mathrm{HH}}=7.1 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 7.19(\mathrm{~d}, 1 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 7.38(\mathrm{~s}, 1 \mathrm{H}, \mathrm{Ar}-\mathrm{H})$. ESIMS (+ve, MeOH): m/z $173[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (ASAP): $m / z$ calc. for $\mathrm{C}_{6} \mathrm{H}_{7} \mathrm{BClO}_{3} \mathrm{Na}[\mathrm{M}+\mathrm{Na}]^{+}$194.0996, found 194.0293; m/z calc. for $\mathrm{C}_{6} \mathrm{H}_{7} \mathrm{BClO}_{3}[\mathrm{M}+\mathrm{H}]^{+} 173.0177$, found 173. 0178.

### 8.4.7 Synthesis of 2-(3'-chlorophenol)-6-ethylpicolinate



The same procedure as that described for 2-phenol-6ethylpicolinate, using ethyl-6-bromopicolinate ( 1.05 g , 4.6 mmol ), 3-chloro-6-hydroxybenzeneboronic acid $\left(\begin{array}{llllll}0.950 & \mathrm{~g}, & 5.52 & \mathrm{mmol}, & 1.2 & \mathrm{eq} .\end{array}\right)$, tetrakis(triphenylphosphine)palladium $(0)\left[\left(\mathrm{Pd}_{( }\left(\mathrm{PPh}_{3}\right)_{4}\right](0.159 \mathrm{~g}, 0.138 \mathrm{mmol}, 0.03\right.$ eq. $)$ in tetrahydrofuran ( 40 ml ) and $1 \mathrm{M} \mathrm{Na}_{2} \mathrm{CO}_{3}$ aqueous solution ( $21 \mathrm{ml}, 21 \mathrm{mmol}, 4.6 \mathrm{eq}$.) gave a yellow oil which was purified by column chromatography ( $\mathrm{SiO}_{2}$, ethyl acetate and hexane, 20:80) to give pure 2-(4'-chlorophenol)-6-ethylpicolinate ( $1.20 \mathrm{~g}, 94 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta 1.33\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.4 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 4.35\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=\right.$ $7.2 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}$ ), $76.83\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.5 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.18\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.7 \mathrm{~Hz}\right.$, ${ }^{4} J_{\mathrm{HH}}=2.4 \mathrm{~Hz}$, Py/Ar-H), $7.86\left(\mathrm{~s}, 1 \mathrm{H}\right.$, Py/Ar-H), $7.96\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.4 \mathrm{~Hz}\right.$, Py/Ar-H), $8.01\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz}\right.$, Py/Ar-H), $8.18\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}\right.$, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $\left.125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}\right): \delta 14.5\left(\mathrm{CH}_{3}\right), 63.2\left(\mathrm{CH}_{2}\right), 121.1(\mathrm{CH}), 122.2(\mathrm{CH}), 124.1(\mathrm{CH})$, 127.4 (CH), 130.2 (CH), 132.7 (CH), 140.7 (C), 145.9 (C), 157.5 (C), 157.7 (C), 159.6 (C), 165.1 (C). IR ( $\mathrm{cm}^{-1}$ ): 3102 (O-H), 1727 (C=O), 1596 (C=N) pyridine, 1261 (C-O). ESIMS (+ve, MeOH): $m / z 278[\mathrm{M}+\mathrm{H}]^{+} ; 300[\mathrm{M}+\mathrm{Na}]^{+}$. HRMS (ASAP): $m / z$ calc. for $\mathrm{C}_{14} \mathrm{H}_{13} \mathrm{ClO}_{3}[\mathrm{M}+\mathrm{H}]^{+}$278.0506, found 278.0577.

### 8.4.8 Synthesis of 2-(3-chlorophenol)-6-carboxylatopyridine (HL6)



The same procedure as that described for 2-phenol-6carboxylatopyridine, using 2-(4'-chlorophenol)-6ethylpicolinate ( $1 \mathrm{~g}, 3.61 \mathrm{mmol}$ ), bench ethanol ( 118 ml ) and sodium hydroxide ( $0.764 \mathrm{~g}, 16.6 \mathrm{~mol}, 4.6 \mathrm{eq}$.$) , pre-dissolved$ in water ( 23.5 ml ) gave 2-(4'-chlorophenol)-6-carboxylatopyridine as a yellow solid ( $0.850 \mathrm{~g}, 95 \%$ ). M.p: $194-196{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta 6.93\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=\right.$ 8.1 Hz, Py/Ar-H), $7.24\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.7 \mathrm{~Hz}, \operatorname{Py} / A r-\mathrm{H}\right), 7.92(\mathrm{~s}, 1 \mathrm{H}, \operatorname{Py} / A r-\mathrm{H}), 7.97(\mathrm{~d}$, $1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.1 \mathrm{~Hz}$, Py/Ar-H), $8.02\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}\right.$, Py/Ar-H$), 8.09\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=\right.$ 7.7 Hz, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta 121.2(\mathrm{CH}), 121.6(\mathrm{CH}), 123.2 .4$ $(\mathrm{CH}), 127.4(\mathrm{CH}), 131.8(\mathrm{CH}), 139.8(\mathrm{CH}), 125.8(\mathrm{C}), 129.5(\mathrm{C}), 133.1(\mathrm{C}), 143.5(\mathrm{C})$, 157.2 (C), 169.4 (C). IR ( $\mathrm{cm}^{-1}$ ): 3032 (O-H), 2956 (br. O-H), 1738 (C=O), 1598(C=N) pyridine, 1214 (C-O). ESIMS ( $+v e, ~ M e O H$ ): $m / z 250[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{12} \mathrm{H}_{9} \mathrm{ClNO}_{3}[\mathrm{M}+\mathrm{H}]^{+} 250.0271$, found 250.0288 . HRMS (ASAP): $\mathrm{m} / \mathrm{z}$ calc. for $\mathrm{C}_{12} \mathrm{H}_{9} \mathrm{ClNO}_{3}[\mathrm{M}+\mathrm{H}]^{+}$250.0271, found 250.0271.

### 8.5 Complexes supported by phenol-substituted $\left[O, N_{P y}, O\right.$ ] pincer ligands

Synthesis of 3a


A clean dry Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was then charged with 2-phenol-6-carboxylatopyridine $(0.080 \mathrm{~g}, 0.372$ $\mathrm{mmol})$ and $\mathrm{Pd}(\mathrm{OAc})_{2}(0.083 \mathrm{~g}, 0.372 \mathrm{mmol})$ in dry acetonitrile ( 10 $\mathrm{ml})$. The reaction was stirred and heated to $70{ }^{\circ} \mathrm{C}$ for 18 h . After cooling to room temperature, the reaction mixture was filtered through a Celite plug. The Celite plug was washed thoroughly with acetonitrile and dried under reduced pressure to give 3a as an orange solid (0.092 g, 69\%). Mp: 256-258 ${ }^{\circ} \mathrm{C}$ (decomp.) ${ }^{1} \mathrm{H}$ NMR (500 MHz, CD ${ }_{3} \mathrm{CN}$ ): $\delta 1.99$ ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{Pd}-\mathrm{NCMe}$ ), 6.67 (t, $1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.7 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-$ $\mathrm{H}), 6.88\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.14\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.7 \mathrm{~Hz}, \operatorname{Py} / A r-\mathrm{H}\right), 7.54(\mathrm{~d}$, $1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.3 \mathrm{~Hz}$, Py/Ar-H), $7.81\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}\right.$, Py/Ar-H), $8.02\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=\right.$ 8.0 Hz, Py/Ar-H), $8.20\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.4 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 0.5\left(\mathrm{CH}_{3} \mathrm{CNPd}\right), 116.1(\mathrm{CH}), 117.0\left(\mathrm{CH}_{3} \mathrm{CNPd}\right), 120.4(\mathrm{CH}), 123.1(\mathrm{CH}), 124.5(\mathrm{CH})$, 128.8 (CH), 130.9 (CH), 139.7 (CH), 148.9 (C), 151.1 (C), 157.9 (C), 161.2 (C), 171.3
(C). IR ( $\mathrm{cm}^{-1}$ ): $1646(\mathrm{C}=\mathrm{O}), 1572(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$. ESIMS ( $+v e, \mathrm{MeCN}$ ): m/z 383 $[\mathrm{M}+\mathrm{Na}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{14} \mathrm{H}_{10} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{NaPd}[\mathrm{M}+\mathrm{Na}]^{+}$382.9624, found 382.9636. Anal. calc. for $\left(\mathrm{C}_{14} \mathrm{H}_{10} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{Pd}\right)$ : 46.62 , H 2.79, N 7.77; found 46.58, H 2.80, N 7.60.

## Synthesis of 3.2a

A clean dry Schlenk flask equipped with a magnetic stir bar was
 evacuated and backfilled with nitrogen. To the flask was added 3a ( $0.015 \mathrm{~g}, 0.0416 \mathrm{mmol}$ ), 3,5-dimethylpyridine $(0.0045 \mathrm{~g}, 0.0416$ $\mathrm{mmol})$ and dry chloroform ( 10 ml ). The reaction was stirred at room temperature for 18 h . The reaction mixture was then filtered through a thin layer of Celite. The Celite plug was washed thoroughly with chloroform and dried under reduced pressure to give 3.2a as a yellow solid ( $0.016 \mathrm{~g}, 93 \%$ ). Mp: 230-232 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 2.32(\mathrm{~s}, 6 \mathrm{H}$, $\left.\mathrm{CH}_{3}\right), 7.06\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.5 \mathrm{~Hz}\right.$, Py/Ar-H$), 7.15\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.5 \mathrm{~Hz}\right.$, Py/Ar-H$), 7.45$ (s, $1 \mathrm{H}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}), 7.70\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.5 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.90\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.5 \mathrm{~Hz}\right.$, Py/Ar-H), 8.03 (d, 1H, ${ }^{3} J_{\mathrm{HH}}=7.4 \mathrm{~Hz}$, Py/Ar-H), 8.37 (s, 2H, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( 125 $\left.\mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right): \delta 18.5\left(\mathrm{CH}_{3}\right), 116.5(\mathrm{CH}), 120.3(\mathrm{C}), 122.1(\mathrm{CH}), 123.4(\mathrm{CH}), 124.1$ $(\mathrm{CH}), 128.8(\mathrm{CH}), 132.1(\mathrm{CH}), 134.5(\mathrm{C}), 138.9(\mathrm{CH}), 140.5(\mathrm{CH}), 146.4(\mathrm{CH}), 150.1$ (C), 152.3 (C), 162.6 (C), 172.3 (C). IR ( $\mathrm{cm}^{-1}$ ): 1657 (C=O), 1595 (C=N) pyridine. ESIMS ( $+v e, \mathrm{MeOH}$ ): $m / z 449[\mathrm{M}+\mathrm{Na}]^{+}$. HRMS (FAB): $m / z$ calc. for $\mathrm{C}_{19} \mathrm{H}_{16} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{Pd}[\mathrm{M}]^{+}$ 426.01958, found 426.01889. HRMS (ASAP): $m / z$ calc. for $\mathrm{C}_{19} \mathrm{H}_{17} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{Pd}[\mathrm{M}+\mathrm{H}]^{+}$ 427.0291, found 427.0274. Anal. calc. for $\left(\mathrm{C}_{19} \mathrm{H}_{16} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{Pd}\right)$ : C 53.47, H 3.78, N 6.56; found: C 50.99, H 3.03, N 6.59 .

## Synthesis of 3.3a



The same procedure as that described for 3.2a, using $\mathbf{3 a}(0.015 \mathrm{~g}$, $0.0416 \mathrm{mmol}), 3,5$-dichloropyridine ( $0.0062 \mathrm{~g}, 0.0416 \mathrm{mmol}$ ) and dry chloroform ( 10 ml ) gave 3.3a as a yellow solid ( 0.016 g , $85 \%$ ). Mp: $245-247{ }^{\circ} \mathrm{C}$ (decomp.) ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 6.64\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.6 \mathrm{~Hz}\right.$, Py/Ar-H), $6.94\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8\right.$ $\mathrm{Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 7.09\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.6 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.60(\mathrm{~d}, 1 \mathrm{H}$, ${ }^{3} J_{\mathrm{HH}}=6.5 \mathrm{~Hz}$, Py/Ar-H), $7.64\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.6 \mathrm{~Hz}\right.$, Py/Ar-H), $7.85(\mathrm{~s}, 2 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H})$, $7.99\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.5 \mathrm{~Hz}\right.$, Py/Ar-H), 8.64 (s, 2H, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( 125 MHz ,
$\left.\mathrm{CD}_{3} \mathrm{CN}\right): \delta 116.8(\mathrm{CH}), 121.8(\mathrm{CH}), 123.7(\mathrm{CH}), 124.2(\mathrm{CH}), 128.6(\mathrm{CH}), 132.2(\mathrm{CH})$, 133.1 (C), 138.9 (CH), 139.2 (CH), 141.1 (C), 146.1 (CH), 149.8 (C), 152.4 (C), 152.3 (C), $171.6(\mathrm{C})$. IR $\left(\mathrm{cm}^{-1}\right): 1650(\mathrm{C}=\mathrm{O}), 1602(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$. ESIMS (+ve, MeOH): m/z $467[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (FAB): $m / z$ calc. for $\mathrm{C}_{17} \mathrm{H}_{10} \mathrm{ClN}_{2} \mathrm{O}_{3} \mathrm{Pd}[\mathrm{M}]^{+} 466.91033$, found 466.90980. Anal. calc. for $\left(\mathrm{C}_{17} \mathrm{H}_{10} \mathrm{Cl}_{2} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{Pd}\right)$ : C 43.67, H 2.16, N 5.99; found C 43.58, H 2.07, N 6.13 .

## Synthesis of 3.5a



The same procedure as that described for $\mathbf{3 . 2 a}$, using $\mathbf{3 a}(0.015 \mathrm{~g}$, $0.0416 \mathrm{mmol})$, triphenylphosphine $(0.011 \mathrm{~g}, 0.0416 \mathrm{mmol})$ and dry chloroform ( 10 ml ) gave $\mathbf{3 . 5 a}$ as a yellow solid $(0.023 \mathrm{~g}$, 96\%). Crystals suitable for single crystal X-ray diffraction study were grown from chloroform/petroleum ether solution. Mp: 240-243 ${ }^{\circ} \mathrm{C}$. ${ }^{1} \mathrm{H}$ NMR (500 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 6.42\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right), 6.63\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.4 \mathrm{~Hz}\right.$, Py/Ar-H), $7.01\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.5 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.39(\mathrm{~m}, 6 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 7.46(\mathrm{t}, 3 \mathrm{H}$, ${ }^{3} J_{\mathrm{HH}}=8.1 \mathrm{~Hz}$, Py/Ar-H), $7.63(\mathrm{~s}, 1 \mathrm{H}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}), 7.66(\mathrm{~m}, 6 \mathrm{H}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}), 7.85(\mathrm{~d}, 1 \mathrm{H}$, ${ }^{3} J_{\mathrm{HH}}=7.3 \mathrm{~Hz}$, Py/Ar-H), $7.95\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.7 \mathrm{~Hz}\right.$, Py/Ar-H), $8.09\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.5\right.$ $\mathrm{Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 115.4$ (CH), 119.8 (C), 121.8 (CH), $122.0(\mathrm{CH}), 123.1(\mathrm{CH}), 123.2(\mathrm{CH}), 126.4(\mathrm{C}), 126.8(\mathrm{C}), 127.6(\mathrm{CH}), 127.8(\mathrm{CH})$, 127.9 (CH), 130.3 (CH), 130.8 (CH), 132.7 (CH), 132.9 (CH), $133.5(\mathrm{CH}), 133.7(\mathrm{CH})$, 138.6 (CH), 149.1 (C), 149.3 (C), 161.7 (C), 172.7 (C). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ ( 161 MHz ): $\delta 32.06$ (s, $\left.1 \mathrm{P}, P \mathrm{Ph}_{3}\right)$. IR $\left(\mathrm{cm}^{-1}\right): 1664(\mathrm{C}=\mathrm{O}), 1598(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$. ESIMS ( $\left.+v e, \mathrm{MeOH}\right): m / z 604$ $[\mathrm{M}+\mathrm{Na}]^{+}$. HRMS (FAB): m/z calc. for $\mathrm{C}_{30} \mathrm{H}_{22} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{Pd}[\mathrm{M}]^{+}$581.03721, found 581.03638. HRMS (ASAP): $m / z$ calc. for $\mathrm{C}_{30} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{Pd}[\mathrm{M}+\mathrm{H}]^{+}$582.0450, found 582.0479 .

## Synthesis of 3.6a



A round bottomed flask, equipped with a magnetic stir bar, was charged with 2-phenyl-6-carboxylatopyridine ( $0.080 \mathrm{~g}, 0.372$ mmol), dry methanol (15 ml) and tris(triphenylphosphine)ruthenium(II) dichloride $(0.356 \mathrm{~g}, 0.372$ $\mathrm{mmol})$. The reaction mixture was then stirred and heated to reflux for 18 hours. After cooling to room temperature, the precipitate was filtered through a Celite plug and washed with methanol. Pure precipitate collected by filtration was
extracted with dichloromethane and dried under reduced pressure to afford 3.6a as a green solid ( $0.312 \mathrm{~g}, 96 \%$ ). Mp: $245{ }^{\circ} \mathrm{C}$ (decomp.). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ ( 161 MHz ): $\delta 34.56$ (s, 2P, $\left.P \mathrm{Ph}_{3}\right)$. IR $\left(\mathrm{cm}^{-1}\right): 1644(\mathrm{C}=\mathrm{O}), 1600(\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1432,1094,693\left(\mathrm{PPh}_{3}\right)$. ESIMS (+ve, $\mathrm{MeOH}): m / z 839[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (TOF): $\mathrm{m} / \mathrm{z}$ calc. for $\mathrm{C}_{48} \mathrm{H}_{3} 7 \mathrm{NO}_{3} \mathrm{P}_{2} \mathrm{Ru}[\mathrm{M}-\mathrm{Cl}]^{+}$ 839.1306, found 839.1324. $\mu_{\text {eff }}=1.91$ BM.

## Synthesis of 3b



A clean dry Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was then charged with 2-(4'-t-butyl-phenol)-6carboxylatopyridine $(0.100 \mathrm{~g}, 0.368 \mathrm{mmol})$ and $\mathrm{Pd}(\mathrm{OAc})_{2}$ $(0.083 \mathrm{~g}, 0.368 \mathrm{mmol})$ in dry acetonitrile $(10 \mathrm{ml})$. The reaction mixture was stirred at room temperature for 3 hours. Red solution was filtered through a Celite plug. which was washed thoroughly with acetonitrile and dried under reduced pressure to give 3b as a red solid $(0.133 \mathrm{~g}$, $87 \%$ ). Single crystals suitable for X-ray determination were grown by slow evaporation of a solution of $\mathbf{3 b}$ in acetonitrile. Mp: 254-256 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta$ $1.35\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 1.97(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Pd}-\mathrm{NCMe}), 6.92\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{H}_{\mathrm{HH}}=8.7 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right)$, $7.81(\mathrm{~s}, 1 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 7.34\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.8 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=2.4 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.62(\mathrm{~d}$, $1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.3 \mathrm{~Hz}$, Py/Ar-H), $8.09\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.1 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 8.32\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=\right.$ $8.6 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 1.1\left(\mathrm{CH}_{3} \mathrm{CNPd}\right), 30.3\left(\left(\mathrm{CH}_{3}\right)_{3}\right), 34.1$ $\left(C\left(\mathrm{CH}_{3}\right)_{3}\right), 117.3\left(\mathrm{CH}_{3} C \mathrm{NPd}\right), 120.3(\mathrm{CH}), 124.4(\mathrm{CH}), 124.7(\mathrm{CH}), 123.2(\mathrm{CH}), 127.1$ (C), 130.0 (CH), 138.8 (C), 139.7 (CH), 142.1 (C), 145.4 (C), 162.5 (C), 176.1 (C). IR $\left(\mathrm{cm}^{-1}\right): 1652(\mathrm{C}=\mathrm{O}), 1595(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$. ESIMS ( $+v e$, MeCN): m/z 417 [MH] ${ }^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{18} \mathrm{H}_{19} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{Pd}[\mathrm{MH}]^{+}$417.0430, found 417.0436. HRMS (FAB): $m / z$ calc. for $\mathrm{C}_{16} \mathrm{H}_{15} \mathrm{NO}_{3} \mathrm{Pd}$ [M-MeCN] ${ }^{+}$375.00868, found 375.00802. Anal. calc. for $\left(\mathrm{C}_{18} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{Pd}\right)$ : C 51.87, H 4.35, N 6.72; found C 50.99, H 4.27, N 6.28 .

## Synthesis of 3.2b



The same procedure as that described for 3.2a, using 3b $(0.010 \mathrm{~g}, 0.024 \mathrm{mmol}), 3,5$-dimethylpyridine ( $0.003 \mathrm{~g}, 0.024$ mmol ) and dry chloroform ( 10 ml ) gave 3.2b as a yellow solid ( $0.010 \mathrm{~g}, 91 \%$ ). Mp: > $260{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR $(500 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right): \delta 1.28\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 2.32\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 7.05(\mathrm{~d}$, $\left.1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.6 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.25\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, Py/Ar-H), 7.45 (s, 1H, Py/Ar-H), 7.63 (s, 1H, Py/Ar-H), 7.73 (d, $1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}$, Py/Ar-H), $7.93\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 8.05\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.4 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right)$, 8.39 (s, 2H, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $\left.125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 17.5\left(\mathrm{CH}_{3}\right), 30.4\left(\left(\mathrm{CH}_{3}\right)_{3}\right), 33.0$ $\left(C\left(\mathrm{CH}_{3}\right)_{3}\right), 121.1(\mathrm{CH}), 122.2(\mathrm{CH}), 123.2(\mathrm{CH}), 123.5(\mathrm{CH}), 129.2(\mathrm{CH}), 138.2(\mathrm{CH})$, 139.1 (CH), 139.4 (CH), 145.5 (C), 146.4 (C), 147.7 (C), 149.5 (C), 151.3 (C), 159.7 (C), $171.4(\mathrm{C})$. IR $\left(\mathrm{cm}^{-1}\right): 1656(\mathrm{C}=\mathrm{O}), 1600(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$. ESIMS (+ve, MeOH): m/z $483[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{23} \mathrm{H}_{25} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{Pd}[\mathrm{M}+\mathrm{H}]^{+}$483.0900, found 483.0915. $[\mathrm{M}+\mathrm{Na}]^{+}$505.0719, found 505.0756. HRMS (FAB): $\mathrm{m} / \mathrm{z}$ calc. for $\left(\mathrm{C}_{25} \mathrm{H}_{32} \mathrm{O}_{3} \mathrm{~N}_{2} \mathrm{Pd}\right)[\mathrm{M}]^{+} 482.08218$, found 482.08269 .

## Synthesis of 3.3b



The same procedure as that described for 3.2a, using 3b ( $0.012 \mathrm{~g}, 0.028 \mathrm{mmol}$ ), 3,5-dichloropyridine $(0.0043 \mathrm{~g}$, $0.028 \mathrm{mmol})$ and dry chloroform ( 10 ml ) gave $\mathbf{3 . 3 b}$ as a yellow solid ( $0.012 \mathrm{~g}, 78 \%$ ). Mp: > $260{ }^{\circ} \mathrm{C}$. ${ }^{1} \mathrm{H}$ NMR ( 500 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 1.28\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 7.02\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=\right.$ $8.8 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 7.26\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.8 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=2.4\right.$ Hz, Py/Ar-H), 7.63 (s, 1H, Py/Ar-H), 7.71 (d, 1H, $\left.{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}, \operatorname{Py} / A r-H\right), 7.88(\mathrm{~s}, 1 \mathrm{H}$, Py/Ar-H), $7.94\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.0 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 8.06\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.6 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right)$, 8.75 (s, 2H, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 31.4\left(\left(\mathrm{CH}_{3}\right)_{3}\right)$, $34.0\left(\mathrm{C}_{\left.\left(\mathrm{CH}_{3}\right)_{3}\right) \text {, }}\right.$ $119.2(\mathrm{CH}), 121.4(\mathrm{CH}), 123.5(\mathrm{CH}), 124.5(\mathrm{CH}), 130.5(\mathrm{CH}), 133.2(\mathrm{CH}), 138.5(\mathrm{CH})$, 139.2 (CH), 139.3 (C), 139.5 (C), 146.3 (C), 150.3 (C), 152.5 (C), 160.1 (C), 171.8 (C). IR ( $\mathrm{cm}^{-1}$ ): $1697(\mathrm{C}=\mathrm{O}), 1601(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$. ESIMS ( $\left.+v e, \mathrm{MeOH}\right): m / z 375$ [M-3,5dichloropyridine] ${ }^{+}$. HRMS (FAB): $m / z$ calc. for $\left(\mathrm{C}_{16} \mathrm{H}_{15} \mathrm{NO}_{3} \mathrm{Pd}\right)[\mathrm{M}]^{+} 375.00868$, found 375.00802. Anal. calc. for $\left(\mathrm{C}_{21} \mathrm{H}_{18} \mathrm{Cl}_{2} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{Pd} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$ : C 43.42 , H 3.31 , N 4.60 ; found: C 45.32, H 3.42, N 5.03.

## Synthesis of 3.4b



The same procedure as that described for 3.2a, using 3b $(0.010 \mathrm{~g}, 0.024 \mathrm{mmol})$, phenylpyridine $(0.0037 \mathrm{~g}, 0.024$ mmol ) and dry chloroform ( 10 ml ) gave $\mathbf{3 . 4 b}$ as a yellow solid $(0.009 \mathrm{~g}, 76 \%) . \mathrm{Mp}:>270^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta 1.34\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 6.73\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=87.7\right.$ Hz, Py/Ar-H), $7.19\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.8,1 \mathrm{~Hz},{ }^{3} J_{\mathrm{HH}}=1.9\right.$, Py/Ar-H), $7.39\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.2 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.47\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.3 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right)$, 7.62 (m, 2H, Py/Ar-H), 7.67 (d, 1H, ${ }^{3} J_{\mathrm{HH}}=7.3 \mathrm{~Hz}$, Py/Ar-H), 7.94 (m, 2H, Py/Ar-H), $8.04\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz}\right.$, Py/Ar-H$), 8.27\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz}\right.$, Py/Ar-H$), 9.07(\mathrm{~s}, 1 \mathrm{H}$, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $\left.125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 31.4\left(\left(\mathrm{CH}_{3}\right)_{3}\right), 34.2\left(C\left(\mathrm{CH}_{3}\right)_{3}\right), 121.2(\mathrm{CH})$, $122.9(\mathrm{CH}), 123.3(\mathrm{CH}), 123.9(\mathrm{CH}), 124.3(\mathrm{CH}), 126.2(\mathrm{CH}), 127.1(\mathrm{CH}), 128.4(\mathrm{CH})$, 129.0 (CH), 129.7 (CH), 131.3 (CH), 137.5 (C), 138.8 (CH), 138.9 (CH), 139.2 (C), 150.5 (C), 151.4 (C), 157.2 (C), 160.7 (C), 162.0 (C), 171.8 (C). IR ( $\left.\mathrm{cm}^{-1}\right): 1660$ (C=O), $1601(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$. ESIMS (+ve, MeOH): $m / z 531[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{27} \mathrm{H}_{24} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{Pd}[\mathrm{M}+\mathrm{Na}]^{+}$553.0730, found 553.0773.

