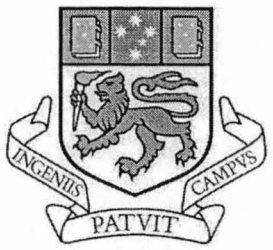

UNIVERSITY
OF TASMANIA

Catalytic Studies of Low Valent Palladium *N*-Heterocyclic Carbene Complexes

By

Anung Riapanitra

A thesis submitted in partial fulfilment of the requirements

for the degree of Master of Science in Chemistry

at the University of Tasmania

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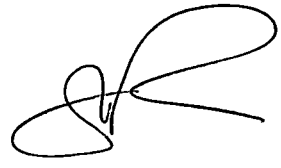
Declaration

To the best of my knowledge, this thesis contains no copy or paraphrase of material previously published or written except where due reference is included in the text.



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Abstract

This thesis describes the synthesis of low valent *N*-heterocyclic carbene palladium complexes. The aim of this project was to investigate the identity of *in situ* formed *N*-heterocyclic carbene palladium species under catalytically relevant reaction conditions from palladium(II) precatalysts. This aim was underpinned by the importance of neutral and cationic palladium(II) complexes widely used as precatalysts for carbon monoxide/ethene copolymerisation as well as various related C-C coupling reactions.

The use of bulky chelating ligands is an important factor for catalytic performance in these reactions. Consequently, we focussed on a variety of aryl-substituted methylene bridged bis(*N*-heterocyclic carbene) palladium complexes. In order to achieve our aims, various attempts to synthesise complexes under reductive/basic conditions were undertaken, which led to the synthesis of several known precursors and novel complexes.

Reaction of the dicationic Pd(II) complexes [{1,1'-di(aryl)-3,3'-methylenediimidazolin-2,2'-diylidene}palladium(II)bis(acetonitrile)][PF_6]$_2$ (aryl = 2,4,6-mesityl and 2,6-diisopropylphenyl) with sodium carbonate in methanol afforded novel dipalladium(I) hydride complexes [{bis(μ-carbene)}$_2$$Pd_2H$][$PF_6$]. Steric influences led to major structural differences; Pd-Pd-H core (for 2,4,6-mesityl) and linear Pd-H-Pd core (for 2,6-diisopropylphenyl). The complexes were characterised by ^1H, ^{13}C, 2D and VT NMR spectroscopy (revealing differences in fluxional behaviour), mass spectroscopy, microanalysis and X-ray and neutron (2,4,6-mesityl only) crystallography. The metal oxidation states of both dipalladium hydride complexes have been shown to be Pd(I) by DFT calculations, but the precise nature of the Pd-Pd-H and Pd-H-Pd interactions remains to be confirmed. The synthesis of analogous complexes with less bulky phenyl and *tert*-butyl substituents were unsuccessful.

The reactivity of these cationic dinuclear Pd(I) hydride complexes as catalysts were examined in carbon monoxide/ethene copolymerisation as well as various C-C coupling reactions (2,4,6-mesityl substituent only for the latter). Their poor performance indicated that the dipalladium(I) hydride complexes were inefficient catalysts for carbon monoxide/ethene copolymerisation, which may suggest that a palladium methoxide species is the actual catalyst instead of palladium hydride species.

Table of Contents

Abbreviations

$(CF_3)_2C(D)OD$	deuterated 1,1,1,3,3,3-hexafluoro-2-propanol
Å	Angström, 10^{-10} m
Ar	aryl
bipy	2,2'-bipiridyl
bs	broad singlet (NMR)
C_6D_6	deuterated benzene
cat.	catalyst
CD_3OD	deuterated methanol
$CDCl_3$	deuterated chloroform
CO	carbon monoxide
COD	1,5-cyclooctadiene
COSY	correlation spectroscopy
Cp	cyclopentadienyl
d	doublet (NMR)
dba	dibenzylideneacetone
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCM	dichloromethane
dippp	1,3-bis(diisopropylphosphino)propane
DMAc	*N*,*N*-dimethylacetamide
DMSO	dimethyl sulfoxide
DMSO-d_6	deuterated dimethyl sulfoxide
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
ESI-MS	electrospray ionisation-mass spectrometry

Et	ethyl
GC-MS	gas chromatography-mass spectrometry
HMBC	heteronuclear multiple bond correlation
HMQC	heteronuclear multiple quantum correlation
R_2Im	1,3-alkyl-imidazolin-2-ylidene
ipso-	*ipso*
*i*Pr	isopropyl
kcal	kilocalorie
KOtBu	potassium *tert*-butoxide
L	ligand
LSI-MS	liquid secondary ion-mass spectrometry
m-	*meta*
M	metal
m	multiplet (NMR)
MAO	methyl aluminoxane
Me	methyl
Mes	mesityl; 2,4,6-trimethylphenyl
n	normal
NHC	*N*-heterocyclic carbene
NMR	nuclear magnetic resonance
o-	*ortho*
p-	*para*
pent	pentet (NMR)
Ph	phenyl
ppm	parts per million
q	quartet (NMR)
R	alkyl, aryl
s	singlet (NMR)

sept	septet (NMR)
t	triplet (NMR)
tert-	tertiary
THF	tetrahydrofuran
THF-d_8	deuterated tetrahydrofuran
TON	turnover number
VT NMR	variable temperature nuclear magnetic resonance

Chapter 1: Introduction

1.1 Carbenes and Traditional Carbene Complexes

A carbene is defined as an uncharged component/molecule with a neutral dicoordinate carbon atom and two unshared electrons. These electrons can be assigned to nonbonding orbitals in different ways. Carbenes were first observed by chemists in 1950's from the work of Doering and Hoffman.[1] They have been used in numerous applications in synthesis and catalysis such as in olefin metathesis and cyclopropanation of olefins.[2]

The carbon atoms of carbenes typically tend to adopt bent geometries, instead of the linear possibility, to possess sp^2 type hybridisation with σ and p_π as the frontier orbitals. Carbene has four electronic configurations available, Figure 1.1.

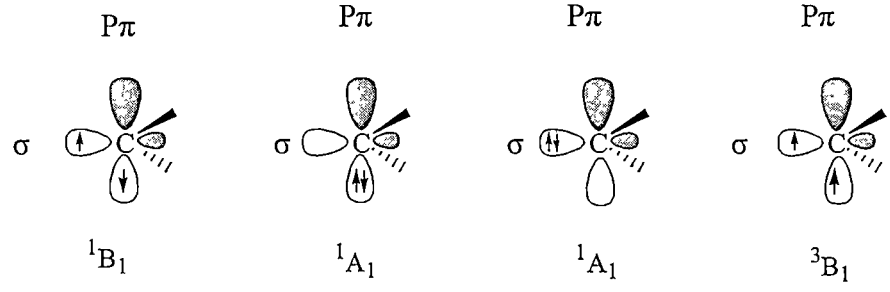


Figure 1.1 Electronic configurations of carbenes

Of the four electronic configurations of carbene, two feature electron pairing in the two nonbonding orbitals in either the same σ or p_π creating orbital (singlet carbene), therefore there are two different $^1A_1$ states. The σ^2 is more stable than the p_π^2 configuration. The other two configurations are triplet carbenes ($^3B_1$, $^1B_1$). Singlet carbenes possess favourable carbene ground-state multiplicity that is easier to be stabilised sterically or electronically with substitution patterns.[3]

Metal carbenes were introduced into organometallic chemistry by Fischer and Maasböl.[4] The development of metal carbene chemistry was continued with the wide development of what, nowadays, are known as traditional carbenes

which was started from Fischer type carbenes, Figure 1.2 (a)[5], and were extended to Schrock type carbenes (b)[6], which are in some ways comparable with Fischer carbenes. The isolation of a stable free carbene by Arduengo[7] in 1991 sparked great activity, which was preceded by the development of metal complexes of this carbene type by Wanzlick[8-10] and Öfele[11] many years prior in 1968. This new class of carbene has very different reaction patterns compared with Fischer and Schrock type carbenes; the *N*-Heterocyclic Carbenes (NHC).

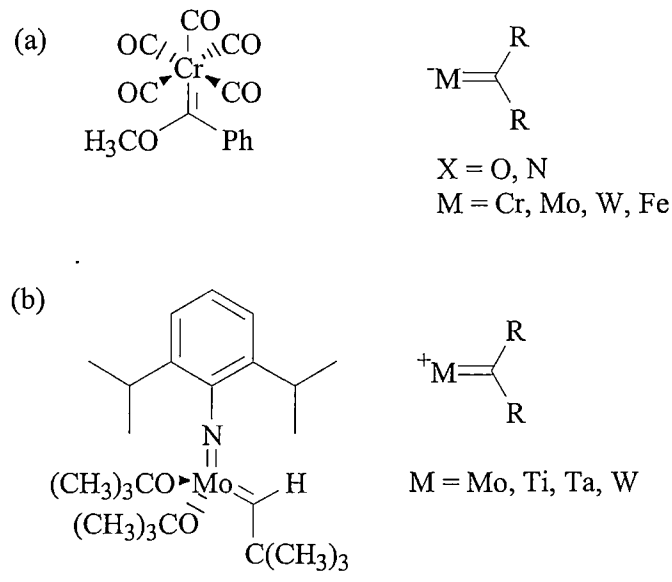


Figure 1.2 Fischer and Schrock carbene complexes

Fischer type carbene complexes are classically comprised of $M(CO)_5$ complexes, where M is chromium, molybdenum or tungsten and bound with CO ligands, prepared by an organolithium reaction. The formula is $(CO)_5M=C(X)R$ where X is a π-donor substituent and R is an alkyl, aryl, unsaturated and alkenyl or alkynyl. The CO ligands act as π-accepting electron withdrawing ligands that stabilise and delocalise the formation of such Fischer carbene complexes. This type of carbene possesses significant carbene to metal σ- donation and the difference between donation and back donation creates a separation of charge. Electron deficiency of the carbene is the reason why this carbene type is electrophilic and is easily attacked by nucleophiles.

Schrock type carbenes are typified by coordination to metals in high oxidation states with strong donor ligands such as alkyl or cyclopentadienyl without π-acceptor ligands. The formula for Schrock type carbenes is, for example $[R_3Ta{=}CHC(CH_3)_3]$. They do not have any stabilising substituents on the carbene ligand. Characteristic of Schrock type carbene complexes is that their interaction with transition metal feature a triplet state, therefore it leads to a balanced electronic interaction.

1.2 Free *N*-Heterocyclic Carbenes

Wanzlick carbene complexes, Figure 1.3, were discovered by Wanzlick and Öfele in between the discovery of Fischer and Schrock type carbenes. However, isolable free carbenes of this type were not obtained for some years later. This complex type is now well known for their role in alkene metathesis catalysis by Herrmann and Grubbs.[12-15] The *N*-substituents that provide a π-donor and σ-acceptor ability increases the stability of the carbene by stabilising the carbon-based lone pair by filling the *p*-orbital of the carbon atom.

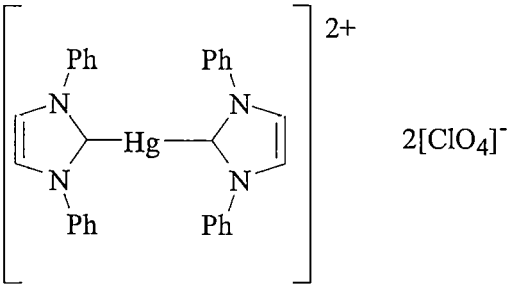


Figure 1.3 The first Wanzlick carbene complex

After the discovery of the first isolable, stable free NHC carbene by Arduengo in 1991[7], *N*-heterocyclic carbenes have been of great interest. The stability of this kind of carbene is one of the main interests, especially when steric bulk is not a requirement for stability, as both aromatic and saturated NHCs with five membered rings are known to be stable.[9,16,17] Imidazolin-2-ylidenes, Figure 1.4, (A) and the saturated imidazolidin-2-ylidenes (D) are stabilised by electron donation from the nitrogen *p*-orbital based lone pairs to the empty p_π-orbital of the carbon. Particularly for imidazolin-2-ylidenes, the cyclic 6π electron

delocalisation within the carbene possesses aromatic character.[18] NHCs show increased donor capacity relative to phosphine or trialkylphosphines and the π-acceptor capacity of NHCs are of the order of nitrile and pyridine ligands.[19] Compared with other non-carbon based heterocyclic analogues such as silylenes and germylenes (B, C, E and F), the order of metal-ligand bond dissociation energy is C > Si > Ge.[20]

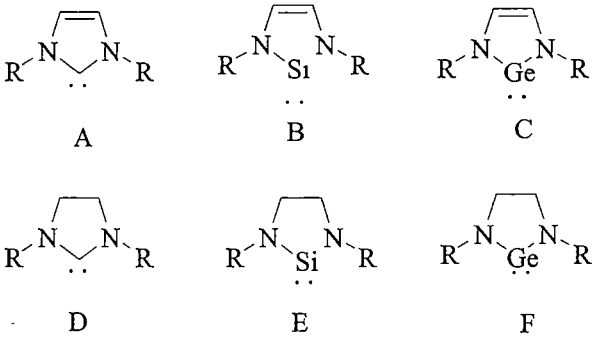


Figure 1.4 Unsaturated and saturated *N*-heterocyclic carbenes, silylene and germylenes

The type and number of heteroatoms in the NHCs determines its suffix naming. For a five-member ring that contains minimal 1 nitrogen atom the saturated system is given suffix (-olidine), one double bond (-oline) and for maximum number of double bond (-ole). Ylidenes refer to compounds where the hydrogen 2-substituent is replaced by two electrons.[21] As an example, Figure 1.5, (a) is the formal tautomer of 1-*H*-imidazole. Protonation of (a) at N3 position results in 1,3-dihydroimidazolium ion (b). Subsequent deprotonation of (b) at the C2 centre yields the 1,3-dihydrosubstituted ylidene (c).

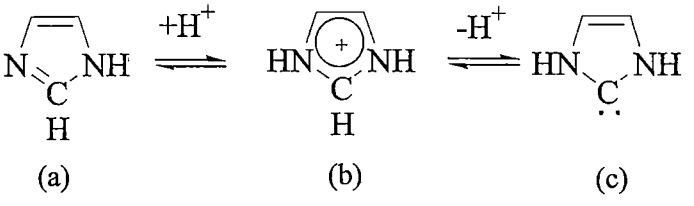


Figure 1.5 Example of nomenclature of ylidene[21]

Since the first reported free *N*-heterocyclic carbene, many different kinds have been synthesised, Figure 1.6, starting from the unsaturated cyclic diamino carbene; imidazolin-2-ylidenes (G), 1,2-pyrazolin-5-ylidenes (H), 1,2,4-triazolin-5-ylidenes (I), saturated imidazolidin-2-ylidenes (J), or systems where the nitrogen was replaced by sulphur (K) as well as the six-membered saturated tetrahydropyrimid-2-ylidenes (L). The development of NHCs has expanded even more with the discovery of C4 bonding in imidazolydenes.[3] Some examples[22] of the less stabilising heteroatom systems (M-R), the so called "abnormal carbenes" includes the imidazolium derivative that binds to metal via C4 or C5 carbon (M-N), pyridylidene carbene (O) with only one heteroatom in the heterocyclic skeleton, as well as remote carbenes (Q). Remote carbenes were derived from pyrazolium, isothiazolium and quinolinium salts with the stabilising heteroatom in a remote position. Low heteroatom stabilised carbenes (R) with only one heteroatom that lack delocalisation through the heterocycle have been discovered and shown to be versatile ligand systems.[22] Larger ring sizes have also been developed.

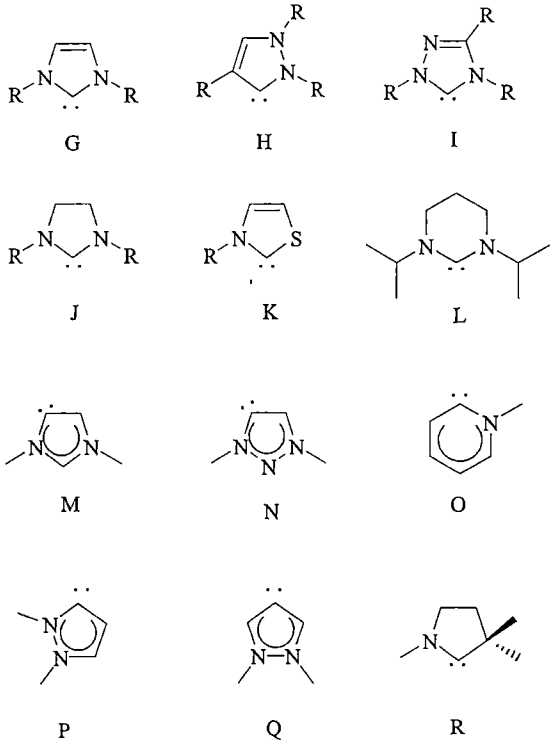


Figure 1.6 Different classes of *N*-heterocyclic carbenes

1.2.1 Structure and properties of *N*-heterocyclic carbenes

NHCs stabilise carbene, CH_2, by substituting two hydrogen atoms with σ-electron withdrawing, π-electron donating heteroatoms. NHCs have singlet carbene characteristics from its N-C-N angle 102.2°.[7] *Ab initio* studies by Arduengo determined that the proton affinity of unsubstituted imidazol-2-ylidene is about 250 kcal mol^{-1} making it one of the strongest organic Brönsted bases.[23] Ylidic resonance forms are a minor influence and the π-back-donation is negligible.[24] The unsaturated carbene based on imidazolin-2-ylidene is more stable than its saturated analogue by 20 kcal mol^{-1}.[25]

Being more σ-donating than Fischer and Schrock carbenes, the metal-carbene bond in NHC complexes is longer and has higher dissociation energies making it quite inert for cleavage. Metal-carbene, M-C, bonds in NHC complexes are generalised by Herrmann to be > 2.10 Å, whereas for Fischer and Schrock carbenes this distance is less than 2.00 Å due to back-bonding.[26]

Representing the true structure of a free NHC is difficult; therefore the general consideration is to draw single bonds between the carbene carbon centre and the flanking heteroatoms. In metal complexes of NHC, the electron pair is involved in the dative single bond between the metal and carbene carbon centre.[27]

1.2.2 Preparation of *N*-heterocyclic carbenes

Arduengo[7] prepared the first free stable carbene that was isolable by deprotonation of 1,3-bis(1-adamantyl)imidazolium chloride, Figure 1.7, which made possible the further preparation of metal-NHC complexes in a direct manner. With this route, various metal precursors can be used regardless of their ligand sphere and oxidation state in direct reaction with the NHC. The stable free carbene isolated by Arduengo has a melting point of 240-241°C, and quickly decomposed at room temperature in solution.[7]

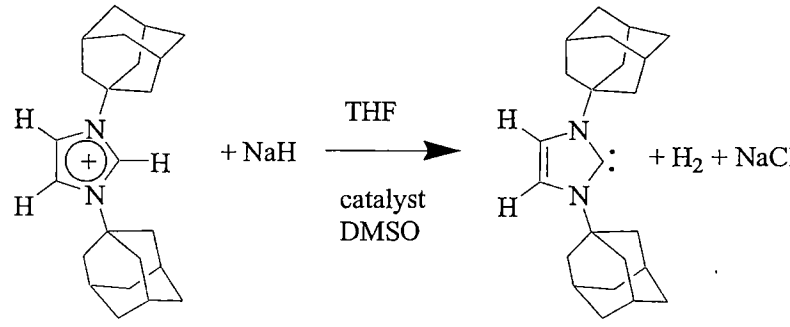
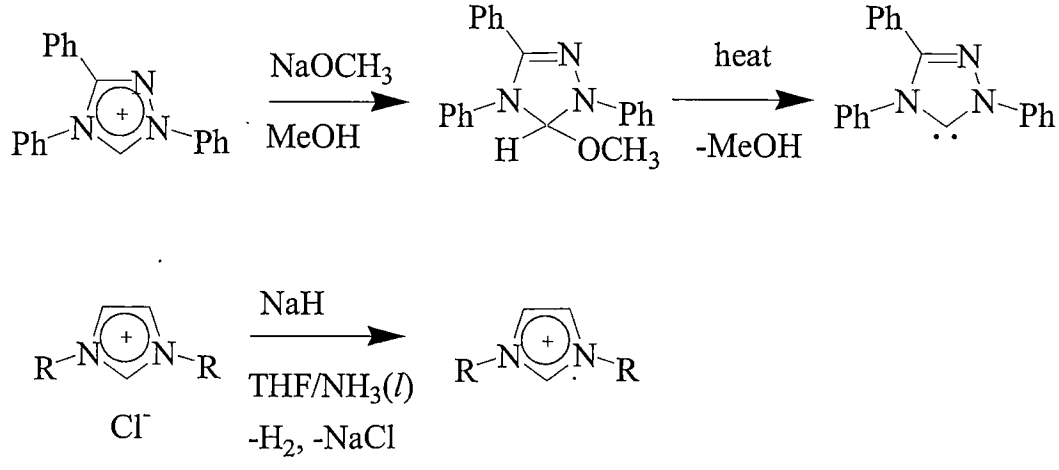


Figure 1.7 Synthesis of the first isolable carbene by Arduengo

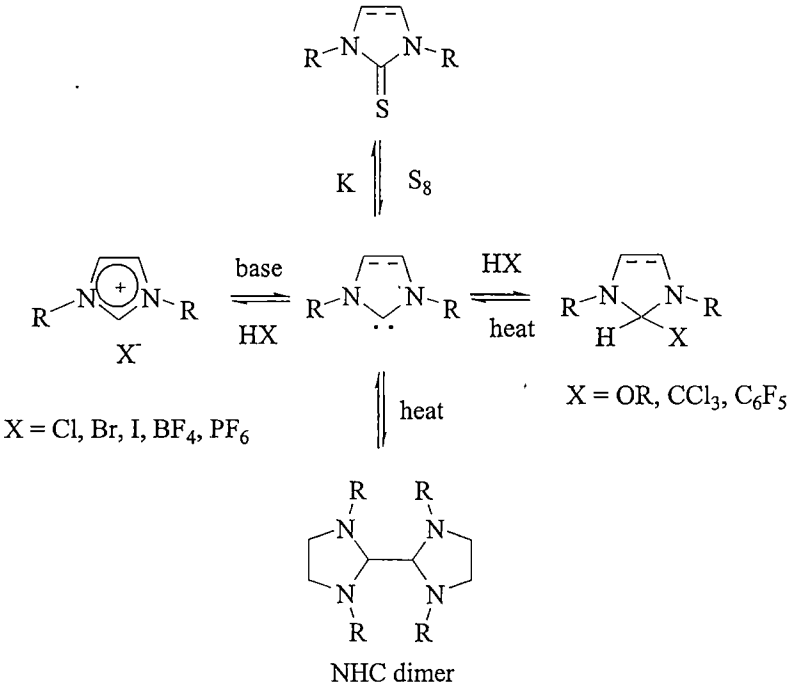
Around 1996, the synthesis of NHCs using liquid ammonia with organic amines and polar aprotic solvents became a standard route known as the ammonia method. In liquid ammonia, deprotonation of the corresponding azolium salts with reagents such as metal hydrides, -alkoxides, and -carboxylates at temperatures between -75 and 0 °C is commonly conducted.[26] Nowadays, the preparation of NHCs is considered as an easy access with various routes of synthesis available which are described below.

NHCs are usually prepared by reacting an azolium salt precursor with a strong base.[7,17,28] Examples include deprotonation of imidazolium salt precursors with sodium hydride, NaOMe in MeOH and KOtBu in THF.[7,28] Generation of NHCs by reaction of NaH and liquid ammonia mixtures is illustrated in Scheme 1.1.