## Synthesis of 3.5b



The same procedure as that described for 3.2a, using 3b $(0.010 \mathrm{~g}, 0.024 \mathrm{mmol}$,$) , triphenylphosphine (0.006 \mathrm{~g}, 0.024$ mmol ) and dry chloroform ( 10 ml ) gave $\mathbf{3 . 5 b}$ as a yellow solid ( $0.014 \mathrm{~g}, 92 \%$ ). Mp: > $260{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta 1.24\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right), 6.39\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.8 \mathrm{~Hz}\right.$, Py/Ar-H), 7.38 (m, 6H, Py/Ar-H), 7.09 (dd, 1H, ${ }^{3} J_{\mathrm{HH}}=8.7,2.1 \mathrm{~Hz}$, Py/Ar-H), 7.46 (m, $3 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}$ ), 7.63 (m, 6H, Py/Ar-H), $7.85\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.3 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.96(\mathrm{t}$, $1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.7 \mathrm{~Hz}$, Py/Ar-H), $8.10\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.5 \mathrm{~Hz}\right.$, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR (125 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 30.4\left(\left(\mathrm{CH}_{3}\right)_{3}\right), 33.0\left(C\left(\mathrm{CH}_{3}\right)_{3}\right), 119.1(\mathrm{C}), 121.4(\mathrm{CH}), 121.8(\mathrm{CH})$, $123.2(\mathrm{CH}), 123.7(\mathrm{CH}), 126.3(\mathrm{CH}), 126.5(\mathrm{C}), 127.0(\mathrm{C}), 127.2(\mathrm{CH}), 127.6(\mathrm{CH})$, $128.8(\mathrm{CH}), 130.2(\mathrm{CH}), 130.5(\mathrm{CH}), 133.3(\mathrm{CH}), 133.5(\mathrm{CH}), 133.6(\mathrm{CH}), 138.0(\mathrm{C})$, $138.5(\mathrm{CH}), 149.2(\mathrm{C}), 149.4(\mathrm{C}), 159.6(\mathrm{C}), 172.8(\mathrm{C}) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ ( 161 MHz ): $\delta 30.12$ (s, $\left.1 \mathrm{P}, \mathrm{PPh}_{3}\right)$. IR $\left(\mathrm{cm}^{-1}\right): 1645(\mathrm{C}=\mathrm{O}), 1578(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$. ESIMS ( $+v e, \mathrm{MeOH}$ ): m/z 638 $[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $\mathrm{m} / \mathrm{z}$ calc. for $\mathrm{C}_{34} \mathrm{H}_{30} \mathrm{NO}_{3} \mathrm{PPdNa}[\mathrm{M}+\mathrm{Na}]^{+}$660.0896, found 660.0925. Anal. calc. for $\left(\mathrm{C}_{34} \mathrm{H}_{30} \mathrm{NO}_{3} \mathrm{PPd}\right)$ : C 64.01, H 2.46, N 2.20 ; found: C 63.89 , H 4.62, N 2.31 .

## Synthesis of 3.6b



A round bottomed flask, equipped with a magnetic stir bar was charged with 2-(4'-t-butyl-phenol)-6-carboxylatopyridine ( 0.060 $\mathrm{g}, \quad 0.221 \mathrm{mmol})$, dry methanol ( 15 ml$)$ and tris(triphenylphosphine)ruthenium(II) dichloride $(0.211 \mathrm{~g}, 0.221$ $\mathrm{mmol})$. The reaction mixture was stirred and heated to reflux for 18 hours. After cooling to room temperature, the precipitate was filtered through a Celite plug and washed with methanol. Pure product collected by filtration was extracted with dichloromethane and dried under reduced pressure to afford 3.6b as a green solid ( $0.191 \mathrm{~g}, 93 \%$ ). Single crystals suitable for X-ray determination were grown by slow evaporation of a solution of $\mathbf{3 . 6 b}$ in dichloromethane. Mp: $245{ }^{\circ} \mathrm{C}$ (decomp.). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ ( 161 MHz ): $\delta 32.08$ (s, 2P, $\mathrm{PPh}_{3}$ ). IR ( $\mathrm{cm}^{-1}$ ): $1644(\mathrm{C}=\mathrm{O}), 1600(\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1432,1094,693\left(\mathrm{PPh}_{3}\right)$. ESIMS (-ve, MeOH): $m / z 926[\mathrm{M}-\mathrm{H}]^{+}$. ESIMS (+ve, MeOH): $m / z 895$ [M-Cl] ${ }^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{5} \mathrm{H}_{45} \mathrm{NO}_{3} \mathrm{P}_{2} \mathrm{Ru}[\mathrm{M}-\mathrm{Cl}]^{+} 895.1918$, found 895.1948 . $\mu_{\text {eff }}=1.94 \mathrm{BM}$.

## Synthesis of 3.1c



A round bottomed flask, equipped with a magnetic stir bar was charged with 2-(3-chlorophenol)-6-carboxylatopyridine ( $0.030 \mathrm{~g}, 0.121 \mathrm{mmol}$ ), pyridine ( $0.019 \mathrm{~g}, 0.241 \mathrm{mmol}, 2 \mathrm{eq}$. ), dry methanol ( 15 ml ) and palladium(II) acetate $(0.027 \mathrm{~g}$, $0.121 \mathrm{mmol})$. The reaction mixture was stirred and heated to reflux for 18 hours. After cooling to room temperature, the precipitate was filtered through a Celite plug and washed with methanol. Pure product collected by filtration was extracted with dichloromethane and dried under reduced pressure to afford 3.1c as a yellow solid ( $0.045 \mathrm{~g}, 88 \%$ ). Mp: > $270{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( 500 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta \quad 6.99\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.08\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.8 \mathrm{~Hz}\right.$, Py/Ar-H), 7.42 (t, 2H, $\left.{ }^{3} J_{\mathrm{HH}}=8.4 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.64(\mathrm{~s}, 1 \mathrm{H}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}), 7.74\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}\right.$ $=6.8 \mathrm{~Hz}$, Py/Ar-H), $7.87\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} \mathrm{H}_{\mathrm{HH}}=8.3 \mathrm{~Hz}\right.$, Py/Ar-H), $7.97(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 8.74$ $\left(\mathrm{d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.5 \mathrm{~Hz}\right.$, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 120.0(\mathrm{CH}), 122.5$ $(\mathrm{CH}), 123.0(\mathrm{CH}), 124.0(\mathrm{CH}), 126.7(\mathrm{CH}), 131.0(\mathrm{CH}), 138.2(\mathrm{CH}), 138.4(\mathrm{CH}), 139.2$ (C), 145.0 (C), 148.1 (CH), 150.8 (C), 156.1 (C), 162.3 (C), 169.2 (C). IR ( $\mathrm{cm}^{-1}$ ): 1661 (C=O), $1596(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$. ESIMS (+ve, MeOH): $m / z 433[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{34} \mathrm{H}_{22} \mathrm{~N}_{4} \mathrm{O}_{6} \mathrm{NaCl}_{2} \mathrm{Pd}[2 \mathrm{M}+\mathrm{Na}]^{+}$888.8888, found 888.8915. HRMS (ASAP):
$m / z$ calc. for $\mathrm{C}_{17} \mathrm{H}_{12} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{ClPd}[\mathrm{M}+\mathrm{H}]^{+}$432.9571, found 432.9579. Anal. calc. for $\left(\mathrm{C}_{17} \mathrm{H}_{11} \mathrm{ClN}_{2} \mathrm{O}_{3} \mathrm{Pd}\right)$ : C 47.14, H 2.56, N 6.47; found: C 46.99, H 2.43, N 6.38.

Synthesis of 3.2c


The same procedure as that described for $\mathbf{3 c}$, using 2-(3-chlorophenol)-6-carboxylatopyridine ( $0.020 \mathrm{~g}, 0.0804 \mathrm{mmol}$ ), 3,5-dimethylpyridine ( $0.017 \mathrm{~g}, 0.161 \mathrm{mmol}, 2 \mathrm{eq}$.), dry methanol ( 15 ml ) and palladium(II) acetate $(0.018 \mathrm{~g}, 0.0804$ mmol ) gave 3.2c as a yellow solid ( $0.034 \mathrm{~g}, 93 \%$ ). Mp: > 270 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}^{\mathrm{H}} \mathrm{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 2.34\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right), 7.00(\mathrm{~d}$, $1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.7 \mathrm{~Hz}$, Py/Ar-H), $7.08\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.51(\mathrm{~s}, 1 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-$ H), $7.65\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.6 \mathrm{~Hz}\right.$, Py/Ar-H), $7.76\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.5 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.98(\mathrm{~m}$, $2 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 8.36$ (s, 2H, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 18.5\left(\mathrm{CH}_{3}\right), 120.8$ (C), $121.0(\mathrm{C}), 123.6(\mathrm{CH}), 123.9(\mathrm{CH}), 124.0(\mathrm{CH}), 127.6(\mathrm{CH}), 131.8(\mathrm{CH}), 134.6$ (C), 139.2 (CH), 140.5 (CH), 146.2 (CH), 148.9 (C), 152.4 (C), 161.3 (C), 172.0 (C). IR $\left(\mathrm{cm}^{-1}\right): 1655(\mathrm{C}=\mathrm{O}), 1598(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$. ESIMS ( $\left.+v e, \mathrm{MeOH}\right): m / z 461[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{19} \mathrm{H}_{15} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{NaClPd}[\mathrm{M}+\mathrm{Na}]^{+}$482.9711, found 482.9704. HRMS (ASAP): $m / z$ calc. for $\mathrm{C}_{19} \mathrm{H}_{16} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{ClPd}[\mathrm{M}+\mathrm{H}]^{+} 460.9884$, found 460.9887 .

## Synthesis of 3.2c- ${ }^{-}$Bu



The same procedure as that described for 3.1c, using 2-(3-chlorophenol)-6-carboxylatopyridine ( $0.030 \mathrm{~g}, 0.121 \mathrm{mmol}$ ), tert-butyl pyridine ( $0.033 \mathrm{~g}, 0.241 \mathrm{mmol}, 2 \mathrm{eq}$.$) , dry methanol$ $(15 \mathrm{ml})$ and palladium(II) acetate $(0.027 \mathrm{~g}, 0.121 \mathrm{mmol})$ gave 3.2c- ${ }^{t} \mathbf{B u}$ as a yellow solid $(0.053 \mathrm{~g}, 91 \%)$. Mp: > $270{ }^{\circ} \mathrm{C}$. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.26$ (s, $\left.9 \mathrm{H}, \mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right)$, 6.91 (d, $1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.6 \mathrm{~Hz}$, Py/Ar-H), $6.99\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.7 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}\right.$ $=2.3 \mathrm{~Hz}$, Py/Ar-H), $7.34\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.5 \mathrm{~Hz}\right.$, Py/Ar-H), $7.56(\mathrm{~s}, 1 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 7.65$ $\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.5 \mathrm{~Hz},{ }^{4} \mathrm{~J}_{\mathrm{HH}}=1.9 \mathrm{~Hz}\right.$, Py/Ar-H), $7.89(\mathrm{~m}, 2 \mathrm{H}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}), 8.52(\mathrm{~d}, 2 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 29.3\left(\mathrm{CH}_{3}\right), 30.4\left(\left(\mathrm{CH}_{3}\right)_{3}\right)$, 119.7 (C), 119.9 (C), $121.0(\mathrm{CH}), 122.5(\mathrm{CH}), 122.9(\mathrm{CH}), 126.0(\mathrm{CH}), 126.6(\mathrm{CH})$, 130.8 (CH), 138.2 (CH), 147.4 (CH), 147.9 (C), 151.3 (C), 160.3 (C), 170.9 (C). IR $\left(\mathrm{cm}^{-1}\right): 1676(\mathrm{C}=\mathrm{O}), 1599(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$. ESIMS ( $\left.+v e, \mathrm{MeOH}\right): m / z 489[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{21} \mathrm{H}_{19} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{NaClPd}[\mathrm{M}+\mathrm{Na}]^{+} 511.0025$, found 511.0017. HRMS
(ASAP): $m / z$ calc. for $\mathrm{C}_{21} \mathrm{H}_{20} \mathrm{~N}_{2} \mathrm{O}_{3} \mathrm{ClPd}[\mathrm{M}+\mathrm{H}]^{+} 489.0197$, found 489.0234. Anal. calc. for $\left(\mathrm{C}_{21} \mathrm{H}_{19} \mathrm{ClN}_{2} \mathrm{O}_{3} \mathrm{Pd} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$ : C 46.02, H 3.14, N 4.88 ; found: C 45.91, H 3.14, N 5.42.

## Synthesis of 3.2c-Br



The same procedure as that described for 3.1c, using 2-(3-chlorophenol)-6-carboxylatopyridine ( $0.030 \mathrm{~g}, 0.121 \mathrm{mmol}$ ), 3-bromopyridine ( $0.038 \mathrm{~g}, 0.241 \mathrm{mmol}, 2 \mathrm{eq}$.), dry methanol $(15 \mathrm{ml})$ and palladium(II) acetate $(0.027 \mathrm{~g}, 0.121 \mathrm{mmol})$ gave $3.2 \mathrm{c}-\mathrm{Br}$ as a yellow solid ( $0.052 \mathrm{~g}, 85 \%$ ). Mp: $>270{ }^{\circ} \mathrm{C}$. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.02\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.7 \mathrm{~Hz}\right.$, Py/Ar-H), $7.11\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.3 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=2.4 \mathrm{~Hz}\right.$, Py/Ar-H), $7.34(\mathrm{~m}, 1 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H})$, $7.66(\mathrm{~s}, 1 \mathrm{H}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}), 7.76\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.4 \mathrm{~Hz},{ }^{4} \mathrm{~J}_{\mathrm{HH}}=1.6 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.97(\mathrm{t}, 1 \mathrm{H}$, ${ }^{3} J_{\mathrm{HH}}=8.1 \mathrm{~Hz}$, Py/Ar-H), $8.02(\mathrm{~m}, 2 \mathrm{H}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}), 8.74\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.5 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=1.3\right.$ $\mathrm{Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}$ ), 8.86 (s, $1 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}$ ). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): Sample insufficiently soluble. IR $\left(\mathrm{cm}^{-1}\right)$ : $1683(\mathrm{C}=\mathrm{O}), 1601(\mathrm{C}=\mathrm{N})_{\text {pyridine }}$. $\mathrm{ESIMS}(+v e, \mathrm{MeOH})$ : $m / z 510[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (ASAP): $m / z$ calc. for $\mathrm{C}_{17} \mathrm{H}_{10} \mathrm{ClBrN}_{2} \mathrm{O}_{3} \operatorname{Pd}[\mathrm{M}+\mathrm{H}]^{+} 510.8676$, found 510.8749. Anal. calc. for $\left(\mathrm{C}_{17} \mathrm{H}_{10} \mathrm{BrClN}_{2} \mathrm{O}_{3} \mathrm{Pd}^{2} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$ : $\mathrm{C} 36.22, \mathrm{H} 2.03, \mathrm{~N} 4.69$; found 37.67, H 2.63, N. 4.87.

## Synthesis of 3.5c



The same procedure as that described for 3.1c, using 2-(3-chlorophenol)-6-carboxylatopyridine ( $0.020 \mathrm{~g}, 0.0804 \mathrm{mmol}$ ), triphenylphosphine ( $0.021 \mathrm{~g}, 0.0804 \mathrm{mmol}$ ), dry methanol ( 15 $\mathrm{ml})$ and palladium(II) acetate $(0.018 \mathrm{~g}, 0.0804 \mathrm{mmol})$ gave
3.5c as a yellow solid ( $0.048 \mathrm{~g}, 97 \%$ ). Single crystals suitable for X-ray determination were grown by slow diffusion of petroleum ether (40-60) into a chloroform solution of $\mathbf{3 . 5 c} . \mathrm{Mp}:>270{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 6.40(\mathrm{~d}, 1 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.00\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.8,{ }^{4} J_{\mathrm{HH}}=2.4 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.46(\mathrm{t}, 5 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{HH}}=7.3 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.55\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.3 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.71(\mathrm{~m}, 7 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H})$, $7.97\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.3 \mathrm{~Hz}\right.$, Py/Ar-H), $8.06\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.5 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 8.12(\mathrm{~d}, 1 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 123.6(\mathrm{CH}), 124.0(\mathrm{CH})$, $124.1(\mathrm{CH}), 124.4(\mathrm{CH}), 127.3(\mathrm{C}), 127.6(\mathrm{C}), 127.8(\mathrm{CH}), 128.6(\mathrm{CH}), 128.7(\mathrm{CH})$, $131.4(\mathrm{CH}), 131.7(\mathrm{CH}), 134.4(\mathrm{CH}), 134.5(\mathrm{CH}), 139.9(\mathrm{CH}), 141.8(\mathrm{CH}), 145.2(\mathrm{CH})$,
147.2 (C), 152.4 (C), 154.7 (C), 159.8 (C), 161.3 (C), 167.2 (C). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}(161 \mathrm{MHz}): \delta$ $29.70\left(\mathrm{~s}, 1 \mathrm{P}, \mathrm{PPh}_{3}\right)$. IR $\left(\mathrm{cm}^{-1}\right): 1662(\mathrm{C}=\mathrm{O}), 1603(\mathrm{C}=\mathrm{N})_{\text {pyridine. }}$. ESIMS ( $\left.+v e, \mathrm{MeOH}\right)$ : $m / z 616[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (ASAP): $m / z$ calc. for $\mathrm{C}_{30} \mathrm{H}_{22} \mathrm{NO}_{3} \mathrm{ClPd}[\mathrm{M}+\mathrm{H}]^{+}$616.0061, found 616.0088.

## Synthesis of 3.6c



The same procedure as that described for 3.6a, using 2-(3-chlorophenol)-6-carboxylatopyridine ( $0.020 \mathrm{~g}, 0.0804 \mathrm{mmol}$ ), tris(triphenylphosphine)ruthenium(II) dichloride $(0.077 \mathrm{~g}, 0.0804$ $\mathrm{mmol})$ and dry methanol $(10 \mathrm{ml})$ gave $\mathbf{3 . 6 c}$ as a green solid $(0.066$ g, $91 \%$ ). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ ( 161 MHz ): $\delta 35.02$ (s, 2P, $P \mathrm{Ph}_{3}$ ). IR $\left(\mathrm{cm}^{-1}\right)$ : 1654 ( $\mathrm{C}=\mathrm{O}$ ), 1597 ( $\mathrm{C}=\mathrm{N})_{\text {pyridine, }}$ 1433, 1092, 693 ( $\mathrm{PPh}_{3}$ ). ESIMS $(+v e, \mathrm{MeOH}): m / z 909[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{30} \mathrm{H}_{21} \mathrm{NO}_{3} \mathrm{PNaCl}_{2} \mathrm{Ru}$ [M$\left.\left(\mathrm{PPh}_{3}\right)+\mathrm{Na}\right]^{+} 668.9579$, found 668.9597 . $\mu_{\text {eff }}=1.96 \mathrm{BM}$. Anal. calc. for $\left(\mathrm{C}_{48} \mathrm{H}_{36} \mathrm{Cl}_{2} \mathrm{NO}_{3}\right.$ $\mathrm{P}_{2} \mathrm{Ru} \cdot 3 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ ): C 52.65, H 3.64, N 1.20. Found C 53.47, H 3.22, N 1.84 .

### 8.6 Experimental procedures for Chapter 4

### 8.6.1 General procedure for transfer hydrogenation of ketones

A small oven-dried Schlenk flask was evacuated and backfilled with nitrogen. Distilled 2-propanol ( 5 mL ), ketone ( mmol ), catalyst ( mmol ), and NaOtBu (mmol) were added under nitrogen in sequential order. The reaction mixture was stirred at $80^{\circ} \mathrm{C}$ for 6 h . On cooling to room temperature, the mixture was filtered through a Celite plug and washed thoroughly with petroleum ether. The volatiles were removed under reduced pressure. The crude product was purified by column chromatography on silica gel (dichloromethane, 100\%) to give the corresponding alcohol.

## 1-Phenylethanol


[CAS 98-85-1] Obtained as clear liquid ( $0.050 \mathrm{~g}, 98 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( 500 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 1.42\left(\mathrm{~d}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.0 \mathrm{~Hz}, \mathrm{CH}_{3}\right), 1.83(\mathrm{bs}, 1 \mathrm{H}, \mathrm{OH}), 4.81$ $\left(\mathrm{q}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.0 \mathrm{~Hz}, H\left(\mathrm{CH}_{3}\right)\right), 7.20\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.6 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 7.22-7-$ 34 (m, 4H, Ar-H). ESIMS (+ve, MeOH): m/z $123[\mathrm{M}+\mathrm{H}]^{+}$.

## 1-(4-Methylphenyl)ethanol


[CAS 536-50-5] Obtained as clear liquid (0.045 g, 89\%). ${ }^{1} \mathrm{H}$ NMR (500 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 1.45\left(\mathrm{~d}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}_{3}\right), 2.10(\mathrm{bs}, 1 \mathrm{H}, \mathrm{OH})$, $2.33\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right), 4.82\left(\mathrm{q}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.1 \mathrm{~Hz}, H\left(\mathrm{CH}_{3}\right)\right), 7.14(\mathrm{~d}, 2 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{HH}}=7.9 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 7.23\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.6 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right)$. ESIMS (+ve, MeOH): $m / z .137$ $[\mathrm{M}+\mathrm{H}]^{+}$.

## 1-(4-Methoxyphenyl)ethanol

 $\left(\mathrm{d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.2 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 7.05\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.4 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right) . \operatorname{ESIMS}(+v e, \mathrm{MeOH}):$ $m / z 153[\mathrm{M}+\mathrm{H}]^{+}$.

## 1-(4-Bromophenyl)ethanol


[CAS 5391-88-8] Obtained as clear liquid ( $0.034 \mathrm{~g}, 68 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.46\left(\mathrm{~d}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.5 \mathrm{~Hz}, \mathrm{CH}_{3}\right), 1.89(\mathrm{bs}, 1 \mathrm{H}$, $\mathrm{OH}), 4.86\left(\mathrm{q}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.7 \mathrm{~Hz}, H\left(\mathrm{CH}_{3}\right)\right), 7.24\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.7 \mathrm{~Hz}\right.$, Ar-H), $7.46\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.7 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right)$. ESIMS (+ve, MeOH): $m / z 202[\mathrm{M}+\mathrm{H}]^{+}$.

## Benzhydrol


[CAS 91-01-0] Obtained as white solid (0.047 g, 94\%). ${ }^{1} \mathrm{H}$ NMR (500 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 3.85\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.7 \mathrm{~Hz}, \mathrm{OH}\right), 5.21\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=\right.$ $6.6 \mathrm{~Hz}, H(\mathrm{OH})$ ), 7.21-7.26 (m, 10H, Ar-H). ESIMS (+ve, MeOH):
$\mathrm{m} / \mathrm{z} 185[\mathrm{M}+\mathrm{H}]^{+}$.

### 8.6.2 Magnetic susceptibility measurements via the Evans' NMR method ${ }^{157,158}$

Magnetic susceptibilities in $\mathrm{CD}_{3} \mathrm{CN}$ or $\mathrm{CD}_{2} \mathrm{Cl}_{2} / t-\mathrm{BuOH}$ solution at 298 K were determined by the Evans' Method ${ }^{8,9}$ using a Bruker 400 MHz spectrometer, a routine 5 mm spinning NMR sample tube along with a loose thin-walled insert tube with ca. 1 mm diameter (a melting point tube that could be flame sealed). Note: the recommended Wilmad Stem Coaxial Small Volume NMR Insert was not available but the
combination of a routine NMR tube and a loose glass insert proved a satisfactory alternative; confirmed using a $\mathrm{Fe}(\mathrm{acac})_{3}$ validation experiment. The concentration of the samples in both the NMR sample tube and insert was kept at 2 mM using the following approach:

1. Insert tube: $t$ - $\mathrm{BuOH}(0.002 \mathrm{mmol}, 0.19 \mathrm{ml})$ was mixed with $\mathrm{CDCl}_{3}(1 \mathrm{ml})$ to give a 2 mM concentration. $c a .0 .1 \mathrm{ml}$ was transferred to the melting point tube and the tube sealed with a hot flame.
2. NMR tube: The paramagnetic sample ( 0.002 mmol ) was dissolved in $\mathrm{CD}_{3} \mathrm{CN}(1 \mathrm{ml})$ in a vial to give a 2 mM concentration. In a separate vial, $t$ - $\mathrm{BuOH}(0.04 \mathrm{mmol})$ was mixed with $\mathrm{CDCl}_{3}(1 \mathrm{ml})$ to give a 2 mM concentration. The two solutions were mixed and 0.5 ml was transferred to the NMR tube once the insert was added.
3. The insert tube was then inserted carefully into the NMR tube and the ${ }^{1} \mathrm{H}$ NMR spectrum was recorded. Two resonance lines were obtained from the methyl protons of the $t$-butyl alcohol in the two solutions owing to the difference in their volume susceptibilities, with the line from the paramagnetic solution lying at higher frequency. The mass susceptibility, $x$, of the dissolved substance was given by the expression:

$$
x=\frac{3 \Delta v}{4 \pi v m}+x_{o}
$$

Where $x_{o}$ was the mass susceptibility of the solvent for dilute $t-\mathrm{BuOH}$ solutions $(-0.72 \mathrm{x}$ $10^{-6}$ ). Diamagnetic corrections were applied using literature values.

### 8.7 Experimental procedures for Chapter 5

### 8.7.1 Synthesis of diethyl pyridine-2,6-dicarboxylate



A three-necked round bottomed flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with pyridine-2,6dicarboxylic acid ( $10.06 \mathrm{~g}, 60.2 \mathrm{mmol}$ ), freshly distilled ethanol ( 70 ml ) and conc. $\mathrm{H}_{2} \mathrm{SO}_{4}(2 \mathrm{ml})$. The mixture was stirred and heated to reflux for 3 h and then allowed to cool to room temperature. The solvent was removed under reduced pressure to give a colourless viscous residue. The residue was dissolved in dichloromethane ( 5 ml ) and the
solution neutralised with saturated aqueous $\mathrm{NaHCO}_{3}$. The aqueous phase was extracted with dichloromethane ( $3 \times 40 \mathrm{~mL}$ ) and the organic phases combined and washed with distilled water ( 3 x 40 mL ). The organic phase was dried with $\mathrm{MgSO}_{4}$, and the volatiles removed under reduced pressure. The product was isolated as off-white crystals ( 8.08 g , $61 \%$ ). Mp: 43-44 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta 1.45\left(\mathrm{t}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}, \mathrm{CH}_{3}\right.$ ), $4.48\left(\mathrm{q}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}, \mathrm{CH}\right), 8.16\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{Py}-\mathrm{H}\right), 8.30\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=\right.$ $7.6 \mathrm{~Hz}, \mathrm{Py}-\mathrm{H})$. The NMR data are consistent with those reported in the literature ${ }^{159}$.

### 8.7.2 Synthesis of ethyl 6-acetyl-2-pyridinecarboxylate



A 250 ml three-necked round bottomed flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was charged with dry ethanol ( 23 ml ), Na metal ( 0.910 $\mathrm{g}, 39.6 \mathrm{mmol}$ ) was added slowly until fully dissolved, and the excess ethanol removed on the Schlenk line to form sodium ethoxide (solid, white powder) in situ. A 100 ml dry round bottomed flask was charged with distilled ethyl acetate ( 35 ml ) and diethyl pyridine-2,6-dicarboxylate ( $8.08 \mathrm{~g}, 36.1 \mathrm{mmol}$ ) was added until fully dissolved. The solution was transferred to a pressure equalised dropping funnel and slowly added dropwise to the prepared sodium ethoxide, then heated to reflux at $80^{\circ} \mathrm{C}$ for 18 h . The yellow mixture was cooled to room temperature, and conc. $\mathrm{HCl}(20 \mathrm{ml})$ was added dropwise. The resultant milky white mixture was heated to reflux at $100^{\circ} \mathrm{C}$ for 18 h , and then allowed to cool to room temperature. Distilled water ( 50 ml ) was added and the precipitate dissolved, affording an orange solution. The aqueous layer was washed with dichloromethane ( $4 \times 25 \mathrm{ml}$ ), and the combined organic layers washed with aqueous $5 \% \mathrm{Na}_{2} \mathrm{CO}_{3}$ ( $3 \times 33 \mathrm{ml}$ ). The organic layer was dried with $\mathrm{MgSO}_{4}$ and the solvent removed under reduced pressure yielding a dark red oil. The product was purified by column chromatography (pet. ether/ ethyl acetate $8: 1$ ) to obtain ethyl 6-acetyl-2-pyridinecarboxylate as a white solid ( $1.87 \mathrm{~g} 27 \%$ ). Mp: 48-50 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.39\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} \mathrm{JHH}_{\mathrm{HH}}=7.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right.$ ), $2.73\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{COCH}_{3}\right), 4.42$ $\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}, \mathrm{CH}_{2}\right), 7.91\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz}, \mathrm{Py}-\mathrm{H}\right), 8.16\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.8\right.$ $\left.\mathrm{Hz},{ }^{3} J_{\mathrm{HH}}=1.2 \mathrm{~Hz}, \mathrm{Py}-\mathrm{H}\right)$. The NMR data are consistent with those reported in the literature ${ }^{159}$.

### 8.7.3 Synthesis of EtL7



A 150 ml three-necked round bottomed flask equipped with a magnetic bar was charged with 2,6diisopropylaniline ( $0.974 \mathrm{~g}, 5.47 \mathrm{mmol}$ ), ethyl 6-acetyl-2pyridinecarboxylate ( $1.0 \mathrm{~g}, 5.18 \mathrm{mmol}$ ) and toluene ( 55 $\mathrm{m})$. $p$-toluene sulfonic acid $(0.004 \mathrm{~g}, 0.0547 \mathrm{mmol}, 0.01$ eq.) was added and the reaction was heated to reflux for 24 h . The solution was allowed to cool to room temperature and the solvent removed under reduced pressure. An orange residue remained was purified by column chromatography (pet. ether/ ethyl acetate $15: 1$ ) to afford pure $\mathrm{EtL}_{7}$ as a pale orange powder ( $1.52 \mathrm{~g}, 84 \%$ ). M.p: $96-98{ }^{\circ} \mathrm{C}$. ${ }^{1} \mathrm{H}^{\mathrm{NMR}}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 1.06\left(\mathrm{~d}, 12 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.38\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}}\right.$ $\left.=7.0 \mathrm{~Hz}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 2.21\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CNCH}_{3}\right), 2.64\left(\mathrm{sept}, 2 \mathrm{H},{ }^{3} \mathrm{JHH}=6.8 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right)$, $4.41\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.0 \mathrm{~Hz}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 7.02\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.1 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 7.08(\mathrm{~d}, 2 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 7.85\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.7 \mathrm{~Hz}\right.$, Py-H), $8.12\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.7 \mathrm{~Hz}\right.$, PyH), $8.49\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.7 \mathrm{~Hz}\right.$, Py-H). IR $\left(\mathrm{cm}^{-1}\right): 1236(\mathrm{C}-\mathrm{O}), 1591(\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1676$ $(\mathrm{C}=\mathrm{N})_{\text {imine }}, 1747(\mathrm{C}=\mathrm{O}), 2967(\mathrm{C}-\mathrm{H})$. The NMR data are consistent with those reported in the literature ${ }^{159}$.

### 8.7.4 Synthesis of 2,4,6-triisopropyl-1-nitrobenzene



A 250 ml three-necked round bottomed flask equipped with a magnetic bar was evacuated and backfilled with nitrogen. The flask was charged with $1,3,5$-triisopropylbenzene $(32.17 \mathrm{~g}, 0.158 \mathrm{~mol})$, acetic anhydride ( 27.7 ml ), and the contents placed in an ice bath and cooled to $0^{\circ} \mathrm{C}$. A mixture of $\mathrm{HNO}_{3}(12 \mathrm{ml})$, ethanoic acid ( 10 ml ) and acetic anhydride ( 10 ml ) was added dropwise to the flask. The yellow solution was stirred for 5 h at $0^{\circ} \mathrm{C}$, then warmed to room temperature. The precipitate was filtered by vacuum filtration to yield 2,4,6-triisopropyl-1-nitrobenzene as yellow crystals ( $37.64 \mathrm{~g}, 96 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( 400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 1.09\left(\mathrm{~d}, 12 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.8 \mathrm{~Hz}\right.$, Tripp-o), $1.10\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.8 \mathrm{~Hz}\right.$, Tripp-p), 2.66 (m, 2H, Tripp-o), 2.76 (m, 1H, Tripp-p), 7.10 (s, 2H, Ar-H). ESIMS $(+v e, \mathrm{MeOH}): m / z 250[\mathrm{M}+\mathrm{H}]^{+}$. The NMR data are consistent with those reported in the literature ${ }^{129}$.

### 8.7.5 Synthesis of 2,4,6-triisopropylaniline



A dry Schlenk flask was equipped with a magnetic stir bar and dry ethanol ( 80 ml ) was added. The ethanol was degassed via the freeze-pump-thaw method three times to thoroughly remove all trace impurities. 2,4,6-triisopropyl-1-nitrobenzene ( $3.76 \mathrm{~g}, 15.1 \mathrm{mmol}$ ), $10 \% \mathrm{Pd} / \mathrm{C}(2.172 \mathrm{~g}, 20.41 \mathrm{mmol})$ and hydrazine ( 55 ml ) were added to the flask. The reaction mixture was heated to reflux for 19 h . After cooling to room temperature, the $\mathrm{Pd} / \mathrm{C}$ solid was filtered from the reaction mixture and the filtrate was removed under reduced pressure. The residue was washed with aqueous $\mathrm{NaOH}(20 \% \mathrm{w} / \mathrm{v}, 20 \mathrm{ml})$ and extracted with diethyl ether ( $4 \times 25 \mathrm{ml}$ ). The organic extracts were combined and dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and the volatiles were removed under reduced pressure to give 2,4,6triisopropylaniline as an orange oil ( $3.08 \mathrm{~g}, 93 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.42$ $\left(\mathrm{d}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.8 \mathrm{~Hz}\right.$, Tripp-p), $1.46\left(\mathrm{~d}, 12 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.8 \mathrm{~Hz}\right.$, Tripp-o), 3.01 (sept, 1 H , ${ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}$, Tripp-p), $3.10\left(\mathrm{sep}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}\right.$, Tripp-o), $3.76\left(\mathrm{~s}, 1 \mathrm{H},-\mathrm{NH}_{2}\right), 7.09$ ( $\mathrm{s}, 2 \mathrm{H}, \mathrm{Ar}-\mathrm{H}$ ). The NMR data are consistent with those reported in the literature ${ }^{129}$.

### 8.7.6 Synthesis of EtL8



The synthesis of EtLs was based on the procedure for EtL7, using 2,4,6-triisopropylaniline ( $1.15 \mathrm{~g}, 5.25$ mmol ), ethyl 6 -acetylpicolinate ( $1.01 \mathrm{~g}, 5.23 \mathrm{mmol}$ ), toluene ( 55 ml ) and $p$-toluene sulfonic acid $(0.005 \mathrm{~g}$, $0.0525 \mathrm{mmol}, 0.01 \mathrm{eq}$. .) to give crude product as an orange residue which was purified by column chromatography (pet. ether/ ethyl acetate 15:1). The pure EtLs was obtained as a yellow powder ( $1.81 \mathrm{~g}, 88 \%$ ). Crystals suitable for X-ray diffraction studies of EtLs were obtained by slow evaporation of a saturated solution in chloroform. Mp: $153-155^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.13(\mathrm{~d}, 12 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{HH}}=6.9 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.27\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.9 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.46\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=\right.$ $7.1 \mathrm{~Hz}, \mathrm{OCH}_{2} \mathrm{CH}_{3}$ ), $2.29\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}=\mathrm{NCH}_{3}\right), 2.70$ (sept., $\left.2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.9 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right)$, 2.90 (sept., $\left.1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.9 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 4.49\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.1 \mathrm{~Hz}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 7.00$ $(\mathrm{s}, 2 \mathrm{H}, \mathrm{Ar}-\mathrm{H}), 7.92\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz}\right.$, Py-H), $8.18\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, Py-H), 8.56 $\left(\mathrm{d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, Py-H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 14.3\left(\mathrm{CH}_{3}\right)$, $17.2\left(\mathrm{CH}_{3}\right)$, $22.9\left(\mathrm{CH}_{3}\right), 23.3\left(\mathrm{CH}_{3}\right), 24.3\left(\mathrm{CH}_{3}\right), 28.4\left(\mathrm{CH}_{3}\right), 30.9(\mathrm{C}), 34.0(\mathrm{CH}), 61.9\left(\mathrm{CH}_{2}\right), 120.9$ $(\mathrm{CH}), 124.3(\mathrm{CH}), 126.0(\mathrm{CH}), 135.2(\mathrm{CH}), 137.2(\mathrm{C}), 143.8(\mathrm{CH}), 144.0(\mathrm{C}), 147.3$
(C), 156.6 (C), 165.2 (C), 166.7 (C). IR ( $\mathrm{cm}^{-1}$ ): 1241 (C-O), 1585 (C=N) pyridine, 1670 $(\mathrm{C}=\mathrm{N})_{\text {imine }}, 1751(\mathrm{C}=\mathrm{O}), 2971(\mathrm{C}-\mathrm{H}) . \operatorname{ESIMS}(+v e, \mathrm{MeCN}): m / z 395[\mathrm{M}+\mathrm{H}]^{+} . \mathrm{HRMS}$ (TOF): $m / z$ calc. for $\mathrm{C}_{25} \mathrm{H}_{34} \mathrm{~N}_{2} \mathrm{O}_{2}[\mathrm{M}+\mathrm{H}]^{+} 395.2699$, found 395.2717.

### 8.7.7 Synthesis of EtL9



The synthesis of EtL9 was based on the procedure for EtL7, using 2,6-diisopropylbromoaniline ( $0.795 \mathrm{~g}, 3.11$ $\mathrm{mmol})$, ethyl 6 -acetylpicolinate ( $0.500 \mathrm{~g}, 2.59 \mathrm{mmol}$ ), toluene ( 50 ml ) and $p$-Toluene sulfonic acid $(0.005 \mathrm{~g}$, 0.0259 mmol ) to obtain crude EtL9 as a brown residue which was further recrystallized from hot methanol to give pure EtL 9 as brown crystals ( $1.064 \mathrm{~g}, 95 \%$ ). Mp: $100-103{ }^{\circ} \mathrm{C}$. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.06\left(\mathrm{~d},{ }^{3} \mathrm{JHH}_{\mathrm{HH}}=7.0 \mathrm{~Hz}, 12 \mathrm{H}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.39(\mathrm{t}, 3 \mathrm{H}$, ${ }^{3} J_{\mathrm{HH}}=8.1 \mathrm{~Hz}, \mathrm{OCH}_{2} \mathrm{CH}_{3}$ ), $2.21\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CNCH}_{3}\right), 2.64$ (sept., $2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}$, $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 4.42\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.0 \mathrm{~Hz}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 7.18(\mathrm{~s}, 1 \mathrm{H}, \mathrm{Ar}-\mathrm{H}), 7.19(\mathrm{~s}, 1 \mathrm{H}, \mathrm{Ar}-$ $\mathrm{H}), 7.87\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz}\right.$, Py-H), $8.13\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz}\right.$, Py-H), $8.46(\mathrm{~d}, 1 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{HH}}=7.9 \mathrm{~Hz}, \mathrm{Py}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 13.3\left(\mathrm{CH}_{3}\right), 16.2\left(\mathrm{CH}_{3}\right), 21.6$ $\left(\mathrm{CH}_{3}\right), 22.0\left(\mathrm{CH}_{3}\right), 27.4(\mathrm{CH}), 61.0\left(\mathrm{CH}_{2}\right), 116.0(\mathrm{C}), 123.2(\mathrm{CH}), 125.3(\mathrm{CH}), 136.3$ (CH), 137.2 (C), 144.3 (CH), 146.5 (C), 155.1 (C), 164.1 (C), 166.4 (C). IR ( $\mathrm{cm}^{-1}$ ): 1264 (C-O), $1583(\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1670(\mathrm{C}=\mathrm{N})_{\text {imine }}, 1746(\mathrm{C}=\mathrm{O})$, 2962 (C-H). ESIMS $(+v e, \mathrm{MeOH}): m / z 431[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{22} \mathrm{H}_{28} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Br}[\mathrm{M}+\mathrm{H}]^{+}$ 431.1334, found 431.1318 .

### 8.8 Complexes supported by imine-substituted $\left[\mathrm{N}, \mathrm{N}_{P y}, \mathrm{O}\right]$ pincer ligands

## Synthesis of 5a



A small round bottomed flask equipped with a stir bar was charged with EtL7 ( $0.010 \mathrm{~g}, 0.028 \mathrm{mmol}), \mathrm{Pd}(\mathrm{OAc})_{2}(0.0063 \mathrm{~g}$, 0.028 mmol ) and chloroform ( 5 ml ). The reaction was stirred at room temperature for 18 h . The yellow precipitate was filtered through a Celite plug, washed with chloroform and the pure product was extracted with acetonitrile. The volatiles were removed under reduced pressure to give $\mathbf{5 a}$ as a yellow powder $(0.013 \mathrm{~g}, 97 \%)$. Crystals suitable for a single crystal X-ray diffraction studies were grown upon slow evaporation of $\mathbf{5 a}$ in acetonitrile
solution. Mp: 250-253 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 1.28\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.7 \mathrm{~Hz}\right.$, $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.51\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.7 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.52\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCOCH}_{3}\right), 2.44(\mathrm{~s}, 3 \mathrm{H}$, $\left.\mathrm{C}=\mathrm{NCH}_{3}\right), 3.41\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 7.42\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 7.53\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}\right.$ $=8.0 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}), 8.06\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}, \mathrm{Py}-\mathrm{H}\right), 8.17\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.0 \mathrm{~Hz}, \mathrm{Py}-\mathrm{H}\right)$, $8.49\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}, \mathrm{Py}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 18.8$ (Py-C(N)$\left.\mathrm{CH}_{3}\right), 24.1\left(\mathrm{Ar}-\mathrm{CH}-\left(\mathrm{CH}_{3}\right)_{2}\right), 24.6\left(\mathrm{Ar}-\mathrm{CH}-\left(\mathrm{CH}_{3}\right)_{2}\right), 29.6\left(\mathrm{OCOCH}_{3}\right), 29.1$ ( $\mathrm{Ar}-\mathrm{CH}-$ $\left.\left(\mathrm{CH}_{3}\right)_{2}\right)$, $124.1(\mathrm{CH}), 124.8(\mathrm{CH}), 125.4(\mathrm{CH}), 128.9(\mathrm{CH}), 129.4(\mathrm{CH}), 130.1(\mathrm{CH})$, 140.9 (C), 142.6 (CH), 155.4 (C), 173.5 (C), 177.4 (C), 181.4 (C). IR ( $\mathrm{cm}^{-1}$ ): 1314 $(\mathrm{COO})_{\text {symm. }} 1595(\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1666(\mathrm{C}=\mathrm{N})_{\text {imine }}, 2963(\mathrm{C}-\mathrm{H})$. ESIMS (+ve, MeCN): m/z $429[(\mathrm{M}+\mathrm{H})-\mathrm{OAc}]^{+}$. HRMS (TOF): $\mathrm{m} / \mathrm{z}$ calc. for $\mathrm{C}_{22} \mathrm{H}_{26} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Pd}[(\mathrm{M}+\mathrm{H})-\mathrm{OAc}]^{+}$ 429.0803, found 429.0886. Anal. calc. for $\left(\mathrm{C}_{22} \mathrm{H}_{26} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Pd} \cdot \mathrm{HOAc}\right)$ : C 52.51, H 5.51, N 5.10; found: C 51.43, H 5.14, N 5.45.

## Synthesis of 5b



A small round bottomed flask equipped with a stir bar was charged with EtLs ( $0.011 \mathrm{~g}, 0.026 \mathrm{mmol}), \mathrm{Pd}(\mathrm{OAc})_{2}$ $(0.006 \mathrm{~g}, 0.026 \mathrm{mmol})$ and chloroform ( 5 ml ). The reaction was stirred at room temperature for 18 h . Hexane ( 5 ml ) was added and the mixture was stirred for 1 h . The yellow precipitate was filtered through a Celite plug, washed with chloroform and the volatiles were removed under reduced pressure to give $\mathbf{5 b}$ as a yellow powder $(0.013 \mathrm{~g}$, $95 \%$ ). Mp: 253-255 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 1.16\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}\right.$, $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.26\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.9 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.45\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.7 \mathrm{~Hz}\right.$, $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.50\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCOCH}_{3}\right), 2.38\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}=\mathrm{NCH}_{3}\right), 2.91$ (sept., $1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.9$ $\left.\mathrm{Hz}, \mathrm{C} H\left(\mathrm{CH}_{3}\right)_{2}\right), 3.26\left(\right.$ sept., $\left.2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{C} H\left(\mathrm{CH}_{3}\right)_{2}\right), 7.07(\mathrm{~s}, 2 \mathrm{H}, \mathrm{Ar}-\mathrm{H}), 7.94(\mathrm{~d}$, $1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}$, Py-H), $8.22\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.3 \mathrm{~Hz}\right.$, Py-H), $8.58\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, Py-H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 17.9\left(\mathrm{CH}_{3}\right), 22.0\left(\mathrm{CH}_{3}\right), 23.6\left(\mathrm{CH}_{3}\right), 23.9$ $\left(\mathrm{CH}_{3}\right), 24.2\left(\mathrm{CH}_{3}\right), 29.0\left(\mathrm{CH}_{3}\right), 29.7(\mathrm{CH}), 34.3(\mathrm{CH}), 121.9(\mathrm{CH}), 127.7(\mathrm{CH}), 129.2$ (CH), 136.5 (CH), 140.32 (C), 142.4 (C), 149.8 (C), 151.6 (C), 153.4 (C), 170.6 (C), 177.2 (C), $177.6(\mathrm{C})$. IR ( $\left.\mathrm{cm}^{-1}\right): 1314(\mathrm{COO})_{\text {symm. }}, 1575(\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1668(\mathrm{C}=\mathrm{N})_{\text {imine }}$, 2960 (C-H). ESIMS (+ve, MeCN): $m / z 471$ [M-OAc] ${ }^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{25} \mathrm{H}_{32} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{Pd}$ [M-OAc] $^{+}$471.1264, found 471.1286; [(M-OAc)+MeCN] ${ }^{+}$512.1529, found 511.1542. HRMS (FAB): $m / z$ calc. for $\mathrm{C}_{25} \mathrm{H}_{32} \mathrm{O}_{4} \mathrm{~N}_{2} \mathrm{Pd}[\mathrm{M}+\mathrm{H}]^{+} 531.1132$, found 531.1137.

## Synthesis of 5c



The same procedure as that described for 5a using HL9 $(0.020 \mathrm{~g}, 0.046 \mathrm{mmol}), \mathrm{Pd}(\mathrm{OAc})_{2}(0.010 \mathrm{~g}, 0.046 \mathrm{mmol})$ and chloroform ( 5 ml ) afforded $\mathbf{2 c}$ as a yellow solid ( 0.025 g, $96 \%$ ). Mp: 251-253 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ $1.19\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}, 1.46\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=\right.\right.$ $\left.6.5 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.63\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCOCH}_{3}\right), 2.39\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}=\mathrm{NCH}_{3}\right), 3.28$ (sept, $2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}$ $\left.=6.9 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 7.39(\mathrm{~s}, 2 \mathrm{H}, \mathrm{Ar}-\mathrm{H}), 8.01\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.6 \mathrm{~Hz}, \mathrm{Py}-\mathrm{H}\right), 8.22(\mathrm{~d}$, $1 \mathrm{H},{ }^{3} \mathrm{JHH}_{\mathrm{HH}}=7.6 \mathrm{~Hz}$, Py-H), $8.51\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.8 \mathrm{~Hz}\right.$, Py-H) ${ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta 18.1\left(\mathrm{Py}-\mathrm{C}(\mathrm{N})-\mathrm{CH}_{3}\right), 22.4\left(\mathrm{OCOCH}_{3}\right), 23.4\left(\mathrm{Ar}-\mathrm{CH}-\left(\boldsymbol{C H}_{3}\right)_{2}\right), 23.8(\mathrm{Ar}-\mathrm{CH}-$ $\left.\left(\mathrm{CH}_{3}\right)_{2}\right), 29.2\left(\mathrm{Ar}-\mathrm{CH}-\left(\mathrm{CH}_{3}\right)_{2}\right), 126.8(\mathrm{CH}), 127.4(\mathrm{CH}), 127.9(\mathrm{C}), 128.1(\mathrm{C}), 129.1$ (CH), 141.6 (CH), 142.1 (C), 142.9 (C), 153.1 (C), 153.3 (C), 177.3 (C), 177.7 (C). IR $\left(\mathrm{cm}^{-1}\right): 1309(\mathrm{COO})_{\text {symm. }}, 1574(\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1667(\mathrm{C}=\mathrm{N})_{\text {imine }}, 2962(\mathrm{C}-\mathrm{H})$. ESIMS (+ve, $\mathrm{MeCN}): \mathrm{m} / \mathrm{z} 507$ [(M+H)-OAc] ${ }^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{20} \mathrm{H}_{22} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{BrPd}$ [(M+H)-OAc] ${ }^{+}$506.9902, found 506.9948 .

## Synthesis of 5.1a



A round bottomed flask equipped with a magnetic stir bar was charged with $5 \mathbf{5 a}(0.013 \mathrm{~g}, 0.016 \mathrm{mmol})$ dissolved in acetonitrile $(10 \mathrm{ml})$, and saturated brine solution $(20 \mathrm{ml})$. The biphasic mixture was stirred vigorously for 1 h at room temperature. The organic layer was separated and dried over $\mathrm{MgSO}_{4}$. The volatiles were removed under reduced pressure to yield 5.1a as an orange powder ( $0.012 \mathrm{~g}, 99 \%$ ). Crystals suitable for a single crystal X-ray diffraction studies were grown upon slow evaporation of 5.1a in acetonitrile solution. $\mathrm{Mp}: 228-231^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right): \delta 1.08\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.31\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8\right.$ $\left.\mathrm{Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.18\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}=\mathrm{NCH}_{3}\right), 3.10\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 7.19\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=\right.$ $8.0 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}), 7.29\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 7.88\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}, \mathrm{Py}-\mathrm{H}\right)$, $8.00\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, Py-H), $8.31\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, Py-H). ${ }^{13} \mathrm{C}$ NMR (100 $\mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 18.4$ ( $\left.\mathrm{Py}-\mathrm{C}(\mathrm{N})-\boldsymbol{C H} 3\right), 23.6$ ( $\left.\mathrm{Ar}-\mathrm{CH}-(\boldsymbol{C H} 3) 2\right), 23.9$ (Ar-CH-( $\left.\boldsymbol{C H} 3\right) 2$ ), 29.2 ( $\mathrm{Ar}-\mathrm{CH}-(\mathrm{CH} 3) 2), 125.5(\mathrm{CH}), 125.8(\mathrm{C}), 130.1(\mathrm{CH}), 130.7(\mathrm{CH}), 131.2(\mathrm{CH})$, 140.9 (C), 143.9 (C), 144.6 (CH), 155.5 (C), 156.7 (C), 184.3 (C). IR ( $\left.\mathrm{cm}^{-1}\right): 1558$ $(\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1663(\mathrm{C}=\mathrm{N})_{\text {imine }}, 2962(\mathrm{C}-\mathrm{H})$. ESIMS ( $\left.+v e, \mathrm{MeCN}\right): m / z 467[\mathrm{M}+\mathrm{H}]^{+}$.

HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{20} \mathrm{H}_{23} \mathrm{ClN}_{2} \mathrm{O}_{2} \mathrm{Pd}[\mathrm{M}]^{-} 466.0487$, found 466.0485; [M-H] 465.0409, found 465.0424.