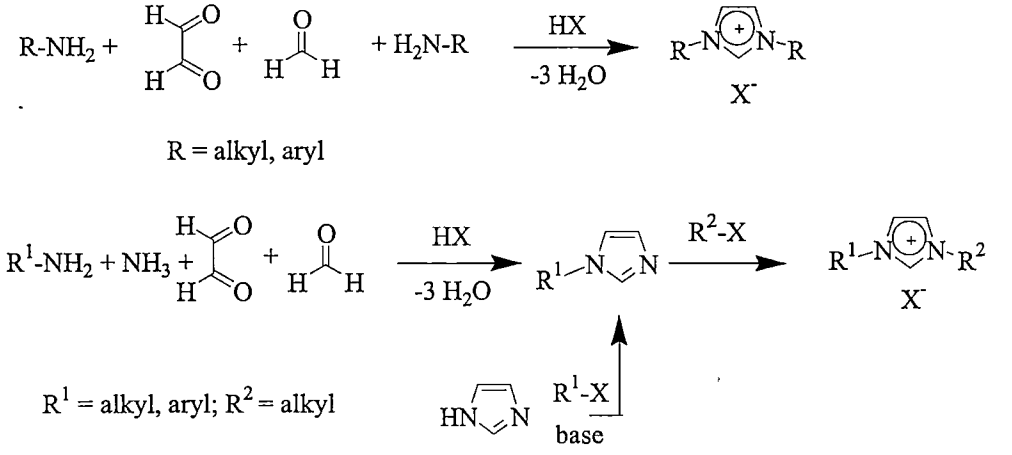
Scheme 1.1 Preparation of free NHCs from imidazolium salts with strong bases

Saturated carbenes can be prepared by 1,1-elimination of alcohol[29,30], chloroform[31,32] and pentafluorobenzene[32]; reduction of thioureas with molten potassium and by heating carbene dimers, Scheme 1.2.[33-35]



Scheme 1.2 Preparation of NHC (⎓ = single or double bond)

Symmetrically substituted imidazolium cations can be prepared by reacting the precursor primary amine, glyoxal and formaldehyde in strong acids while unsymmetrical imidazolium salts can be prepared by alkylation of *N*-aryl or *N*-alkyl imidazoles, Scheme 1.3.[36-38]



Scheme 1.3 Preparation of symmetrical and unsymmetrical imidazolium salts

1.2.3 *N*-Heterocyclic carbenes and phosphines

NHCs are stronger σ electron donors than phosphines, proven by comparisons of CO stretches in infrared spectra of the following complexes $[LNi(CO)_2]$ or $[LNi(CO)_3]$, $[LIr(CO)_2Cl]$ or $[LRh(CO)_2Cl]$, where L is NHC or PR_3.[39,40] A carbene with non linear sp^2 hybridisation of the carbon atom can have either a singlet or triplet carbene ground state, but only the former have been isolated as crystalline compounds.[3,41]

One of the advantages of NHC ligands is that the nitrogen substituents that determine the bulkiness of ligand are not directly connected to the carbene carbon atom and, thus, create only limited effects on the electron density of the carbene donor atom.[27] Therefore, electronic and steric properties of NHC can be tuned independently. Based on topology properties, the nitrogen substituents of an NHC ligand are directed forward to the metal centre while the opposite is the case for phosphine ligands. This arrangement leads to stronger steric effects of NHCs on the metal centres.[27]

Varying the steric bulk at the substituents on the NHC will give a positive effect on the tuning of NHC ligands. For example, 2,6-diisopropylphenyl substituents give the best option, while mesityl and adamantyl follow subsequently.[42-44] NHCs act as neutral 2 electron donors to form a single bond to metal centres.[26,45,46] π-back bonding donation of metal to NHC π*-orbital is negligible.[24,47] The heterocyclic moiety is responsible for electronic properties of the NHC ligand.[48] Unsaturated NHCs have advantages over its saturated counterparts since its aromatic-supported stability helps its life span, especially under high temperature cross-coupling reaction conditions. The possibility to fine tune the metal centre by varying the substituents in the 4,5-positions of the aromatic ring was apparent from the ^{13}C NMR resonance of carbene carbon atom, which is shifted for different substituents. Electron withdrawing groups like halogens lead to shifts of the carbene carbon signal to lower field due to the higher partial negative charge at the carbene carbon atom of the complex, *vice versa* for the use of electron donating group such as 4-methoxyphenyl.[49]

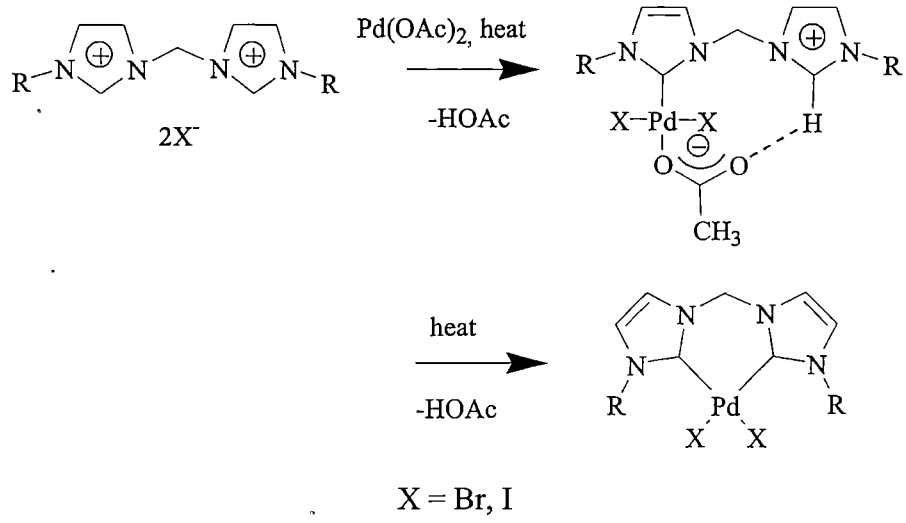
Gusev[50] reported that small unsaturated and saturated *N*-heterocyclic carbenes with *N*-Me groups have net donor properties similar to PMe_3 and PEt_3, respectively. For unsaturated carbenes, extending the bulkiness of ligand will improve the donor properties and create the same effect as for trialkylphosphines. Abnormal carbenes with methyl attached on C_1 and C_4 outperform the use of NMe_3. The thermodynamic parameters of the reaction of $Ir(C_5H_5)(CO)L$ + $Ir(C_5H_5)(L')$ $\leftrightharpoons$ $Ir(C_5H_5)(CO)L'$ + $Ir(C_5H_5)(L)$, with L = NHC and L' = PF_3 confirmed that bulky *N*-heterocyclic carbenes are described as the best ligands for $Ir(C_5H_5)(CO)L$ complexes, that arises for ligands giving better σ- and π-bonding of the CO to the metal. However, it also showed that NHCs might not be the best ligands to support reactions involving high formal oxidation states of the metal centre, in contrast of what has been reported by Nolan and co-workers.[45]

1.3 *N*-Heterocyclic Carbene Metal Complexes

There are three major routes for the synthesis of NHC metal complexes.[51]

1. Deprotonation of azolium salts

In situ deprotonation enabled the creation of metal-carbene complexes without the need to prepare the free carbene, Scheme 1.4. This method was used firstly by Öfele to create the first metal complex.[11] Deprotonation of azolium salts by basic metal complexes that also functioned as the ligand acceptor has been used to prepare benzimidazolium, pyrazolium, triazolium and tetrazolium salts, although the metal precursor is sometimes hard to obtain.[52-54] Acetate salts, acetylacetonate salts or metal alkoxides are frequently used as the Brönsted base to provide the NHC ligand by *in situ* deprotonation. The new complex may incorporate new anionic ligands arising from counter anions of the azolium salts unless a non-coordinating anion is used. This route is especially useful for the preparation of methylene bridged chelated NHC complexes.[55-57]



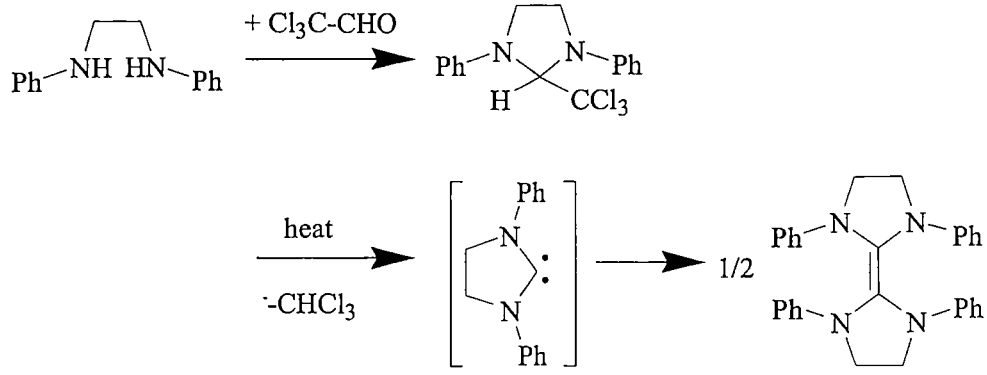
Scheme 1.4 Preparation of palladium(II) NHC complexes by deprotonation of azolium salts

2. Complexation of preformed free NHC

This method has been discussed in Section 1.2.2.

3. Cleavage of electron rich olefins

Electron rich olefins are nucleophilic. Dimerisation of non stable NHCs can be used to make tetraaminoethenes as electron rich olefins that can be converted to metal-NHC complexes in several ways, including thermal cleavage by heating in refluxing toluene in the presence of Mn, Fe, Ru, Co and Ni carbonyl complexes, for example.[34,58,59] Tetraaminoethenes can be prepared by deprotonation of imidazolium salts with Grignard reagent followed by autocoupling of these species, or other approaches such as shown in, Scheme 1.5.[60]



Scheme 1.5 Preparation of electron rich tetraaminoethenes

1.4 Palladium NHC Complexes and Catalysis

Transition metal NHC complexes have been used extensively in organic synthesis for over a decade. The study of these complexes is mainly concerned with the use of the carbene ligand/s as non-participatory ligand/s in catalytic processes where the carbene is not consumed during the reaction. Interestingly, free NHCs, themselves, are finding applications in organocatalysis.

Since 1972 carbene complexes have been used as olefin metathesis and hydrosilylation catalysts with ruthenium and rhodium, repectively.[61] Later it was the Herrmann group that realised the similarity of the properties of *N*-heterocyclic carbenes as a mimic of phosphines.[61] They utilised palladium NHC complexes as catalysts for the Heck carbon-carbon coupling reaction. This study was regarded as highly successful and since then interest on *N*-heterocyclic carbenes continues to grow and new catalysts are being developed for various C-C and C-N coupling reactions such as Heck, Suzuki, Stille, etc. NHC metal complexes can also catalyse other reactions such as transesterification/acylation of various enol esters with primary alcohols.[62]

Palladium is the most widely used transition metal in organometallic catalysis. This is due to its versatility for carbon-carbon bond formations.[63] Compared to other metal such as Rh, Pt and Os, palladium is less expensive and less toxic as well. Carbon-carbon coupling reactions build new single bonds between a nucleophilic and an electrophilic (organic halide or pseudo halide)

carbon.[64] They are often driven thermodynamically by the formation of inorganic salt. Palladium is so far the best metal for this reaction type. The advantages of using NHC ligands in these reactions are; the NHC ligand helps the metal centre undergo the oxidative addition step into both activated and non-activated aryl halides since it has good σ-donating properties.[65-67] It also helps the reductive elimination process by the steric bulk of the ligand and, in addition, a strong Pd-C bond to the NHC disfavours the decomposition to palladium black during and after the reaction.[68,69]

Specifically in comparison to phosphine catalysis, there are several advantages of the use of *N*-heterocyclic carbene complexes as catalysts in cross-coupling reactions that emphasise that they are not just mimics of phosphine catalysts but rather they offer more than that. Phosphine catalysts are usually air sensitive and susceptible to ligand oxidation. At high temperature P-C bond degradation may also occur which results in deactivation of the catalyst, which is why higher concentration loadings are often needed. NHC ligands can overcome these weaknesses; they are non toxic, require low loading and are more stable with respect to decomposition at high temperature.[57] NHCs appear to be stronger ligands which show low dissociation from the metal in solution.[70]

The role of NHCs in catalytic reactions is to stabilise reactive intermediates or transition states as well as affecting activity and selectivity through electronic and steric effects.[71,72] In cross-coupling reactions, the choice of supporting ligand is particularly important since it can affect both oxidative addition and reductive elimination steps via stabilisation of metal centre at each stage of the catalytic cycle.[73] NHC complexes of Pd(II) salts as precatalysts in Heck and Suzuki reactions show that they are able to activate chloro- and bromo-arenes,[57,73,74] reacting with the difficult aryl chloride substrates due to high thermal stability and tuneability of steric and electronic parameters. Generation of the active catalysts *in situ* gives poor control over the amount of active catalyst produced and the chemical composition. Therefore a well defined Pd(0) NHC complex is needed to allow quantitative performance analysis and allow improved development.

Several groups are now extensively studying the utilisation of *N*-heterocyclic carbene complexes as precatalysts in catalytic reactions, especially C-C cross-coupling reactions. Herrmann *et al.* utilised NHC complexes of Pd(II) in Heck and Suzuki reactions, showing that they can activate chloro- and bromoarenes.[57] The Herrmann group have also utilised NHCs mixed with the traditional phosphine ligands,[75] phosphapalladacyclic ligands,[76] as well as Pd NHC complexes immobilised on Wang resin[70], Figure 1.8. The use of homoleptic NHC Pd(0) catalysts has also been reviewed, showing the necessity of bulky ligands for increased activity.[77]

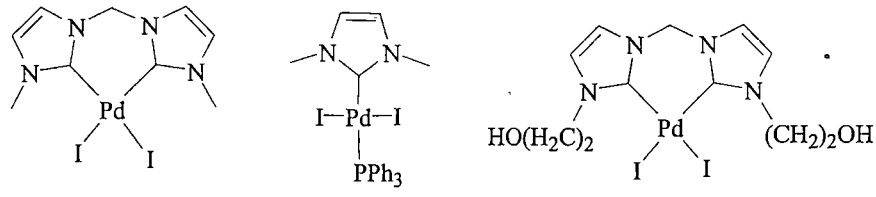
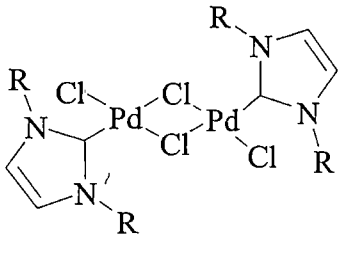
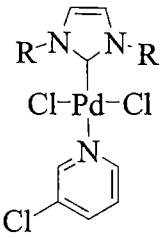


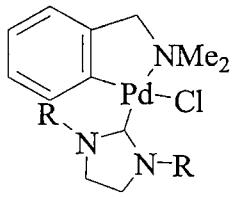
Figure 1.8 Examples of Pd NHC systems reported by Herrmann

Whilst not necessarily being the first group to develop particular catalysts or catalytic reactions, another group that examines the use of NHC complexes is Nolan *et al.* using monodentate[78-82] and bidentate[83] NHC Pd(II) complexes as precatalysts in Suzuki and Heck reactions as well as other reactions such as aryl amination, Figure 1.9. Some Pd(II) precatalysts range from dimeric complexes with bridging halides,[84] palladacycles,[85] palladium acetates and acetylacetonate complexes,[86] π-allyl palladium complexes: [(NHC)Pd(allyl)Cl],[78-81] and pyridine-containing palladium complexes.[87] They also utilise mixed NHC ligands with NC-palladacycles. Simple NHC based Pd acetate complexes have been synthesised and used as efficient catalysts in Suzuki coupling reactions.[88] Palladacyclic scaffolds stabilised by highly donating NHC ligands have been used for coupling reactions.[85] Cavell *et al.* have also demonstrated the use of monodentate methyl Pd(II) NHC complexes.[72,74]



R = mesityl, 2,6-diisopropylphenyl





R = phenyl

Figure 1.9 Examples of Pd NHC complexes reported by Nolan

Bulky NHC ligand *N*-substituents such as adamantyl are found to afford higher activity in catalytic reactions such as Suzuki reaction compared to less bulky analogues such as the *tert*-butyl substituted ligand.[77,89] Stable palladium complexes with chelating and pincer carbenes tend to be less effective catalysts than monodentate complexes.[74,90]

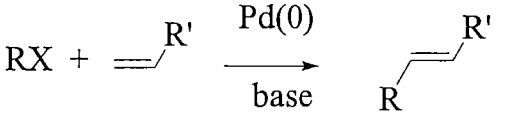
Combining NHCs and phosphines result in extraordinarily high thermal stability and high Pd-C bond dissociation energy of the ligand as well as triggering higher catalyst activity.[75,91] The Herrmann group utilised this system type for the first time as a catalyst for the Stille reaction and other coupling reactions. Thermochemical studies showed that some NHCs have greater electron donating properties compared to tertiary phosphines. Steric bulk also has influence on the preparation of the complexes and, furthermore, their M-C bond dissociation energy to the NHC ligand.[92]

NHCs can form singly and doubly ligated complexes both with Pd(0) and Pd(II) centres. Pd(0) is oxophilic and synthetic routes are more difficult while Pd(II) precatalysts are air and moisture stable as well as thermally stable. $Pd(OAc)_2$ acts as both base and Pd source through *in situ* deprotonation synthesis with diimidazolium salts, therefore is often used. So far only NHC complexes derived from imidazolium or 4,5-dihydro imidazolium salts have been extensively developed as capable catalysts for coupling reactions and are widely used in organic reaction synthesis.[27]

1.5 Palladium Catalysed Coupling Reactions

1.5.1 Heck reaction

The Heck reaction is defined as the reaction, typically, of a haloarene or haloalkene with an alkene to yield arylated or alkenylated alkenes, respectively. The reaction was invented by Richard F. Heck in the late 1960's, Scheme 1.6.[93] After the invention of the Heck reaction, many impressive advances related to metal mediated catalytic transformations with arene, alkene and alkyne derivatives continue to be reported, especially after many in-depth studies focussing on mechanism. Control of substrate selectivity and increasing efficiency was greatly improved during the mid-1980's. After that period of time, this method of C-C bond formation has become an indisputably important method for organic synthesis and is finding its way into applications in industrial synthesis.[94,95]



X= I, Br, Cl, Triflate

Scheme 1.6 Heck Reaction

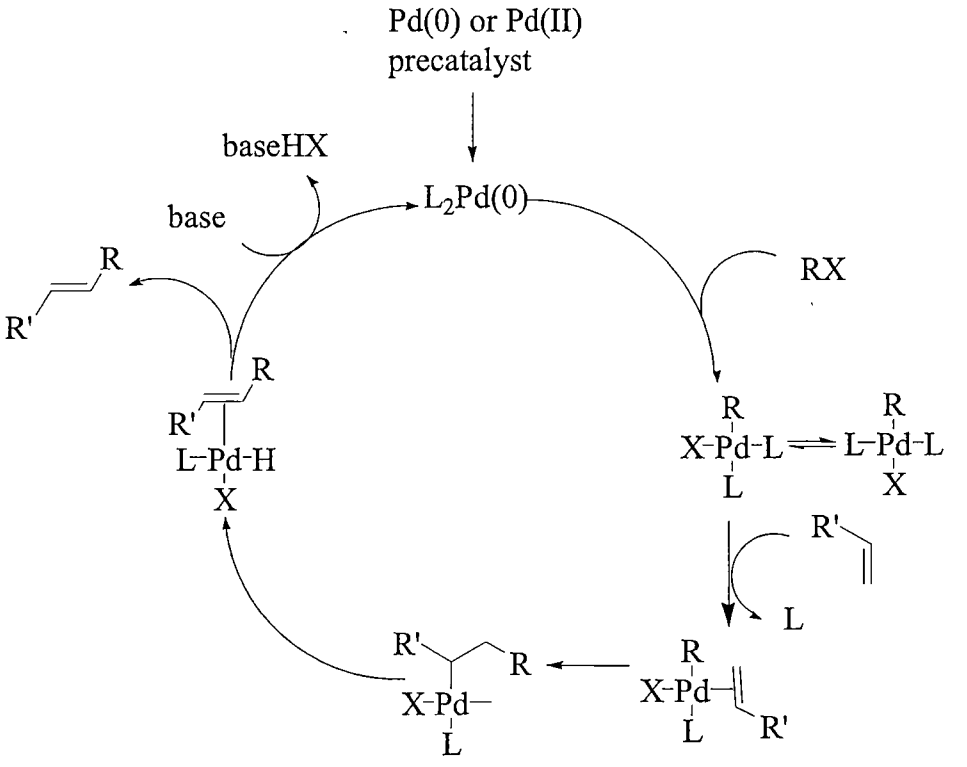
Traditional Heck coupling reactions involve aryl iodides or bromides (electrophilic) and alkenes (nucleophilic) where the terminal alkene possesses an electron withdrawing group like COOR, CN or phenyl.[96] Heck reactions are usually palladium mediated, complexed by tertiary phosphines as weak donor ligands.[97] The palladium species used can be sources of Pd(0), such as $Pd_2(dba)_3$ (dba = dibenzylideneacetone), $Pd(PPh_3)_4$, or can be a source of Pd(II), such as $Pd(OAc)_2$ and $PdCl_2(NCMe)_2$.[98] The most common procedure for the Heck reaction is to use triphenylphosphine.[99] The use of "ligand free" systems is also possible, as the initial Heck reaction were reported in ligand free environments.[100] Improvements from the traditional Heck reaction have followed various directions, such as the use of ionic liquid solvents,[101] phase transfer agents,[102] the use of palladacycle[103] and carbene complexes.[104]

Recent developments of the Heck reaction have focussed on the point of developing high turnover catalysis and has been reviewed by Farina, and many others in recent years.[105] Several palladium catalysts and precatalysts are described: with ligands such as NHCs and bi- or multidentate P- or N- based ligands, ligandless catalysts such as Pd colloids and heterogeneous catalysts, palladacycle and polymer-supported catalysts having shown high turnover numbers (TON) for a given Heck or other related coupling reaction. Some improvements have been made such as the use of liquid-solid phase transfer agents for near room temperature reaction developed by Jeffery, later known as Jeffery's conditions.[102] Some other different aspects of the use of the Heck reaction has been established such as the intramolecular Heck reaction,[106] intermolecular asymmetric Heck reaction,[107,108] carbon-carbon bond formation via 1,2-addition of organopalladium reagents to heteroatom-substituted olefins[109] and bimetallic catalysed Heck reactions.[94]

Despite these many developments and improvements, the role of the Heck reaction in organic syntheses is still facing obstacles. Problems arise when attempts are made to utilise the Heck reaction for unsymmetrical alkenes due to the lack of regioselectivity, causing isomeric products to be generated. Another obstacle is employing the Heck reaction very efficiently to aryl and alkenyl chlorides for more economic and ease of accessibility benefits. So far, widely used Heck reactions are restricted to aryl and alkenyl bromide and iodide substrates.[110,111] Lastly, there should be improved ways to minimise the cost of the catalyst and catalyst contamination in the products. The need to replace traditional phosphine ligands is huge due to their toxic properties.[97] The answers for those questions are the key for the Heck reaction to be implemented in industrial scale synthesis.

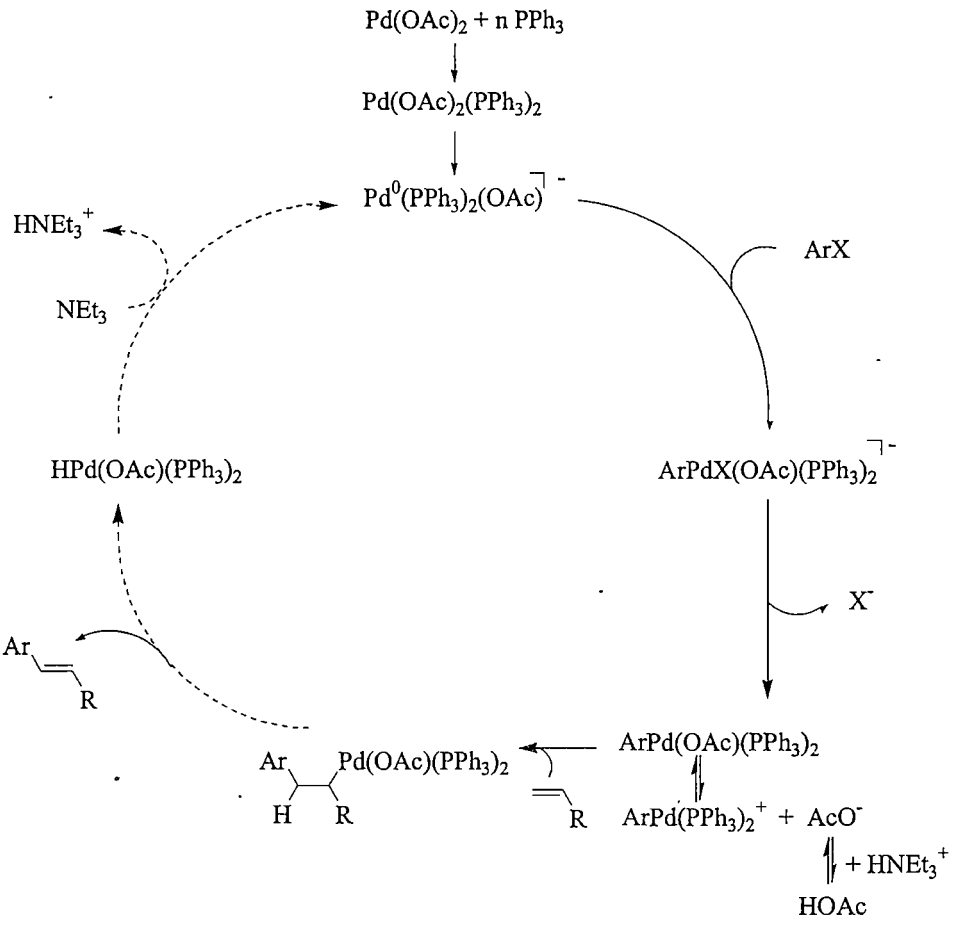
The mechanism of the traditional Heck reaction is usually presented with coordinated tertiary phosphine ligands bound to an unsaturated 14 electron Pd(0) species which acts as the active catalyst.[110] This traditional catalytic system has been well studied and has resulted in detailed information of the elementary steps of the catalytic system.[97,112] Bis(phosphine)Pd(0) complexes have been isolated

and fully characterised.[99,112-115] The active catalyst may be generated by reduction of a Pd(II) complex precursor *in situ* or by displacement of weakly coordinating ligands from higher coordinate Pd(0) precursors. Beletskaya *et al.* described in her detailed review of the mechanism of the Heck reaction as it consisting of five steps: pre-activation, oxidative addition, migratory insertion, β-hydride elimination and termination of reaction. The commonly used textbook mechanism for the Heck reaction follows, Scheme 1.7.[97]



Scheme 1.7 Early mechanism of the Heck reaction developed by Beletskaya

Oxidative addition of the aryl halide to the Pd(0) species forms a Pd(II) intermediate. The olefin is then bound to the Pd(II) complex, inserting it into the Pd-C bond to the aryl to create the new C-C bond. The product species is then generated after the β-hydride elimination step, forming a $L_2Pd(H)X$ species. The role of base is to remove the bound HX from the palladium, regenerating the $L_2Pd(0)$ catalyst.[111] Another approach to honing the details of the Heck reaction mechanism was developed by Amatore and Jutand who suggested an anionic, pentacoordinated species as an important Pd(II) intermediate, Scheme 1.8.[113]

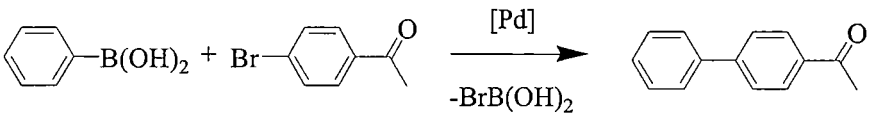


Scheme 1.8 Alternative Heck reaction mechanism Developed by Jutand and Amatore

The Heck reaction shares similarity with other coupling reactions, such as the Suzuki, Sonogashira, Stille, Negishi and Kumada reactions in which the oxidative addition of the aryl halide to the catalytically active Pd(0) species forms a Pd(II) species. In cross coupling reactions this step is followed by a transmetallation step and suspected reductive elimination of product to regenerate the active palladium(0) catalyst.[98] The Heck reaction, however, does not use organometallic substances as the coupling partner like in most of these other C-C coupling reactions. The widely accepted general mechanism for all these coupling reactions is an initial oxidative addition of the halide to Pd(0) catalyst.[114]

1.5.2 Suzuki reaction

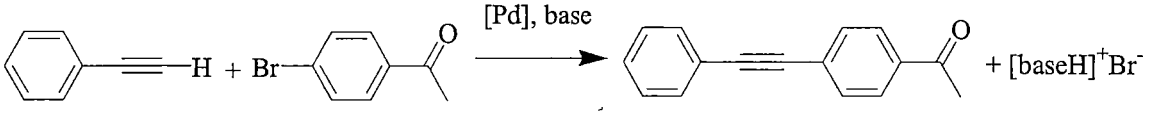
The Suzuki reaction is a cross-coupling reaction of an organoboron derivative with an aryl halide, Scheme 1.9.[115,116] It is one the most widely used cross-coupling reactions because of the availability of a wide range of stable boronic acids.[117-119] Some advantages of Suzuki reactions are that the by product is non toxic and the reaction can run well in methanol or water. The reaction permits the use of a variety of functional groups. Addition of base is necessary to activate the boron derivatives. Herrmann demonstrated the efficient application of Pd(II) NHC complexes with chelating ligands in the Suzuki coupling reaction of deactivated aryl bromides and aryl boronic acids, focussing on the importance of unsymmetrically substituted biaryl derivatives which are important for drug intermediates and nonlinear optic materials. This study showed that Pd NHC complexes can successfully activate a wide variety of bromo and chloro arenes.[77]



Scheme 1.9 Suzuki Reaction

1.5.3 Sonogashira alkyne cross-coupling reaction

In the Sonogashira reaction[120], a *sp*-hybridised carbon nucleophile is generated and coupled to the aryl, Scheme 1.10. Cu salts are often used as co-catalyst with the addition of amine bases. Copper free alkyne coupling reactions have been studied by Cavell as well as the Herrmann group using NHC complexes.[57,74]

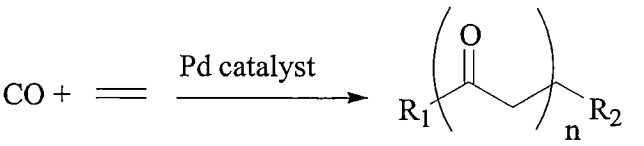


Scheme 1.10 Sonogashira Reaction

1.6 Carbon Monoxide/Ethene Copolymerisation

Dimerisation, oligomerisation and polymerisation of alkenes often depend on alkene insertion into M-C bonds forming new C-C bonds through the Cossee mechanism.[121] Alkene polymerisation is one of the most important catalytic reactions in commercial use, with most polyethene and polypropene being produced with organometallic based methods. The invention of alkene polymerisation catalysts brought Ziegler and Natta the Nobel Prize in 1963. The catalysts used are mixtures of alkyl aluminium reagents and early transition metal complexes, such as $TiCl_4/Et_2AlCl$, active under mild room temperature and 1 atm conditions. Another rapidly developing catalyst class in the polymer industry are the aluminium cocatalyst activated metallocene catalysts, where Zr, Hf and Ti is used with cyclopentadienyl (Cp) or substituted Cp ligands, Cp_2MX_2. Dimerisation, oligomerisation and polymerisation of alkenes are often related one to another since they often differ mainly in the relative rates of chain growth (k_g) by insertion to termination (k_t), through β-H-elimination. More efficient chain termination will result in fewer new C-C bonds forming, while the opposite occurs in Ziegler-Natta and metallocene catalyst alkene polymerisation, where high molecular weight polymers are produced.[121]

The carbon monoxide/ethene copolymerisation reaction was discovered in 1950's by Reppe through the palladium catalysed alternating carbon monoxide/ethene copolymerisation reaction at Shell Company, Scheme 1.11. The work has been continued by Drent.[122-124] This was the turning point for the synthesis of polyketones to be of commercial importance. Nickel, rhodium and palladium complexes were firstly used as active catalysts for the production of carbon monoxide/ethene copolymers during 1970's. These catalysts yielded low g polymer/per gram M returns.[123]



Scheme 1.11 Carbon monoxide/ethene copolymerisation reaction

Afterwards, Pd catalyst systems were developed which were based on bis(phosphine)Pd dichloride complexes that yielded higher amounts of high molecular weight polymer over oligomeric formylation products, Scheme 1.11. High temperature and pressure are needed for this system as well as high loading of Pd per gram polymer yielded. During the 1980's period Shell invented Pd-containing tertiary phosphine systems giving high rates with high yield per gram of Pd with mild conditions.[122,125] This catalyst was also easy to prepare. Later on this new family of catalysts was found to be active in copolymerisation with alkenes other than ethene to create a new range of copolymer materials. Chelating bidentate ligands give significant effects in enhancing the performance of the catalyst in terms of reaction rate and product molecular weight. Bidentate ligands are always *cis* coordinated, making them favourable for the C-C bond formation insertion in the polymer chain growth step. Palladium diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ have been widely used in variation with several types of chelating ligands such as bipyridines, Figure 1.10, dithioesters and bisoxazolines. Non-coordinating anions within the complex also improve reaction rates.[123]

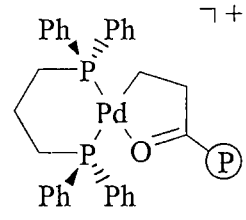
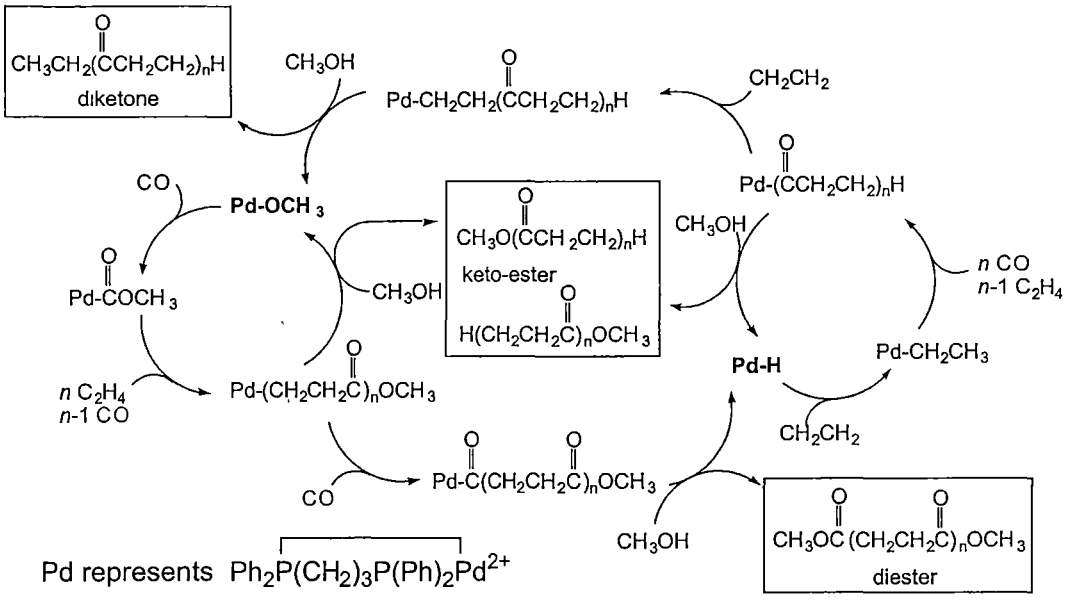


Figure 1.10 Bidentate ligand as catalyst for copolymerisation reaction

The mechanism of carbon monoxide/ethene and higher olefin copolymerisation has been studied by numerous reports.[123,126-129] *In situ* monitoring of a palladium based polyketone catalyst has been reported by Mul.[124] Alternating[130] and non alternating copolymerisation[131] has also been discussed.

The copolymerisation reaction is most successfully undertaken using precatalysts consisting of a bidentate ligand coordinated dicationic palladium complex having weakly coordinated anion using methanol as solvent under high CO pressures. A two cycle copolymer mechanism was developed by Drent, Scheme 1.12.[123] Many of the steps relate generically to common fundamental reaction steps known across a wide range of formylation reactions. The

propagation step involves alternating steps: the migratory insertion of CO onto a palladium-alkyl bond followed by migratory insertion of ethene into the resulting palladium-acyl bond.



Scheme 1.12 Copolymerisation reaction mechanism developed by Drent[123]

The active catalyst formed is believed to be a monocationic palladium hydride or methoxy species which initiates the copolymerisation. For some systems, the active species have been distinguished, but not in all cases. Based on end group analysis of many systems, there are two possible initiation mechanisms. CO insertion in a palladium methoxide or direct attack of methanol on CO will give result in an ester end group, while insertion of ethene in palladium hydride will give result in a ketone end group. Doubt still remains about the active catalyst, whether it is a palladium hydride species or palladium methoxy species. The chain termination step involves the formation of alkyl or ester polymer end groups from protonolysis of the metal-alkyl bond or methanolysis of the palladium-acyl bond.[122] It is known that the copolymer typically does not have diester or diketone end groups. Molecular weight estimates can be estimated by ^{13}C NMR integration of the end groups relative to the intensity of the backbone carbon resonances (the copolymer is soluble in $(CF_3)_2C(D)OD$)).

A recent study characterised the CO coordinated and inserted products of a cationic Pd(II)Me complex rarely isolated species in regard to mechanistic

understanding of C_2H_4/CO copolymerisation using a chelated NHC Pd(II)Me catalyst.[132-135] C_2H_4/CO copolymerisation activities were not reported, but detailed kinetic data highlighted the process as being slow relative to the highly active 1,3-bis(diphenylphosphino)propane (dppp) chelated systems possessing a larger chelate bite angle. This recent study relates more to secondary CO insertion subsequent to ethene insertion into a hydride precursor (*i.e.*, an ethyl species). Thus, the doubt of palladium methoxy species or palladium hydride species act as initiating species was not resolved in this recent article.

1.7 Project Aim

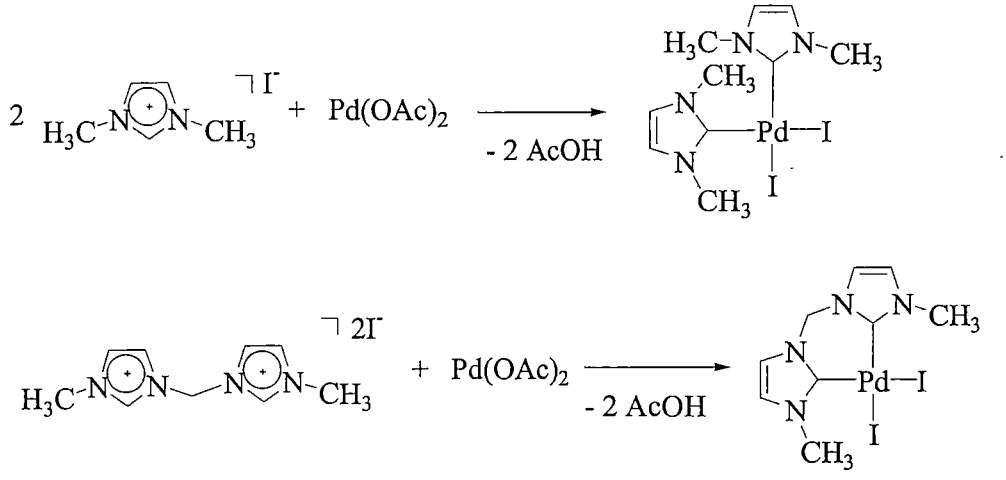
The aim of this project was to investigate the identity of *in situ* formed palladium *N*-heterocyclic carbene complexes formed under catalytically relevant reaction conditions. Aims included:

i) Synthesis of a variety of methylene bridged *N*-heterocyclic carbene complexes of Pd(II).
ii) Investigation of the base promoted activation of Pd(II) NHC complexes as preformed catalysts, which may include low oxidation state complex formation.
iii) To investigate the application of these Pd NHC complexes as catalysts for the copolymerisation of carbon monoxide/ethene and C-C coupling reactions.

Chapter 2: Complex Synthesis and Catalytic Studies

2.1 Introduction

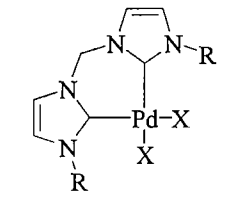
The resurgence in the development of palladium NHC and other transition metal NHC complexes as catalysts was initiated by Herrmann. This work has featured both monodentate and chelated bidentate NHC complexes that have been reported to be readily accessible, Scheme 2.1.[136] The palladium(II) NHC carbene complexes showed high thermal stability as well as being versatile in Heck and various coupling reactions such as the Stille and Suzuki reaction.[57] X-ray crystal structure analyses of some palladium complexes of methylene linked bis(NHC) complexes revealed them to be chelated bidentate complexes.[57,136]



Scheme 2.1 Early palladium(II) complexes developed by Herrmann

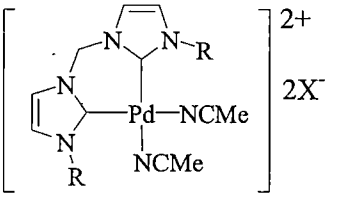
A selection of the various neutral and cationic chelated bis(carbene) palladium(II) complexes have been summarised, Figure 2.1. Some of the complexes were synthesised by Herrmann's group[137], Figure 2.1 (A, B) have been used as catalysts for coupling reactions, and furthermore, other research groups have shown activity in other reactions such as the conversion of methane into methanol.[138] The chelated complexes have also been attached to polymer supports and applied in ionic liquid solvents for the Heck reaction in attempts to allow recyclability of the catalyst.[70,139] The development of cationic Pd NHC complexes

for the copolymerisation of carbon monoxide/ethene has also been reported, Figure 2.1 (B).[140] The mechanistic and structural detail of this area was studied by Drent and attempts to create dicationic *cis*-chelated NHC systems of palladium have also been explored by Herrmann.[122,123,140]



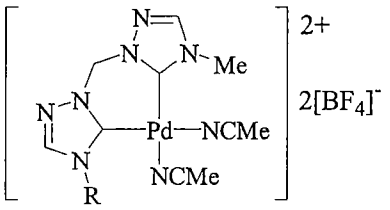
X = Cl, R = $CH_2(p\text{-}C_6H_4)CH{=}CH_2$
X = Br, R = $CH(C_6H_5)CH_3$, *t*-Bu, Mes **(3a)**
X = I, R = ethyl, benzyl, cyclohexyl, phenyl

A



R = $CH(C_6H_5)CH_3$, X = BF_4
R = *t*-Bu, X = BF_4
R = Mes, X = PF_6 **(4a)**

B



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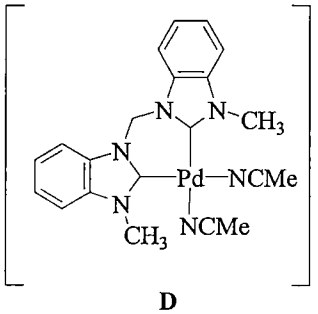

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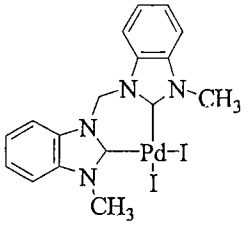


E

Figure 2.1 Various type of chelated bis(NHC) Pd complexes

The *N*-heterocyclic systems employed in chelated Pd(II) systems has also been broadened to a wide array, including the use of triazolin-2-ylidene and benzimidazolin-2-ylidene, Figure 2.1 (C,D).[141,142] Biffis modified the structure of Pd NHC complexes from Herrmann's group with increasing substituent bulk and also changed the NHC system into benzimidazolin-2-ylidene, Figure 2.1 (E), to obtain a better performance in the Heck reaction.[143] Several tetracarbene methylene linked mono and dinuclear complexes with bridging, Figure 2.2 (A[142],B[144]) and chelated Figure 2.2 (C[145],D[56]) structures have also been reported.

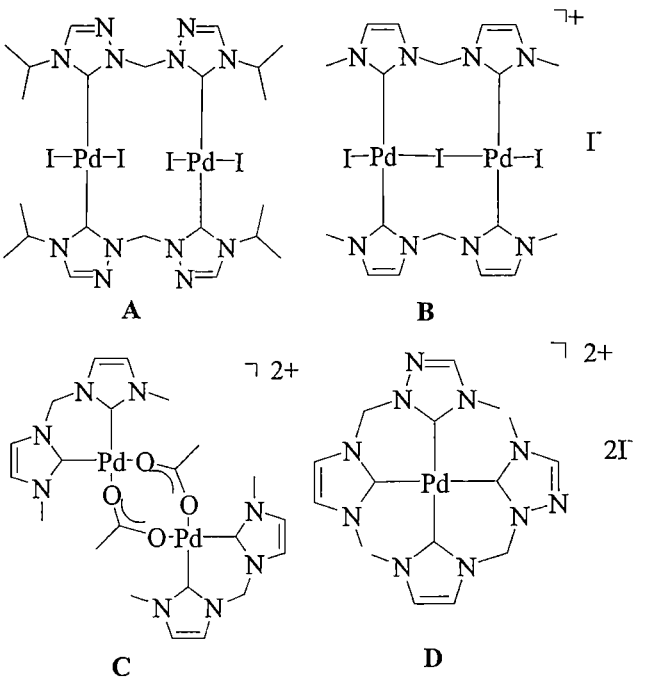


Figure 2.2 Tetracarbene Pd NHC complexes with a methylene bridge

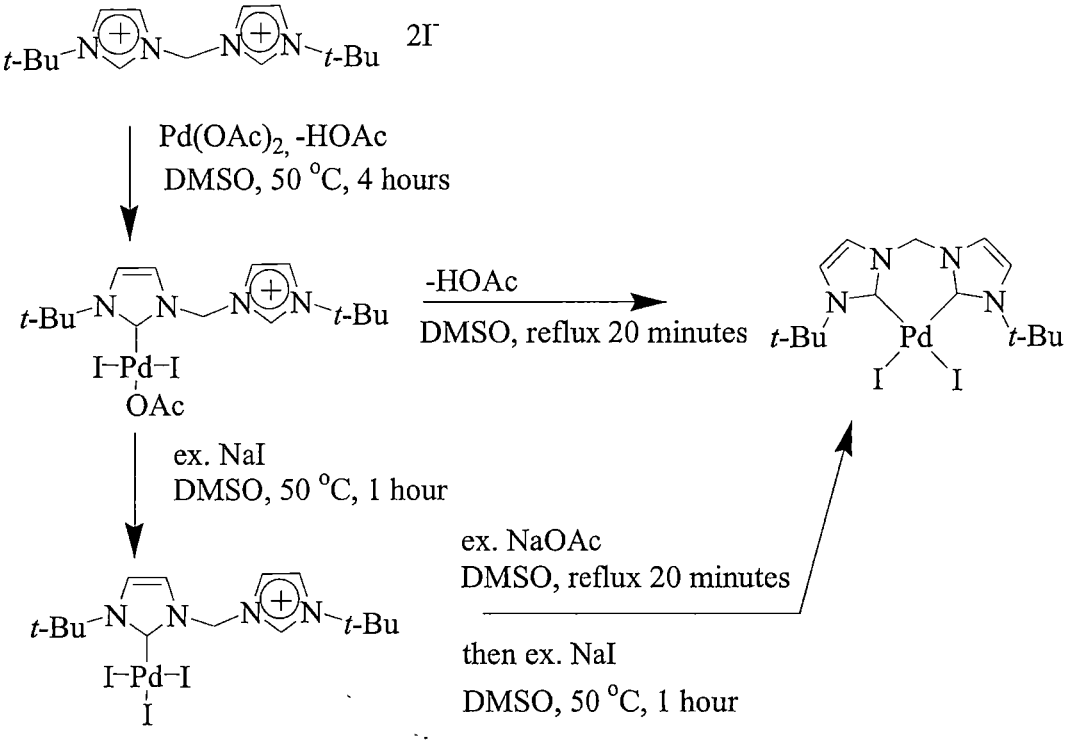
The synthesis of chelated methylene linked bis(NHC) complexes is usually achieved from diimidazolium salts and a metal salt containing basic ligands such as palladium acetate, $Pd(OAc)_2$.[104] Especially for platinum, the general protocol for bis(NHC) complexes was using platinum(II) acetylacetonate as a commercially available metal precursor.[49]

2.1.1 Bridged versus chelated binding of linked bis(NHC) complexes

The formation of methylene linked bis(NHC) palladium complexes from diimidazolium salts and $Pd(OAc)_2$ has been investigated in detail using the *tert*-butyl substituted system, Scheme 2.2.[146] Initially a palladate species, [1,1'-di-*tert*-butyl-3,3'-methylenediimidazolium]$^{2+}$[$PdI_2(OAc)_2$]$^{2-}$, was formed upon dissolution of the diimidazolium salts and $Pd(OAc)_2$ in DMSO. This intermediate is then converted into a further NHC intermediate complex and subsequently into the product of the reaction through various heating stages, as described below.