## Synthesis of 5.1b



The same procedure as that described for 5.1a using $\mathbf{5 b}$ $(0.0134 \mathrm{~g}, 0.026 \mathrm{mmol})$, chloroform $(10 \mathrm{ml})$ and saturated brine solution ( 10 ml ) gave 5.1b as an orange solid ( 0.012 g, $96 \%$ ). Mp: > $250{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ $1.08\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.18\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=\right.$ $\left.6.8 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.34\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.26\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}=\mathrm{NCH}_{3}\right), 2.83$ (sept, $\left.1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.0 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.97\left(\mathrm{sept}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 6.97(\mathrm{~s}$, $2 \mathrm{H}, \mathrm{Ar}-\mathrm{H}), 7.99\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.9 \mathrm{~Hz}\right.$, Py-H), $8.05\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.9 \mathrm{~Hz}\right.$, Py-H), 8.34 $\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.9 \mathrm{~Hz}, \mathrm{Py}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 17.9\left(\mathrm{Py}-\mathrm{C}(\mathrm{N})-\mathrm{CH}_{3}\right), 23.7$ ( $\left.\mathrm{Ar}-\mathrm{CH}-\left(\boldsymbol{C H}_{3}\right)_{2}\right), 23.8\left(\mathrm{Ar}-\mathrm{CH}-\left(\boldsymbol{C H}_{3}\right)_{2}\right), 28.8\left(\mathrm{Ar}-\boldsymbol{C H}-\left(\mathrm{CH}_{3}\right)_{2}\right), 29.8\left(\mathrm{Ar}-\mathrm{CH}-\left(\boldsymbol{C H}_{3}\right)_{2}\right)$, 34.1 ( $\mathrm{Ar}-\mathrm{CH}-\left(\mathrm{CH}_{3}\right), 35.5(\mathrm{CH}), 121.8(\mathrm{C}), 128.6(\mathrm{CH}), 128.8(\mathrm{CH}), 138.6(\mathrm{CH}), 141.7$ $(\mathrm{CH}), 149.5(\mathrm{C}), 153.0(\mathrm{CH}), 152.6(\mathrm{C}), 178.9(\mathrm{C}), 179.1(\mathrm{C}) . \mathrm{IR}\left(\mathrm{cm}^{-1}\right): 1556$ $(\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1655(\mathrm{C}=\mathrm{N})_{\text {imine }}, 2962(\mathrm{C}-\mathrm{H}) . \mathrm{ESIMS}(+v e, \mathrm{MeOH}): m / z 507[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{23} \mathrm{H}_{29} \mathrm{ClN}_{2} \mathrm{O}_{2} \mathrm{Pd}[\mathrm{M}+\mathrm{H}]^{+} 507.1031$, found 507.1030. Anal. calc. for ( $\mathrm{C}_{23} \mathrm{H}_{29} \mathrm{ClN}_{2} \mathrm{O}_{2} \mathrm{Pd}$ ): C 54.45, H 5.76, N 5.52; found: C 54.51, H 5.60, N 5.56.

## Synthesis of 5.1c



The same procedure as that described for 5.1a using 5c
 $(0.020 \mathrm{~g}, 0.035 \mathrm{mmol})$, chloroform $(10 \mathrm{ml})$ and saturated brine solution $(10 \mathrm{ml})$ gave $\mathbf{5 . 1} \mathbf{c}$ as a yellow solid $(0.018 \mathrm{~g}$, $98 \%$ ). Crystals suitable for a single crystal X-ray diffraction studies were grown upon slow evaporation of 5.1 c in acetonitrile solution. Mp: 245-247 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 1.07(\mathrm{~d}, 6 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.30\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.22(\mathrm{~s}, 3 \mathrm{H}$, $\mathrm{C}=\mathrm{NCH}_{3}$ ), 3.07 (sept, $\left.2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 7.35$ (s, $2 \mathrm{H}, \mathrm{Ar}-\mathrm{H}$ ), $7.89(\mathrm{~d}, 1 \mathrm{H}$, ${ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}$, Py-H), $8.02\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, Py-H), $8.31\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, Py$\mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $\left(125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right): \delta 18.1\left(\mathrm{Py}-\mathrm{C}(\mathrm{N})-\mathrm{CH}_{3}\right), 22.3\left(\mathrm{Ar}-\mathrm{CH}-\left(\mathrm{CH}_{3}\right)_{2}\right), 22.9$ ( $\left.\mathrm{Ar}-\mathrm{CH}-\left(\mathrm{CH}_{3}\right)_{2}\right), 28.8\left(\mathrm{Ar}-\boldsymbol{C H}-\left(\mathrm{CH}_{3}\right), 127.1(\mathrm{CH}), 128.2(\mathrm{C}), 129.5(\mathrm{CH}), 139.7(\mathrm{CH})\right.$, 141.5 (CH), 142.8 (C), 143.3 (C), 151.3 (C), 153.7 (C), 154.1 (C), 181.6 (C). IR ( $\mathrm{cm}^{-1}$ ): $1598(\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1638(\mathrm{C}=\mathrm{N})_{\text {imine }}, 2995(\mathrm{C}-\mathrm{H})$. ESIMS ( $+v e$, MeCN): m/z 509
$[(\mathrm{M}+\mathrm{H})-\mathrm{Cl}]^{+}$. HRMS (TOF): $\mathrm{m} / \mathrm{z}$ calc. for $\mathrm{C}_{22} \mathrm{H}_{25} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{BrPd}[(\mathrm{M}-\mathrm{Cl})+\mathrm{MeCN}]^{+}$ 550.0169 , found 550.0167 .

## Synthesis of 5.2a



A small Schlenk flask equipped with a magnetic stir bar was charged with 5.1a ( $0.012 \mathrm{~g}, 0.026 \mathrm{mmol}$ ), dry acetonitrile ( 10 ml ) and $\mathrm{AgPF}_{6}(0.0072 \mathrm{~g}, 0.028 \mathrm{mmol}$, 1.1 eq.). The solution was stirred at room temperature for 2 h . The mixture was filtered through a plug containing $\mathrm{MgSO}_{4} /$ Celite and the volatiles were removed under reduced pressure to afford 5.2a as a pale green solid ( $0.0144 \mathrm{~g}, 90 \%$ ). Mp: 217-220 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}\right): \delta 1.13\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}\right.$, $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.32\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} \mathrm{JHH}_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.15\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C} \equiv \mathrm{NCH}_{3}\right), 2.33(\mathrm{~s}, 3 \mathrm{H}$, $\left.\mathrm{C}=\mathrm{NCH}_{3}\right), 3.41\left(\mathrm{sept}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{C} H\left(\mathrm{CH}_{3}\right)_{2}\right), 7.30\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.5 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right)$, $7.40\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 7.90\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, Py-H), $8.08\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=\right.$ 8.0 Hz, Py-H), $8.42\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, Py-H) $.{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}(161 \mathrm{MHz}): \delta-144.50(\mathrm{~m}$, $\left.{ }^{1} J_{\mathrm{PF}}=705.8 \mathrm{~Hz}, 1 \mathrm{P}, P \mathrm{~F}_{6}\right) .{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}(376 \mathrm{MHz}): \delta-72.9\left(\mathrm{~d},{ }^{1} J_{\mathrm{FP}}=705.8 \mathrm{~Hz}, 6 \mathrm{~F}\right.$, PF6). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 1.1\left(\mathrm{CH}_{3} \mathrm{CN}-\mathrm{Pd}\right)$, $18.4\left(\mathrm{Py}-\mathrm{C}(\mathrm{N})-\mathrm{CH}_{3}\right), 23.9$ ( $\mathrm{Ar}-$ $\left.\mathrm{CH}-\left(\mathrm{CH}_{3}\right)_{2}\right), 24.2\left(\mathrm{Ar}-\boldsymbol{C H}-\left(\mathrm{CH}_{3}\right)_{2}\right), 29.4$ ( $\left.\mathrm{Ar}-\mathrm{CH}-(\boldsymbol{C H} 3)_{2}\right), 118.2\left(\mathrm{CH}_{3} \mathbf{C N}-\mathrm{Pd}\right), 125.7$ (C), 130.4 (C), $130.6(\mathrm{CH}), 131.7(\mathrm{CH}), 140.4(\mathrm{CH}), 140.9(\mathrm{CH}), 141.1(\mathrm{C}), 152.5$ (CH), 155.6 (C), $155.8(\mathrm{C}), 184.2(\mathrm{C})$. IR ( $\left.\mathrm{cm}^{-1}\right): 1598(\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1671(\mathrm{C}=\mathrm{N})_{\text {imine }}$, 2967 (C-H). ESIMS ( $+v e, \mathrm{MeCN}$ ): m/z 470 [M] ${ }^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{22} \mathrm{H}_{26} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{Pd}[\mathrm{M}]^{+} 470.1060$, found 470.1067.

## Synthesis of 5.2b



The same procedure as that described for 5.2a, using 5.1b ( $0.0122 \mathrm{~g}, 0.024 \mathrm{mmol}$ ), acetonitrile ( 5 ml ), chloroform ( 5 ml ) and $\mathrm{AgPF}_{6}(0.0066 \mathrm{~g}, 0.026$ mmol, 1.1 eq.) afforded $\mathbf{5 . 2 b}$ as a brown solid ( $0.0144 \mathrm{~g}, 92 \%$ ). Mp: $230-232^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR (300
$\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 1.12\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.18\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}\right.$, $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.19\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{N} \equiv \mathrm{CCH}_{3}\right), 1.33\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.33(\mathrm{~s}, 3 \mathrm{H}$, $\left.\mathrm{C}=\mathrm{NCH}_{3}\right), 2.88\left(\mathrm{sept}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 3.11\left(\mathrm{sep}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}\right.$,
$\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 7.17(\mathrm{~s}, 2 \mathrm{H}, \mathrm{Ar}-\mathrm{H}), 8.41\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.0 \mathrm{~Hz}, \operatorname{Py}-\mathrm{H}\right), 7.88\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=\right.$ 6.0 Hz, Py-H), $8.08\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.0 \mathrm{~Hz}\right.$, Py-H). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}(161 \mathrm{MHz}): \delta-144.50(\mathrm{~m}$, $\left.{ }^{1} J_{\mathrm{PF}}=706.7 \mathrm{~Hz}, 1 \mathrm{P}, P \mathrm{~F}_{6}\right) .{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}(376 \mathrm{MHz}): \delta-72.9\left(\mathrm{~d},{ }^{1} J_{\mathrm{FP}}=706.7 \mathrm{~Hz}, 6 \mathrm{~F}, \mathrm{PF} 6\right) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}, 300 \mathrm{~K}$ ): $\delta 1.2\left(\mathrm{CH}_{3} \mathrm{CN}-\mathrm{Pd}\right)$, 17.5 ( $\left.\mathrm{Py}-\mathrm{C}(\mathrm{N})-\mathrm{CH}_{3}\right), 23.9$ (Ar-$\left.\mathrm{CH}-\left(\mathrm{CH}_{3}\right)_{2}\right), 22.7$ ( $\left.\mathrm{Ar}-\mathrm{CH}-\left(\mathrm{CH}_{3}\right)_{2}\right), 22.8\left(\mathrm{Ar}-\mathrm{CH}-\left(\mathrm{CH}_{3}\right)_{2}\right), 28.14\left(\mathrm{Ar}-\mathrm{CH}-\left(\mathrm{CH}_{3}\right)_{2}\right), 33.8$ ( $\left.\mathrm{Ar}-\mathrm{CH}-\left(\mathrm{CH}_{3}\right)_{2}\right), 117.5\left(\mathrm{CH}_{3} \mathrm{CN}-\mathrm{Pd}\right), 122.3(\mathrm{CH}), 122.5(\mathrm{C}), 129.0(\mathrm{CH}), 130.1(\mathrm{CH})$, 138.8 (C), $139.5(\mathrm{CH}), 150.6(\mathrm{CH}), 150.9$ (C), 160.1 (C), 183.5 (C). IR ( $\mathrm{cm}^{-1}$ ): 1595 $(\mathrm{C}=\mathrm{N})_{\text {pyridine }} 1642(\mathrm{C}=\mathrm{N})_{\text {imine }}, 2975(\mathrm{C}-\mathrm{H})$. ESIMS ( $\left.+v e, \mathrm{MeCN}\right)$ : m/z 512 [M] ${ }^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{25} \mathrm{H}_{32} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{Pd}[M]^{+} 512.1529$, found 512.1539.

Synthesis of 5.2c


A small dry Schlenk flask was evacuated and backfilled with nitrogen. The flask was charged with $\mathrm{PdCl}_{2}(\mathrm{MeCN})_{2}(0.0091 \mathrm{~g}, 0.035 \mathrm{mmol}), \mathrm{AgPF}_{6}$ ( $0.026 \mathrm{~g}, 0.105 \mathrm{mmol}, 3$ eq.) and dry acetonitrile. The flask was left to stir for 30 minutes at room temperature. EtL9 ( $0.015 \mathrm{~g}, 0.035 \mathrm{mmol})$ was added to the flask and the reaction mixture was allowed to stir for 24 h at room temperature. The solid was filtered through a Celite plug and washed thoroughly with acetonitrile. The volatiles were removed under reduced pressure to afford 5.2 c as a dark orange solid ( $0.022 \mathrm{~g}, 92 \%$ ). Mp: 232-235 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 1.08\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=\right.$ $\left.6.6 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.28\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.6 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.85\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C} \equiv \mathrm{NCH}_{3}\right), 2.30$ (s, $3 \mathrm{H}, \mathrm{C}=\mathrm{NCH}_{3}$ ), 3.08 (sept., $2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.9 \mathrm{~Hz}, \mathrm{C} H\left(\mathrm{CH}_{3}\right)_{2}$ ), 7.43 (s, $2 \mathrm{H}, \mathrm{Ar}-\mathrm{H}$ ), 7.90 $\left(\mathrm{d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, Py-H), $8.05\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}\right.$, Py-H), $8.39\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0\right.$ $\mathrm{Hz}, \mathrm{Py}-\mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 1.8\left(\mathrm{CH}_{3} \mathrm{CN}-\mathrm{Pd}\right), 18.2$ ( $\left.\mathrm{Py}-\mathrm{C}(\mathrm{N})-\mathrm{CH}_{3}\right)$, 22.5 ( $\left.\mathrm{Ar}-\mathrm{CH}-\left(\mathrm{CH}_{3}\right)_{2}\right), 22.6\left(\mathrm{Ar}-\mathrm{CH}-\left(\mathrm{CH}_{3}\right)_{2}\right), 28.5\left(\mathrm{Ar}-\mathrm{CH}-(\boldsymbol{C H})_{2}\right), 117.4\left(\mathrm{CH}_{3} \mathbf{C N}-\mathrm{Pd}\right)$, 123.4 (C), 128.3 (C), 129.3 (CH), 130.4 (CH), 142.4 (CH), 142.8 (C), 143.4 (CH), 151.2 (C), 154.6 (C), 155.1 (C), $184.0(\mathrm{C}) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ ( 161 MHz ): $\delta-144.5$ (m, 1P, ${ }^{1} J_{\mathrm{PF}}=$ $706 \mathrm{~Hz}, P \mathrm{~F}_{6}$ ). ${ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (376MHz): $\delta-72.8\left(\mathrm{~d}, 6 \mathrm{~F},{ }^{1} J_{\mathrm{FP}}=705.8 \mathrm{~Hz}, \mathrm{P} F_{6}\right)$. IR $\left(\mathrm{cm}^{-1}\right)$ : $1598(\mathrm{C}=\mathrm{N})_{\text {pyridine }} 1673(\mathrm{C}=\mathrm{N})_{\text {imine. }}$. ESIMS ( $+v e$, MeCN): $m / z 550[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{22} \mathrm{H}_{25} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{BrPd}[\mathrm{M}]^{+} 550.0169$, found 550.0163.

## Synthesis of 5.3a



A small round bottomed flask equipped with stir bar was charged with 5.2a ( $0.020 \mathrm{~g}, 0.0325 \mathrm{mmol}$ ) and pyridine $(0.0026 \mathrm{~g}, 0.0325 \mathrm{mmol})$ in chloroform ( 10 ml ). The reaction was stirred at room temperature for 18 h . The filtrate was removed under reduced pressure to give 5.3a as a yellow solid ( $0.015 \mathrm{~g}, 73 \%$ ). Mp: > $260{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 0.98\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.0 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.16\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.0\right.$ $\left.\mathrm{Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.54\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}=\mathrm{NCH}_{3}\right), 3.06\left(\mathrm{sept}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.9 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 7.19-$ $7.25\left(\mathrm{~m}, 3 \mathrm{H}\right.$, Py/Ar-H), $7.42\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.0 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.55\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.0 \mathrm{~Hz}\right.$, Py/Ar-H), $7.80\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.1 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 8.02\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.4 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right)$, $8.36\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.4 \mathrm{~Hz}\right.$, Py-H), $8.47\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.3 \mathrm{~Hz}\right.$, Py-H). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}(161$ MHz ): $\delta-144.5\left(\mathrm{~m}, 1 \mathrm{P},{ }^{1} J_{\mathrm{PF}}=706 \mathrm{~Hz}, P \mathrm{~F}_{6}\right) .{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 376 MHz ): $\delta-72.9(\mathrm{~d}, 6 \mathrm{~F}$, ${ }^{1} J_{\mathrm{FP}}=705.8 \mathrm{~Hz}, \mathrm{PF} F_{6}$. ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 171.5(\mathrm{C}), 165.9(\mathrm{C}), 160.3(\mathrm{C})$, 152.6 (C), $149.3(\mathrm{CH}), 143.9(\mathrm{CH}), 140.6(\mathrm{C}), 140.4(\mathrm{CH}), 138.6(\mathrm{C}), 131.2(\mathrm{CH})$, $130.4(\mathrm{CH}), 129.8(\mathrm{CH}), 125.7(\mathrm{CH}), 125.3(\mathrm{CH}), 28.7\left(\mathrm{Ar}-\mathrm{CH}-(\mathrm{CH} 3)_{2}\right), 23.8(\mathrm{Ar}-\mathrm{CH}-$ $\left.\left(\mathrm{CH}_{3}\right)_{2}\right)$, $22.9\left(\mathrm{Ar}-\mathrm{CH}-\left(\boldsymbol{C H}_{3}\right)_{2}\right), 18.8\left(\mathrm{Py}-\mathrm{C}(\mathrm{N})-\mathrm{CH}_{3}\right)$. IR $\left(\mathrm{cm}^{-1}\right): 1582(\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1682$ $(\mathrm{C}=\mathrm{N})_{\text {imine. }}$. ESIMS ( $+v e, \mathrm{MeOH}$ ): $m / z 508\left[\mathrm{M}^{2} \mathrm{PF}_{6}\right]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{25} \mathrm{H}_{28} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{Pd}\left[\mathrm{M}-\mathrm{PF}_{6}\right]^{+}$508.1216, found 508.1228.

## Synthesis of 5.4a



The same procedure as that described for 5.3a using 5.2a $(0.020 \mathrm{~g}, 0.0325 \mathrm{mmol})$, 4-tert-Butylpyridine $(0.0044 \mathrm{~g}$, 0.0325 mmol ) in chloroform ( 10 ml ) gave 5.4a as a yellow solid ( $0.017 \mathrm{~g}, 75 \%$ ). Mp: > $260^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( 500 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 1.05\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.6 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right)$, $1.23\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.7 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.26(\mathrm{~s}, 9 \mathrm{H}$, ${ }^{t} \mathrm{BuPy}$ ), 2.61 (s, $3 \mathrm{H}, \mathrm{C}=\mathrm{NCH}_{3}$ ), 3.12 (sept., $2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.3$ $\left.\mathrm{Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 7.18\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.0 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right), 7.29\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.6 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\right.$ H), $7.42\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.0 \mathrm{~Hz}\right.$, Py/Ar-H), $7.47\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.7 \mathrm{~Hz}\right.$, Py/Ar-H), 8.08 (d, $1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}$, Py/Ar-H), $8.48\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}\right.$, Py-/ArH), $8.57\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=\right.$ 8.8 Hz, Py/Ar-H), 8.99 (d, 1H, ${ }^{3} J_{\mathrm{HH}}=6.5 \mathrm{~Hz}$, Py/Ar-H). ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}(161 \mathrm{MHz}): \delta-146.2$ (m, 1P, ${ }^{1} J_{\mathrm{PF}}=705 \mathrm{~Hz}, P \mathrm{~F}_{6}$ ). ${ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}(376 \mathrm{MHz}): \delta-72.4\left(\mathrm{~d}, 6 \mathrm{~F},{ }^{1} J_{\mathrm{FP}}=706 \mathrm{~Hz}\right.$, $\mathrm{PF} 6) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 22.5\left(\mathrm{Py}-\mathrm{C}(\mathrm{N})-\mathrm{CH}_{3}\right), 22.9\left(\mathrm{Ar}-\mathrm{CH}-\left(\mathrm{CH}_{3}\right)_{2}\right), 23.8$
( $\left.\mathrm{Ar}-\mathrm{CH}-\left(\mathrm{CH}_{3}\right)_{2}\right), 28.7$ ( $\left.\mathrm{Ar}-\mathrm{CH}-(\mathrm{CH} 3)_{2}\right), 30.0\left(\mathrm{Py}-\left(\mathrm{CH}_{3}\right)_{3}\right), 122.6(\mathrm{CH}), 124.3(\mathrm{CH})$, $125.2(\mathrm{CH}), 130.2(\mathrm{CH}), 138.7(\mathrm{CH}), 140.9(\mathrm{CH}), 144.0(\mathrm{CH}), 148.7(\mathrm{C}), 150.6(\mathrm{C})$, 153.4 (C), 165.1 (C), 165.8 (C), 170.2 (C). IR ( $\mathrm{cm}^{-1}$ ): 1618 (C=N) $)_{\text {pyridine, }} 1683$ $(\mathrm{C}=\mathrm{N})_{\text {imine. }}$ ESIMS ( $+v e, \mathrm{MeOH}$ ): $m / z 564$ [M-PF $]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{29} \mathrm{H}_{36} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{Pd}\left[\mathrm{M}-\mathrm{PF}_{6}\right]^{+} 564.1842$, found 564.1855.

## Synthesis of 5.5a



The same procedure as that described for 5.3a, using 5.2a ( $0.020 \mathrm{~g}, 0.0325 \mathrm{mmol}$ ), 3-bromopyridine ( 0.0051 $\mathrm{g}, 0.0325 \mathrm{mmol}$ ) in chloroform ( 10 ml ) gave $\mathbf{5 . 5 a}$ as a yellow solid ( $0.019 \mathrm{~g}, 82 \%$ ). Single crystals of $\mathbf{5 . 5 a}$ suitable for analysis by X-ray diffraction were grown by slow diffusion of petroleum ether into a solution of the complex in chloroform. Mp: > $260{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.09\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}\right.$ $\left.=6.5 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.23\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.7 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 2.61\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}=\mathrm{NCH}_{3}\right)$, 3.14 (sept., $\left.2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 7.29-7.31$ (m, 2H, Py/Ar-H), 7.33 (d, 2H, ${ }^{3} J_{\mathrm{HH}}=7.6 \mathrm{~Hz}$, Py/Ar-H) $7.52\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.5 \mathrm{~Hz}\right.$, Py/Ar-H), $8.01(\mathrm{~m}, 2 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H})$, $8.05\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.6 \mathrm{~Hz}\right.$, Py/Ar-H), $8.42\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{JHH}_{\mathrm{HH}}=7.6 \mathrm{~Hz}\right.$, Py-H), $8.56(\mathrm{~d}, 1 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{HH}}=7.1 \mathrm{~Hz}, \mathrm{Py}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}, 300 \mathrm{~K}$ ): $\delta 18.7\left(\mathrm{Py}-\mathrm{C}(\mathrm{N})-\mathrm{CH}_{3}\right)$, 23.1 ( $\left.\mathrm{Ar}-\mathrm{CH}-\left(\mathrm{CH}_{3}\right)_{2}\right), 23.8$ ( $\left.\mathrm{Ar}-\mathrm{CH}-\left(\mathrm{CH}_{3}\right)_{2}\right), 28.6$ ( $\left.\mathrm{Ar}-\mathrm{CH}-(\boldsymbol{C H} 3)_{2}\right), 121.6(\mathrm{CH}), 125.3$ (CH), $126.6(\mathrm{CH}), 129.6(\mathrm{CH}), 131.3(\mathrm{CH}), 138.4(\mathrm{CH}), 140.9(\mathrm{CH}), 143.2(\mathrm{CH}), 144.1$ (C), 149.7 (C), $151.6(\mathrm{C}), 153.5(\mathrm{C}), 170.2(\mathrm{C}) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}(161 \mathrm{MHz}): \delta-144.5(\mathrm{~m}, 1 \mathrm{P}$, ${ }^{1} J_{\mathrm{PF}}=706 \mathrm{~Hz}, P \mathrm{~F}_{6}$ ). ${ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 376 MHz ): $\delta-72.0\left(\mathrm{~d}, 6 \mathrm{~F},{ }^{1} J_{\mathrm{FP}}=706 \mathrm{~Hz}, \mathrm{PF}\right.$ ) . IR $\left(\mathrm{cm}^{-1}\right): 1576(\mathrm{C}=\mathrm{N})_{\text {pyridine }} 1682(\mathrm{C}=\mathrm{N})_{\text {imine. }}$. ESIMS ( $\left.+v e, \mathrm{MeOH}\right): m / z 586[\mathrm{M}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{25} \mathrm{H}_{27} \mathrm{~N}_{3} \mathrm{O}_{2} \operatorname{BrPd}[\mathrm{M}]^{+} 586.0321$, found 586.0347.