The formation of the chelated Pd(II) complex followed the formation of an acetate-mono(carbene) intermediate generated in the first mild stage of heating, which is somewhat unstable and can give the product after the second stage of

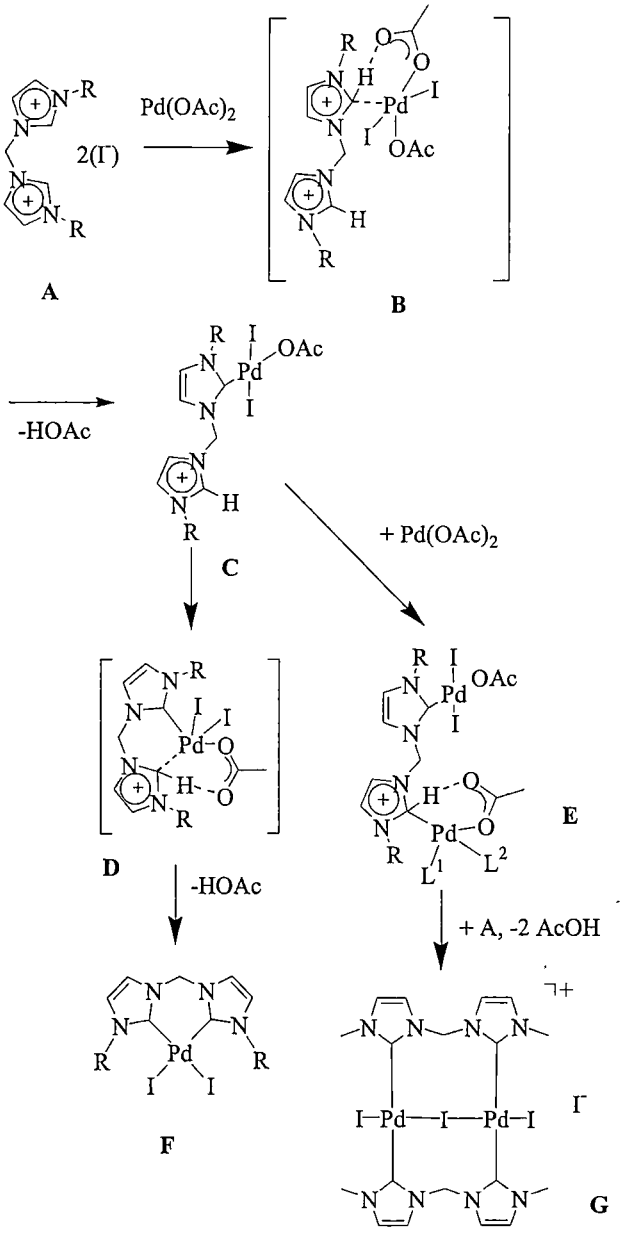
more forcing heating, or converted into a stable triiodo derivative that in turn can also be converted into the product on reaction with added sodium acetate. This is the reason that reaction of the diimidazolium salt with palladium acetate needs two stages of mild heating. The approach has been used many times by other research groups and modified, accordingly, to meet the varying conditions needed in each case. Evidence for both intermediates is supported by *in situ* ^{1}H NMR spectroscopy as well as single crystal X-ray crystal structure determinations.



Scheme 2.2 Optimised reaction conditions for the synthesis of chelated methylene bridged Pd NHC complexes

Other groups have shown that non-chelated methylene bridged complexes can be obtained from these systems. Rationalisation of the formation of chelated or bridged complexes is given in Scheme 2.3. The formation of the palladium-bound carbene ligands from diimidazolium salts and $Pd(OAc)_2$ is assumed to proceed *via* an initial six-membered ring transition state (B). The acetate ion is coordinated into both metal centre and the acidic 2-H proton of the imidazolium cation by each oxygen centre. The palladium mono-carbene complex containing both halides from the imidazolium salt and the remaining acetate ligand is then

formed after releasing HOAc. Subsequently, cyclometallation occurs by the metal-bound acetate *via* formation of another six-membered transition state. This process favours intramolecular deprotonation from the monocarbene complex (D) to give the chelated 1:1 complex, (F). The formation of bridging ligand complex (G), however, is achieved by either reaction with another $Pd(OAc)_2$ or the intermolecular reaction of two units of the monocarbene complex, (E).



Scheme 2.3 Formation of chelated or bridged methylene linked palladium NHC complexes[144]

Reaction conditions strongly influence the ligand environment in the formation of alkylene bridged bis(NHC) palladium carbene complexes from diimidazolium salts. Some relevant factors include the concentration of the reactants, the *N*-substituents of the diimidazolium salt and the presence of base. The larger groups (alkyl) mostly give mononuclear chelated complexes while smaller substituents tend to give a mixture of mono and bimetallic complexes. The presence of base can result in the formation of tetracarbene complexes.[144] When a longer bridge than methylene is used in the diimidazolium salt, decomposition of the starting material and formation of palladium black during the reaction is observed.[146] Some successful attempts have been reported when steric and conformational constraints are imposed by a rigid spacer, which prevent this side reaction, such as for the *o*-phenylene bridge, Figure 2.3.[143]

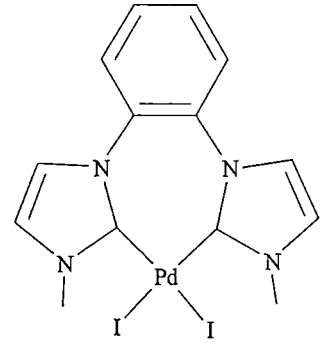
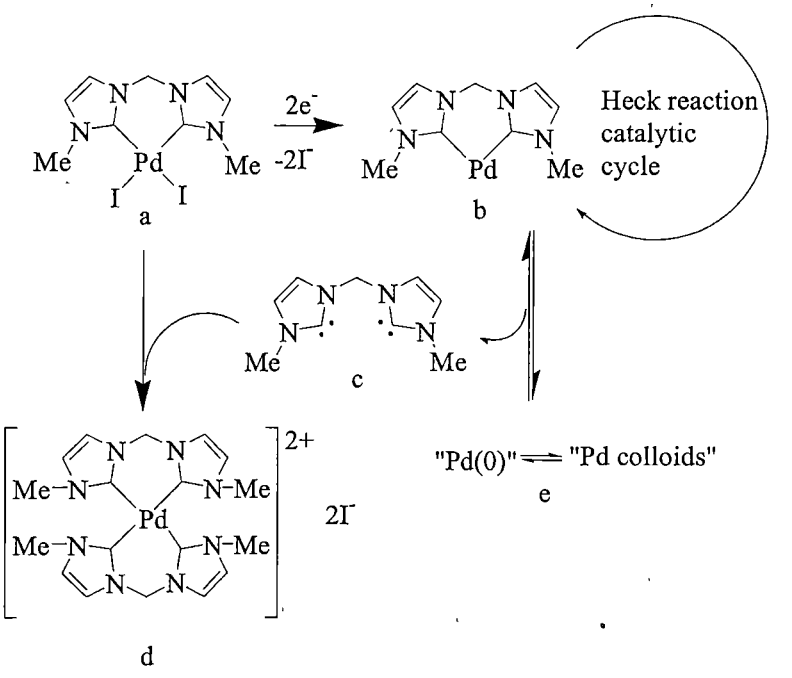


Figure 2.3 Pd complex with rigid *o*-phenylene bridge spacer

The chelated bis(carbene) complexes are often less successful catalysts than simple bis(carbene) analogues for the Heck reaction. This is because the chelated bis(carbene) complexes can have an inhibiting effect on Heck reaction, especially when non-activated aryl halides were used, Scheme 2.4. This inhibiting effect can be correlated with their ability to form inactive tetracarbene Pd(II) derivatives during the reaction and appears to depend on their steric features with catalytic activity increasing along with the bulkiness of the ligand, Scheme 2.4.[143] This hypothesis is supported by a report that cationic dinuclear Pd(II) complexes with two bridging bis(carbene) ligands may form instead of the favourable chelated mononuclear complexes at high temperature.[2,11,16] Catalyst poisoning may occur because of the decomposition of the *in situ* formed Pd(0) species

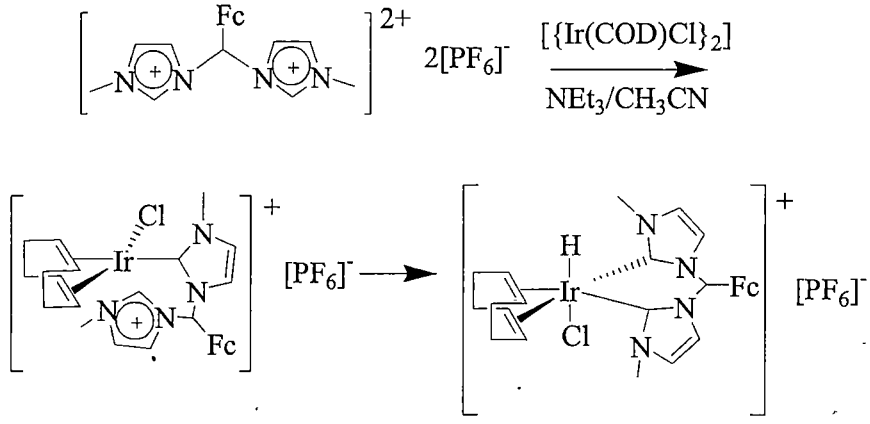
(formation of Pd colloid was proven by darkening reaction solution from apparent catalyst decomposition) that liberates free bis(carbene) leading to the formation of the dicationic of tetracarbene species, Scheme 2.4 (d). Bulky substituents can reduce the catalytic poisoning, since it sterically prevents the formation of the homoleptic dicationic tetracarbene complex.[143] The isolation of these thermally stable, dicationic complexes from the methylene linked bis(carbene) complexes from catalytic runs suggest that Pd-C bond is kinetically labile,[136] undergoing transient association and dissociation from the metal centre.[147]



Scheme 2.4 Formation of inactive species from a catalyst[143]

Reaction between a methylene bridged bis(methylimidazolium) salt with [M(COD)Cl_2 (where COD = 1,5-cyclooctadiene; M = rhodium, iridium), in the presence of the weak base NEt_3 resulted in a monodentate complex with rhodium, while iridium gave both monodentate and bidentate complexes, Scheme 2.5.[148] The Ir bidentate complexes have a carbene carbon atom with ^{13}C-NMR resonances at 145 ppm. X-ray diffraction showed the C-Ir-C bite angle to be 83.5° and the Ir-C bond distances measure 2.056(5) and 2.043(5) Å. The monodentate Ir complex, analogous to Rh was also produced, but converted into the bidentate complex at room temperature over two hours. The addition of base is

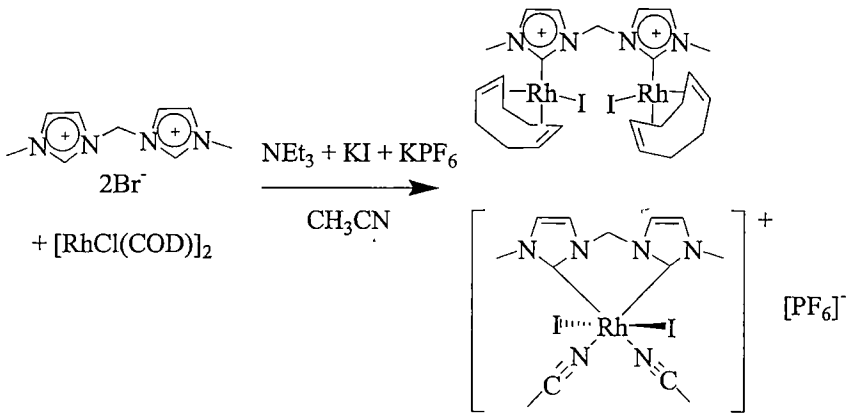
important in the synthesis of the monodentate compound. However, it is not needed in the case of Ir to form the bidentate complex. This is because an oxidative addition step is responsible for the formation of the second carbene centre, whereas, base is required for the initial metallation derived carbene generation. This provides proof that oxidative addition may be an alternative general method to synthesise NHC metal complexes.



Fc = ferrocenyl

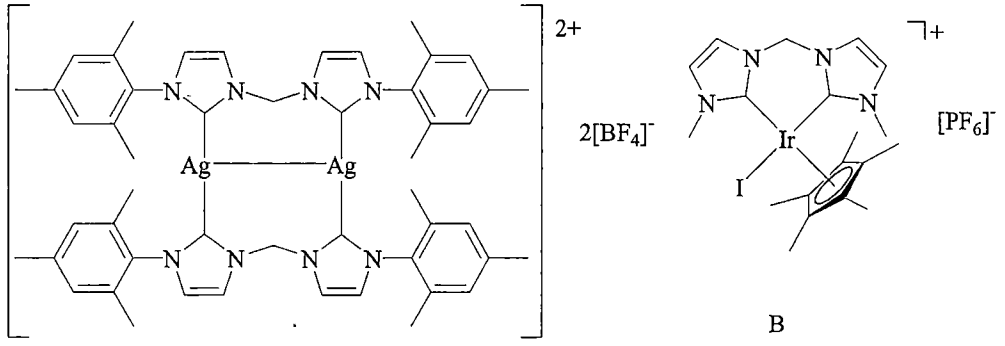
Scheme 2.5 monodentate and bidentate Ir NHC complexes

A study of Rh(I) and Rh(III) methylene linked NHC complexes appear to show some preference for bis(NHC) bridging over chelation from the lower oxidation state metal centres, Scheme 2.6. Whilst the Rh(III) complex forms a chelated bis(carbene), the Rh(I) outcome afforded a binuclear bridged species.[149] However, there are other examples of chelated Rh(I) bis(carbene) complexes,[150] so this observation is not entirely general.



Scheme 2.6 Rh(I) and Rh(III) NHC complexes

The dimesityl substituted imidazolin-2-ylidene carbene with a methylene linkage was shown to form a dimeric complex with Ag(I) that surprisingly shows a short Ag···Ag distance of 3.2039(3) Å with a boat conformation and the bridging NHC ligand. This Ag···Ag interaction was merely because of the influence of the *N*-mesityl substituent, Figure 2.4 (A).[151] Vogt[152] reported the structure of a cationic bis(carbene) Ir(III) with a cyclopentadienyl ligand $[(C_5Me_5)Ir(bis\text{-}NHC)I][PF_6]$, Figure 2.4 (B), that is similar to the reported Herrmann Pd(II) bis(carbene) complexes,[153] as well as Ir(III) complexes reported by Crabtree,[154] with the C-M-C bite angle of 86.4 °.



A B

Figure 2.4 Ag(I) and Ir(III) NHC complexes

2.1.2 Structural details

Examples of typical structurally characterised non palladium metal NHC complexes with methylene bridged bis(NHC) ligands are summarised in Figure

2.5. For Ni(II) complexes, such as the chelated complex (A), the Ni-C bond distances are 1.942(4) and 1.871(4) Å, with a C-Ni-C bite angle of 84.82(18) °, which is comparable to its chelated 1,2-bis(phosphine)ethane analogue.[155] The chelated Cr(II) complex [$LCrBr_2(THF)$] has Cr-C distances of 2.162(7) and 2.173(6) Å with C-Cr-C of 86.5(2) ° (B).[156] For the Pt(II) bis(carbene) complex (C), the Pt-C distance is 1.968(5) Å and C-Pt-C bond angle is 84.9(2) °.[49] The cationic chelated bis(carbene) iridium complex [(C_5Me_5)Ir(bis-NHC)I][PF_6] has both Ir-C distances of 2.019(8) Å and C-Ir-C bond angle of 86.4(4) °.[152] For the chelated Rh complex (E), the Rh-C distances are 1.976(5) and 1.978(5) Å with a C-Rh-C bond angle of 87.3(2) °.[149]

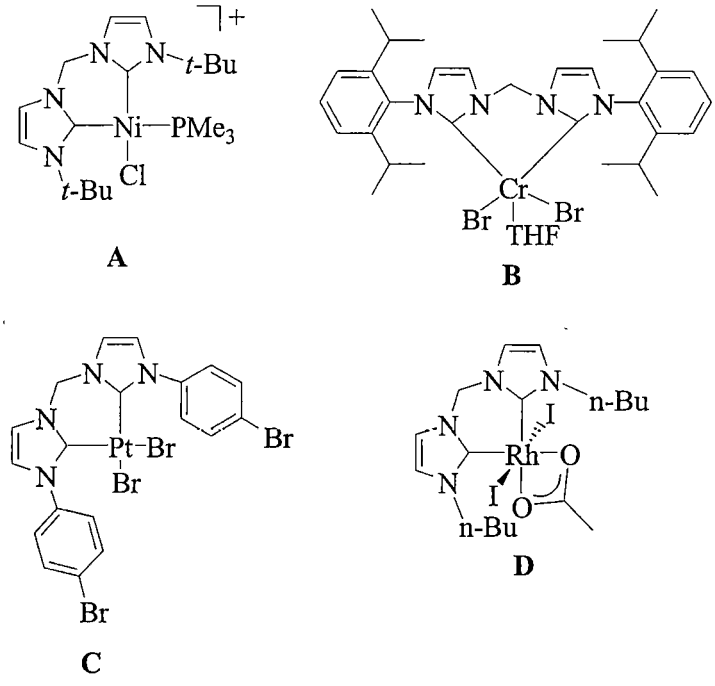


Figure 2.5 Non-palladium methylene bridged metal complexes

Crabtree reported that bis(imidazolium) salts react with basic Rh(I) metal complexes to give chelated or dinuclear bridged structures depending on the linker between the two NHCs. The coordination modes of these complexes are heavily influenced by the interplay between linker, *N*-substituent and counter ion effect for bulkier substituent, Figure 2.6.[157] This owes to the NHC plane preferring to lie in the ±*z* direction on steric grounds, so that with short bridges (n= 1 or 2) bridging structures are adopted so that both NHCs can adopt strictly ±*z*

conformations. Longer linkers will prefer chelate arrangements to avoid steric clashes between the *N*-substituent and the other ligands (L) when the NHC rings lie along the ±*z* axis, Figure 2.6 (a). Longer bridges still will disfavour chelate conformations due to interactions between the *N*-substituents at each end of the bis(NHC) for bulky substituents, Figure 2.6 (b,c). The use of the less bulky ligands will prefer chelated conformations. The use of a non coordinating anion has a positive influence on the adoption of chelate conformations.[158]

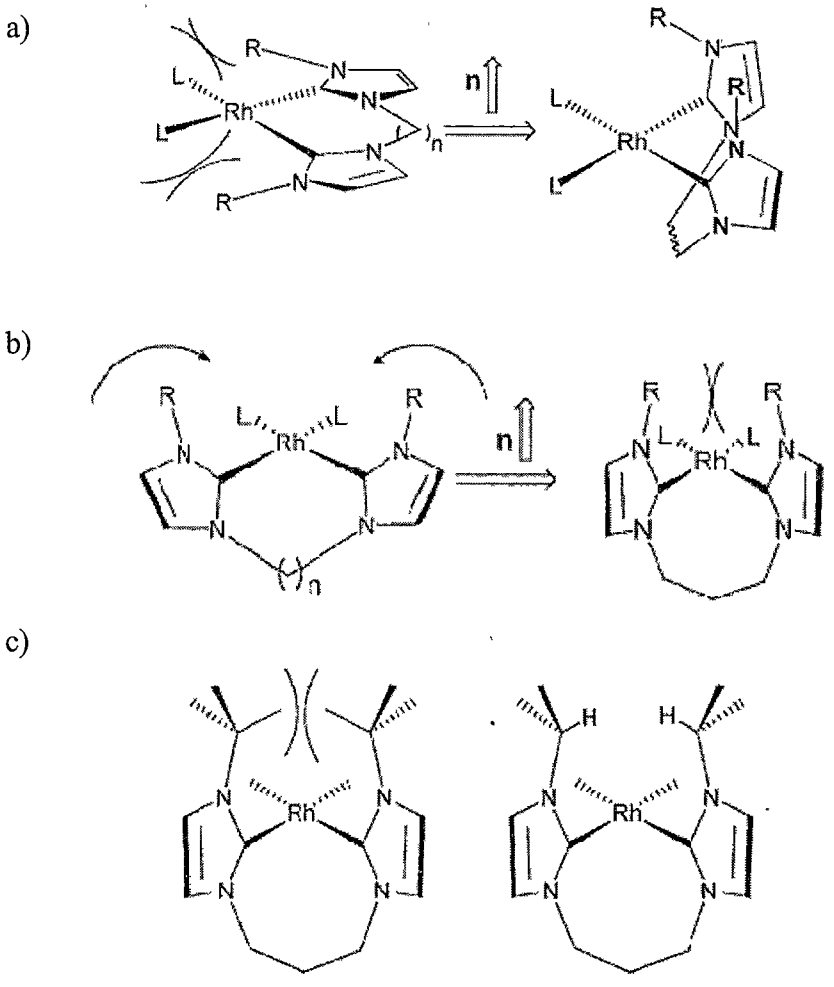
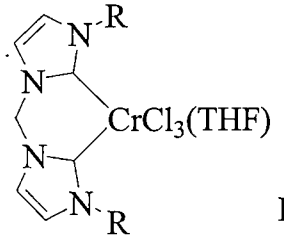


Figure 2.6 Effect of linker and bulky substituents on Rh NHC complexes[157]

Theopold[156] reported the use of chelated bis(NHC) complexes in chromium chemistry as catalysts, Figure 2.7. The bis(carbene) Cr(III) complexes catalyse the polymerisation of ethene with methyl aluminoxane (MAO) as cocatalyst. However, the bis(carbene) ligand influences the easily achieved

reduction of Cr(III) to Cr(II) due to the affinity of the strong σ-donation of the carbene ligand with the softer character of lower valent chromium Cr(II). Unfortunately the Cr(II) complexes failed to polymerise ethene even with added MAO. The complex $LCrCl_3(THF)$ has Cr-C bond lengths of 2.109(5) Å, which is within the range commonly reported for Cr NHC complexes.



R = 2,6-diisopropylphenyl

Figure 2.7 bis(carbene) Cr(III) complex[156]

Chelated bis(carbene) metal complexes with various lengths of alkyl bridges have also been reported by Herrmann and the other groups.[3,7,27,29,31] For chelated palladium(II) dihalide complexes with a methylene bridge, the NHC ligand planes tend to form a "v-shape" at some angle to the metal coordination plane.[157] This is due to the influence of restricted conformational freedom of the chelated carbenes. This has been invoked as a reason why such complexes are expected to be very thermally stable with respect to decomposition by slowing the reductive elimination of the carbene during catalysis. The "v-shape" is shallower for complexes with the extension of the alkylene bridge. The thermal stability of these complexes maybe reduced with this extension of the alkylene linkage, as seen by the decreasing melting point values for such complexes, Figure 2.6 (b). The synthesis of palladium(II) complexes with methylene and ethylene bridges was undertaken by deprotonation of the bis(imidazolium) salts with $Pd(OAc)_2$, while for longer chain linkers, they were synthesised *via* the silver salt method to avoid decomposition. The C-Pd-C bite angles were increased with the length of the bridge, from 83.87 °, for a methylene bridge, through 87.81, 87.63 and 91.15(9) ° with successive addition of one CH_2 unit to the bridges, respectively.[157] The distance between the *N*-methyl substituents of the NHC units become smaller with growing alkylene bridge length and would be expected to cause crowding in bulkier complexes.