## Synthesis of 5.6a



To a round bottom flask open to the air was added EtL $7_{7}$ $(0.020 \mathrm{~g}, 0.057 \mathrm{mmol}), \mathrm{K}_{2} \mathrm{PtCl}_{4}(0.023 \mathrm{~g}, 0.057 \mathrm{mmol})$ and acetic acid ( 5 ml ). A reflux condenser was attached and the reaction mixture then stirred and heated to $130{ }^{\circ} \mathrm{C}$ for 24 h . After cooling to room temperature, the resulting suspension was filtered to give $\mathbf{5 . 6 a}$ as a brown powder $(0.029 \mathrm{~g}, 85 \%) . \mathrm{Mp}:>270{ }^{\circ} \mathrm{C}$. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.10\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} \mathrm{JHH}_{\mathrm{HH}}=6.9 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.17(\mathrm{~d}, 6 \mathrm{H}$,
$\left.{ }^{3} J_{\mathrm{HH}}=7.1 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.39\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.4 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 2.73\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}=\mathrm{NCH}_{3}\right)$, $2.92\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 4.42\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 6.95\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.8\right.$ Hz, Py/Ar-H), $6.97\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.1 \mathrm{~Hz}\right.$, Py/Ar-H), $7.02\left(\mathrm{~d}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.0 \mathrm{~Hz}\right.$, Py/Ar$\mathrm{H}), 7.91\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}\right.$, Py/Ar-H), $8.12\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=1.2 \mathrm{~Hz}\right.$, Py/Ar-H), $8.20\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz},{ }^{4} \mathrm{~J}_{\mathrm{HH}}=1.2 \mathrm{~Hz}\right.$, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR $(100 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right): ~ \delta 14.2\left(\mathrm{CH}_{3}\right), 22.7\left(\mathrm{CH}_{3}\right), 23.7\left(\mathrm{CH}_{3}\right), 24.3\left(\mathrm{CH}_{3}\right), 25.6\left(\mathrm{CH}_{3}\right), 28.9\left(\mathrm{CH}_{3}\right), 33.9$ (C), $34.3(\mathrm{CH}), 62.1\left(\mathrm{CH}_{2}\right), 121.5(\mathrm{CH}), 121.8(\mathrm{CH}), 124.4(\mathrm{CH}), 124.5(\mathrm{CH}), 128.1$ (CH), 137.9 (C), 145.9 (C), 146.2 (C), 147.8 (C), 153.6 (C), 164.7 (C), 170.2 (C). IR $\left(\mathrm{cm}^{-1}\right): 1235(\mathrm{C}-\mathrm{O}), 1582(\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1653(\mathrm{C}=\mathrm{N})_{\text {imine }}, 1701(\mathrm{C}=\mathrm{O}), 2961(\mathrm{C}-\mathrm{H})$. ESIMS ( $+v e, \mathrm{MeOH}$ ): $m / z 618[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{22} \mathrm{H}_{28} \mathrm{~N}_{2} \mathrm{O}_{2}{ }^{194} \mathrm{Pt}$ $\left[_{\mathrm{M}-2 \mathrm{Cl}]^{+}} 546.4123\right.$, found 546.4117.

## Synthesis of 5.6b



The same procedure as that described for 5.6a, using $\mathrm{EtL} 8(0.020 \mathrm{~g}, 0.051 \mathrm{mmol}), \mathrm{K}_{2} \mathrm{PtCl}_{4}(0.021 \mathrm{~g}, 0.051$ mmol ) and acetic acid ( 5 ml ) afforded $\mathbf{5 . 6}$ b as a brown solid $(0.027 \mathrm{~g}, 83 \%) . \mathrm{Mp}:>270{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR (400 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.08\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}\right.$, $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.12\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.17\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.8 \mathrm{~Hz}\right.$, $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.39\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.1 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right), 2.72\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}=\mathrm{NCH}_{3}\right), 3.03(\mathrm{~m}, 2 \mathrm{H}$, $\left.\mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 3.07$ (sept., $\left.1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.8 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 4.42\left(\mathrm{q}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}\right.$, $\mathrm{CH}_{2} \mathrm{CH}_{3}$ ), 7.14 (m, 2H, Py/Ar-H), 7.91 (t, $\left.1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.9 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 8.12(\mathrm{dd}, 1 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=1.2 \mathrm{~Hz}, \operatorname{Py} / \mathrm{Ar}-\mathrm{H}\right), 8.19\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.7 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=1.2 \mathrm{~Hz}\right.$, Py/Ar-H). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 14.2\left(\mathrm{CH}_{3}\right), 20.0\left(\mathrm{CH}_{3}\right), 22.6\left(\mathrm{CH}_{3}\right), 23.7$ $\left(\mathrm{CH}_{3}\right)$, $24.3\left(\mathrm{CH}_{3}\right), 25.6\left(\mathrm{CH}_{3}\right), 27.6\left(\mathrm{CH}_{3}\right), 28.3\left(\mathrm{CH}_{3}\right), 28.5(\mathrm{C}), 28.8(\mathrm{CH}), 62.1$ $\left(\mathrm{CH}_{2}\right), 123.5(\mathrm{CH}), 123.9(\mathrm{CH}), 124.4(\mathrm{CH}), 128.1(\mathrm{CH}), 137.9(\mathrm{CH}), 144.4(\mathrm{C}), 146.3$ (C), 146.6 (C), 147.8 (C), 153.6 (C), 164.7 (C), 170.1 (C). IR ( $\mathrm{cm}^{-1}$ ): 1236 (C-O), 1582 ( $\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1646(\mathrm{C}=\mathrm{N})_{\text {imine, }} 1700(\mathrm{C}=\mathrm{O})$, $2962(\mathrm{C}-\mathrm{H}), 3249(\mathrm{C}-\mathrm{H})$. ESIMS (+ve, $\mathrm{MeOH}): m / z 660[\mathrm{M}+\mathrm{H}]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{25} \mathrm{H}_{34} \mathrm{~N}_{2} \mathrm{O}_{2}{ }^{196} \mathrm{Pt}[\mathrm{M}-2 \mathrm{Cl}+\mathrm{H}]^{+}$ 591.0810, found 591.0802.

## Synthesis of 5.6c



The same procedure as that described for 5.6a, using EtL9 ( $0.020 \mathrm{~g}, 0.046 \mathrm{mmol}), \mathrm{K}_{2} \mathrm{PtCl}_{4}(0.019 \mathrm{~g}, 0.046$ mmol ) and acetic acid ( 5 ml ) afforded $\mathbf{5 c}$ as a brown solid $(0.025 \mathrm{~g}, 81 \%)$. Crystals suitable for a single crystal X-ray diffraction studies were grown upon slow evaporation of 5.6 c in chloroform solution. Mp: >270 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.07\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=\right.$ $\left.6.7 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.11\left(\mathrm{~d}, 6 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.1 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.39\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.9 \mathrm{~Hz}\right.$, $\mathrm{CH}_{2} \mathrm{CH}_{3}$ ), 2.73 (s, $3 \mathrm{H}, \mathrm{C}=\mathrm{NCH}_{3}$ ), 2.92 (sept., $\left.2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.1 \mathrm{~Hz}, \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}\right), 4.42(\mathrm{q}$, $2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{CH}_{3}$ ), $7.19(\mathrm{~s}, 2 \mathrm{H}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}), 7.90\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.1 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\right.$ H), $8.12\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.7 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=1.2 \mathrm{~Hz}\right.$, Py/Ar-H), $8.19\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz}\right.$, $\left.{ }^{4} J_{\mathrm{HH}}=1.2 \mathrm{~Hz}, \mathrm{Py} / \mathrm{Ar}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 13.2\left(\mathrm{CH}_{3}\right), 20.7\left(\mathrm{CH}_{3}\right), 21.4$ $\left(\mathrm{CH}_{3}\right)$, $22.2\left(\mathrm{CH}_{3}\right), 23.2\left(\mathrm{CH}_{3}\right)$, $24.6\left(\mathrm{CH}_{3}\right), 27.6(\mathrm{C}), 27.9(\mathrm{CH}), 61.1\left(\mathrm{CH}_{2}\right), 121.8$ (CH), $125.9(\mathrm{CH}), 126.4(\mathrm{CH}), 126.7(\mathrm{CH}), 127.1(\mathrm{CH}), 136.9(\mathrm{C}), 146.8(\mathrm{C}), 147.7$ (C), 152.6 (C), 160.1 (C), 163.7 (C), 169.3 (C). IR ( $\mathrm{cm}^{-1}$ ): 1235 (C-O), 1575 $(\mathrm{C}=\mathrm{N})_{\text {pyridine }}, 1653(\mathrm{C}=\mathrm{N})_{\text {imine, }} 1701(\mathrm{C}=\mathrm{O}), 2960(\mathrm{C}-\mathrm{H}), 3225(\mathrm{C}-\mathrm{H})$. ESIMS (+ve, $\mathrm{MeOH}): m / z 696[\mathrm{M}+\mathrm{H}]^{+}$. FABMS: $m / z 625[\mathrm{M}-2 \mathrm{Cl}]^{+}$.

### 8.9 Experimental procedures for Chapter 6

### 8.9.1 Preparation of HL 10



An oven dried Schlenk flask was evacuated and backfilled with nitrogen. The flask was charged with diethylenetriamine ( $1.06 \mathrm{~g}, 10.3 \mathrm{mmol}$ ), 2-bromo- $m$-xylene $(2.74 \mathrm{ml}, 3.81 \mathrm{~g}, 20.6 \mathrm{mmol}), \mathrm{Pd}_{2}(\mathrm{dba})_{3}(0.047 \mathrm{~g}, 0.052$ mmol, 0.005 eq.), $\mathrm{NaOBu}^{\mathrm{t}}(2.97 \mathrm{~g}, 30.9 \mathrm{mmol})$, $r a c-B I N A P(0.096 \mathrm{~g}, 0.155 \mathrm{mmol}$, 0.015 eq.) and toluene ( 40 ml ). The mixture was heated and stirred at reflux for 4 days. After cooling to room temperature, the solvent was removed under reduced pressure to give an oily residue. The residue was dissolved in diethyl ether ( 30 ml ) and washed with water ( $3 \times 30 \mathrm{ml}$ ) and saturated sodium chloride solution ( $3 \times 30 \mathrm{ml}$ ). The organic phase was separated and dried over magnesium sulphate. The solvent was removed under reduced pressure and the resulting residue was left under vacuum at $50{ }^{\circ} \mathrm{C}$ for 24 h to afford $\mathrm{HL}_{10}$ as a viscous oil ( $2.25 \mathrm{~g}, 70 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 2.22(\mathrm{~s}, 12 \mathrm{H}$,
$\mathrm{Me}), 2.76\left(\mathrm{t}, 4 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=5.5 \mathrm{~Hz}, \mathrm{CH}_{2}\right), 3.00\left(\mathrm{t}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.0 \mathrm{~Hz}, \mathrm{CH}_{2}\right), 6.72\left(\mathrm{t}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}\right.$ $=7.4 \mathrm{~Hz}, \operatorname{Ar}-\mathrm{H}), 6.89\left(\mathrm{~d}, 4 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.3 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ $18.7\left(\mathrm{CH}_{3}\right), 48.3\left(\mathrm{CH}_{2}\right), 50.1(\mathrm{C}), 121.8(\mathrm{C}), 128.9(\mathrm{C}), 129.4(\mathrm{C}), 146.4(\mathrm{C}) . \mathrm{IR}\left(\mathrm{cm}^{-1}\right)$ : $3357(\mathrm{~N}-\mathrm{H})$. ESIMS (+ve, MeOH$): m / z 312[\mathrm{M}+\mathrm{H}]^{+}$. The data are in agreement with the literature ${ }^{135}$.

### 8.9.2 Preparation of HL 11



An oven dried Schlenk flask was evacuated and backfilled with nitrogen. The flask was charged with $N$ methyldiethylenetriamine ( $1.20 \mathrm{~g}, 10.3 \mathrm{mmol}$ ), 2-bromo-mxylene ( $2.74 \mathrm{ml}, 3.81 \mathrm{~g}, 20.6 \mathrm{mmol}$ ), $\mathrm{Pd}_{2}(\mathrm{dba})_{3}(0.047 \mathrm{~g}$, $0.052 \mathrm{mmol}, 0.005 \mathrm{eq}$.$) , \mathrm{NaOBu}^{\mathrm{t}}$ ( $2.97 \mathrm{~g}, 30.9 \mathrm{mmol}$ ), rac-BINAP ( $0.096 \mathrm{~g}, 0.155$ $\mathrm{mmol}, 0.015 \mathrm{eq}$.$) and toluene ( 40 \mathrm{ml}$ ). The mixture was heated and stirred at reflux for 4 days. After cooling to room temperature, the solvent was removed under reduced pressure to give an oily residue. The residue was dissolved in diethyl ether ( 30 ml ) and washed with water ( $3 \times 30 \mathrm{ml}$ ) and saturated sodium chloride solution ( $3 \times 30 \mathrm{ml}$ ). The organic phase was separated and dried over $\mathrm{MgSO}_{4}$. The solvent was removed under reduced pressure and the resulting residue was left under vacuum at $50^{\circ} \mathrm{C}$ for 24 h to afford $\mathrm{HL}_{11}$ as a viscous oil ( $2.46 \mathrm{~g}, 77 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 2.15(\mathrm{~s}, 3 \mathrm{H}$, $\mathrm{NMe}), 2.20(\mathrm{~s}, 12 \mathrm{H}, \mathrm{Me}), 2.73\left(\mathrm{t}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=5.7 \mathrm{~Hz}, \mathrm{CH}_{2}\right), 3.02\left(\mathrm{t}, 4 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.1 \mathrm{~Hz}\right.$, $\left.\mathrm{CH}_{2}\right), 6.73\left(\mathrm{t}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.5 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 6.90\left(\mathrm{~d}, 4 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.1 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 18.7\left(\mathrm{CH}_{3}\right), 40.6\left(\mathrm{CH}_{3}\right), 47.1\left(\mathrm{CH}_{2}\right), 55.1\left(\mathrm{CH}_{2}\right), 121.5(\mathrm{C}), 127$ (C), 129.1 (C), 146.5 (C). IR ( $\mathrm{cm}^{-1}$ ): 3357 (N-H). ESIMS (+ve, MeOH): m/z $326[\mathrm{M}+\mathrm{H}]$ ${ }^{+}$. HRMS (ASAP): $m / z 326[\mathrm{M}+\mathrm{H}]^{+}$. The data are in agreement with the literature ${ }^{135}$.

### 8.10 Complexes supported by $[N, N, N]$ tridentate ligands

## Synthesis of 6a



A small dry Schlenk flask was evacuated and backfilled with nitrogen. The flask was charged with $\mathrm{HL}_{10}(0.010 \mathrm{~g}, 0.0322 \mathrm{mmol})$ and $\mathrm{Pd}(\mathrm{OAc})_{2}$ $(0.0072 \mathrm{~g}, 0.032 \mathrm{mmol})$ and $\mathrm{CHCl}_{3}(5 \mathrm{ml})$. The reaction mixture was allowed to stir for 24 h at room temperature. The solid was filtered
through a Celite plug and washed thoroughly with chloroform. The volatiles were removed under reduced pressure to afford $\mathbf{6 a}$ as a yellow solid ( $0.0131 \mathrm{~g}, 71 \%$ ). Layering of a chloroform solution of $\mathbf{6 a}$ with petroleum ether gave orange crystals after 2 days at room temperature. Mp: decomposes at $135{ }^{\circ} \mathrm{C}$. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ 0.93 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{OAc}$ ), 1.23 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{OAc}$ ), 2.34 (s, $6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}$ ), 2.97 (dd, $2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=13.1$ $\left.\mathrm{Hz},{ }^{4} J_{\mathrm{HH}}=4.1 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 3.06\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=12.6 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=3.3 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 3.36$ (s, $6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}$ ), $3.69\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=12.2 \mathrm{~Hz},{ }^{4} \mathrm{~J}_{\mathrm{HH}}=4.8 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 3.75\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}\right.$ $\left.=12.4 \mathrm{~Hz},{ }^{4} \mathrm{~J}_{\mathrm{HH}}=5.1 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 4.18(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 7.03(\mathrm{~m}, 6 \mathrm{H}, \mathrm{Ar}-\mathrm{H}), 8.56(\mathrm{~s}, 1 \mathrm{H}$, NH). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{MeOD}$ ): $\delta 1.10$ ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{OAc}$ ), 1.82 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{OAc}$ ), 2.30 ( $\mathrm{s}, 6 \mathrm{H}$, Ar-Me), $2.75\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=12.0 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=3.1 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 3.08\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=12.9\right.$ $\mathrm{Hz},{ }^{4} J_{\mathrm{HH}}=4.3 \mathrm{~Hz}, \mathrm{NHCH}_{2}$ ), $3.21(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}), 3.24\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=9.9 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=3.4\right.$ $\left.\mathrm{Hz}, \mathrm{NHCH}_{2}\right), 3.36\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=12.9 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.7, \mathrm{NHCH}_{2}\right), 6.90\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.18\right.$ $\mathrm{Hz}, \mathrm{Ar}-\mathrm{H}), 6.98\left(\mathrm{t}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 7.04\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.5 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 22.1\left(\mathrm{CH}_{3}\right), 25.0\left(\mathrm{CH}_{3}\right), 52.6\left(\mathrm{CH}_{2}\right), 52.8\left(\mathrm{CH}_{2}\right), 55.7$ $\left(\mathrm{CH}_{2}\right), 57.2\left(\mathrm{CH}_{2}\right), 125.8(\mathrm{CH}), 128.7(\mathrm{CH}), 129.5(\mathrm{CH}), 130.7(\mathrm{CH}), 131.2(\mathrm{CH}), 131.3$ (CH), 132.3 (C), $139.5(\mathrm{C}), 140.1(\mathrm{CH}), 143.2(\mathrm{C})$. IR $\left(\mathrm{cm}^{-1}\right): 3257(\mathrm{~N}-\mathrm{H})$. ESIMS (+ve, $\mathrm{MeOH}) m / z 416$ [M-OAc] ${ }^{+}$. HRMS (FAB): $m / z$ calc. for $\mathrm{C}_{20} \mathrm{H}_{29} \mathrm{~N}_{3} \mathrm{Pd} 416.1396$, found 416.1412 [M-OAc] $^{+}$.

## Synthesis of 6b



The same procedure as that described for for $\mathbf{6 a}$ using HL ${ }_{11}(0.010 \mathrm{~g}, 0.0308 \mathrm{mmol}), \mathrm{Pd}(\mathrm{OAc})_{2}$ ( $0.0068 \mathrm{~g}, 0.0302 \mathrm{mmol}$ ) and $\mathrm{CHCl}_{3}(5 \mathrm{ml})$ gave $\mathbf{6 b}$ as a yellow solid ( $0.013 \mathrm{~g}, 73 \%$ ). Layering of a chloroform solution of $\mathbf{6 b}$ with petroleum ether gave orange crystals at room temperature. Mp: decomposes at $140{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 1.31$ (s, 3H, $\mathrm{OAc}), 1.96(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OAc}), 2.16\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{N}-\mathrm{CH}_{3}\right), 2.46\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=12.5 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=3.3\right.$ $\left.\mathrm{Hz}, \mathrm{NHCH}_{2}\right), 2.56(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}), 3.20\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=12.2 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.7 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right)$, $3.31(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}), 3.40\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=11.6 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=5.1 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 3.69(\mathrm{dd}$, $\left.2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=12.3 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.9 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 7.23(\mathrm{~m}, 6 \mathrm{H}, \mathrm{Ar}-\mathrm{H}), 4.98(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 8.52$ (s, 1H, NH). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{MeOD}$ ): $\delta 1.13$ (s, 3H, OAc), 1.93 (s, 3H, OAc), 2.47 (s, 6H, Ar-Me), $3.14(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NMe}), 3.28\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=13.8 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=3.6 \mathrm{~Hz}\right.$, $\mathrm{NHCH}_{2}$ ), 3.36 ( $\mathrm{s}, 6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}$ ), $3.57\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=13.9 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.2 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right.$ ),
$3.92\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=13.9 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=5.1 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 2.81\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=13.4 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}\right.$ $\left.=3.5, \mathrm{NHCH}_{2}\right), 7.06\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.3 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 7.13\left(\mathrm{t},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.9 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{Ar}-\mathrm{H}\right)$, $7.18\left(\mathrm{~d},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.3 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{Ar}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 17.5\left(\mathrm{CH}_{3}\right), 18.5$ $\left(\mathrm{CH}_{3}\right), 20.4\left(\mathrm{CH}_{3}\right), 21.5\left(\mathrm{CH}_{3}\right), 45.3\left(\mathrm{CH}_{2}\right), 54.7\left(\mathrm{CH}_{2}\right), 62.0\left(\mathrm{CH}_{2}\right), 126.9(\mathrm{CH}), 129.2$ $(\mathrm{CH}), 130.4(\mathrm{C}), 131.2(\mathrm{C}), 132.2(\mathrm{C}), 140.3(\mathrm{C}), 176.8(\mathrm{C}), 178.4(\mathrm{C})$. IR ( $\left.\mathrm{cm}^{-1}\right): 3286$ (N-H). ESIMS: (+ve, MeOH): m/z 430 [M-OAc] ${ }^{+}$. HRMS (FAB): $m / z$ calc. for $\mathrm{C}_{21} \mathrm{H}_{31} \mathrm{~N}_{3} \mathrm{Pd} 430.1469$, found 430.1479 [M-OAc] $^{+}$.

## Synthesis of 6.1a



A small dry Schlenk flask was evacuated and backfilled with nitrogen. The flask was charged with $\mathrm{HL}_{10}(0.010 \mathrm{~g}, 0.0322 \mathrm{mmol})$ and $\mathrm{PdCl}_{2}(\mathrm{MeCN})_{2}$ ( $0.0082 \mathrm{~g}, 0.032 \mathrm{mmol}$ ) and $\mathrm{CHCl}_{3}(5 \mathrm{ml})$. The reaction mixture was allowed to stir for 24 h at room temperature. The yellow precipitate was filtered through a Celite plug and washed thoroughly with chloroform. The volatiles were removed under reduced pressure and then extracted into methanol. The solvent was removed under reduced pressure to afford 6.1a as a yellow solid ( $0.0132 \mathrm{~g}, 77 \%$ ). Crystals were grown from cold methanol on prolonged standing at room temperature. Mp: decomposes at $155{ }^{\circ} \mathrm{C}$. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{MeOD}$ ): $\delta 2.32$ (s, $6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}), 2.82\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=12.0 \mathrm{~Hz},{ }^{4} \mathrm{JHH}_{\mathrm{HH}}=3.4 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 3.09\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=\right.$ $\left.12.4 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.1 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 3.15(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}), 3.26\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=12.7 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}\right.$ $\left.=3.9, \mathrm{NHCH}_{2}\right), 3.36\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=13.8 \mathrm{~Hz},{ }^{4} \mathrm{JHH}_{\mathrm{HH}}=3.9 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 6.90\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}\right.$ $=6.90 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}), 6.96\left(\mathrm{t}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.04 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 7.02\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=4.45 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right)$. ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz} ; \mathrm{MeOD}$ ): the sample was insufficiently soluble to give an assignable spectrum. IR $\left(\mathrm{cm}^{-1}\right)$ : 3247 (N-H). ESIMS: (+ve, MeOH): m/z $452[\mathrm{M}]^{+}, 430$ $[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (FAB): $m / z$ calc. for $\mathrm{C}_{20} \mathrm{H}_{29} \mathrm{ClN}_{3} \mathrm{Pd} 452.1085$, found $452.1075[\mathrm{M}]^{+}$.

## Synthesis of 6.1b



The same procedure as that described for 6.1a using


HL11 ( $0.010 \mathrm{~g}, 0.0308 \mathrm{mmol}), \mathrm{PdCl}_{2}(\mathrm{MeCN})_{2}(0.008$ $\mathrm{g}, 0.0308 \mathrm{mmol})$ and $\mathrm{CHCl}_{3}(5 \mathrm{ml})$ afforded $\mathbf{6 . 1 b}$ as a yellow solid ( $0.0114 \mathrm{~g}, 68 \%$ ). Crystals were grown from cold methanol on prolonged standing at room temperature. Mp: decomposes at $153{ }^{\circ}{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{MeOD}$ ): $\delta 2.36$ (s, 6H, Ar-Me), 2.74 (dd, $2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=12.9$
$\mathrm{Hz},{ }^{4} J_{\mathrm{HH}}=3.6, \mathrm{NHCH}_{2}$ ), 3.07 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{NMe}$ ), $3.15\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=13.0 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=3.9\right.$ $\mathrm{Hz}, \mathrm{NHCH}_{2}$ ), 3.17 (s, $6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}$ ), $3.51\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=13.7 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=3.3 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right.$ ), $3.86\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=13.7 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=3.8 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 6.93\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.85 \mathrm{~Hz}, \mathrm{Ar}-\right.$ $\mathrm{H}), 6.98\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.80 \mathrm{~Hz}, \operatorname{Ar}-\mathrm{H}\right), 7.02\left(\mathrm{t}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.20 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right) .{ }^{13} \mathrm{C}$ NMR (100MHz; MeOD): the sample was insufficiently soluble to give an assignable spectrum. IR ( $\mathrm{cm}^{-1}$ ): $3235(\mathrm{~N}-\mathrm{H})$. ESIMS: (+ve, MeOH): $m / z 466[\mathrm{M}]^{+}, 430[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (FAB): $m / z$ calc. for $\mathrm{C}_{21} \mathrm{H}_{31} \mathrm{ClN}_{3} \mathrm{Pd} 466.1241$, found 466.1231 [M] ${ }^{+}$.

## Synthesis of 6.2b



A round bottomed flask, equipped with a magnetic stir bar was charged with $\mathbf{6 . 1 b}(0.010 \mathrm{~g}, 0.0200$ $\mathrm{mmol})$, silver acetate $(0.0033 \mathrm{~g}, 0.0200 \mathrm{mmol})$ and dichloromethane $(5 \mathrm{ml})$. The reaction mixture was then stirred at room temperature for 18 hours. Pure product was collected by filtration through a Celite plug, washed with dichloromethane and dried under reduced pressure to afford 6.2b as a yellow solid ( $0.010 \mathrm{~g}, 97 \%$ ). Single crystals suitable for X-ray determination were grown from a dichloromethane/hexane solution. Mp: decomposes at $192{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ): $\delta 2.36\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=12.7 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=3.7\right.$, $\mathrm{NHCH}_{2}$ ), 2.98 ( $\mathrm{s}, 6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}$ ), $2.96(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NMe}), 3.05\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=12.6 \mathrm{~Hz},{ }^{4} \mathrm{~J}_{\mathrm{HH}}=\right.$ $4.5 \mathrm{~Hz}, \mathrm{NHCH}_{2}$ ), $3.15(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}), 3.65\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=12.7 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.6 \mathrm{~Hz}\right.$, $\left.\mathrm{NHCH}_{2}\right), 4.60(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH}), 4.85\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=12.7 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.5 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 6.90$ $\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} \mathrm{JHH}_{\mathrm{HH}}=7.5 \mathrm{~Hz}, \operatorname{Ar}-\mathrm{H}\right), 6.98\left(\mathrm{~d}, 3 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.1 \mathrm{~Hz}, \operatorname{Ar}-\mathrm{H}\right), 8.42(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH})$. IR $\left(\mathrm{cm}^{-1}\right): 3199$ (N-H). ESIMS: (+ve, MeOH): m/z 430 [M-Cl-OAc] ${ }^{+}$. ESIMS: (-ve, MeOH ): $m / z 59$ [OAc]. HRMS (FAB): $m / z$ calc. for $\mathrm{C}_{21} \mathrm{H}_{30} \mathrm{~N}_{3} \mathrm{Pd}$ 430.1457, found 430.1475 [M-Cl-OAc] ${ }^{+}$.