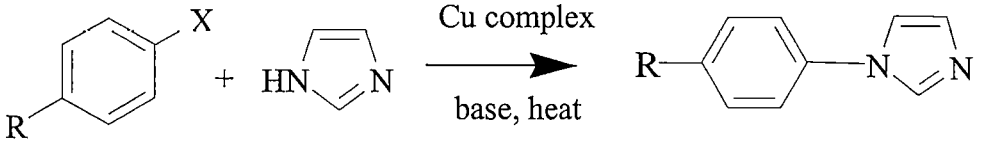
The typical structure for methylene bridged chelated metal complexes are monomeric, in which the metal centre is chelated by the bis(NHC) ligand in *cis* fashion forming the six-membered C_3N_2Pd ring in a boat conformation. The length of Pd-C bonds are comparable; 1.991(5) and 1.994(5) Å for the neutral chelated [*cis*-CH_2{N(H)C=C(H)N(R)C}$_2PdX_2$] (X = Br, I; R = $(CH_2)_nOH$; n = 2, 3)[70], cationic chelated[140] [*cis*-$CH_2(NC{=}CN(Me)C)_2Pd(NCCH_3)_2][PF_6]_2$ at 1.966(2) and 1.972(3) Å, and, for neutral chelated[57] [*cis*-CH_2{NC=CN(Me)C}$_2PdI_2$] at 1.966(2) and 1.972(3) Å. The typical Pd-C bond length of 2.01 Å was obtained from a theoretical calculation of the model chelate compound [*cis*-$CH_2(NC{=}CN(H)C)_2PdCl_2$]. Inversion rates of the boat shaped six-membered chelate can be determined by the appearance of the methylene proton resonance in the ^{1}H NMR spectrum. Fast inversion will give equivalent methylene proton resonances as singlets.[70] Complexes of 1,1'-dialkyl systems with substituents such as methyl, ethyl, isopropyl and *tert*-butyl are found to be fluxional.[137,159] The coalescence temperature trend observed by NMR spectroscopy were reported, showing that increasing steric bulk of the alkyl groups leads to increasing coalescence temperatures. Interestingly, ^{1}H NMR spectra of *N,N'*-diaryl substituted CH_2-linked bis(NHC)Pd(II) complexes often have singlet resonances for the CH_2 protons, despite all being similar of or greater steric bulk than *N*-alkyl analogues displaying AB spin systems.[56,137,142,159] No evidence has appeared for dynamic or permanent conversion to dinuclear forms for the *N,N'*-diaryl cases (where singlet CH_2 resonances are more likely). Such dimeric species are known for *N,N'*-dialkyl substituted CH_2-linked bis(triazol-2-ylidene)Pd(II) complexes (no Pd···Pd interaction, 4.20 Å) *via* conversion under forcing conditions (160 °C, > 1 day) from the initially isolated chelated mononuclear species.[142,160] A detailed study has shown that *N,N'*-dialkyl substituted cationic A-frame bis(NHC)Pd(II) complexes as accessible in direct *in situ* deprotonation methods from bis(imidazolium) precursors (no Pd···Pd interaction, 3.60 Å).[144]

2.2 Results and Discussion

2.2.1 *N*-Arylimidazole synthesis

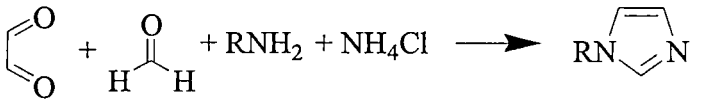
N-Substituted heterocycles are an important structural motif occurring in natural products and many synthetic materials. Some of the most commonly utilised *N*-substituted heterocycles are *N*-arylimidazoles that have commercial uses as pharmaceuticals and are common intermediates in many applications.[161,162] In organometallic synthesis, *N*-arylimidazoles are used to synthesise imidazolium salts as precursors to metal NHC complexes having a growing number of uses, including as homogenous catalysts.

N-Arylimidazoles are often made by substitution of the parent heterocycle *via* the copper promoted coupling of an imidazole with an aryl halide, known as the Ullmann reaction, Scheme 2.7. A variety of *N*-arylated imidazoles can be prepared with this way. However, it is limited to strongly electron-withdrawing substituents. Another difficulty with the reaction is that high temperatures and extended reaction times are needed, and that stoichiometric quantities of the copper reagent are required.[163,164]



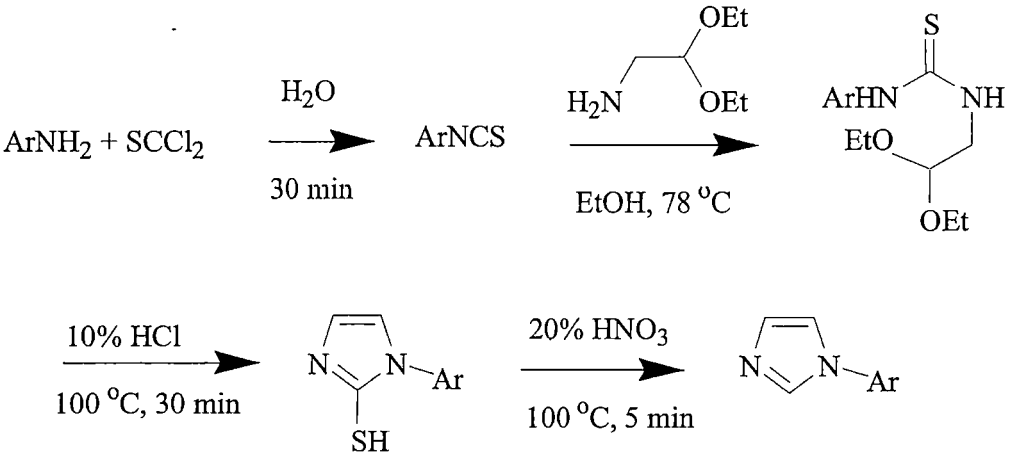
Scheme 2.7 Preparation of *N*-arylimidazoles by the Ullmann reaction

The 'one pot' cyclisation shown in Scheme 2.8 drew attention because of the easy procedural detail as well as low cost of technical reagents that can be used. This method was perfected by Gridnev[165] with 95% yields being obtained. The reaction employs glyoxal; ammonium chloride and formaldehyde in acidic conditions, where phosphoric acid or hydrochloric acid is used. Herrmann[140] modified this one pot reaction for easier access and higher yields of some *N*-alkyl imidazoles. The modification has since been implemented by other research groups to synthesise various *N*-arylimidazoles.[166] Newer methods have involved microwave assistance.[164]



Scheme 2.8 Preparation of *N*-arylimidazoles *via* a one pot cyclisation reaction

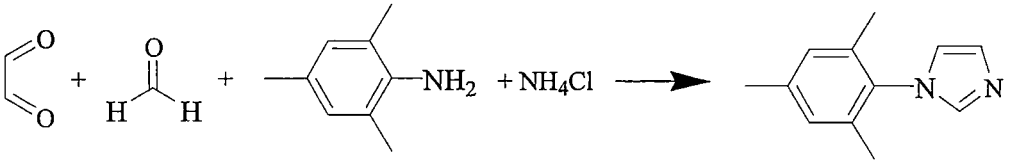
Another reported method for the synthesis of *N*-arylimidazoles is *via* the formation of an isothiocyanate intermediate, Scheme 2.9.[167]



Scheme 2.9 Synthesis of *N*-arylimidazoles *via* an isothiocyanate intermediate

2.2.1.1 Preparation of 1-(2,4,6-mesityl)imidazole, MesIm 1a

1-(2,4,6-mesityl)imidazole, MesIm **1a**, was prepared *via* a modified literature method by Herrmann based on the method by Gridnev.[140,165] It was noted that the use of methanol as solvent gave better yields compared to 1,4-dioxane. The reaction was achieved in a one pot reaction in which 2,4,6-trimethylphenylamine (mesidine), glyoxal, formaldehyde and ammonium chloride in the presence of phosphoric acid at pH of 1 in methanol was refluxed for four hours to build the imidazole ring bearing the *N*-mesityl group as its aryl substituent, Scheme 2.10.

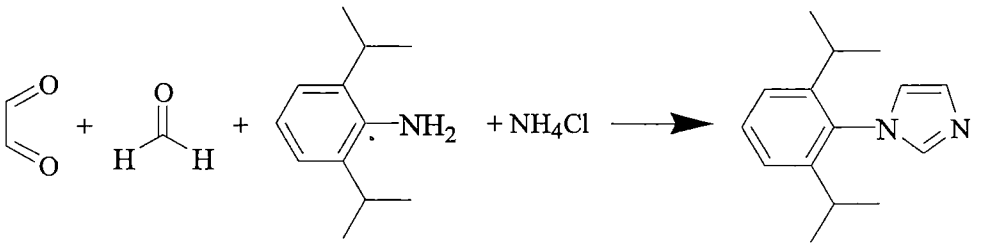


Scheme 2.10 Preparation of 1-(2,4,6-mesityl)imidazole, MesIm **1a**

After the reaction, the solvent was evaporated and the concentrated mixture basified in an ice bath with potassium hydroxide until the pH was > 9. The dark brown mixture was then extracted into dichloromethane and washed with water, brine and dried over anhydrous magnesium sulphate and evaporated to dryness. The resulting product was washed with hexane and then purified *via* soxhlet extraction with hexane. This yielded the product in good yield as a yellow solid that was shown by ^{1}H NMR spectroscopy to be pure and consistent with literature data.[140] The purity of the product, as shown by ^{1}H NMR spectroscopy, was significantly better with the use of methanol as the reaction solvent as compared to 1,4-dioxane.

2.2.1.2 Preparation of 1-(2,6-diisopropylphenyl)imidazole, *i*Pr$_2$PhIm 1b

The synthesis of 1-(2,6-diisopropylphenyl)imidazole, *i*Pr$_2$PhIm **1b**, was attempted by two methods. The first attempted method was via the preparation of the isothiocyanate intermediate, Scheme 2.11.[167] Thiophosgene was suspended in water and then 2,6-diisopropylphenylamine was added, giving a yellow solution of the isothiocyanate. The aminoacetaldehyde was then added to the isothiocyanate in ethanol and the solution refluxed. Once the solvent was removed, the product was suspended in HCl again and refluxed. The solution was cooled and the solid that formed was collected by filtration, washed with water and left to air dry. The product was suspended in HNO_3 and warmed, creating a vigorous reaction which was then cooled. The product was basified with ammonia solution and was extracted in dichloromethane at room temperature. This reaction gave an impure sample of the target product as a yellow solid which was collected by filtration and dried in air. This reaction scheme was considered a lengthy pathway and did not yield the targeted product with satisfactory purity. Therefore another procedure was conducted following Gridnev's one pot reaction.



Scheme 2.11 Preferred method synthesis of 1-(2,6-diisopropylphenyl)imidazole **1b**

The method used was similar to that utilised to prepare 1-(mesityl)imidazole, discussed in Section 2.2.1.1. The product was initially isolated as a brown sticky solid that can be purified *via* vacuum sublimation at 110 °C, 10 mbar, resulting in colourless crystals of the target compound. The product was shown by ^{1}H NMR spectroscopy to be pure and consistent with literature data.[168] This one pot reaction procedure was thus found to be the preferred method compared to synthesis *via* the isothiocyanate intermediate.

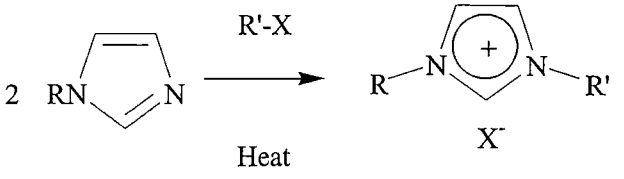
2.2.1.3 Preparation of 1-phenylimidazole, PhIm 1c

The synthesis of 1-phenylimidazole, PhIm **1c**, was attempted *via* Gridnev's one pot reaction using both 1,4-dioxane and methanol as solvents. However, both solvents resulted in a black sticky tar that was unable to be purified *via* vacuum distillation. Low yields of a yellowish solution could only be achieved and analysis of these products by ^{1}H NMR spectroscopy showed product peaks along with a substantial amount of various impurities. Attempts to use the impure sample in the subsequent imidazolium salt formation step were also unsuccessful. Since **1c** was not obtained pure *via* this method, it is not discussed further herein. 1-phenylimidazole was eventually purchased from Sigma-Aldrich and used without further purification.

2.2.2 Diimidazolium salt synthesis

Imidazolium salts are commonly prepared by S_N2 substitution of alkyl halides with an imidazolide nucleophilic species, Scheme 2.12. The substitution can be adapted to diimidazolium salts by the use of dibromomethane or other CH_2X_2 reagents to give various diimidazolium salts. Extension of the alkylene bridge of the dihaloalkylene to create diimidazolium salts has led to, ethylene;

propylene and butylene bridged diimidazolium salts.[157] The main concern of this reaction is long reaction times and high temperatures, often above the boiling point of a reagent/solvent and thus the requirement of a high pressure reactor may be necessary. Even though often used as precursors for *N*-heterocyclic carbene complexes, only a few crystal structures of alkyl-bridged diimidazolium compounds have been reported.[169]

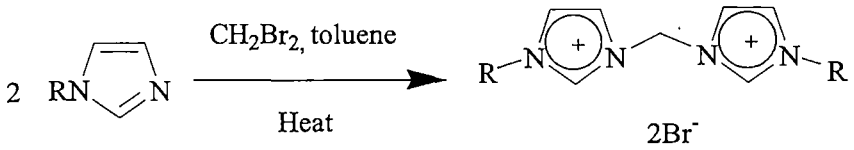


Scheme 2.12 Synthesis of imidazolium salts

2.2.2.1 Preparation of methylene bridged diimidazolium dihalides

Diimidazolium salts **2a-c**, derived from MesIm **1a**, *i*Pr$_2$PhIm **1b** and PhIm **1c** were prepared according to literature procedures.[140] Dibromomethane was used as the source of the methylene bridge of the diimidazolium dication giving these, thus, as dibromide salts. The reactions were attempted with reaction of the *N*-arylimidazoles with dibromomethane in toluene above its boiling point in a pressure vessel for 24 to 48 hours, Scheme 2.13. It was noted that toluene was the best choice for solvent rather than THF or 1,4-dioxane. When THF or 1,4-dioxane was used as solvent, the incomplete reaction mixtures went brown after 24 hours of reaction. The products were obtained as white solids by filtration that were then washed with THF and dried *in vacuo*. The resulting products were shown by ^{1}H and ^{13}C NMR spectroscopy to be pure and consistent with literature data.[140,168] 1,1'-di(2,4,6-mesityl)-3,3'-methylenediimidazolium dibromide [(MesImH)$_2$CH$_2$]Br$_2$ **2a** was prepared by heating MesIm **1a** with dibromomethane in toluene at 150 °C for 48 hours. Similarly, the diimidazolium salt with 2,6-diisopropylphenyl substituents, [(*i*Pr$_2$PhImH)$_2$CH$_2$]Br$_2$ **2b** was prepared in the same manner. However, better yields were obtained when the reaction was undertaken at 120 °C heating with toluene solvent for 24 hours. 1,1'-diphenyl-3,3'-methylenediimidazolium dibromide [(PhImH)$_2$CH$_2$]Br$_2$ **2c** was prepared in toluene by heating 1-phenylimidazole in toluene at 120 °C for 24 hours. The main

spectroscopic identifier of the formation of the imidazolium salts **2a-2c** is the ^{1}H NMR resonance of methylene protons at *ca.* 6.00 ppm.

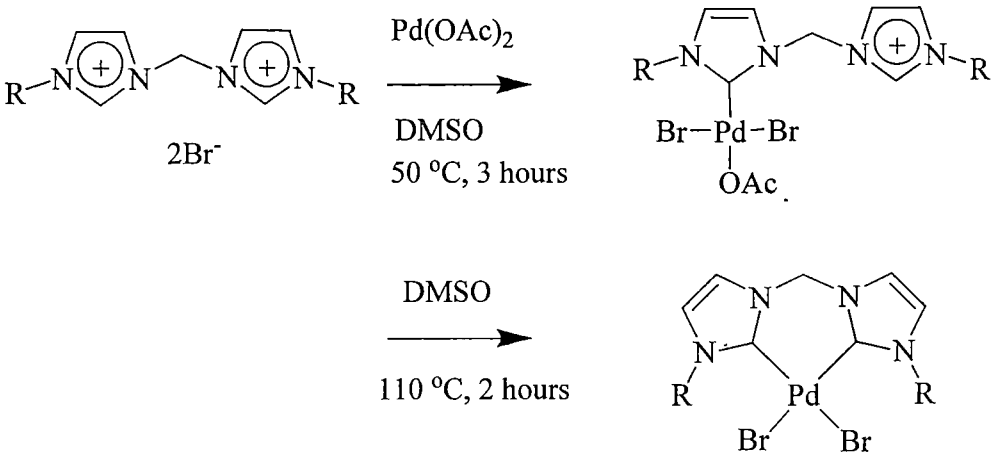


R = 2,4,6-mesityl **2a**, 2,6-diisopropylphenyl **2b** and phenyl **2c**

Scheme 2.13 Synthesis of methylene bridged diimidazolium salts

2.2.3 Palladium(II) NHC dihalide complexes

The neutral chelated bis(carbene)palladium(II) dibromide complexes $[\{(ArIm)_2CH_2\}PdBr_2]$ were prepared *via* the *in situ* carbene complex generation procedure. {1,1'-di(2,4,6-mesityl)-3,3'-methylenediimidazolin-2,2'-diylidene}palladium(II) dibromide, $[\{(MesIm)_2CH_2\}PdBr_2]$ **3a**, was prepared following the procedure developed by Herrmann[140] in which $[(MesImH)_2CH_2]Br_2$ **2a** was heated at two stages under an inert atmosphere with palladium(II) acetate in dry DMSO, Scheme 2.14. The first stage of heating is at a mild temperature, 50 °C for 3 hours, in which deprotonation of one of the imidazolium rings of the salt occurs to form a mono(carbene) palladium intermediate complex. The next stage is required to deprotonate the second imidazolium ring to yield the chelated bis(carbene) palladium dihalide by increased heating at 110 °C for 2 hours. The solvent was then removed *in vacuo* and the product obtained as a yellow solid once washed with dichloromethane and purified by recrystallisation from acetonitrile. The product was shown by ^{1}H and ^{13}C NMR spectroscopy to be pure and consistent with literature data.[140]



R = 2,4,6-mesityl **3a**, 2,6-diisopropylphenyl **3b** and phenyl **3c**

Scheme 2.14 Preparation of chelated NHC Pd(II) dihalide complexes

Attempts to synthesise 1,1'-di(2,6-diisopropylphenyl)-3,3'-methylenediimidazolium dibromide, $[\{(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}\text{PdBr}_2]$ **3b** from its precursor $[(i\text{Pr}_2\text{PhImH})_2\text{CH}_2]\text{Br}_2$ **2b** followed a patent by Straβner.[168] The precursor compound was gradually heated in DMSO with palladium(II) acetate for an hour at 40 °C, one hour at 60 °C, 2 hours at 80 °C, 2 hours at 100 °C and another hour at 130 °C. At the end of the reaction, the solvent was removed *in vacuo* and the product rinsed in dichloromethane, giving a pale yellow solid in good yield. The product can be purified by recrystallisation from acetonitrile. The product was shown by ^{1}H and ^{13}C NMR spectroscopy to be pure and consistent with literature data.[140] The yield was found to be improved and the formation of palladium black avoided when the diimidazolium salt and palladium(II) acetate were dried by heating at *ca.* 70 °C for 15 minutes *in vacuo* prior to the addition of DMSO.

Attempts to synthesise 1,1'-diphenyl-3,3'-methylenediimidazolium dibromide $[\{(\text{PhIm})_2\text{CH}_2\}\text{PdBr}_2]$ **3c** from its precursor $[(\text{PhImH})_2\text{CH}_2]\text{Br}_2$ followed the reported method of Okuyama.[170] The precursor compound was gradually heated in DMSO with palladium(II) acetate for an hour at 40 °C and 10 minutes at 110 °C. At the end of the reaction the solvent was removed in high vacuum, the product is rinsed dichloromethane and then dried *in vacuo*.

Electrospray ionisation-mass spectrometry (ESI-MS) showed that the product was a minor component of the mixture with *m/z* 487 (M-Br, $C_{19}H_{16}N_4BrPd$) as well as an envelope at 405 (M-2Br, $C_{19}H_{16}N_4Pd$) being low abundance ions, with a large ion of *m/z* 631 corresponding to the pendant imidazolium mono-NHC complex [{(PhImH)CH_2(PhIm)}$PdBr_2$(OAc)], but further heating was not successful. Longer heating was undertaken following a method more similar to Herrmann,[140] with 50 °C heating for 3 hours and increased heating of 110 °C for 2 hours. By the end of this reaction a significant amount of palladium black had formed, from which no product could be obtained. Since the synthesis of **3c** was unsuccessful, the reaction sequence was not continued for the phenyl substituted palladium complexes.

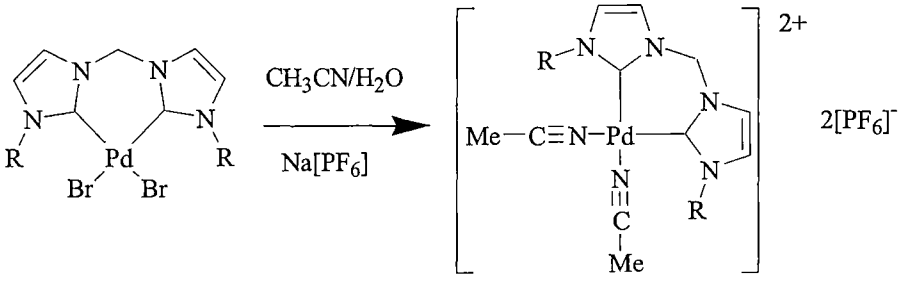
^{1}H NMR spectroscopic characterisation of the chelated NHC Pd(II) dihalides complexes **3a** and **3b** showed singlet resonances for the methylene groups at 5.89 ppm for **3a** and 6.55 ppm for **3b**. The two-stage-heating method by Herrmann has universally given chelated mononuclear complexes, as opposed to dinuclear bridging carbene complexes, for which singlet resonances for methylene protons might be expected, as mentioned in Section 2.1.2.

2.2.4 Dicationic palladium(II) NHC complexes

The dicationic complexes [{(MesIm)$_2$$CH_2$}Pd(NCMe)$_2$][$PF_6$]$_2$ **4a** and [{(*i*Pr$_2$PhIm)$_2$$CH_2$}Pd(NCMe)$_2$][$PF_6$]$_2$ **4b** were synthesised in acetonitrile : H_2O (1 : 1) solutions with Na[PF_6] by heating at 80 °C for an hour before the acetonitrile was removed by rotary evaporation, Scheme 2.15. The colourless solids that deposited after all of the acetonitrile was removed were collected, washed with H_2O and dried *in vacuo*. The products were purified *via* recrystallisation by vapour diffusion of diethyl ether into saturated acetonitrile solutions. Products were obtained as colourless needle-like crystals.

The 2,4,6-mesityl substituted of the dicationic Pd(II) complex [{(MesIm)$_2$$CH_2$}Pd(NCMe)$_2$][$PF_6$]$_2$ **4a** has been reported, while the 2,6-diisopropylphenyl analogue [{(*i*Pr$_2$PhIm)$_2$$CH_2$}Pd(NCMe)$_2$][$PF_6$]$_2$ **4b** is a new compound. The methods used for the synthesis were as reported for the mesityl complex.[140] Both dicationic complexes are air stable and can be stored in open air

conditions for long periods. The mesityl substituted complex was shown by ^{1}H and ^{13}C NMR spectroscopy to be pure and consistent with literature data.[140] The 2,6-diisopropylphenyl complex was characterised by ^{1}H and ^{13}C NMR spectroscopy, LSIMS, microanalysis and single crystal X-ray structure determination.



R = 2,4,6-mesityl **4a**, 2,6-diisopropylphenyl **4b**

Scheme 2.15 Preparation of dicationic NHC Pd(II) complexes **4a** and **4b**

The ^{1}H NMR spectrum of the cationic complex **4b** has similar proton resonances to the previously reported mesityl substituted analogue, **4a**. Like its mesityl analogue **4a**, **4b** also exhibits a singlet resonance for the methylene protons at room temperature, Figure 2.8. The proton resonances from the four methyls of the diisopropylphenyl unit appeared as two equal intensity doublets at 1.02 and 1.28 ppm. A septet resonance appears for the methine group of the diisopropylphenyl units at 2.51 ppm. This is consistent with free rotation of the aryl substituents (about the C(*ipso*)-N bond) in solution at room temperature on the NMR time scale so as to make both isopropyl groups of the aryl substituents equivalent. This behaviour has previously been reported for the mesityl analogue. Similarly, the methylene proton resonance appears as a singlet at 6.61 ppm. This is in accordance with fluxional behaviour of the six-membered chelate ring of the bis-NHC ligand, which has also been previously reported for system for 1,1'-diaryl substituted complexes (neutral dihalides as well as dicationic species). The aromatic resonances occur in the 7.3-8.0 ppm region and have been assigned through COSY, HMQC and HMBC spectra. The ^{13}C NMR spectrum of **4b** showed two isopropyl methyl carbons at 23.6 and 26.0 ppm and the methine carbon at 28.9 ppm. The methyl carbon of MeCN is at 1.9 ppm, while the

methylene carbon of the NHC ligand resonates at 62.8 ppm. The nitrile carbon of acetonitrile is at 119.0 ppm. The carbon resonances at 123.1 and 128.7 are assigned to the 4,5-positions of the imidazolin-2-ylidene rings. The carbon resonances at 124.6, 131.1, 135.3, and 145.7 are resonances for *m*-, *p*-, *ipso*- and *o*- carbon of the aryl substituent, respectively. The carbene carbon resonance at 143.6 ppm is in accordance with its mesityl analogue of 145.5 ppm. The Pd(II) complex **4b** showed *m/z* ions of 619.1 $[\{(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}\text{Pd(NCMe)}]^+$ and 573.2 $[\{(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}\text{Pd}]^+$, with no dimer-derived ions or half mass ion for dicationic ions.