## Synthesis of 6.3b



The same procedure as that described for 6.2b using 6.1b $(0.010 \mathrm{~g}, 0.0200 \mathrm{mmol})$, silver triflate ( $0.0051 \mathrm{~g}, 0.0200 \mathrm{mmol}$ ) and dichloromethane ( 5 ml ) to give $\mathbf{6 . 3 b}$ as a yellow solid $(0.010 \mathrm{~g}, 82 \%)$.
Single crystals suitable for X-ray determination were grown from a dichloromethane/hexane solution. Mp: decomposes at $171{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz ,

MeOD): $\delta 2.79$ (dd, $2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=13.2 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=3.9, \mathrm{NHCH}_{2}$ ), 3.23 (s, $6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}$ ), 3.32 (s, $3 \mathrm{H}, \mathrm{NMe}$ ), $3.35\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=13.1 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.1 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 3.41(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Ar}-$ $\mathrm{Me}), 3.66\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=14.2 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.1 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 4.15\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=13.7 \mathrm{~Hz}\right.$, $\left.{ }^{4} J_{\mathrm{HH}}=4.2 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 7.22\left(\mathrm{~d}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.2 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 7.23\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.8 \mathrm{~Hz}\right.$, Ar-H). ${ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 376 MHz ): $\delta-80.0$ (s, 3F, $\mathrm{SO}_{3} \mathrm{CF}_{3}$ ).IR ( $\mathrm{cm}^{-1}$ ): 2929 (N-H). ESIMS: (+ve, MeOH): m/z 430 [M-Cl-SO $\left.3_{3} \mathrm{CF}_{3}\right]^{+}$. ESIMS: (-ve, MeOH): m/z 149 [ $\left.\mathrm{SO}_{3} \mathrm{CF}_{3}\right]^{-}$. HRMS (FAB): $m / z$ calc. for $\mathrm{C}_{21} \mathrm{H}_{30} \mathrm{~N}_{3} \mathrm{Pd} 430.1458$, found 430.1475 [M-Cl$\left.\mathrm{SO}_{3} \mathrm{CF}_{3}\right]^{+}$.

## Synthesis of 6.4b



The same procedure as that described for $\mathbf{6 . 2 b}$ using 6.1b $(0.010 \mathrm{~g}, 0.0200 \mathrm{mmol})$, silver tetrafluoroborate ( $0.0038 \mathrm{~g}, 0.0200 \mathrm{mmol}$ ) and dichloromethane ( 5 ml ) to give 6.4b as a yellow solid ( $0.0093 \mathrm{~g}, 85 \%$ ). Single crystals suitable for X-ray determination were grown from a dichloromethane/hexane solution. Mp: decomposes at $183{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ): $\delta 2.36$ (s, 6H, Ar-Me), $2.56\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=12.7 \mathrm{~Hz},{ }^{4} \mathrm{~J}_{\mathrm{HH}}=\right.$ $4.2, \mathrm{NHCH}_{2}$ ), $3.02(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NMe}), 3.10(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}), 3.13\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=12.6 \mathrm{~Hz}\right.$, $\left.{ }^{4} J_{\mathrm{HH}}=4.5 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 3.26\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=13.4 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.6 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 4.23(\mathrm{td}$, $\left.2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=13.2 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.9 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 6.82(\mathrm{br} \mathrm{s}, 2 \mathrm{H}, \mathrm{NH}), 6.96\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=6.5\right.$ $\mathrm{Hz}, \mathrm{Ar}-\mathrm{H}$ ), 7.04 (m, 3H, Ar-H). ${ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ( 376 MHz ): $\delta$-147.1 (s, 4F, BF4). IR $\left(\mathrm{cm}^{-1}\right): 2964(\mathrm{~N}-\mathrm{H})$. ESIMS: (+ve, MeOH): m/z 430 [M-Cl-BF4] ${ }^{+}$. ESIMS: (-ve, MeOH ): $m / z 87\left[\mathrm{BF}_{4}\right]^{-}$. HRMS (FAB): $m / z$ calc. for $\mathrm{C}_{21} \mathrm{H}_{30} \mathrm{~N}_{3} \operatorname{Pd} 430.1455$, found $430.1470\left[\mathrm{M}-\mathrm{Cl}-\mathrm{BF}_{4}\right]^{+}$.

## Synthesis of 6.5b



The same procedure as that described for $\mathbf{6 . 2 b}$ using
6.1b $\quad(0.010 \mathrm{~g}, \quad 0.0200 \mathrm{mmol})$, silver hexafluorophosphate ( $0.005 \mathrm{~g}, 0.0200 \mathrm{mmol}$ ) and dichloromethane ( 5 ml ) to give $\mathbf{6 . 5 b}$ as a yellow solid ( $0.011 \mathrm{~g}, 91 \%$ ). Single crystals suitable for X-ray determination were grown from a dichloromethane/hexane solution. Mp: decomposes at $175{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ ): $\delta 2.34$ (s, $6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}$ ), $2.66\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=12.8 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.6, \mathrm{NHCH}_{2}\right.$ ), 3.04
(s, 3H, NMe), $3.10(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}), 3.15\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=12.5 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.5 \mathrm{~Hz}\right.$, $\left.\mathrm{NHCH}_{2}\right), 3.35\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=13.2 \mathrm{~Hz},{ }^{4} \mathrm{~J}_{\mathrm{HH}}=4.6 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 4.05\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=13.4\right.$ $\mathrm{Hz},{ }^{4} \mathrm{JH}_{\mathrm{HH}}=4.7 \mathrm{~Hz}, \mathrm{NHCH}_{2}$ ), ), 6.82 (br s, 2H, NH), 7.05 (br m, $\left.6 \mathrm{H}, \mathrm{Ar}-\mathrm{H}\right) .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ ( 161 MHz ): $\delta-143.8\left(\mathrm{~m}, 1 \mathrm{P},{ }^{1} \mathrm{~J}_{\mathrm{PF}}=705 \mathrm{~Hz}, P \mathrm{~F}_{6}\right) .{ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\} \mathrm{NMR}(376 \mathrm{MHz}): \delta-71.2$ (d, 6F, ${ }^{1} J_{\mathrm{FP}}=707 \mathrm{~Hz}, \mathrm{PF}$ ) . IR $\left(\mathrm{cm}^{-1}\right): 2933(\mathrm{~N}-\mathrm{H})$. ESIMS: $(+\mathrm{ve}, \mathrm{MeOH}): m / z 430[\mathrm{M}-$ $\left.\mathrm{Cl}-\mathrm{PF}_{6}\right]^{+}$. ESIMS: (-ve, MeOH): $m / z 145$ [PF6]. HRMS (FAB): $m / z$ calc. for $\mathrm{C}_{21} \mathrm{H}_{30} \mathrm{~N}_{3} \mathrm{Pd} 430.1462$, found 430.1475 [M-Cl-PF $]^{+}$.

## Synthesis of 6.6b



The same procedure as that described for $\mathbf{6 . 2 b}$ using
6.1b $(0.010 \mathrm{~g}, 0.0200 \mathrm{mmol})$, silver nitrate $(0.0034 \mathrm{~g}$, 0.0200 mmol ) and dichloromethane ( 5 ml ) to give 6.6b as a yellow solid ( 0.0098 g , $95 \%$ ). Single crystals suitable for X-ray determination were grown from a dichloromethane/hexane solution. Mp: decomposes at $184{ }^{\circ} \mathrm{C}$. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ): $\delta 2.41$ (s, $6 \mathrm{H}, \mathrm{Ar}-$ Me), $2.72\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=12.7 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.6, \mathrm{NHCH}_{2}\right), 3.14\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=12.8 \mathrm{~Hz}\right.$, $\left.{ }^{4} J_{\mathrm{HH}}=4.4 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 3.18(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NMe}), 3.21(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}), 3.50\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=\right.$ $\left.15.2 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.3 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 3.87\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=15.5 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.1 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right)$, $6.92\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=6.9 \mathrm{~Hz}\right.$, Ar-H), 7.02 (m, 4H, Ar-H). IR $\left(\mathrm{cm}^{-1}\right): 2964(\mathrm{~N}-\mathrm{H})$. ESIMS: (+ve, MeOH): $m / z 430\left[\mathrm{M}-\mathrm{Cl}-\mathrm{NO}_{3}\right]^{+}$. ESIMS: (-ve, MeOH): $m / z 62\left[\mathrm{NO}_{3}\right]^{-}$. HRMS (FAB): $m / z$ calc. for $\mathrm{C}_{21} \mathrm{H}_{30} \mathrm{~N}_{3} \mathrm{Pd} 430.1451$, found $430.1468\left[\mathrm{M}-\mathrm{Cl}^{2}-\mathrm{NO}_{3}\right]^{+}$.

## Synthesis of 6.7b



The same procedure as that described for $\mathbf{6 . 2 b}$ using 6.1b $(0.010 \mathrm{~g}, 0.0200 \mathrm{mmol})$, benzoic acid $(0.0024 \mathrm{~g}, 0.0200 \mathrm{mmol})$ and dichloromethane ( 5 ml ) to give $\mathbf{6 . 7 b}$ as a yellow solid $(0.011 \mathrm{~g}$, $95 \%$ ). Single crystals suitable for X-ray determination were grown from a dichloromethane/hexane solution. Mp : decomposes at $193{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{MeOD}$ ): $\delta 2.36$ (s, 6H, Ar-Me), 2.74 (dd, $2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=12.8$ $\mathrm{Hz},{ }^{4} J_{\mathrm{HH}}=3.8, \mathrm{NHCH}_{2}$ ), 3.07 (s, $3 \mathrm{H}, \mathrm{NMe}$ ), $3.15\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=12.8 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=3.7\right.$ $\mathrm{Hz}, \mathrm{NHCH}_{2}$ ), 3.19 (s, $6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}$ ), $3.51\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=13.5 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.2 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right.$ ), $3.83\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=13.6 \mathrm{~Hz},{ }^{4} \mathrm{~J}_{\mathrm{HH}}=4.1 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 6.99\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.6 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right)$, $7.03\left(\mathrm{~d}, 3 \mathrm{H},{ }^{3} \mathrm{JHH}_{\mathrm{HH}}=7.0 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 7.37\left(\mathrm{t}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.7 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 7.49\left(\mathrm{t}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=\right.$
8.4 Hz, Ar-H), $7.92\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=7.7 \mathrm{~Hz}, \operatorname{Ar-H}\right)$. IR $\left(\mathrm{cm}^{-1}\right): 2985(\mathrm{~N}-\mathrm{H})$. ESIMS (+ve, MeOH ): $m / z 430$ [M-Cl-benzoic acid] ${ }^{+}, m / z 552\left[\mathrm{M}^{+}-\mathrm{Cl}\right]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{28} \mathrm{H}_{36} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{Pd}^{106} 552.1842$, found $552.1842[\mathrm{M}-\mathrm{Cl}]^{+}$.

## Synthesis of 6.8b



The same procedure as that described for $\mathbf{6 . 2 b}$ using 6.1b $(0.010 \mathrm{~g}, \quad 0.0200 \mathrm{mmol})$, 4tertButylbenzoic acid $(0.0035 \mathrm{~g}, 0.0200 \mathrm{mmol})$ and dichloromethane ( 5 ml ) to give $\mathbf{6 . 8 b}$ as a yellow solid $(0.012 \mathrm{~g}, 93 \%)$. Single crystals suitable for X-ray determination were grown from a dichloromethane/hexane solution. Mp: decomposes at $188{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 1.83\left(\mathrm{~s}, 9 \mathrm{H},\left(\mathrm{CH}_{3}\right)_{3}\right), 7.86$ $\left(\mathrm{d}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=7.2 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 2.15\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{HH}}=13.4 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.3, \mathrm{NHCH}_{2}\right), 2.37(\mathrm{~s}$, $6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}), 2.60\left(\mathrm{dd}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=13.1 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.3 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 2.98(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NMe})$, 3.11 (s, 6H, Ar-Me), $3.38\left(\mathrm{td}, 2 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=14.5 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=4.9 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right.$ ), $4.18(\mathrm{td}, 2 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{HH}}=14.6 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=5.1 \mathrm{~Hz}, \mathrm{NHCH}_{2}\right), 6.95\left(\mathrm{t}, 3 \mathrm{H},{ }^{3} J_{\mathrm{HH}}=8.5 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 7.02(\mathrm{~d}, 3 \mathrm{H}$, $\left.{ }^{3} J_{\mathrm{HH}}=6.7 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right), 7.45\left(\mathrm{~d}, 2 \mathrm{H},{ }^{3} \mathrm{JHH}_{\mathrm{HH}}=7.3 \mathrm{~Hz}, \mathrm{Ar}-\mathrm{H}\right)$. IR $\left(\mathrm{cm}^{-1}\right): 2987(\mathrm{~N}-\mathrm{H})$. ESIMS (+ve, MeOH ): $m / z 430$ [M-Cl-(4-'Bubenzoic acid)] ${ }^{+}, m / z 608[\mathrm{M}-\mathrm{Cl}]^{+}$. HRMS (TOF): $\mathrm{m} / \mathrm{z}$ calc. for $\mathrm{C}_{32} \mathrm{H}_{44} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{Pd}^{106} 608.2468$, found $608.2496[\mathrm{M}-\mathrm{Cl}]^{+}$.

## Synthesis of 6.9b



The same procedure as that described for $\mathbf{6 . 2 b}$ using 6.1b $(0.010 \mathrm{~g}, \quad 0.0200 \mathrm{mmol})$, 4Chlorobenzoic acid $(0.0031 \mathrm{~g}, 0.0200 \mathrm{mmol})$ and dichloromethane $(5 \mathrm{ml})$ to give $\mathbf{6 . 9 b}$ as a yellow solid $(0.0107 \mathrm{~g}, 87 \%)$. Single crystals suitable for X-ray determination were grown from a dichloromethane/hexane solution. Mp: decomposes at $177{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}$ ): $\delta 2.30\left(\mathrm{dd},{ }^{3} J_{\mathrm{HH}}=12.8 \mathrm{~Hz}\right.$, ${ }^{4} J_{\mathrm{HH}}=3.8,2 \mathrm{H}, \mathrm{NHCH}_{2}$ ), $2.37(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}), 3.07(\mathrm{~s}, 3 \mathrm{H}, \mathrm{NMe}), 2.64\left(\mathrm{dd},{ }^{3} J_{\mathrm{HH}}=12.7\right.$ $\mathrm{Hz},{ }^{4} J_{\mathrm{HH}}=3.5 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{NHCH}_{2}$ ), $3.12(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Ar}-\mathrm{Me}), 3.39\left(\mathrm{td},{ }^{3} J_{\mathrm{HH}}=13.3 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=\right.$ $\left.4.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{NHCH}_{2}\right), 4.12\left(\mathrm{td},{ }^{3} J_{\mathrm{HH}}=13.1 \mathrm{~Hz},{ }^{4} J_{\mathrm{HH}}=3.8 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{NHCH}_{2}\right), 6.95(\mathrm{~d}$, $\left.{ }^{3} J_{\mathrm{HH}}=7.5 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{Ar}-\mathrm{H}\right), 7.90\left(\mathrm{~d},{ }^{3} J_{\mathrm{HH}}=8.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{Ar}-\mathrm{H}\right), 7.04\left(\mathrm{t},{ }^{3} J_{\mathrm{HH}}=8.2 \mathrm{~Hz}, 3 \mathrm{H}\right.$, Ar-H), 7.41 (d, ${ }^{3} J_{\mathrm{HH}}=8.2 \mathrm{~Hz}, 2 \mathrm{H}$, Ar-H). IR $\left(\mathrm{cm}^{-1}\right): 2992(\mathrm{~N}-\mathrm{H})$. ESIMS (+ve, MeOH):
$m / z 430$ [M-Cl-(4-Clbenzoic acid)] ${ }^{+}, m / z 586[M-C l]^{+}$. HRMS (TOF): $m / z$ calc. for $\mathrm{C}_{28} \mathrm{H}_{35} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{ClPd}^{106} 586.1453$, found 586.1469 [M-Cl] ${ }^{+}$.

### 8.11 Crystallographic studies

Data for all crystalographically characterised compounds were collected on a Bruker APEX 2000 CCD diffractometer. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections applied. Structure solution by direct methods and structure refinement based on full-matrix least-squares on $\mathrm{F}^{2}$ employed SHELXTL version $6.10^{160,161,162}$. Hydrogen atoms were included in calculated positions $(\mathrm{C}-\mathrm{H}=0.95-1.00 \AA$ ) riding on the bonded atom with isotropic displacement parameters set to $1.5 \mathrm{U}_{\mathrm{eq}}(\mathrm{C})$ for methyl H atoms and $1.2 \mathrm{U}_{\mathrm{eq}}(\mathrm{C})$ for all other H atoms. All non-H atoms were refined with anisotropic displacement parameters. Details of data collection, refinement and crystal data are listed in the Appendix.

## Appendix

## Crystal data and structure refinement for 2a

| Identification code | 17074 |
| :---: | :---: |
| Empirical formula | C42 H32 N6 O7 Pd3 |
| Formula weight | 1051.94 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Unit cell dimensions | $a=10.215(3) \AA$ 風 $\quad \alpha=90^{\circ}$. |
|  | $b=18.041(5) \AA \quad \beta=100.623(5)^{\circ}$. |
|  | $\mathrm{c}=21.212(5) \AA \quad \gamma=90^{\circ}$. |
| Volume | 3842.1(17) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.819 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $1.450 \mathrm{~mm}^{-1}$ |
| $F(000)$ | 2080 |
| Crystal size | $0.32 \times 0.12 \times 0.08 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.49 to $26.00^{\circ}$. |
| Index ranges | $-12<=\mathrm{h}<=12,-21<=\mathrm{k}<=22,-26<=1<=26$ |
| Reflections collected | 29631 |
| Independent reflections | $7532[\mathrm{R}(\mathrm{int})=0.1400]$ |
| Completeness to theta $=26.00^{\circ}$ | 99.7 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.837 and 0.614 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 7532 / 9 / 526 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.912 |
| Final R indices $[\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0633, \mathrm{wR} 2=0.1108$ |
| R indices (all data) | $\mathrm{R} 1=0.1354, \mathrm{wR} 2=0.1292$ |
| Largest diff. peak and hole | 1.190 and -0.810 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 2c

| Identification code | 17069 |
| :---: | :---: |
| Empirical formula | C15 H9 F3 N2 O2 Pd |
| Formula weight | 412.64 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 £ |
| Crystal system | Monoclinic |
| Space group | C2/c |
| Unit cell dimensions | $a=13.597(5) \AA \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=21.082(7) \AA \AA^{\circ} \quad \beta=97.722(6)^{\circ}$ |
|  | $\mathrm{c}=20.185(7) \AA \AA^{\text {A }}$ |
| Volume | 5733(3) $\AA^{3}$ |
| Z | 16 |
| Density (calculated) | $1.912 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $1.339 \mathrm{~mm}^{-1}$ |
| $F(000)$ | 3232 |
| Crystal size | $0.19 \times 0.17 \times 0.09 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.79 to $26.00^{\circ}$. |
| Index ranges | $-16<=\mathrm{h}<=16,-26<=\mathrm{k}<=26,-24<=1<=24$ |
| Reflections collected | 22236 |
| Independent reflections | $5634[\mathrm{R}(\mathrm{int})=0.0610]$ |
| Completeness to theta $=26.00^{\circ}$ | 99.9 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.547 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 5634 / 132 / 453 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.980 |
| Final R indices $[\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0419, \mathrm{wR} 2=0.0883$ |
| R indices (all data) | $\mathrm{R} 1=0.0545, \mathrm{wR} 2=0.0928$ |
| Largest diff. peak and hole | 1.175 and -0.966 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 2.4b

| Identification code | 17092 |
| :---: | :---: |
| Empirical formula | C27 H24 N2 O2 Pd |
| Formula weight | 514.88 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Unit cell dimensions | $a=10.639(5) \AA \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=10.319(5) \AA \quad \beta=91.637(10)^{\circ}$ |
|  | $\mathrm{c}=20.542(10) \AA \AA^{\circ} \mathrm{A}$ |
| Volume | 2254.4(19) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.517 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.850 \mathrm{~mm}^{-1}$ |
| $\mathrm{F}(000)$ | 1048 |
| Crystal size | $0.14 \times 0.13 \times 0.09 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.91 to $26.00^{\circ}$. |
| Index ranges | $-13<=\mathrm{h}<=13,-12<=\mathrm{k}<=12,-25<=\mathrm{l}<=24$ |
| Reflections collected | 17246 |
| Independent reflections | $4421[\mathrm{R}(\mathrm{int})=0.1534]$ |
| Completeness to theta $=26.00^{\circ}$ | 99.9 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.859 and 0.314 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 4421 / 0 / 292 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.909 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0564, \mathrm{wR} 2=0.1083$ |
| R indices (all data) | $\mathrm{R} 1=0.0896, \mathrm{wR} 2=0.1177$ |
| Largest diff. peak and hole | 0.995 and -0.867e. $\AA^{-3}$ |

## Crystal data and structure refinement for 2.2c

| Identification code | 17087 |
| :---: | :---: |
| Empirical formula | C20 H19 F3 N2 O4 Pd |
| Formula weight | 514.77 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | $a=6.3417(14) \AA \quad \alpha=105.051(3)^{\circ}$. |
|  | $\mathrm{b}=10.514(2) \AA \quad \beta=91.718(4)^{\circ}$. |
|  | $\mathrm{c}=16.194(4) \AA \quad \gamma=106.784(3)^{\circ}$. |
| Volume | 991.8(4) $\AA^{3}$ |
| Z | 2 |
| Density (calculated) | $1.724 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.993 \mathrm{~mm}^{-1}$ |
| $\mathrm{F}(000)$ | 516 |
| Crystal size | $0.44 \times 0.13 \times 0.08 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.31 to $25.99^{\circ}$. |
| Index ranges | $-7<=\mathrm{h}<=7,-12<=\mathrm{k}<=12,-19<=\mathrm{l}<=19$ |
| Reflections collected | 7702 |
| Independent reflections | $3839[\mathrm{R}(\mathrm{int})=0.0402]$ |
| Completeness to theta $=25.99^{\circ}$ | 98.7 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.850 and 0.611 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 3839 / 2 / 273 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.053 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0376, \mathrm{wR} 2=0.0861$ |
| R indices (all data) | $\mathrm{R} 1=0.0432, \mathrm{wR} 2=0.0884$ |
| Largest diff. peak and hole | 1.037 and -1.185 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 2.5a

| Identification code | 17083 |
| :---: | :---: |
| Empirical formula | C31 H23 Cl3 N O2 P Pd |
| Formula weight | 685.22 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | C2/c |
| Unit cell dimensions | $\mathrm{a}=32.329(7) \AA \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=13.294(3) \AA \quad \beta=103.324(4)^{\circ}$ |
|  | $\mathrm{c}=13.878(3) \AA \quad \gamma=90^{\circ}$. |
| Volume | 5804(2) $\AA^{3}$ |
| Z | 8 |
| Density (calculated) | $1.568 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $1.001 \mathrm{~mm}^{-1}$ |
| $\mathrm{F}(000)$ | 2752 |
| Crystal size | $0.39 \times 0.10 \times 0.05 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.66 to $26.00^{\circ}$. |
| Index ranges | $-39<=\mathrm{h}<=39,-16<=\mathrm{k}<=16,-17<=\mathrm{l}<=17$ |
| Reflections collected | 22118 |
| Independent reflections | $5710[\mathrm{R}(\mathrm{int})=0.0863]$ |
| Completeness to theta $=26.00^{\circ}$ | 99.9 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.620 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 5710 / $1 / 316$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.919 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0474, \mathrm{wR} 2=0.0969$ |
| R indices (all data) | $\mathrm{R} 1=0.0744, \mathrm{wR} 2=0.1033$ |
| Largest diff. peak and hole | 0.831 and -0.343 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 2.6b

| Identification code | 16012 |
| :---: | :---: |
| Empirical formula | C53 H49 Cl N O3 P2 Ru |
| Formula weight | 946.39 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Monoclinic |
| Space group | $\mathrm{P} 2(1) / \mathrm{n}$ |
| Unit cell dimensions | $a=12.205(3) \AA \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=27.836(7) \AA \quad \beta=105.491(6)^{\circ}$. |
|  | $\mathrm{c}=13.950(4) \AA \quad \gamma=90^{\circ}$. |
| Volume | 4567(2) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.376 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.516 \mathrm{~mm}^{-1}$ |
| $\mathrm{F}(000)$ | 1956 |
| Crystal size | $0.29 \times 0.13 \times 0.08 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.46 to $26.00^{\circ}$. |
| Index ranges | $-15<=\mathrm{h}<=15,-34<=\mathrm{k}<=34,-17<=1<=17$ |
| Reflections collected | 35789 |
| Independent reflections | $8978[\mathrm{R}($ int $)=0.2374]$ |
| Completeness to theta $=26.00^{\circ}$ | 100.0 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.639 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 8978 / 0 / 554 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.742 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0658, \mathrm{wR} 2=0.0938$ |
| R indices (all data) | $\mathrm{R} 1=0.1857, \mathrm{wR} 2=0.1212$ |
| Largest diff. peak and hole | 0.649 and -1.440 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 2.6c

| Identification code | 17127 |
| :---: | :---: |
| Empirical formula | C49 H36 Cl F3 N O2 P2 Ru |
| Formula weight | 926.25 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 £ |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Unit cell dimensions | $a=9.9364(16) \AA \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=18.756(3) \AA$ A $\quad \beta=94.908(4)^{\circ}$ |
|  | $\mathrm{c}=22.142(3) \AA \AA^{\circ} \mathrm{A}$ |
| Volume | 4111.4(11) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.496 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.580 \mathrm{~mm}^{-1}$ |
| $F(000)$ | 1884 |
| Crystal size | $0.27 \times 0.18 \times 0.06 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.43 to $26.00^{\circ}$. |
| Index ranges | $-12<=\mathrm{h}<=12,-23<=\mathrm{k}<=23,-27<=\mathrm{l}<=27$ |
| Reflections collected | 28069 |
| Independent reflections | $8066[\mathrm{R}(\mathrm{int})=0.1078]$ |
| Completeness to theta $=26.00^{\circ}$ | 100.0 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.553 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 8066 / 0 / 532 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.862 |
| Final R indices $[\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0521, \mathrm{wR} 2=0.0828$ |
| R indices (all data) | $\mathrm{R} 1=0.0871, \mathrm{wR} 2=0.0922$ |
| Largest diff. peak and hole | 0.579 and -0.869 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 2.7b

| Identification code | 16054 |
| :---: | :---: |
| Empirical formula | C26.75 H33 Cl N O2.75 Ru |
| Formula weight | 549.06 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Trigonal |
| Space group | R-3 |
| Unit cell dimensions | $a=35.31(2) \AA \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=35.31(2) \AA \quad \beta=90^{\circ}$. |
|  | $\mathrm{c}=10.493(9) \AA \AA^{\circ} \mathrm{A}$ |
| Volume | 11332(14) ${ }^{\text {A }}$ |
| Z | 18 |
| Density (calculated) | $1.448 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.755 \mathrm{~mm}^{-1}$ |
| F(000) | 5103 |
| Crystal size | $0.27 \times 0.12 \times 0.07 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 2.00 to $24.70^{\circ}$. |
| Index ranges | $-41<=\mathrm{h}<=20,0<=\mathrm{k}<=41,0<=1<=12$ |
| Reflections collected | 4298 |
| Independent reflections | $4298[\mathrm{R}(\mathrm{int})=0.0000]$ |
| Completeness to theta $=24.70^{\circ}$ | 100.0 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.364 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 4298 / 0 / 305 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.899 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0804, \mathrm{wR} 2=0.1445$ |
| R indices (all data) | $\mathrm{R} 1=0.1859, \mathrm{wR} 2=0.1690$ |
| Largest diff. peak and hole | 0.576 and -1.078 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 3b

| Identification code | 17123 |
| :---: | :---: |
| Empirical formula | C18 H18 N2 O3 Pd |
| Formula weight | 416.74 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Unit cell dimensions | $\mathrm{a}=24.620(7) \AA \AA^{\circ} \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=8.455(2) \AA \AA^{\text {A }}$ |
|  |  |
| Volume | 1665.5(8) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.662 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $1.132 \mathrm{~mm}^{-1}$ |
| F(000) | 840 |
| Crystal size | $0.33 \times 0.21 \times 0.03 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.67 to $26.00^{\circ}$. |
| Index ranges | $-30<=\mathrm{h}<=30,-10<=\mathrm{k}<=10,-9<=\mathrm{l}<=9$ |
| Reflections collected | 12505 |
| Independent reflections | $3268[\mathrm{R}(\mathrm{int})=0.0881]$ |
| Completeness to theta $=26.00^{\circ}$ | 99.8\% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.563 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 3268 / 59 / 251 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.013 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0521, \mathrm{wR} 2=0.1113$ |
| R indices (all data) | $\mathrm{R} 1=0.0758, \mathrm{wR} 2=0.1191$ |
| Largest diff. peak and hole | 1.614 and -0.860 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 3.5a

| Identification code | 17081 |
| :---: | :---: |
| Empirical formula | C31 H23 Cl3 N O3 P Pd |
| Formula weight | 701.22 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2(1)/n |
| Unit cell dimensions | $a=8.5086(11) \AA$ ¢ $\quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=21.422(3) \AA \quad \beta=100.661(3)^{\circ}$ |
|  |  |
| Volume | 2943.6(7) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.582 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.991 \mathrm{~mm}^{-1}$ |
| $\mathrm{F}(000)$ | 1408 |
| Crystal size | $0.21 \times 0.17 \times 0.10 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.58 to $26.00^{\circ}$. |
| Index ranges | $-10<=\mathrm{h}<=10,-26<=\mathrm{k}<=26,-20<=\mathrm{l}<=20$ |
| Reflections collected | 22877 |
| Independent reflections | $5796[\mathrm{R}(\mathrm{int})=0.0887]$ |
| Completeness to theta $=26.00^{\circ}$ | 99.9 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.665 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 5796 / 0 / 361 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.914 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0497, \mathrm{wR} 2=0.0953$ |
| R indices (all data) | $\mathrm{R} 1=0.0727, w R 2=0.1025$ |
| Largest diff. peak and hole | 0.910 and -0.660 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 3.4c

| Identification code | 17095 |
| :---: | :---: |
| Empirical formula | C30 H21 Cl N O3 P Pd |
| Formula weight | 616.30 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | $a=8.946(2) \AA \quad \alpha=103.501(6)^{\circ}$. |
|  | $b=9.611(3) \AA \quad \beta=100.595(6)^{\circ}$. |
|  | $\mathrm{c}=14.802(4) \AA \quad \gamma=90.878(7)^{\circ}$. |
| Volume | 1214.1(6) $\AA^{3}$ |
| Z | 2 |
| Density (calculated) | $1.686 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.976 \mathrm{~mm}^{-1}$ |
| $F(000)$ | 620 |
| Crystal size | $0.16 \times 0.11 \times 0.03 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.44 to $26.00^{\circ}$. |
| Index ranges | $-11<=\mathrm{h}<=11,-11<=\mathrm{k}<=11,-18<=1<=18$ |
| Reflections collected | 9548 |
| Independent reflections | $4695[\mathrm{R}(\mathrm{int})=0.1359]$ |
| Completeness to theta $=26.00^{\circ}$ | 98.7\% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.537 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 4695 / 24 / 334 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.957 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0920, \mathrm{wR} 2=0.1839$ |
| R indices (all data) | $\mathrm{R} 1=0.1690, \mathrm{wR} 2=0.2081$ |
| Largest diff. peak and hole | 1.527 and -0.835 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 3.6b

| Identification code | 17097 |
| :---: | :---: |
| Empirical formula | C52 H45 Cl N O3 P2 Ru |
| Formula weight | 930.35 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | $\mathrm{a}=9.8829(17) \AA \quad \alpha=73.420(3)^{\circ}$. |
|  | $\mathrm{b}=12.067(2) \AA \quad \beta=77.906(3)^{\circ}$. |
|  | $\mathrm{c}=19.431(3) \AA \AA^{\circ} \quad \gamma=74.278(4)^{\circ}$. |
| Volume | 2115.8(6) $\AA^{3}$ |
| Z | 2 |
| Density (calculated) | $1.460 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.556 \mathrm{~mm}^{-1}$ |
| $F(000)$ | 958 |
| Crystal size | $0.18 \times 0.11 \times 0.10 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.81 to $26.00^{\circ}$. |
| Index ranges | $-12<=\mathrm{h}<=12,-14<=\mathrm{k}<=14,-23<=\mathrm{l}<=22$ |
| Reflections collected | 16734 |
| Independent reflections | $8221[\mathrm{R}(\mathrm{int})=0.0907]$ |
| Completeness to theta $=26.00^{\circ}$ | 98.8\% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.603 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 8221 / 0 / 544 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.953 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0734, \mathrm{wR} 2=0.1458$ |
| R indices (all data) | $\mathrm{R} 1=0.1135, \mathrm{wR} 2=0.1600$ |
| Largest diff. peak and hole | 1.236 and -1.253 e. $\AA^{-3}$ |

## Crystal data and structure refinement for EtLs

| Identification code | 16035 |
| :---: | :---: |
| Empirical formula | C25 H34 N2 O2 |
| Formula weight | 394.54 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Monoclinic |
| Space group | P2(1)/n |
| Unit cell dimensions | $\mathrm{a}=8.651(2) \AA \quad \alpha=90^{\circ}$. |
|  | $b=11.157(3) \AA$ A $\quad \beta=98.941(5)^{\circ}$. |
|  | $\mathrm{c}=24.055(6) \AA \quad \gamma=90^{\circ}$. |
| Volume | 2293.6(10) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.143 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.072 \mathrm{~mm}^{-1}$ |
| $\mathrm{F}(000)$ | 856 |
| Crystal size | $0.43 \times 0.38 \times 0.17 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.71 to $26.00^{\circ}$. |
| Index ranges | $-10<=\mathrm{h}<=10,-13<=\mathrm{k}<=13,-29<=\mathrm{l}<=29$ |
| Reflections collected | 17615 |
| Independent reflections | $4515[\mathrm{R}(\mathrm{int})=0.0925]$ |
| Completeness to theta $=26.00^{\circ}$ | 99.9 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.981 and 0.638 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 4515 / 0 / 270 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.871 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0540, \mathrm{wR} 2=0.0999$ |
| R indices (all data) | $\mathrm{R} 1=0.1027, w R 2=0.1125$ |
| Largest diff. peak and hole | 0.177 and -0.189 e. $\AA^{-3}$ |

## Crystal data and structure refinement for $\mathbf{4 a}$

| Identification code | 17110 |
| :---: | :---: |
| Empirical formula | C23.50 H29 N2.75 O4.37 Pd |
| Formula weight | 526.39 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 £ |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | $a=10.431(3) \AA$ 成 $\quad \alpha=70.100(4)^{\circ}$. |
|  | $\mathrm{b}=15.416(4) \AA \quad \beta=89.649(5)^{\circ}$. |
|  | $\mathrm{c}=15.950(4) \AA \AA^{\text {A }}$ ( |
| Volume | 2323.8(11) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.505 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.834 \mathrm{~mm}^{-1}$ |
| $F(000)$ | 1081 |
| Crystal size | $0.22 \times 0.11 \times 0.03 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.36 to $26.00^{\circ}$. |
| Index ranges | $-12<=\mathrm{h}<=12,-19<=\mathrm{k}<=18,-19<=\mathrm{l}<=19$ |
| Reflections collected | 18097 |
| Independent reflections | $9003[\mathrm{R}(\mathrm{int})=0.1254]$ |
| Completeness to theta $=26.00^{\circ}$ | 98.6 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.931 and 0.390 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 9003 / 10 / 544 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.841 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0743, \mathrm{wR} 2=0.1342$ |
| R indices (all data) | $\mathrm{R} 1=0.1454, \mathrm{wR} 2=0.1541$ |
| Largest diff. peak and hole | 0.886 and -1.318 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 4.1a

| Identification code | 16003 |
| :---: | :---: |
| Empirical formula | C22 H26 Cl N3 O2 Pd |
| Formula weight | 506.31 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Unit cell dimensions | $a=15.468(2) \AA \quad \alpha=90^{\circ}$. |
|  | $b=10.4664(16) \AA \quad \beta=97.824(3)^{\circ}$. |
|  |  |
| Volume | 2261.1(6) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.487 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.961 \mathrm{~mm}^{-1}$ |
| $\mathrm{F}(000)$ | 1032 |
| Crystal size | $0.16 \times 0.12 \times 0.05 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.33 to $25.99^{\circ}$. |
| Index ranges | $-18<=\mathrm{h}<=19,-12<=\mathrm{k}<=12,-17<=\mathrm{l}<=17$ |
| Reflections collected | 17275 |
| Independent reflections | $4435[\mathrm{R}(\mathrm{int})=0.0954]$ |
| Completeness to theta $=25.99^{\circ}$ | 100.0 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.592 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 4435 / 0 / 268 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.963 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0424, \mathrm{wR} 2=0.0839$ |
| R indices (all data) | $\mathrm{R} 1=0.0597, \mathrm{wR} 2=0.0889$ |
| Largest diff. peak and hole | 0.845 and -0.937e. $\AA^{-3}$ |

## Crystal data and structure refinement for 4.1c

| Identification code | 16097 |
| :---: | :---: |
| Empirical formula | C21 H24 Br Cl N2 O3 Pd |
| Formula weight | 574.18 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Unit cell dimensions | $a=8.2728(12) \AA$ ¢ $\quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=13.772(2) \AA \AA^{\circ} \quad \beta=95.875(3)^{\circ}$ |
|  | $\mathrm{c}=20.908(3) \AA$ A $\quad \gamma=90^{\circ}$. |
| Volume | 2369.6(6) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.609 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $2.605 \mathrm{~mm}^{-1}$ |
| $\mathrm{F}(000)$ | 1144 |
| Crystal size | $0.17 \times 0.11 \times 0.09 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.77 to $26.00^{\circ}$. |
| Index ranges | $-10<=\mathrm{h}<=10,-16<=\mathrm{k}<=16,-25<=1<=24$ |
| Reflections collected | 18296 |
| Independent reflections | $4646[\mathrm{R}(\mathrm{int})=0.1136]$ |
| Completeness to theta $=26.00^{\circ}$ | 99.8\% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.615 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 4646 / 23 / 287 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.859 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0498, \mathrm{wR} 2=0.0874$ |
| R indices (all data) | $\mathrm{R} 1=0.0977, \mathrm{wR} 2=0.0965$ |
| Largest diff. peak and hole | 0.683 and -0.744 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 4.5a

| Identification code | 17108 |
| :---: | :---: |
| Empirical formula | C25 H27 Br F6 N3 O2 P Pd |
| Formula weight | 732.78 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | $\mathrm{a}=8.613(2) \AA \quad \alpha=102.391(5)^{\circ}$. |
|  | $b=11.842(3) \AA$ A $\quad \beta=97.046(5)^{\circ}$. |
|  | $\mathrm{c}=14.325(4) \AA \quad \gamma=106.117(5)^{\circ}$. |
| Volume | 1344.8(6) $\AA^{3}$ |
| Z | 2 |
| Density (calculated) | $1.810 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $2.306 \mathrm{~mm}^{-1}$ |
| $\mathrm{F}(000)$ | 728 |
| Crystal size | $0.13 \times 0.09 \times 0.04 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.48 to $26.00^{\circ}$. |
| Index ranges | $-10<=\mathrm{h}<=10,-14<=\mathrm{k}<=14,-17<=\mathrm{l}<=17$ |
| Reflections collected | 10604 |
| Independent reflections | $5226[\mathrm{R}(\mathrm{int})=0.1405]$ |
| Completeness to theta $=26.00^{\circ}$ | 98.7 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.691 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 5226 / 25 / 357 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.887 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0855, \mathrm{wR} 2=0.1400$ |
| R indices (all data) | $\mathrm{R} 1=0.1898, \mathrm{wR} 2=0.1714$ |
| Largest diff. peak and hole | 0.867 and -1.086 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 4.6c

| Identification code | 16092 |
| :---: | :---: |
| Empirical formula | C24 H29 Br Cl8 N2 O2 Pt |
| Formula weight | 936.09 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Unit cell dimensions | $a=12.499(2) \AA$ 風 $\quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=21.958(4) \AA \quad \beta=116.401(4)^{\circ}$. |
|  |  |
| Volume | $3310.9(11) \AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.878 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $6.116 \mathrm{~mm}^{-1}$ |
| F(000) | 1808 |
| Crystal size | $0.22 \times 0.05 \times 0.03 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.82 to $26.00^{\circ}$. |
| Index ranges | $-15<=\mathrm{h}<=15,-27<=\mathrm{k}<=26,-16<=\mathrm{l}<=16$ |
| Reflections collected | 25739 |
| Independent reflections | $6510[\mathrm{R}(\mathrm{int})=0.1909]$ |
| Completeness to theta $=26.00^{\circ}$ | 100.0 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.549 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 6510 / 26 / 367 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.746 |
| Final R indices $[\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0613, \mathrm{wR} 2=0.0797$ |
| R indices (all data) | $\mathrm{R} 1=0.1457, \mathrm{wR} 2=0.0948$ |
| Largest diff. peak and hole | 1.842 and -1.213 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 6a

| Identification code | 14105 |
| :---: | :---: |
| Empirical formula | C99 H151 C19 N12 O20 Pd4 |
| Formula weight | 2573.97 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | $a=13.046(4) \AA \quad \alpha=71.163(5)^{\circ}$. |
|  | $\mathrm{b}=15.038(4) \AA \quad \beta=86.521(5)^{\circ}$. |
|  | $\mathrm{c}=17.160(5) \AA$ A $\quad \gamma=69.080(5)^{\circ}$ |
| Volume | 2970.7(15) $\AA^{3}$ |
| Z | 1 |
| Density (calculated) | $1.439 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.864 \mathrm{~mm}^{-1}$ |
| $F(000)$ | 1326 |
| Crystal size | $0.43 \times 0.24 \times 0.06 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.53 to $26.00^{\circ}$. |
| Index ranges | $-16<=\mathrm{h}<=16,-18<=\mathrm{k}<=18,-21<=1<=21$ |
| Reflections collected | 23276 |
| Independent reflections | $11532[\mathrm{R}(\mathrm{int})=0.0790]$ |
| Completeness to theta $=26.00^{\circ}$ | 98.6 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.656 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 11532 / 11 / 679 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.000 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0698, \mathrm{wR} 2=0.1701$ |
| R indices (all data) | $\mathrm{R} 1=0.1120, \mathrm{wR} 2=0.1889$ |
| Largest diff. peak and hole | 1.632 and -1.243 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 6b

| Identification code | 14106 |
| :---: | :---: |
| Empirical formula | C25 H41 N3 O6 Pd |
| Formula weight | 586.01 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2(1)/n |
| Unit cell dimensions | $a=12.617(3) \AA$ ¢ $\quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=13.536(3) \AA \quad \beta=107.164(4)^{\circ}$. |
|  | $\mathrm{c}=16.371(4) \AA \quad \gamma=90^{\circ}$. |
| Volume | 2671.4(10) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.457 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.738 \mathrm{~mm}^{-1}$ |
| F(000) | 1224 |
| Crystal size | $0.44 \times 0.25 \times 0.07 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.80 to $27.00^{\circ}$. |
| Index ranges | $-16<=\mathrm{h}<=16,-17<=\mathrm{k}<=17,-20<=\mathrm{l}<=20$ |
| Reflections collected | 21934 |
| Independent reflections | $5815[\mathrm{R}(\mathrm{int})=0.0615]$ |
| Completeness to theta $=27.00^{\circ}$ | 99.7 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.825 and 0.644 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 5815 / 0 / 323 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.006 |
| Final R indices $[\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0385, \mathrm{wR} 2=0.0754$ |
| R indices (all data) | $\mathrm{R} 1=0.0538, \mathrm{wR} 2=0.0800$ |
| Largest diff. peak and hole | 0.861 and -0.430 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 6.1a

| Identification code | 14107 |
| :---: | :---: |
| Empirical formula | C21 H33 Cl2 N3 O Pd |
| Formula weight | 520.80 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Unit cell dimensions | $a=18.992(3) \AA$ A $\quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=9.3489(16) \AA \quad \beta=100.162(3)^{\circ}$. |
|  | $\mathrm{c}=13.476(2) \AA \quad \gamma=90^{\circ}$. |
| Volume | 2355.2(7) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.469 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $1.031 \mathrm{~mm}^{-1}$ |
| F(000) | 1072 |
| Crystal size | $0.45 \times 0.24 \times 0.17 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 2.18 to $27.00^{\circ}$. |
| Index ranges | $-24<=\mathrm{h}<=24,-11<=\mathrm{k}<=11,-17<=\mathrm{l}<=17$ |
| Reflections collected | 19187 |
| Independent reflections | $5119[\mathrm{R}(\mathrm{int})=0.0472]$ |
| Completeness to theta $=27.00^{\circ}$ | 99.9 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.671 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 5119 / 0 / 258 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.018 |
| Final R indices $[\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0288, \mathrm{wR} 2=0.0641$ |
| R indices (all data) | $\mathrm{R} 1=0.0339, \mathrm{wR} 2=0.0661$ |
| Largest diff. peak and hole | 0.503 and -0.574 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 6.1b

| Identification code | 14135 |
| :---: | :---: |
| Empirical formula | C21 H35 Cl2 N3 O2 Pd |
| Formula weight | 538.82 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | $\mathrm{a}=9.565(3) \AA \quad \alpha=114.997(4)^{\circ}$. |
|  | $\mathrm{b}=15.591(4) \AA \quad \beta=95.296(5)^{\circ}$. |
|  | $\mathrm{c}=17.511(5) \AA$ A $\quad \gamma=91.337(5)^{\circ}$. |
| Volume | 2350.9(11) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.522 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $1.038 \mathrm{~mm}^{-1}$ |
| $\mathrm{F}(000)$ | 1112 |
| Crystal size | $0.46 \times 0.43 \times 0.38 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.44 to $27.00^{\circ}$. |
| Index ranges | $-12<=\mathrm{h}<=12,-19<=\mathrm{k}<=19,-22<=1<=22$ |
| Reflections collected | 19748 |
| Independent reflections | $10057[\mathrm{R}(\mathrm{int})=0.0332]$ |
| Completeness to theta $=27.00^{\circ}$ | 97.9 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.669 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 10057 / 4 / 533 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.010 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0347, \mathrm{wR} 2=0.0741$ |
| R indices (all data) | $\mathrm{R} 1=0.0458, \mathrm{wR} 2=0.0775$ |
| Largest diff. peak and hole | 0.870 and -0.583 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 6.2b

| Identification code | 15015 |
| :---: | :---: |
| Empirical formula | C25.50 H39 C12 N3 O4 Pd |
| Formula weight | 628.90 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Unit cell dimensions | $a=11.612(3) \AA \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=18.326(5) \AA \quad \beta=109.405(6)^{\circ}$ |
|  |  |
| Volume | 2861.4(14) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.460 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.870 \mathrm{~mm}^{-1}$ |
| $\mathrm{F}(000)$ | 1300 |
| Crystal size | $0.36 \times 0.08 \times 0.07 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.86 to $26.00^{\circ}$. |
| Index ranges | $-14<=\mathrm{h}<=14,-22<=\mathrm{k}<=22,-17<=\mathrm{l}<=17$ |
| Reflections collected | 22389 |
| Independent reflections | $5636[\mathrm{R}(\mathrm{int})=0.1663]$ |
| Completeness to theta $=26.00^{\circ}$ | 99.9 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.862 and 0.649 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 5636 / 0 / 315 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.779 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0602, \mathrm{wR} 2=0.0939$ |
| R indices (all data) | $\mathrm{R} 1=0.1250, \mathrm{wR} 2=0.1091$ |
| Largest diff. peak and hole | 0.744 and -0.823 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 6.3b

| Identification code | 15067 |
| :---: | :---: |
| Empirical formula | C22 H31 Cl F3 N3 O3 Pd S |
| Formula weight | 616.41 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Monoclinic |
| Space group | C2/c |
| Unit cell dimensions | $\begin{array}{ll} \mathrm{a}=32.779(6) \AA & \alpha=90^{\circ} . \\ \mathrm{b}=7.9867(13) \AA & \beta=107.540(4)^{\circ} . \\ \mathrm{c}=19.918(3) \AA & \gamma=90^{\circ} . \end{array}$ |
| Volume | 4972.1(14) $\AA^{3}$ |
| Z | 8 |
| Density (calculated) | $1.647 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.990 \mathrm{~mm}^{-1}$ |
| $\mathrm{F}(000)$ | 2512 |
| Crystal size | $0.30 \times 0.16 \times 0.05 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 2.14 to $27.00^{\circ}$. |
| Index ranges | $-41<=\mathrm{h}<=41,-10<=\mathrm{k}<=10,-24<=\mathrm{l}<=25$ |
| Reflections collected | 20101 |
| Independent reflections | $5419[\mathrm{R}(\mathrm{int})=0.0433]$ |
| Completeness to theta $=27.00^{\circ}$ | 99.9 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.681 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 5419 / 0 / 312 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.989 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0281, \mathrm{wR} 2=0.0647$ |
| R indices (all data) | $\mathrm{R} 1=0.0346, \mathrm{wR} 2=0.0668$ |
| Largest diff. peak and hole | 0.524 and -0.439 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 6.4b

| Identification code | 15093 |
| :---: | :---: |
| Empirical formula | C88 H138 B4 Cl12 F16 N12 O3 Pd4 |
| Formula weight | 2610.34 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Monoclinic |
| Space group | C2/c |
| Unit cell dimensions | $\mathrm{a}=29.898(7) \AA \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=7.8525(18) \AA$ A $\quad \beta=93.414(4)^{\circ}$. |
|  | $\mathrm{c}=23.044(5) \AA$ ¢ $\quad \gamma=90^{\circ}$. |
| Volume | 5401(2) $\AA^{3}$ |
| Z | 2 |
| Density (calculated) | $1.605 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $1.032 \mathrm{~mm}^{-1}$ |
| $\mathrm{F}(000)$ | 2652 |
| Crystal size | $0.31 \times 0.08 \times 0.07 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.36 to $26.00^{\circ}$. |
| Index ranges | $-36<=\mathrm{h}<=35,-9<=\mathrm{k}<=9,-28<=\mathrm{l}<=28$ |
| Reflections collected | 20345 |
| Independent reflections | $5314[\mathrm{R}(\mathrm{int})=0.0657]$ |
| Completeness to theta $=26.00^{\circ}$ | 99.9 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.689 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 5314 / 6/329 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.998 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0466, \mathrm{wR} 2=0.1157$ |
| R indices (all data) | $\mathrm{R} 1=0.0605, \mathrm{wR} 2=0.1242$ |
| Largest diff. peak and hole | 1.393 and -1.060 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 6.5b

| Identification code | 15026 |
| :---: | :---: |
| Empirical formula | C21 H31 Cl F6 N3 P Pd |
| Formula weight | 612.31 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Monoclinic |
| Space group | P2(1)/n |
| Unit cell dimensions | $a=9.0780(13) \AA$ ¢ $\quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=22.272(3) \AA \quad \beta=100.455(3)^{\circ}$. |
|  | $\mathrm{c}=24.785(4) \AA \AA^{\circ} \mathrm{C}=90^{\circ}$. |
| Volume | 4928.1(12) $\AA^{3}$ |
| Z | 8 |
| Density (calculated) | $1.651 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.986 \mathrm{~mm}^{-1}$ |
| F(000) | 2480 |
| Crystal size | $0.21 \times 0.14 \times 0.08 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.67 to $26.00^{\circ}$. |
| Index ranges | $-11<=\mathrm{h}<=11,-27<=\mathrm{k}<=27,-30<=1<=30$ |
| Reflections collected | 38336 |
| Independent reflections | $9691[\mathrm{R}(\mathrm{int})=0.1496]$ |
| Completeness to theta $=26.00^{\circ}$ | 99.9 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.690 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 9691 / 0 / 605 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.791 |
| Final R indices $[\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0574, \mathrm{wR} 2=0.0767$ |
| R indices (all data) | $\mathrm{R} 1=0.1206, \mathrm{wR} 2=0.0889$ |
| Largest diff. peak and hole | 0.622 and -0.794 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 6.6b

| Identification code | 15147 |
| :---: | :---: |
| Empirical formula | C23 H33 Cl7 N4 O3 Pd |
| Formula weight | 768.08 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | $\mathrm{a}=8.149(2) \AA \quad \alpha=70.648(6)^{\circ}$. |
|  | $\mathrm{b}=12.815(4) \AA \quad \beta=77.539(6)^{\circ}$. |
|  | $\mathrm{c}=16.491(5) \AA$ ¢ $\quad \gamma=83.331(6)^{\circ}$ |
| Volume | 1584.7(8) $\AA^{3}$ |
| Z | 2 |
| Density (calculated) | $1.610 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $1.207 \mathrm{~mm}^{-1}$ |
| $F(000)$ | 776 |
| Crystal size | $0.15 \times 0.05 \times 0.03 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.33 to $26.00^{\circ}$. |
| Index ranges | $-10<=\mathrm{h}<=10,-15<=\mathrm{k}<=15,-20<=\mathrm{l}<=19$ |
| Reflections collected | 12481 |
| Independent reflections | $6133[\mathrm{R}(\mathrm{int})=0.1182]$ |
| Completeness to theta $=26.00^{\circ}$ | 98.6\% |
| Absorption correction | Empirical |
| Max. and min. transmission | 1.00 and 0.603 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 6133 / 12 / 348 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.754 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0637, \mathrm{wR} 2=0.0916$ |
| R indices (all data) | $\mathrm{R} 1=0.1336, \mathrm{wR} 2=0.1092$ |
| Largest diff. peak and hole | 0.646 and -0.792 e. $\AA^{-3}$ |