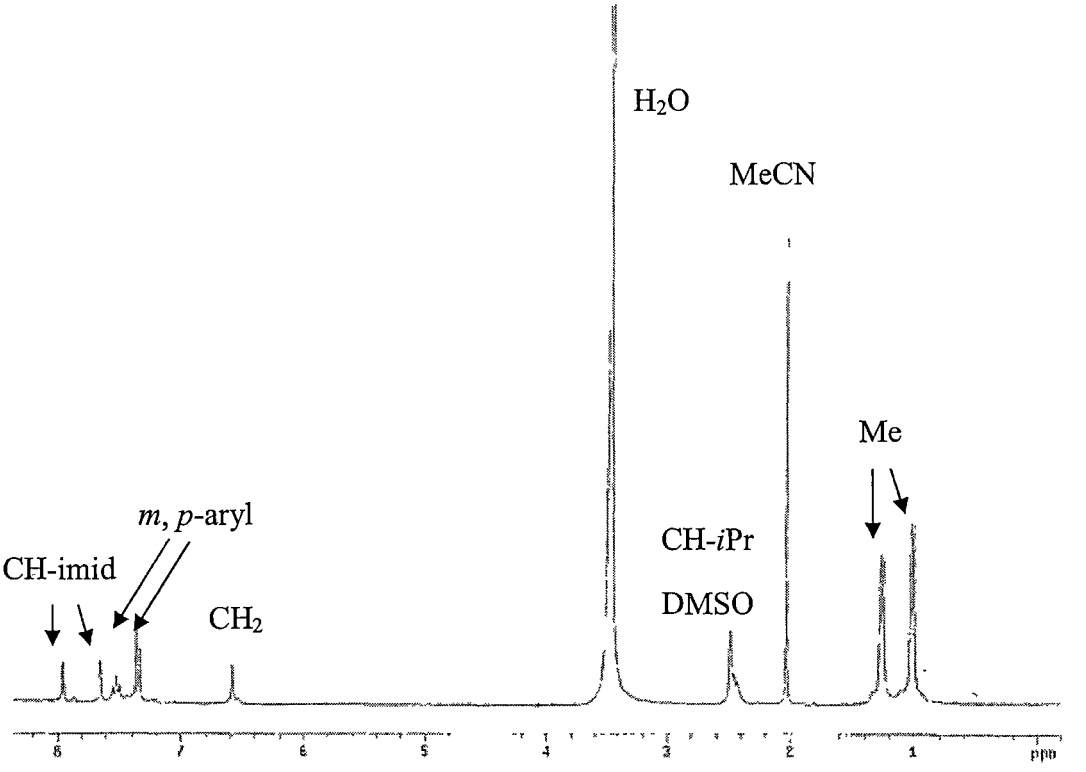


Figure 2.8 ^{1}H NMR spectrum of **4b** at 300 MHz in DMSO-d_6

Crystals of **4b** suitable for X-ray structure determination were grown by vapour diffusion of a diethyl ether into a nearly saturated acetonitrile solution at room temperature overnight. The colourless needles are air stable, belonging to the orthorhombic space group *Pbca*, with a = 21.359(4), b = 16.974(3), c = 23.780(5) Å. The asymmetric unit contains one dication, a well ordered

hexafluorophosphate anion and one that is disordered as well as a non-coordinated acetonitrile molecule.

Complex **4b** is best described as a monomeric dicationic chelated bis(NHC) complex of palladium(II) with a puckered six-membered chelate ring formed from the bis(NHC) ligand, Figures 2.9-2.11. Complex **4b** is isostructural with its mesityl analogue $[\{(MesIm)_2CH_2\}Pd(NCMe)_2][PF_6]_2$ **4a**.[137] The remaining two coordination sites of the palladium centre are occupied by molecules of acetonitrile. The distorted square planar coordinated metal centre and the methylene carbon atom lie on a non-crystallographic, approximate, mirror plane symmetry element of the dication. Summaries of important bond distances and angles are given in Table 2.1.

The Pd-C distances of 1.974(3) and 1.988(3) Å in **4b,** are in accordance with its close analogues $[\{(MesIm)_2CH_2\}Pd(NCMe)_2][BF_4]_2$ at 1.966(2) and 1.972(3) Å,[140] $[\{(MesIm)_2CH_2\}Pd(NCMe)_2][PF_6]_2$ **4a** at 1.965(8) and 1.989(5) Å,[137] as well as a diiodide neutral chelated complex $[\{(MeIm)_2CH_2\}PdI_2]$ at 1.988(7) and 1.989(8) Å,[57] and the related non-chelated complex $[(Me_2Im)_2PdI_2]$ at 1.990(3) and 1.997(3) Å.[104] The Pd-N distances measure 2.036(3) and 2.045(3) Å, again being similar to the mesityl analogue[137] $[\{(MesIm)_2CH_2\}Pd(NCMe)_2][PF_6]_2$ **4a** at 2.066(2) and 2.059(4) Å and $[\{(MesIm)_2CH_2\}Pd(NCMe)_2][BF_4]_2$ at 2.055(2) and 2.064(2) Å.[140] The C-Pd-C bite angle is increased to 87.65(11) ° in comparison to the mesityl analogues at 84.05(11)°[140] and 85.05(3)°.[137] Presumably this relates to steric interactions between the diisopropylphenyl substituents at each end of the bis(NHC) ligand on one face of the metal coordination plane. This steric effect consequently flattens the chelate ring puckering (methylene carbene 1.248(4) Å out of the metal coordination plane, *c.f.*, 1.6_2 Å in **4a**) and the angle of the NHC heterocyclic planes to the metal coordination plane are reduced at 28.5(1) ° (C1-N5) and 27.51(9) ° (C7-N11), in comparison to $40._1$ ° in **4a**. The space filling representations in Figure 2.9 display the steric interferences of the 2,6-diisopropylphenyl substituents that lead to these changes in comparison to the less bulky mesityl analogue **4a**.

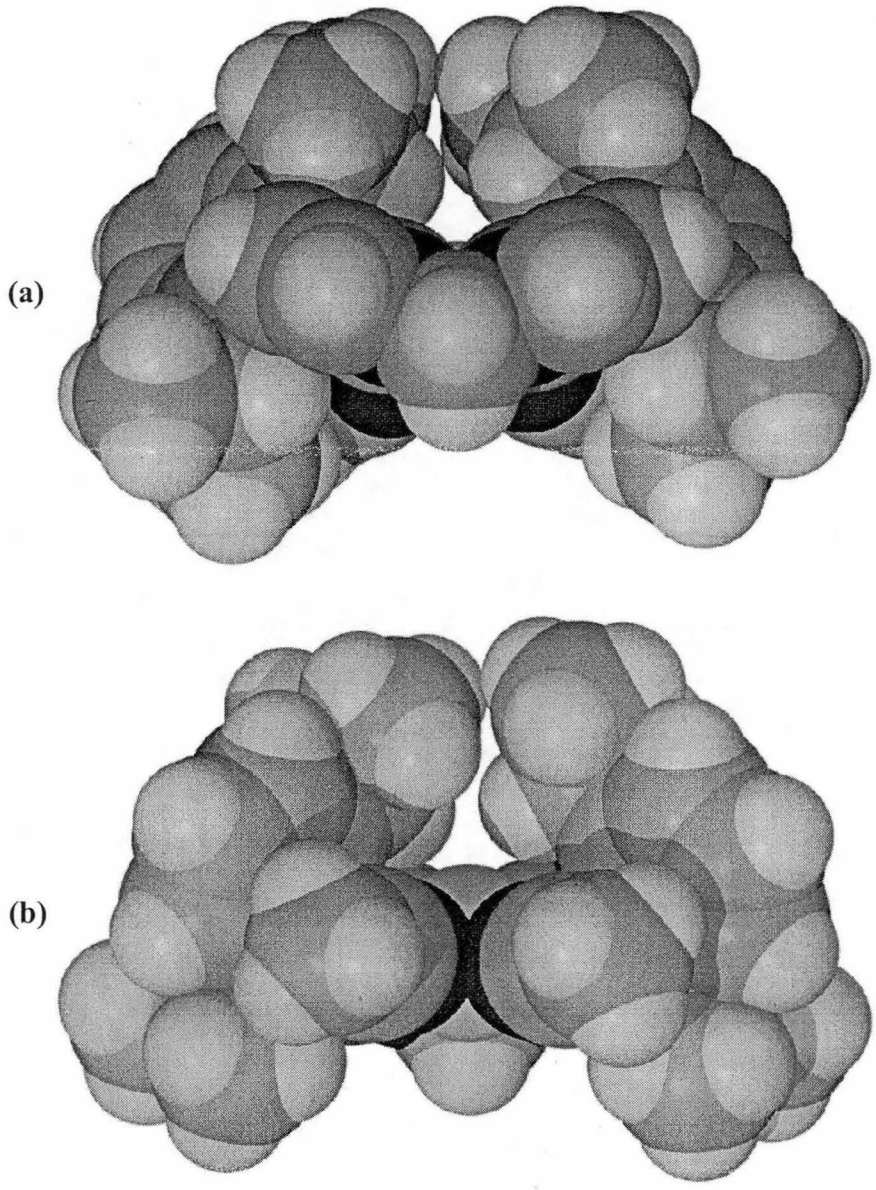


Figure 2.9 Spacefilling representations of $[\{(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}\text{Pd}(\text{NCMe})_2][\text{PF}_6]_2$ **4b** revealing the steric influences of the 2,6-diisopropylphenyl substituents on the top side of the dication (as drawn). (a) viewed along the planes of the NHC rings highlighting the flattened "v-shape" formed by these units and, (b) into the N-Pd-N ligand bite angle which shows their influence on the remaining coordination sites.

The inequivalent N-C-Pd angles to the NHC ligands, 124.4(2)/131.5(2) and 124.60(19)/131.4(2) °, are clear indications of the strain caused by not only chelate ring formation but the additional steric effects of the 2,6-diisopropylphenyl substituents compared to the mesityl analogues. The N-Pd-N angle to the NCMe ligands are reduced to 83.64(10) Å owing to the bulk of the

2,6-diisopropylphenyl substituents at the wingtips of the chelate structure, shrouding the metal centre and the acetonitrile molecules. The influence of the bulky substituents is apparent when compared to the mesityl substituted analogue, bulky in itself, in which the N-Pd-N angle is free from distortion, being closer to ideal at 87.41(3)°. Further, there are significantly reduced Pd-N-C angles of 166.4(2) and 165.3(2)° to the acetonitrile molecules due to this steric effect. The C-C and C-N bond distances of the imidazolin-2-ylidene based ring systems, as well as the Pd-C bond distances in complex **4b** are in accordance with the π-stabilisation of the carbene onto the nitrogen centres and contribution from *s*- and *p*-donation to the metal centre. Other bond angles within the molecule are unexceptional and do not require comment.

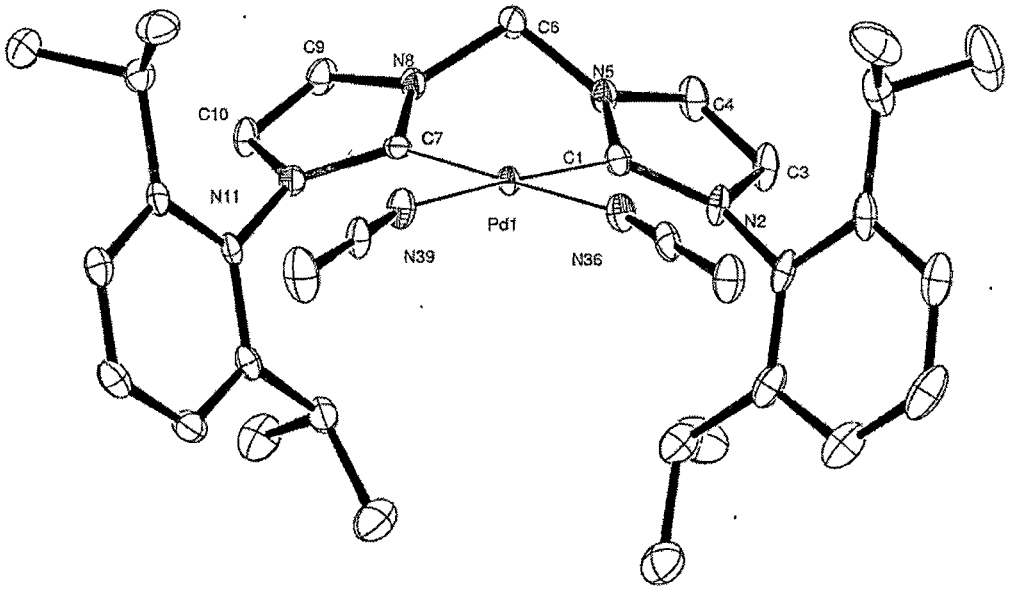


Figure 2.10 ORTEP representations of $[\{(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}\text{Pd}(\text{NCMe})_2][\text{PF}_6]_2$ **4b** with 50% probability level thermal ellipsoids, highlights the environment of the metal centre. All hydrogen atoms omitted for clarity.

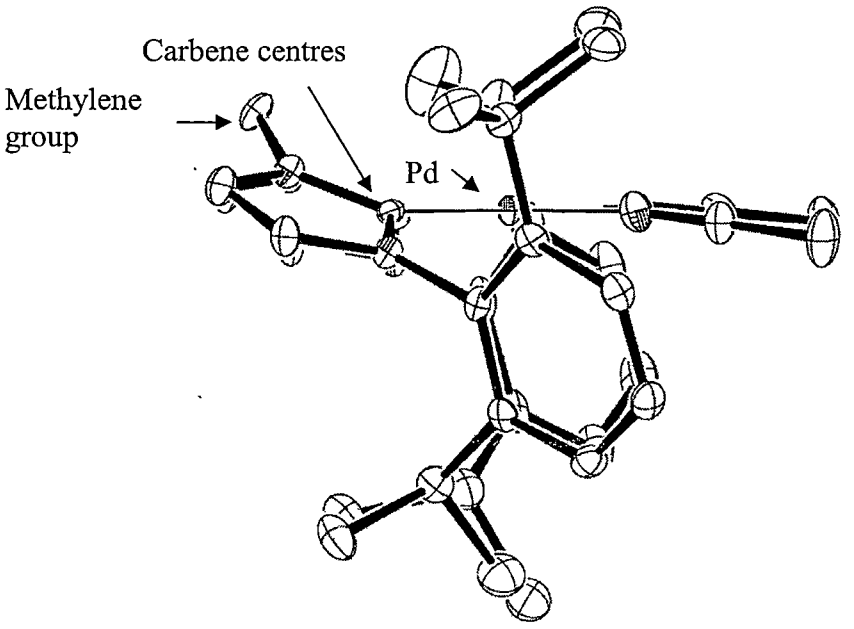


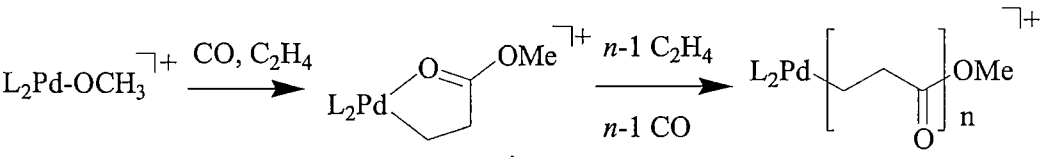
Figure 2.11 ORTEP representations of $[\{(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}\text{Pd}(\text{NCMe})_2][\text{PF}_6]_2$ **4b** with 50% probability level thermal ellipsoids viewed from the side of the dication along the metal coordination plane. All hydrogen atoms omitted for clarity.

Table 2.1 Selected bond lengths (Å) and bond angles (°) for **4b**

Pd1-C1	1.974(3)
Pd1-C7	1.988(3)
Pd1-N36	2.036(3)
Pd1-N39	2.045(3)
C1-Pd1-C7	87.65(11)
C1-Pd1-N36	93.88(11)
C7-Pd1-N36	178.22(10)
C1-Pd1-N39	176.93(10)
C7-Pd1-N39	94.86(10)
N36-Pd1-N39	83.64(10)
C7-N11-C10	110.5(2)
C37-N36-Pd1	166.4(2)
C40-N39-Pd1	165.3(2)
N5-C1-N2	104.0(2)
N5-C1-Pd1	124.4(2)
N2-C1-Pd1	131.5(2)
N8-C7-N11	104.0(2)
N8-C7-Pd1	124.60(19)
N11-C7-Pd1	131.4(2)

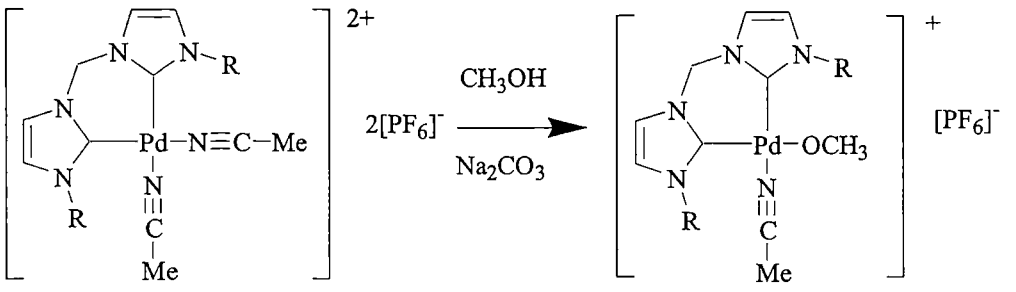
2.2.5 [{bis(μ-carbene)}$_2$Pd$_2$H]$^+$ systems

Previous work by Herrmann on dicationic bis(NHC) palladium(II) complexes in carbon monoxide/ethene copolymerisation studies relied on *in situ* formation of the active species. The polymer yield was poor, but the molecular weight was deemed to be very high. Thus, we aimed to prepare the supposed catalytically active cationic Pd(II) methoxide complex and use this directly in the copolymerisation in an effort to increase polymer yields, Scheme 2.16. The mechanistic discussion of ethene/CO copolymerisation presented in Section 1.6 highlighted the active species as likely being either a cationic Pd(II) hydride or methoxide complex, [L_2Pd(H)(solvent)]$^+$ or [L_2Pd(OMe)(solvent)]$^+$. These monocationic species represent the initial coordination site, L_2PdR^+, for the copolymerisation reaction, where L_2 represents the bidentate ligand and R is the growing polymer chain, where initiation of the copolymerisation reaction commences by alternating CO and ethene insertions, Scheme 2.16.



Scheme 2.16 Initiation step of carbon monoxide/ethene copolymerisation

Reaction of the dicationic bis(NHC) palladium(II) complexes **4a** and **4b** in methanol solvent in the presence of base were envisaged to result in the cationic palladium methoxide species as presented in Scheme 2.17. However, the reaction did not produce the targeted monocationic Pd(II) methoxy complex according to this mechanism. Rather, the reaction of the dicationic palladium(II) precursors with sodium carbonate in methanol afforded stable dipalladium(I) hydride complexes [{bis(μ-carbene)}$_2$Pd$_2$H][PF_6] of varying structure, see Sections 2.2.5.1-2.2.5.2.

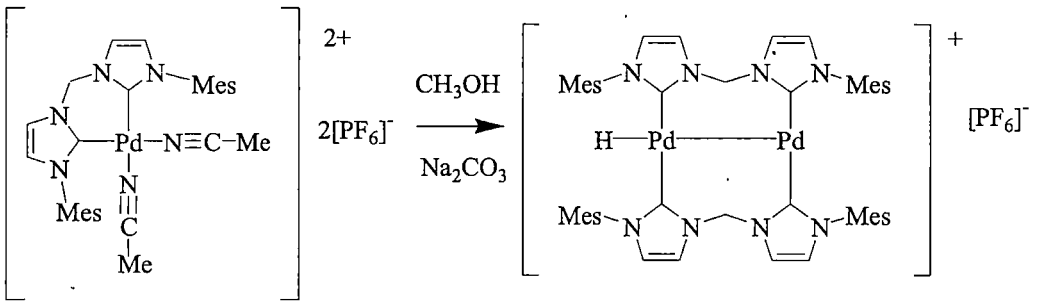


Scheme 2.17 Proposed synthesis of Pd(II) methoxide complexes

2.2.5.1 [{μ-(MesIm)$_2$CH$_2$}$_2$Pd$_2$H][PF$_6$] 5a

2.2.5.1.1 Synthesis and characterisation of [{μ-(MesIm)$_2$CH$_2$}$_2$Pd$_2$H][PF$_6$] 5a

The reaction of [{(MesIm)$_2$CH$_2$}Pd(NCMe)$_2$][PF$_6$]$_2$ **4a** with an excess amount of sodium carbonate in dry methanol was undertaken by heating at 50 °C under an argon atmosphere for two hours, Scheme 2.18. The red solution was filtered from the excess sodium carbonate *via* cannula transfer and the methanol slowly removed *in vacuo*. Crystallisation was achieved from the concentrated solution by slow cooling in an acetone bath to -20 °C. This afforded a mixture of red needle and prismatic crystals that were isolated by removal of the methanolic mother liquor, which could be cropped for further product yield. The crystals were dried *in vacuo* and stored in the glove box. Complex **5a** could not be formed from extensive heating of **4a** in MeOH or DMSO in the absence of base. Characterisation revealed the red crystalline solid to be a novel cationic dipalladium(I) hydride complex. Complex **5a** is air sensitive, stable and soluble in methanol and THF over long periods and is tolerant to water. It has low solubility in 1,4-dioxane and is insoluble in acetone and hydrocarbons. Complex **5a** decomposes over minutes in DMSO. It can be stored in the glove box for a long time period as a solid (> 1 year).

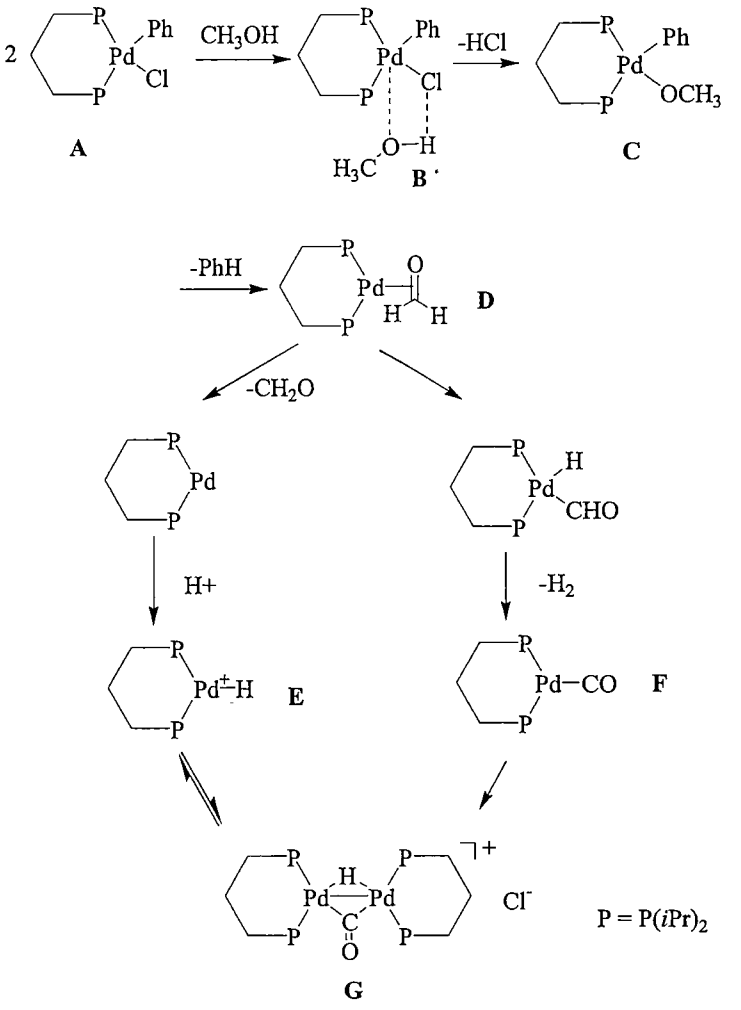


Scheme 2.18 Synthesis of $[\{\mu\text{-}(MesIm)_2CH_2\}_2Pd_2H][PF_6]$, **5a**

Mass spectrometry of **5a** gave initial evidence for the formation of the cationic dipalladium(I) hydride complex. The presence of the hydride was confirmed by ^1H NMR spectroscopy, which was subsequently located by a neutron crystallographic study. These characterisation details, along with the X-ray crystallography study enabled unambiguous structural assignment as shown in Scheme 2.18.

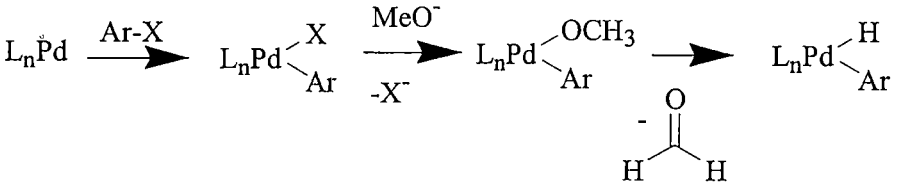
The formation of the dipalladium(I) complex **5a** from the Pd(II) precursor must proceed via a number of steps. However, no intermediates were observed when the reaction was followed by ^1H NMR spectroscopy and mass spectrometry (gives **5a** as the monodeuteride from d_4-methanol). The reaction proceeds cleanly to the single product in apparent quantitative yield. The reaction at room temperature is greatly slowed (relative to 50 °C), but again no intermediates are observable. No information is available regarding the stage at which the chelated bis(NHC) mononuclear to bridged dipalladium conversion takes place. The formation of the dipalladium(I) hydride complex system from the reduction of methanol in the presence of base can be rationalised from several reported supporting mechanisms. A dipalladium(I) hydride complex has a been reported by Milstein where methanol reduced (dippp)Pd(Ph)Cl (dippp = 1,3-bis(diisopropylphosphino)propane), Scheme 2.19.[171,172] The mechanism of this reaction involved the electrophilic attack of a cationic palladium(II) hydride intermediate on a Pd(0) carbonyl complex as described by reaction of (dippp)Pd(Ph)Cl in CD_3OD in the presence of NEt_3 as base, Scheme 2.19. The first step of the reaction is the methanolysis of the Pd(II) complex (A) which

involves the methoxide attack at the metal centre (B). Reductive elimination and β-hydride elimination gives the Pd(0) formaldehyde species (D). The formation of the product (G) is probably the result from the reaction between the outcomes of two competing pathways. Oxidative addition followed by hydride migration and reductive elimination would lead to the formation of Pd(0) carbonyl species (F), meanwhile the Pd(II) complex (E) is formed from formaldehyde dissociation followed by protonation. Reaction between (E) and (F) results in the dinuclear Pd(I) complex (G). This type of reaction is similar to what occurred during the reaction of **4a** in methanol in the presence of base, except that in the formation of **5a** the hydride ligand does not bridge and CO is not retained.

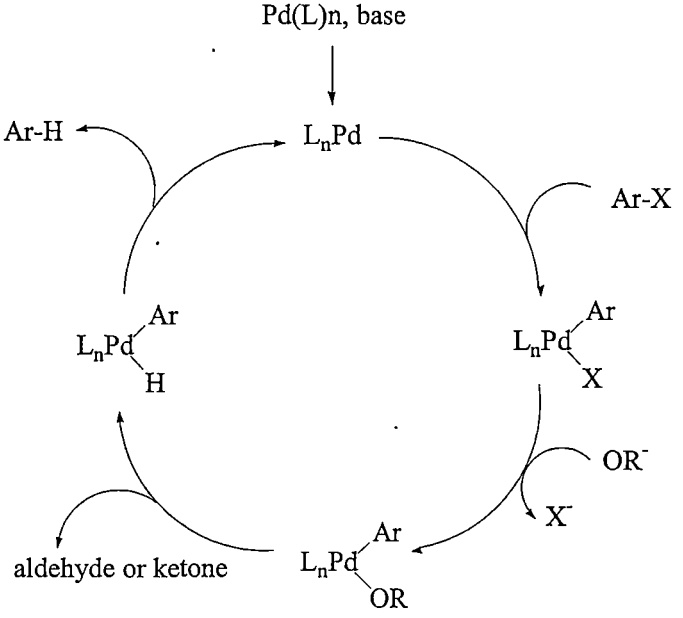


Scheme 2.19 Reduction of a Pd(II) complex into a Pd(I) hydride complex in methanol[171]

The Nolan group[173,174] reported that oxidative addition of aryl halides to Pd(0) NHC complexes may generate NHC palladium(II) hydride species in the presence of methanol that are involved in the catalytic dehalogenation of aryl halides, Scheme 2.20. This condition may promote the formation of a palladium(II) methoxide intermediate, simultaneously with the β-elimination of formaldehyde from an alkoxide, similar to the Milstein intermediate.[171] The proposed mechanism for the catalytic dehalogenation of an aryl halide itself is described in Scheme 2.21. This mechanism is also followed when dehalogenation reactions were catalysed by (NHC)Pd(allyl)Cl,[81] palladacycle NHC[175] or Ni imidazolium chloride complexes.[176] This proposed mechanism supports the possibility of (NHC)Pd(II) hydride systems forming from reactions of palladium(0) complexes.



Scheme 2.20 Proposed mechanism of the formation of the (NHC)Pd(II) hydrides by the β-H elimination from OMe complexes



Scheme 2.21 Proposed mechanism for catalytic dehalogenation of aryl halide[173]

Other (NHC)Pd(II) hydride complexes have been reported from Pd(0) precursors. Cavell[177] reported the synthesis of stable Ni(II) and Pd(II) tris(NHC) hydrides *via* oxidative insertion of the metal centre into the C2-H bond of imidazolium salts under mild conditions. The monocationic tris(carbene)palladium(II) hydride complex was isolated with a characteristic Pd-H resonance in the ^{1}H NMR spectrum at δ = -10.17 ppm, Figure 2.12. Crystal structure determination showed the Pd-H distance to be 1.57(3) Å. This direct *in situ* generated complex could be an important route to active cationic species, especially since metal hydrides are often implicated in catalytic processes.

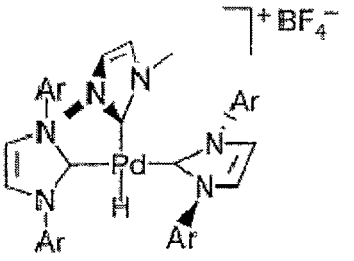


Figure 2.12 Monocationic tris(carbene) Pd(II) hydride complex[177]

Some examples of dinuclear Pd(I) hydride complexes have been reported. Milstein reported a hydride and carbonyl bridged Pd(I) complex [(dippp)Pd_2(μ-H)(μ-CO)]Cl, Figure 2.13 (A).[171] A similar complex with 2,2'-bipyridine, [{(bipy)Pd_2}(μ-H)(μ-CO)]Cl (bipy = 2,2'-bipyridine) (B), was reported by Wong.[178] Another binuclear palladium complex with two bridging hydrides, [(dippp)Pd_2(μ-H)$_2$] (C) was reported by Fryzuk.[179] There are no examples of dinuclear Pd(I) hydride complexes reported with terminal hydride ligands to the best of our knowledge.

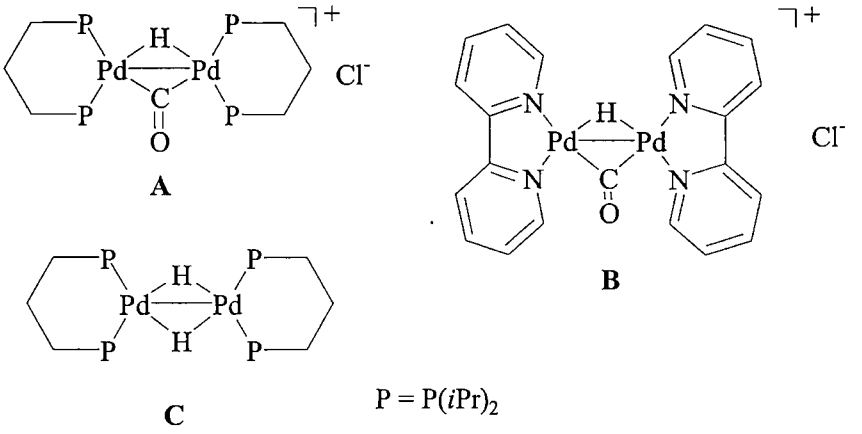


Figure 2.13 [{(dippp)Pd}$_2$(μ-H)(μ-CO)]Cl (A), [{(bipy)Pd}$_2$(μ-H)(μ-CO)]Cl (B) and [{(dippp)Pd}$_2$(μ-H)$_2$] (C)

NMR spectroscopy of **5a** was undertaken using CD_3OD solvent, including ^1H, ^{13}C, COSY and HMQC spectra. ^1H NMR spectroscopy showed three methyl proton resonances for the mesityl substituents of varying line width at 1.48, 1.64 ppm and 2.41 ppm. This shows that each *ortho*-methyl group of the mesityl substituents are non-equivalent, presumably due to restricted rotation about the C(*ipso*)-N bond, Figure 2.14. The presence of two inequivalent *m*-H aryl protons of the mesityl group at 6.87 and 6.93 ppm are also seen, consistent with the restricted rotation of the bulky aryl substituent. There are also two methylene resonances, appearing as doublets at 5.97 and 7.88 ppm in an AX spin system. This indicates that each methylene group is in the same environment, but the methylene protons of these are inequivalent. Their differing line width is indicative of an additional process affecting one of the inequivalent methylene protons. A hydride resonance appears at -16.21 ppm which is exchangeable over *ca.* one hour heating at 50 °C in d^4-methanol. The hydride chemical shift is typical and compares with -15.84 ppm for a neutral bis(NHC) palladium(II) hydride complex.[177] Nolan and co-worker reported a Pd-H resonance for an unidentified complex that was formed during a reaction of a Pd(0) NHC complex and an imidazolium salt at -14.85 ppm.[173]

There are only two imidazolin-2-ylidene ring proton resonances observed that are assigned to C4 and C5 protons at 6.82 and 7.48 ppm, which indicates that

each NHC unit in the bridging NHC ligand is equivalent and that both NHC ligands are equivalent. The relatively high symmetry, variable broad resonances and restricted rotation at the mesityl substituents observed in the room temperature ^{1}H NMR spectrum of $[\{\mu\text{-}(MesIm)_2CH_2\}_2Pd_2H][PF_6]$ **5a** led us to examine the fluxionality in solution through variable temperature studies, see Section 2.2.5.1.2.

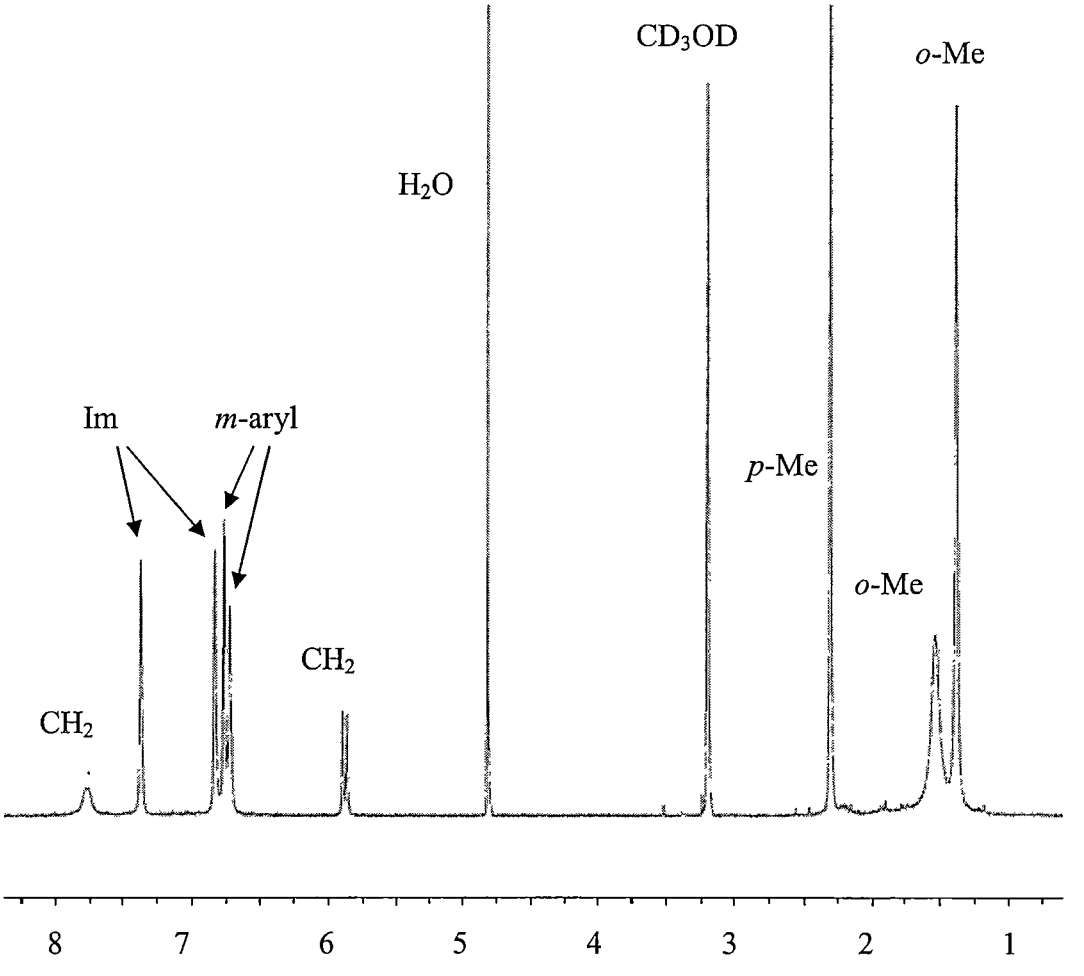


Figure 2.14 ^{1}H NMR spectrum of $[\{\mu\text{-}(MesIm)_2CH_2\}_2Pd_2H][PF_6]$ **5a** at 400 MHz in CD_3OD. Hydride resonance at *ca.* -16 ppm is not shown

Crystals of $[\{\mu\text{-}(MesIm)_2CH_2\}_2Pd_2H][PF_6]$ **5a** suitable for single crystal X-ray crystal structure determination were grown from both saturated methanol and THF solutions that were slowly cooled to -20 °C. Two morphologies of the red crystals from methanol could be identified, both needles and prismatic, which

were shown to relate to different crystal structure forms. Further, the red prismatic crystals obtained from THF were shown to be a tetra(THF) solvate, for which different temperature forms were identified that relate by a phase change in the range 100 – 193 K. Quantitative structural details of the cations in each case are similar (for all located non-hydrogen atoms). Only the structure of the prismatic crystals from methanol is discussed in detail below. Figure 2.15 depicts the structure of the cationic portion of the complex. Selected bond distances and angles are listed in Table 2.2. The atom numbering given for the structure is not systematic and is for X-ray structural discussion only.

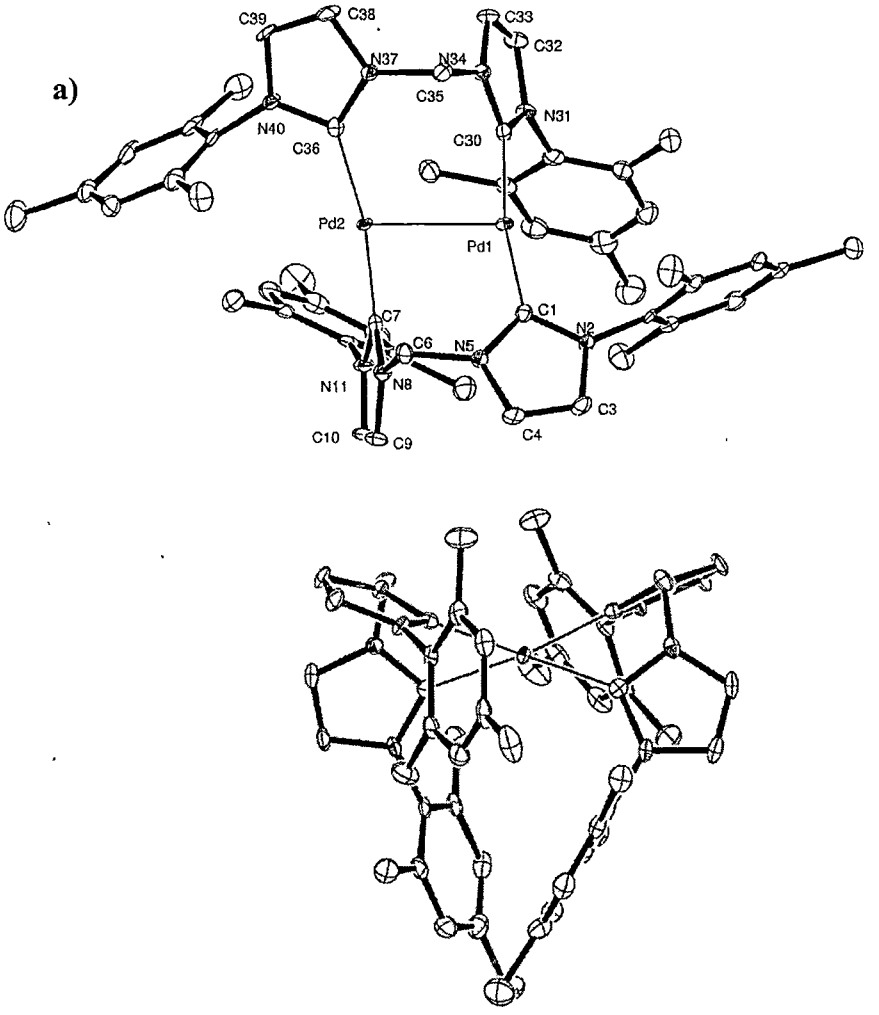


Figure 2.15 ORTEP representations of $[\{\mu\text{-}(MesIm)_2CH_2\}_2Pd_2H][PF_6]$ **5a** with thermal ellipsoids scaled to the 50% probability level. (a) highlights the environment of the metal centre, (b) highlights the relative twist of the metal coordination planes. Hydrogen atoms are omitted for clarity. Pd1 bears the hydride ligand (as determined from neutron diffraction).

Table 2.2 Selected bond distances (Å) and bond angles (°) for the X-ray crystal structure of $[\{\mu\text{-}(MesIm)_2CH_2\}_2Pd_2H][PF_6]$ **5a**

Pd1-Pd2	2.7527(7)
Pd1-C1	2.034(3)
Pd1-C30	2.012(3)
Pd2-C7	2.008(3)
Pd2-C36	2.041(3)
C1-Pd1-Pd2	105.44(9)
C7-Pd2-Pd1	85.67(9)
C30-Pd1-Pd2	85.04(9)
C36-Pd2-Pd1	103.08(9)
C7-Pd2-C36	168.98(12)
C30-Pd1-C1	169.43(12)
N2-C1-Pd1	126.5(2)
N5-C1-Pd1	130.3(2)
N8-C7-Pd2	121.9(2)
N11-C7-Pd2	134.1(2)
N2-C1-N5	103.3(3)
N8-C7-N11	102.4(3)
N31-C30-Pd1	131.1(2)
N34-C30-Pd1	124.8(2)
N40-C36-N37	102.2(3)
N40-C36-Pd2	123.7(2)

The needles of complex **5a** obtained from methanol belong to the tetragonal space group *P4/ncc*, a = 28.514(5), c = 25.560(5) Å with 16 formula units in the unit cell, the asymmetric unit containing one cation and portions of hexafluorophosphate anions residing on symmetry sites (one in net total). In comparison, the prismatic form of complex **5a** obtained from methanol belong to the monoclinic space group $P2_1/c$, a = 13.240(3) b = 18.190(4), c = 21.610(4) Å, β = 105.49(3) °, with 4 formula units in the unit cell, the asymmetric unit containing one cation and a hexafluorophosphate anion. The higher temperature phase of the prismatic crystals of the tetra(THF) solvate of complex **5a** determined at 193 K belong to the orthorhombic space group *Aba2*, a = 20.270(9), b = 14.440(4), c = 23.529(5) Å, with four formula units and 16 THF molecules in the unit cell, the asymmetric unit containing one half of the cation and anion

components, each residing on sites of C_2 symmetry, as well as four THF molecules. Data collection at 100 K revealed that a phase change occurs at an undetermined temperature, giving crystals of the monoclinic space group *C2/c*, a = 26.514(12), b = 40.585(10), c = 14.293(9) Å, β = 118.851(9)°, with 16 formula units and 64 THF molecules in the unit cell, the asymmetric unit containing two cations and two hexafluorophosphate anions as well as eight THF molecules. The crystal symmetry of the higher temperature phase of **5a** from THF implies either a disorder of the hydride location or fluxional motion of the hydride in the solid state at 193 K (see Section 2.2.5.1.2).

All four X-ray crystal structure refinements of **5a** failed to locate the hydride ligand, which is not uncommon for hydridic species of heavy metals. This structural issue was resolved by a neutron crystal structure determination on the prismatic form of the complex obtained from methanol. The neutron structure is shown in Figure 2.16. Whilst the accuracy of the refinement based on neutron data is relatively poor owing to weak diffraction that limited thermal motion modelling to isotropic refinement for all atoms, it was successful in unambiguously locating the hydride ligand in a terminal position attached to Pd1 (clearly visible in difference maps following initial refinement using coordinates of all non-hydrogen atoms obtained from the X-ray crystal structure). Table 2.3 gives selected structural data derived from the neutron crystal structure of **5a**, limited to the hydride geometry. All other structural details are similar to that obtained by X-ray diffraction means.

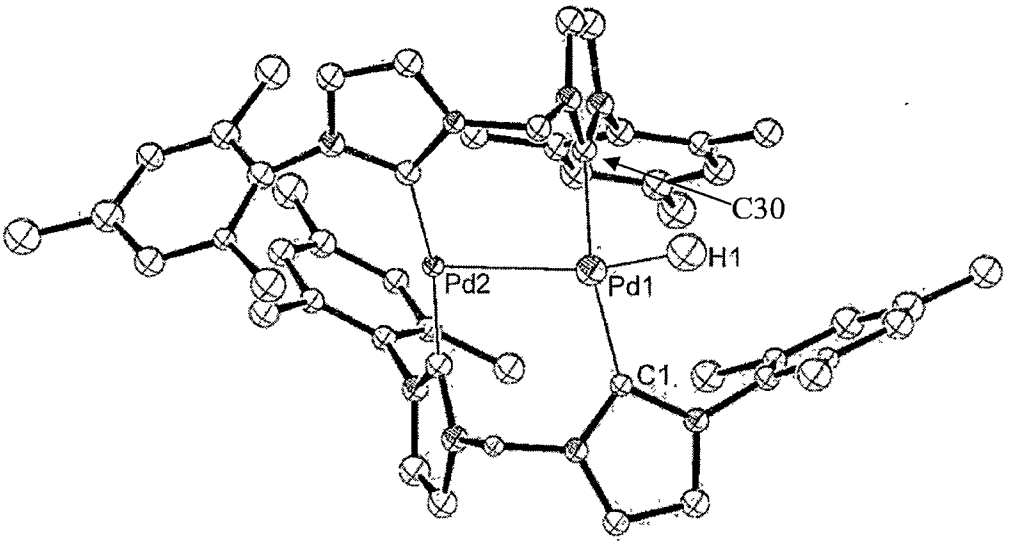


Figure 2.16 ORTEP representation of $[\{\mu\text{-}(MesIm)_2CH_2\}_2Pd_2H][PF_6]$ **5a** obtained from the neutron diffraction data with thermal ellipsoids scaled to the 50% probability level. All hydrogen atoms are omitted for clarity, except for the hydride.