## Crystal data and structure refinement for 6.7b

| Identification code | 15156 |
| :---: | :---: |
| Empirical formula | C29 H39 Cl4 N3 O3 Pd |
| Formula weight | 725.83 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Monoclinic |
| Space group | P2(1)/c |
| Unit cell dimensions | $a=12.096(4) \AA \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=25.808(9) \AA \AA^{\circ} \quad \beta=103.135(7)^{\circ}$. |
|  | $\mathrm{c}=10.690(4) \AA \quad \gamma=90^{\circ}$. |
| Volume | 3249.8(19) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.484 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.934 \mathrm{~mm}^{-1}$ |
| F(000) | 1488 |
| Crystal size | $0.15 \times 0.08 \times 0.03 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.58 to $26.00^{\circ}$. |
| Index ranges | $-14<=\mathrm{h}<=14,-31<=\mathrm{k}<=31,-13<=1<=13$ |
| Reflections collected | 25332 |
| Independent reflections | $6376[\mathrm{R}($ int $)=0.1704]$ |
| Completeness to theta $=26.00^{\circ}$ | 99.9 \% |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.831 and 0.666 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 6376 / 0 / 366 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.821 |
| Final R indices $[\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0640, \mathrm{wR} 2=0.1100$ |
| R indices (all data) | $\mathrm{R} 1=0.1430, w R 2=0.1260$ |
| Largest diff. peak and hole | 1.418 and -0.829 e. $\AA^{-3}$ |

## References

(1) Gunanathan, C.; Milstein, D. Chem. Rev. 2014, 114, 12024-12087.
(2) Moulton, B. C. J.; Shaw, B. L. Dalton Trans. 1976, 11, 1020-1024.
(3) Morales-Morales, D. Rev. la Soc. Química México 2004, 48, 338-346.
(4) Tomasik, P.; Ratajewicz, Z.; Newcome, R. G.; Strekowski, L. Pyridine-metal complexes; John Wiley \& Sons, Inc., 1985.
(5) Grüger, N.; Wadepohl, H.; Gade, L. H. Eur. J. Inorg. Chem. 2013, 5358-5365.
(6) Gruger, N.; Wadepohl, H.; Gade, L. H. Dalton Trans. 2012, 41, 14028-14030.
(7) Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. J. Am. Chem. Soc. 2005, 127, 10840-10841.
(8) Balaraman, E.; Gnanaprakasam, B.; Shimon, L. J. W.; Milstein, D. J. Am. Chem. Soc. 2010, 132, 16756-16758.
(9) Balaraman, E.; Ben-david, Y.; Milstein, D. Angew. Chem. Int. Ed. 2011, 50, 11702-11705.
(10) Balaraman, E.; Gunanathan, C.; Zhang, J.; Shimon, L. J. W.; Milstein, D. Nat. Chem. 2011, 3, 609-614.
(11) Balaraman, E.; Fogler, E.; Milstein, D. Chem. Commun. 2012, 48, 1111-1113.
(12) Coupling, R. P. C. Adv. Synth. Catal. 2012, 354, 2403-2406.
(13) Balaraman, E.; Khaskin, E.; Leitus, G.; Milstein, D. Nat. Chem. 2013, 5, 122125.
(14) Vlugt, J. I. Van Der; Pidko, E. a; Vogt, D.; Lutz, M.; Spek, A. L. Inorg. Chem. Commun. 2008, 47, 1-10.
(15) Huff, C. A.; Kampf, J. W.; Sanford, M. S. Organometallics 2012, 31, 46434645.
(16) Huff, C. A.; Kampf, J. W.; Sanford, M. S. Chem. Commun. 2013, 49, 7147-7149.
(17) Huff, C. A.; Sanford, M. S. ACS Catal. 2013, 3, 2412-2416.
(18) Van Der Vlugt, J. I.; Siegler, M. A.; Janssen, M.; Vogt, D.; Spek, A. L. Organometallics 2009, 28, 7025-7032.
(19) Feller, M.; Ben-Ari, E.; Iron, M. A.; Diskin-Posner, Y.; Leitus, G.; Linda, L. J.; Konstantinovski, L.; Milstein, D. Inorg. Chem. 2010, 49, 1615-1625.
(20) Bailey, W. D.; Kaminsky, W.; Kemp, R. a; Goldberg, K. I. Organometallics 2014, 33, 2503-2509.
(21) Konrad, F.; Fillol, J. L.; Wadepohl, H.; Gade, L. H. Inorg. Chem. 2009, 48, 8523-8535.
(22) Zeng, F.; Yu, Z. Organometallics 2008, 27, 2898-2901.
(23) Zhao, M.; Yu, Z.; Yan, S.; Li, Y. Tetrahedron Lett. 2009, 50, 4624-4628.
(24) Jin, W.; Wang, L.; Yu, Z. Organometallics 2012, 31, 5664-5667.
(25) Zhao, M.; Yu, Z.; Yan, S.; Li, Y. J. Organomet. Chem. 2009, 694, 3068-3075.
(26) Ye, W.; Zhao, M.; Du, W.; Jiang, Q.; Wu, K.; Wu, P.; Yu, Z. Eur. J. Org. Chem 2011, 17, 4737-4741.
(27) Du, W.; Wu, P.; Wang, Q.; Yu, Z. Organometallics 2013, 32, 3083-3090.
(28) Asay, M.; Morales-Morales, D. Dalton Trans. 2015, 44, 17432-17447.
(29) Small, B. L.; Brookhart, M.; Bennett, A. M. A. J. Am. Chem. Soc. 1998, 120, 4049-4050.
(30) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mctavish, S. J.; Solan, G. A.; White, J. P.; Williams, D. J. Chem. Commun. 1998, 311, 849850.
(31) Zhang, W.; Wang, Y.; Yu, J.; Redshaw, C.; Hao, X.; Sun, W.-H. Dalton Trans. 2011, 40, 12856-12865.
(32) Eshtiagh-Hosseini, H.; Aghabozorg, H.; Mirzaei, M.; Amini, M. M.; Chen, Y. G.; Shokrollahi, A.; Aghaei, R. J. Mol. Struct. 2010, 973, 180-189.
(33) Park, H.; Lough, A. J.; Kim, J. C.; Jeong, M. H.; Kang, Y. S. Inorganica Chim. Acta 2007, 360, 2819-2823.
(34) Ebina, M.; Kobayashi, A.; Ogawa, T.; Yoshida, M.; Kato, M. Inorg. Chem. 2015, 54, 8878-8880.
(35) Funaki, T.; Otsuka, H.; Onozawa-Komatsuzaki, N.; Kasuga, K.; Sayama, K.; Sugihara, H. Inorg. Chem. Commun. 2014, 46, 137-139.
(36) Zhang, Y. H.; Yu, J. Q. J. Am. Chem. Soc. 2009, 131, 14654-14655.
(37) Zhang, J.; Khaskin, E.; Anderson, N. P.; Zavalij, P. Y.; Vedernikov, A. N. Chem. Comтии. 2008, 3625-3627.
(38) Wang, D.; Zavalij, P. Y.; Vedernikov, A. N. Organometallics 2013, 32, pp 48824891.
(39) Kettler, P. B. Org. Process Res. Dev. 2003, 7, 342-354.
(40) Apps, M. G.; Choi, E. H. Y.; Wheate, N. J. Endocr. Relat. Cancer 2015, 22, R219-R233.
(41) Davies, M. S.; Berners-Price, S. J.; Hambley, T. W. Inorg. Chem. 2000, 39, 5603-5613.
(42) Todd, R. C.; Lippard, S. J. J. Inorg. Biochem. 2010, 104, 902-908.
(43) Wheate, N. J.; Walker, S.; Craig, G. E.; Oun, R. Dalton Trans. 2010, 39, 81138127.
(44) Reithofer, M. R.; Bytzek, A. K.; Valiahdi, S. M.; Kowol, C. R.; Groessl, M.; Hartinger, C. G.; Jakupec, M. A.; Galanski, M.; Keppler, B. K. J. Inorg. Biochem. 2011, 105, 46-51.
(45) Puddephatt, R. J. Angew. Chem. Int. Ed. 2002, 41, 261-263.
(46) Albrecht, M., Van Koten, G. Angew. Chem. Int. Ed. 2001, 40, 3750-3781.
(47) Albrecht, M.; Lutz, M.; Schreurs, A. M. M.; Lutz, E. T. H.; Spek, A. L.; van Koten, G. Dalton Trans. 2000, 3797-3804.
(48) Elsevier, C. J. Coord. Chem. Rev. 1999, 186, 809-822.
(49) Herrmann, W. A.; Brossmer, C.; Öfele, K.; Reisinger, C.-P.; Priermeier, T.; Beller, M.; Fischer, H. Angew. Chem. Int. Ed. 1995, 34, 1844-1848.
(50) Bianchini, C.; Lenoble, G.; Oberhauser, W.; Parisel, S.; Zanobini, F. Eur. J. Inorg. Chem. 2005, 4794-4800.
(51) Torrente-Murciano, L.; Lapkin, A.; Nielsen, D. J.; Fallis, I.; Cavell, K. J. Green Chem. 2010, 12, 866-869.
(52) Colacot, B. T. J. Platin. Met. Rev. 2012, 2, 110-116.
(53) Ang, W. H.; Casini, A.; Sava, G.; Dyson, P. J. J. Organomet. Chem. 2011, 696, 989-998.
(54) Gallagher, M.; Wieder, N. L.; Dioumaev, V. K.; Carroll, P. J.; Berry, D. H. Organometallics 2010, 29, 591-603.
(55) Yoo, H.; Carroll, P. J.; Berry, D. H. J. Am. Chem. Soc. 2006, 128, 6038-6039.
(56) Nielsen, M.; Alberico, E.; Baumann, W.; Drexler, H.-J.; Junge, H.; Gladiali, S.; Beller, M. Nature 2013, 495, 85-89.
(57) Tseng, K. N. T.; Rizzi, A. M.; Szymczak, N. K. J. Am. Chem. Soc. 2013, 135, 16352-16355.
(58) Manson, A. J. J. Am. Chem. Soc. 1955, 77, 4925-4926.
(59) MacInnis, M. C.; Maclean, D. F.; Lundgren, R. J.; Mcdonald, R.; Turculet, L. Organometallics 2007, 26, 6522-6525.
(60) Baratta, W.; Rigo, P. Eur. J. Inorg. Chem. 2008, 4041-4053.
(61) Uson, R.; Oro, L. A.; Sariego, R.; Esteruelas, M. A. J. Organomet. Chem. 1981, 214, 399-404.
(62) Tabata, T.; Honda, Y.; Yamaguchi, M.; Amano, H. Chem. Commun. 1991, 10631064.
(63) Baratta, W.; Chelucci, G.; Gladiali, S.; Siega, K.; Toniutti, M.; Zanette, M.; Zangrando, E.; Rigo, P. Angew. Chem. Int. Ed. 2005, 44, 6214-6219.
(64) Baratta, W.; Ballico, M.; Zotto, A. Del; Herdtweck, E.; Peloso, S. M. R.; Siega, K.; Toniutti, M.; Zangrando, E.; Rigo, P. Organometallics 2009, 28, 4421-4430.
(65) Moore, C. M.; Szymczak, N. K. Chem. Commun. 2013, 49, 400-402.
(66) Bergman, R. G. Nature 2007, 446, 391.
(67) Shilov, A. E.; Shul'pin, G. B. Chem. Rev. 1997, 97, 2879-2932.
(68) Labinger, J. A.; Bercaw, J. E. Nature 2002, 417, 507.
(69) Boutadla, Y.; Davies, D. L.; Macgregor, S. A.; Poblador-Bahamonde, A. I. Dalton Trans. 2009, 5820-5831.
(70) Berkowitz, J.; Ellison, G. B.; Gutman, D. J. Phys. Chem. 1994, 98, 2744-2765.
(71) Lyons, T.; Sanford, M. Chem. Rev. 2010, 1147-1169.
(72) Crabtree, R. H. J. Chem. Soc., Dalton Trans. 2001, 0, 2437-2450.
(73) Bennett, M. A.; Milner, D. L. Chem. Commun. 1967, 581.
(74) Chatt, J.; Davidson, J. M. J. Chem. Soc. 1965, 843-855.
(75) Clot, E.; Oelckers, B.; Klahn, A. H.; Eisenstein, O.; Perutz, R. N. Dalton Trans. 2003, 4065-4074.
(76) Bergman, R. G. Science 1984, 223, 902-908.
(77) Jones, W. D.; Feher, F. J. Acc. Chem. Res. 1989, 22, 91-100.
(78) J.Tsuji. Palladium Reagents and Catalysts: New Perspectives for the $21 S t$ Century; 2005; Vol. 9.
(79) Topczewski, J. J.; Cabrera, P. J.; Saper, N. I.; Sanford, M. S. Nature 2016, 531, 220-224.
(80) Shi, Z.; Li, B.; Wan, X.; Cheng, J.; Fang, Z.; Cao, B.; Qin, C.; Wang, Y. Angew. Chem. Int. Ed. 2007, 46, 5554-5558.
(81) Gary, J. B.; Cook, A. K.; Sanford, M. S. ACS Catal. 2013, 3, 700-703.
(82) Baratta, W.; Bosco, M.; Chelucci, G.; Del Zotto, A.; Siega, K.; Toniutti, M.; Zangrando, E.; Rigo, P. Organometallics 2006, 25, 4611-4620.
(83) Hosseini-Kharat, M.; Karami, K.; Saeidifar, M.; Rizzoli, C.; Zahedi-Nasab, R.; Sohrabijam, Z.; Sharifi, T. New J. Chem. 2017, 41, 9897-9907.
(84) Cross, W. B.; Hope, E. G.; Lin, Y.-H.; Macgregor, S. A.; Singh, K.; Solan, G. A.; Yahya, N. Chem. Commun. 2013, 49, 1918-1920.
(85) Rao, A. R. B.; Pal, S. J. Organomet. Chem. 2013, 731, 67-72.
(86) Li, H. H.; Maitra, R.; Kuo, Y. T.; Chen, J. H.; Hu, C. H.; Lee, H. M. Appl. Organomet. Chem. 2017, 1-16.
(87) Simayi, R.; Hope, E. G.; Singh, K.; Cross, W. B.; Solan, G. A. J. Organomet. Chem. 2017, 851, 254-264.
(88) Du, W.; Wang, L.; Wu, P.; Yu, Z. Eur. J. Org. Chem 2012, 18, 11550-11554.
(89) Baratta, W.; Ballico, M.; Baldino, S.; Chelucci, G.; Herdtweck, E.; Siega, K.; Magnolia, S.; Rigo, P. Eur. J. Org. Chem 2008, 14, 9148-9160.
(90) Zhao, C.-J.; Xue, D.; Jia, Z.-H.; Wang, C.; Xiao, J. Synlett 2014, 25, 1577-1584.
(91) Venkatachalam, G.; Ramesh, R. Tetrahedron Lett. 2005, 46, 5215-5218.
(92) Choi, J.; MacArthur, A. H. R.; Brookhart, M.; Goldman, A. S. Chem. Rev. 2011, 111, 1761-1779.
(93) O'Reilly, M. E.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. J. Am. Chem. Soc. 2012, 134, 11185-11195.
(94) Dauth, A.; Love, J. A. Dalton Trans. 2012, 41, 8144-8152.
(95) Heyduk, A. F.; Zarkesh, R. A.; Nguyen, A. I. Inorg. Chem. 2011, 50, 9849-9863.
(96) Pontiggia, A. J.; Chaplin, A. B.; Weller, A. S. J. Organomet. Chem. 2011, 696, 2870-2876.
(97) Elliott, P. I. P.; Haslam, C. E.; Spey, S. E.; Haynes, A. Inorg. Chem. 2006, 45, 6269-6275.
(98) O'Reilly, M. E.; Veige, A. S. Chem. Soc. Rev. 2014, 43, 6325-6369.
(99) Sues, P. E.; John, J. M.; Schrock, R. R.; Müller, P. Organometallics 2016, 35, 758-761.
(100) Hanh Nguyen, D.; Pérez-Torrente, J. J.; Lomba, L.; Victoria Jiménez, M.; Lahoz, F. J.; Oro, L. A. Dalton Trans. 2011, 40, 8429-8435.
(101) El, P. C. Polyhedron 1983, 2, 317-322.
(102) Arumugam, V.; Kaminsky, W.; Bhuvanesh, N. S. P.; Nallasamy, D. RSC Adv.

2015, 5, 59428-59436.
(103) Espinet, P.; García-Orodea, E.; Miguel, J. A. Inorg. Chem. 2000, 39, 3645-3651.
(104) Shi, J.; Hu, B.; Gong, D.; Shang, S.; Hou, G.; Chen, D. Dalton Trans. 2016, 45, 4828-4834.
(105) Pandiarajan, D.; Ramesh, R. Inorg. Chem. Commun. 2011, 14, 686-689.
(106) Filonenko, G. A.; van Putten, R.; Hensen, E. J. M.; Pidko, E. A. Chem. Soc. Rev. 2018, 47, 1459-1483.
(107) Fu, S.; Chen, N. Y.; Liu, X.; Shao, Z.; Luo, S. P.; Liu, Q. J. Am. Chem. Soc. 2016, 138, 8588-8594.
(108) Ren, P.; Vechorkin, O.; Csok, Z.; Salihu, I.; Scopelliti, R.; Hu, X. Dalton Trans. 2011, 40, 8906-8911.
(109) Ghoochany, L. T.; Farsadpour, S.; Sun, Y.; Thiel, W. R. Eur. J. Inorg. Chem. 2011, 2011, 3431-3437.
(110) Li, Y.-H.; Ding, X.-H.; Zhang, Y.; He, W.-R.; Huang, W. Inorg. Chem. Commun. 2012, 15, 194-197.
(111) Gagliardo, M.; Chase, P. A.; Brouwer, S.; Van Klink, G. P. M.; Van Koten, G. Organometallics 2007, 26, 2219-2227.
(112) Amoroso, D.; Jabri, A.; Yap, G. P. A.; Gusev, D. G.; Dos Santos, E. N.; Fogg, D. E. Organometallics 2004, 23, 4047-4054.
(113) Chen, T.; He, L.-P.; Gong, D.; Yang, L.; Miao, X.; Eppinger, J.; Huang, K.-W. Tetrahedron Lett. 2012, 53, 4409-4412.
(114) Chowdhury, R. L.; Backvall, J.-E. J. Chem. Soc., Chem. Commun. 1991, 10631064.
(115) Baratta, W.; Siega, K.; Rigo, P. Eur. J. Org. Chem 2007, 13, 7479-7486.
(116) Zacharopoulos, N.; Koukoulakis, K.; Bakeas, E.; Philippopoulos, A. I. Open Chem. 2016, 14, 308-315.
(117) Zhou, C.; Zhang, J.; Daković, M.; Popović, Z.; Zhao, X.; Liu, Y. Eur. J. Inorg. Chem. 2012, 3435-3440.
(118) De Araujo, M. P.; De Figueiredo, A. T.; Bogado, A. L.; Von Poelhsitz, G.; Ellena, J.; Castellano, E. E.; Donnici, C. L.; Comasseto, J. V.; Batista, A. A. Organometallics 2005, 24, 6159-6168.
(119) Standfest-Hauser, C.; Slugove, C.; Mereiter, K.; Schmid, R.; Kirchner, K.; Xiao, L.; Weissensteiner, W. J. Chem. Soc. Dalt. Trans. 2001, 108, 2989-2995.
(120) Brooke L. Small, M.; Brookhart, A. M. A. B. J. Am. Chem. Soc. 1998, 120, 4049-4050.
(121) Britovsek, George J. P., Vernon C. Gibson, Brian S. Kimberley, Peter J. Maddox, Stuart J. McTavish, Gregory A. Solan, Andrew J.P. White, D. J. W. Chem. Соттии. 1998, 0, 849-850.
(122) Bianchini, C.; Mantovani, G.; Meli, A.; Migliacci, F.; Laschi, F. Organometallics 2003, 22, 2545-2547.
(123) Bianchini, C.; Gatteschi, D.; Giambastiani, G.; Guerrero Rios, I.; Ienco, A.; Laschi, F.; Mealli, C.; Meli, A.; Sorace, L.; Toti, A.; Vizza, F. Organometallics 2007, 26, 726-739.
(124) Sun, W. H.; Tang, X.; Gao, T.; Wu, B.; Zhang, W.; Ma, H. Organometallics 2004, 23, 5037-5047.
(125) Tang, X.; Sun, W. H.; Gao, T.; Hou, J.; Chen, J.; Chen, W. J. Organomet. Chem. 2005, 690, 1570-1580.
(126) Su, B. Y.; Zhao, J. S. Polyhedron 2006, 25, 3289-3298.
(127) Su, B.; Zhao, J.; Zhang, Q.; Qin, W. Polym. Int. 2009, 58, 1051-1057.
(128) Jie, S.; Ai, P.; Zhou, Q.; Li, B.-G. J. Organomet. Chem. 2011, 696, 1465-1473.
(129) Liu, J.-Y.; Zheng, Y.; Li, Y.-G.; Pan, L.; Li, Y.-S.; Hu, N.-H. J. Organomet. Chem. 2005, 690, 1233-1239.
(130) Wenjuan Zhang, Biao Wu, W.-H. S. Stud. Surf. Sci. Catal. 2006, 161, 141-146.
(131) Emig, N.; Nguyen, H.; Krautscheid, H.; Réau, R.; Cazaux, J.-B.; Bertrand, G. Organometallics 1998, 17, 3599-3608.
(132) Schrock, R. R.; Bonitatebus, P. J.; Schrodi, Y. Organometallics 2001, 20, 1056-
1058.
(133) Feghali, K.; Harding, D. J.; Reardon, D.; Gambarotta, S.; Yap, G.; Wang, Q. Organometallics 2002, 21, 968-976.
(134) Cowdell, R.; Davies, J. C.; Hilton, J. S.; Marechal, J.-D.; Solan, G. A.; Thomas, O.; Fawcett, J. Dalton Trans. 2004, 3231-3240.
(135) Davies, C. J.; Hilton, S. J.; Solan, G. A.; Stannard, W.; Fawcett, J. Polyhedron 2005, 24, 2017-2026.
(136) Ward, B. D.; Dubberley, S. R.; Maisse-Francois, A.; Gade, L. H.; Mountford, P. J. Chem. Soc., Dalton Trans. 2002, 2, 4649-4657.
(137) Whitesides, G. M.; Boncheva, M. Proc. Natl. Acad. Sci. 2002, 99, 4769-4774.
(138) Park, J.; Lang, K.; Abboud, K. A.; Hong, S. Eur. J. Org. Chem 2011, 17, 22362245.
(139) Steiner, T. Angew. Chem. Int. Ed. 2002, 41, 48-76.
(140) Kluge, T.; Bette, M.; Rüffer, T.; Bruhn, C.; Wagner, C.; Ströhl, D.; Schmidt, J.; Steinborn, D. Organometallics 2013, 32, 7090-7106.
(141) Steed, J. W. Chem. Soc. Rev. 2009, 38, 506-519.
(142) Raynal, M.; Ballester, P.; Vidal-Ferran, A.; van Leeuwen, P. W. N. M. Chem. Soc. Rev. 2014, 43, 1660-1733.
(143) Park, J.; Lang, K.; Abboud, K. A.; Hong, S. J. Am. Chem. Soc. 2008, 130, 16484-16485.
(144) Hammes, G. G.; Lillford, P. J. J. Am. Chem. Soc. 1970, 92, 7578-7585.
(145) Weis, M.; Waloch, C.; Seiche, W.; Breit, B. J. Am. Chem. Soc. 2006, 128, 41884189.
(146) Klare, H.; Neudörfl, J. M.; Goldfuss, B. Beilstein J. Org. Chem. 2014, 10, $224-$ 236.
(147) Gu, Q.; You, S.-L. Chem. Sci. 2011, 2, 1519-1522.
(148) Johnson, J. S.; Evans, D. A. Acc. Chem. Res. 2000, 33, 325-335.
(149) Nishizawa, S.; Bühlmann, P.; Iwao, M.; Umezawa, Y. Tetrahedron Lett. 1995, 36, 6483-6486.
(150) Kelly, T. R.; Kim, M. H. J. Am. Chem. Soc. 1994, 116, 7072-7080.
(151) Riggio, G.; Hopff, W. H.; Hofmann, A. A.; Waser, P. G. Helv. Chim. Acta 1980, 63, 488-497.
(152) Paul, F.; Patt, J.; Hartwig, J. F. J. Am. Chem. Soc. 1994, 116, 5969-5970.
(153) Wolfe, J. P.; Wagaw, S.; Buchwald, S. L. J. Am. Chem. Soc. 1996, 118, 72157216.
(154) In Inorganic Syntheses; John Wiley \& Sons, Inc., 2007; pp 121-124.
(155) Matthews, C. J. J. Mol. Catal. A Chem. 2003, 206, 77-82.
(156) Miecznikowski, J. R.; Caradonna, J. P.; Foley, K. M.; Kwiecien, D. J.; Lisi, G. P.; Martinez, A. M. J. Chem. Educ. 2011, 88, 657-661.
(157) Evans, D. F. J. Chem. Soc. 1959, 2003-2005.
(158) Evans, D. F.; Jakubovic, D. A. J. Chem. Soc., Dalton Trans. 1988, 2927-2933.
(159) Sun, W. H.; Tang, X.; Gao, T.; Wu, B.; Zhang, W.; Ma, H. Organometallics 2004, 23, 5037-5947.
(160) Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. J. Am. Chem. Soc. 1999, 121, 2674-2678.
(161) Kingsbury, J. S.; Garber, S. B.; Giftos, J. M.; Gray, B. L.; Okamoto, M. M.; Farrer, R. A.; Fourkas, J. T.; Hoveyda, A. H. Angew. Chem. Int. Ed. 2001, 40, 4251-4256.
(162) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. Org. Lett. 1999, 1, 953-956.