Table 2.3 Selected bond length (Å) and bond angles (°) for the neutron crystal structure of $[\{\mu\text{-}(MesIm)_2CH_2\}_2Pd_2H][PF_6]$ **5a**

Pd1-Pd2	2.716(17)
Pd1-H1	1.61(3)
Pd2-Pd1-H1	167.0(12)
C1-Pd1-H1	86.0(11)
C30-Pd1-H1	82.6(11)

The monocationic dipalladium complex **5a** exhibits a Pd-Pd interaction and two bridging methylene-linked imidazolin-2-ylidene ligands. Overall, the ligand skeleton of the cation displays approximate, non-crystallographic, C_2 symmetry (broken by the hydride ligand) resulting in significant variation in regard to the shielding of the metal core by the mesityl substituents, which all lie on one face of the metal coordination planes, Figure 2.17. Thus, Pd1 has a distorted square planar coordination geometry (including hydride ligand) and Pd2 is chemically distinct, having a distorted T-shape. The metal coordination planes are twisted somewhat, 41.78(7) °. The chemical inequivalence of the palladium centres result in each end of the bis(NHC) ligand being inequivalent. In addition,

the twist between the metal coordination planes results in a further reduction in symmetry of the cation in the solid state, such that each of the four NHC units are inequivalent. The space filling representation in Figure 2.17 highlights the congested nature of the cation and rationalises the observation that ^{1}H NMR spectroscopy of **5a** is consistent with restricted rotation of the mesityl substituents in solution even at elevated temperature, whilst a fluxional process involving interconversion of the twisted metal coordination planes raises the time averaged symmetry of the cation to C_{2v} down to ~ -20 °C (see below). Indeed, low temperature ^{1}H NMR spectroscopic studies of **5a** can be interpreted in terms of the cation being locked in the same low symmetry state as observed in the solid state, with only free rotation of the methyl groups of the mesityl substituents occurring. The solution fluxional behaviour of **5a** is discussed in detail in Section 2.5.2.1.2.

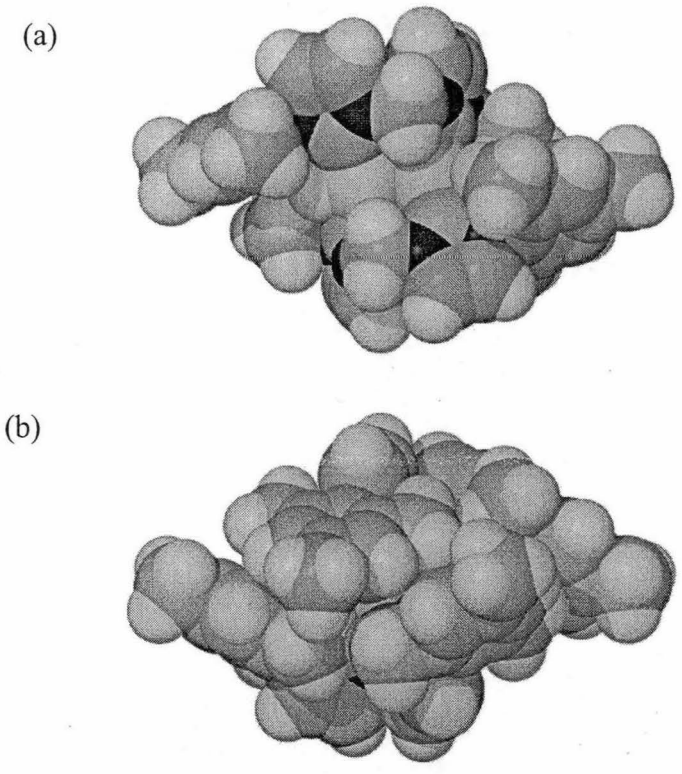


Figure 2.17 Space filling representations of [{μ-(MesIm)$_2$CH$_2$}$_2$Pd$_2$H][PF$_6$] **5a** obtained from neutron data from each side of the Pd coordination planes (a) viewed onto the open face of the metal coordination planes, and (b) onto the mesityl protected face of the metal coordination planes

The Pd1-Pd2 bond length of 2.7527(7) Å in **5a** is much less than the sum of Van der Waals radii of Pd atoms (3.26 Å) indicating that there is an obvious Pd-Pd bond. A range between 2.8 to 2.9 Å is typical for a single Pd-Pd bond.[180-185] Compared to the bridging hydride Pd(I)-Pd(I) complex [{(bipy)Pd}$_2$(μ-H)(μ-CO)]Cl, Figure 2.13 (B), with Pd-Pd distance 2.691(3) Å[178], **5a** is slightly longer. However, it is shorter compared to the other bridging hydride complexes [{(dippp)Pd}$_2$(μ-H)(μ-CO)]Cl[171] at 2.767(4) Å, Figure 2.13 (A), and [(dippp)Pd$_2$(μ-H)$_2$][179] at 2.8248(5) Å, Figure 2.13 (C). Compared to the dinuclear Pd(II) hydride [Pd$_2$HMe(μ-Cl)(μ-dppm)$_2$][BPh$_4$] (dppm = bis(diphenylphosphino)methane), Figure 2.18 (A), with the Pd Pd distance of 3.031(1) Å, the Pd-Pd distance of **5a** is much shorter.[185] Pd-Pd distance of **5a** is also shorter compared to a PCP pincer type mixed-valence binuclear Pd(0)-Pd(II) complex, Figure 2.18 (B), with a Pd-Pd distance of 3.0389(11) Å.[186]

The Pd-C bond distances in **5a** are typical for Pd-NHC interactions.[57,70,140] Pd-C distances Pd1-C30 2.012(3), Pd1-C1 2.034(3), Pd2-C7 2.008(3) and Pd2-C36 2.041(3) Å indicate no significant difference between each palladium centre. Compared to its Pd(II) precursor **4a**, with Pd distances of 1.9653(8) and 1.9893(5) Å, these distances is **5a** appear to be slightly longer. Pd-C distances in the range 1.970(17) - 2.018(17) Å were found for a Pd(II) complex [{PdX$_2$(μ-dicarbene)}$_2$], Figure 2.18 (C).[142] The Pd-C distances in **5a** are also nearly equal to those in the Pd(II) cationic triscarbene palladium hydride complex being trans to another NHC ligand, Figure 2.12 with Pd-C distances of 2.030(2) and 2.031(2) Å.[177] Compared to the (NHC)$_2$Pd(0) complex with the bulky substituted 1,3-bisadamantylimidazolin-2-ylidene, Figure 2.18 (D), with Pd-C distances of 2.076(5) and 2.084(5) Å, **5a** is shorter.[89] The Pd-C distance does not seem to be greatly affected by the oxidation state of the Pd centres in these complexes (slight trend to longer distances for low oxidation states) and there is no significant difference between Pd-C distances with or without the bound hydride. The C-Pd-C angles are 169.43(12) °, for C30-Pd1-C1, and 168.98(12) °, for C7-Pd2-C36, show non linear geometries surrounding both Pd atoms and similar distortions in geometry around both Pd atoms. All the carbene centres of the NHC units are bent

away from the Pd-Pd bond, again with little influence of the hydride ligand being noted.

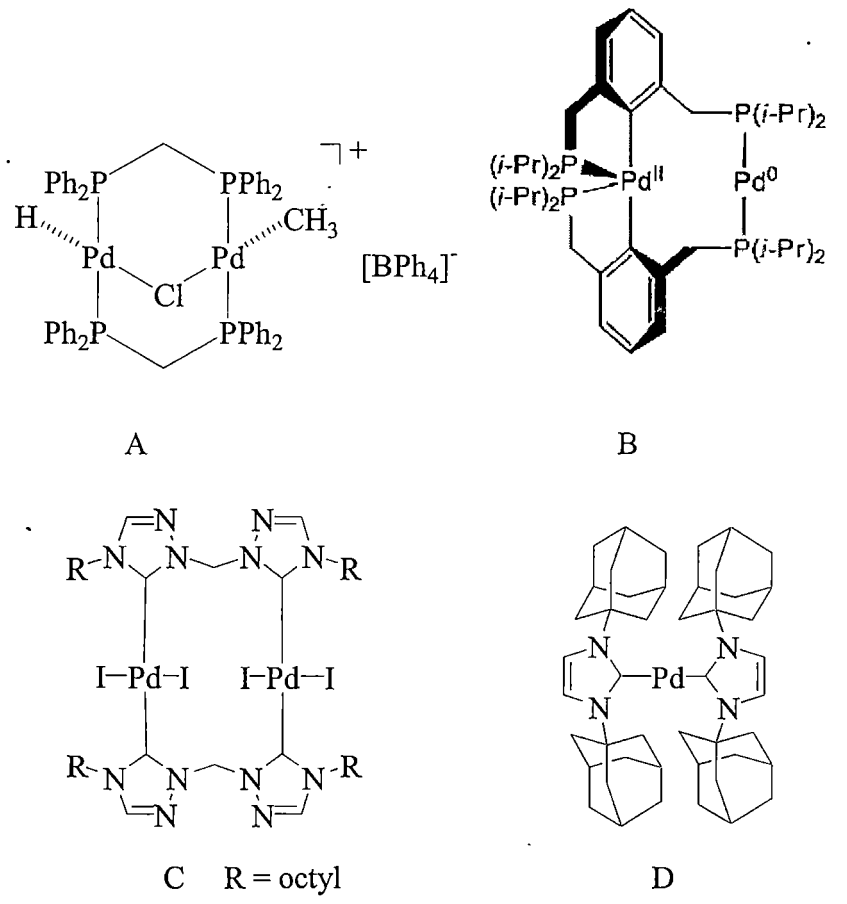


Figure 2.18 [{(μ-dppm)Pd}$_2$HMe(μ-Cl)][BPh$_4$] (A)[185], mixed valence Pd(0)-Pd(II) complex (B)[186] [(PdI)$_2$(μ-4-octyl-4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene)$_2$] (C)[142] and (NHC)$_2$Pd(0) complex (D)[89]

The neutron crystal structure determination showed the hydride to be terminally bound to Pd1. The Pd1-H1 distance of 1.61(3) Å is comparable to the Pd-H distance of a tris(carbene)palladium hydride complex[177] of 1.57(3) Å, as well as for the bridging hydride in the Pd(I)-Pd(I) complex [{(bipy)Pd}$_2$(μ-H)(μ-CO)]$^+$, with Pd-H distances of 1.6$_8$ and 1.6$_4$ Å, both the comparisons being based on X-ray data.[178] The position of the hydride is nearly linear along the H1-Pd1-Pd2 vector, with an angle of 167.0(12) °. The C-Pd1-H angles of 86.0(11) ° and 82.6(11) ° for C1-Pd1-H1 and C30-Pd1-H1, respectively, showed that the hydride is bent away from the mesityl group attached to N11 relative to the steric interaction with the mesityl substituents. The near equal C-Pd-C angles show that

the distinct square planar Pd1 and T-shaped Pd2 metal coordination geometries are not significantly influenced by the presence of the hydride bound to Pd1. Subtle differences exist between the conformations of the mesityl group at each end of the cation, which is expected owing to the terminal location of the hydride ligand.

2.2.5.1.2 Solution fluxionality of [{μ-(MesIm)$_2$CH$_2$}$_2$Pd$_2$H][PF$_6$] 5a

A number of fluxional processes which increase the time averaged molecular symmetry beyond that seen in the solid state determined structure are observed for **5a** by ^{1}H NMR spectroscopy. Variable temperature NMR spectroscopy at high temperature was unable to achieve coalescence of the *ortho*-methyl groups of the mesityl substituents. Although broadening is seen at 50 °C, Figure 2.19 and 2.20. Higher temperature spectra were not possible to be achieved with CD_3OD as solvent. In an attempt to collect higher temperature spectra using 1,4-dioxane-d_8 failed due to low solubility, while DMSO-d_6 decomposed the complex. Broadening was also seen above 40 °C for the methylene protons, indicative of nearing the coalescence point of a fluxional process involving a conformational change of the seven-membered ring structure of the Pd_2 bridging bis(NHC) ligand systems.

At low temperatures, there is a chemical shift movement of the hydride resonance at *ca.* -16.2 ppm involving line broadening (maximised at *ca.* -20 °C) and finally sharpening again to *ca.* -16.5 ppm into a single resonance at -70 °C, Figure 2.21. At around this approximate temperature range, many of the bis(NHC) ligand proton resonances appear to go through various coalescences, which is very likely linked to the observations of the hydride resonance. Of the proton types amenable to analysis due to minimal signal overlap, the *o*-Me groups of the mesityl substituents split into seven resolvable regions (two presumably overlapped), assigned to eight inequivalent methyl groups through COSY experiments, Figure 2.19. This is consistent with two plausible fluxional processes; i) a hydride ligand migrating over both Pd centres at high temperature, and, ii) a flipping of the relatively twisted metal coordination planes at high temperature. Similarly, one of the ring protons of the imidazolin-2-ylidene rings

splits into four equal intensity signals at low temperature, Figure 2.20. Interestingly, one of the methylene protons exhibits significant broadening at intermediate low temperatures. We speculate that this may relate to one proton, of each methylene set which is located above the metal coordination planes (Pd··H 2.72 and 2.77 Å, calculated proton geometries) and these may play a role in the mobile hydride ligand via fluxional Pd H agostic interactions, else their proximity to the metal coordination plane (where the hydride fluxionality occurs) otherwise gives rise to this effect.

A similar twisted arrangement and fluxional process was reported for the C_2 symmetric dicationic Ag_2^{2+} complex featuring the same sterically hindered bis(NHC) ligand set, though in that case the equivalence of the Ag^+ centres decreases spectral complexity.[151] C_i and C_{2v} symmetric isomers lacking the twisted arrangement have been characterised for the less bulky *N,N'*-dimethyl substituted Ag_2^{2+} analogues that have far reduced stability and higher fluxionality in solution.[187-190]

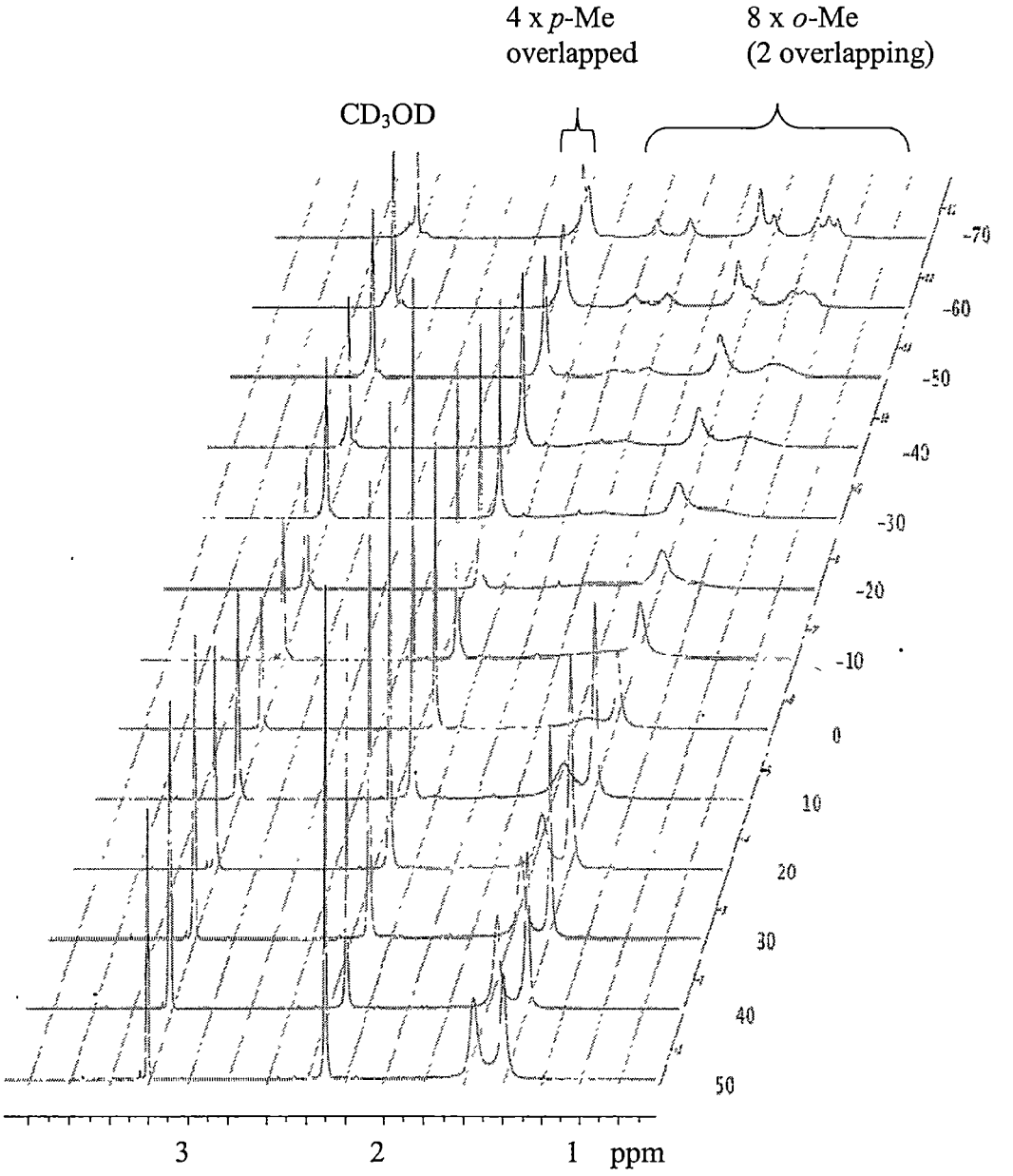


Figure 2.19 Variable temperature ^{1}H NMR spectrum of **5a** at 400 MHz in CD_3OD, 0.6-4.0 ppm region

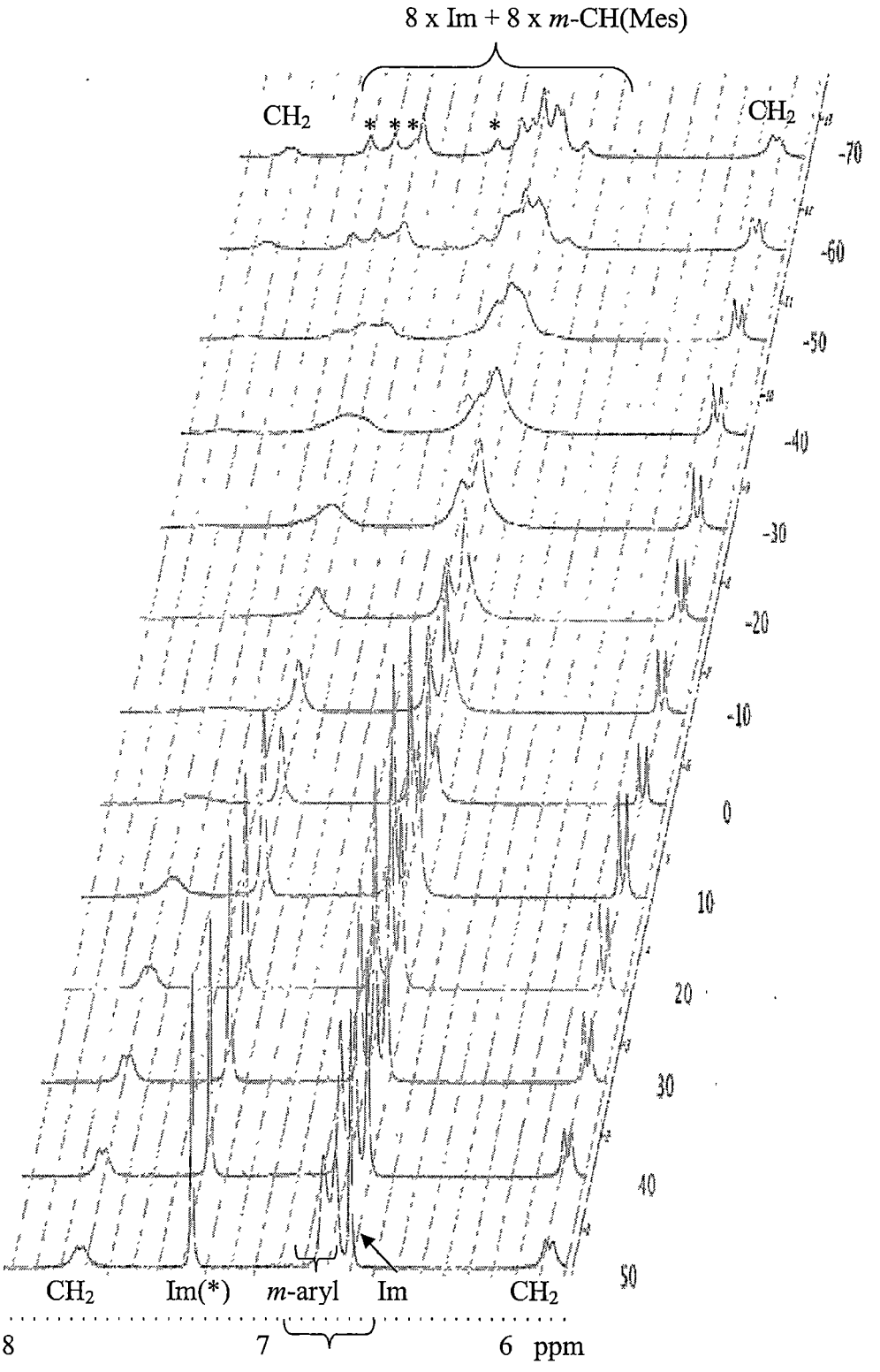


Figure 2.20 Variable temperature ^{1}H NMR spectrum of **5a** at 400 MHz in CD_3OD, 5.8-8.1 ppm region

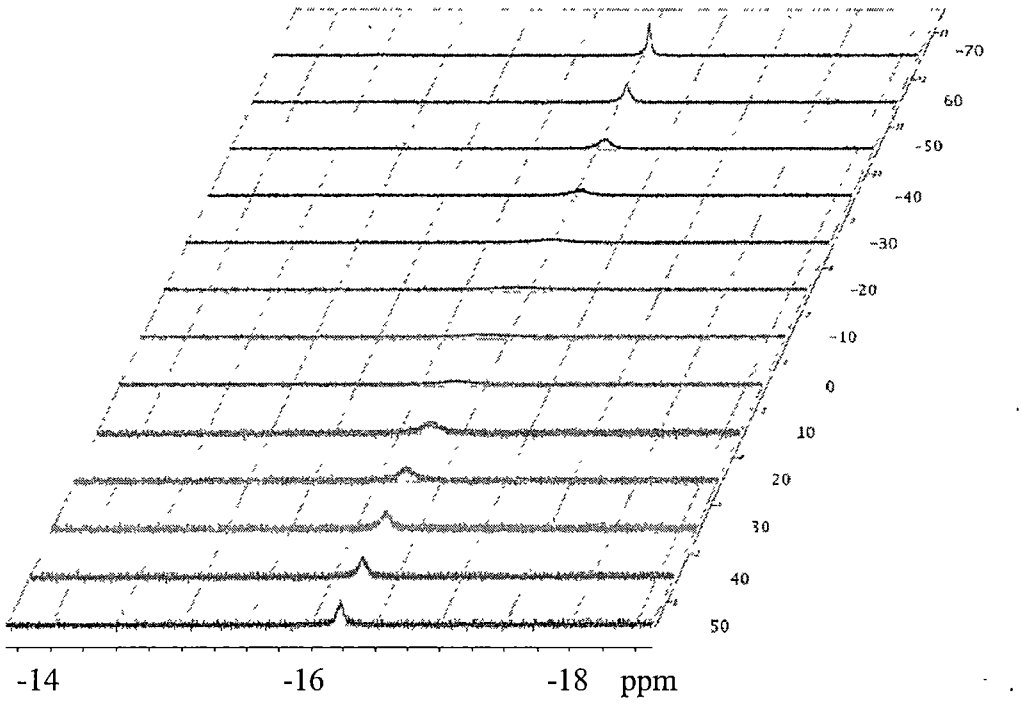


Figure 2.21 Variable temperature ^{1}H NMR spectrum of **5a** at 400 MHz in CD_3OD, Pd-H region

2.2.5.1.3 $[Pd_2H]^+$ bonding in $[\{\mu\text{-}(MesIm)_2CH_2\}_2Pd_2H][PF_6]$ 5a

The H-Pd-Pd core of **5a** is novel and also represents the first Pd(I) NHC complex. The Pd-Pd interaction has been established by DFT calculations as a Pd(I)-Pd(I) arrangement (performed by Prof Brian F. Yates and Dr. Damien N. Stringer). Reference examples of mixed valence, Pd(II)-Pd(0), as well as common Pd(I)-Pd(I) complexes are available for comparative purposes. Clearly, the inequivalent Pd coordination geometries in **5a** warranted this determination. An example of a Pd(I)-Pd(I) interaction for a square planar/T-shaped complex was reported by Kempe's group, Figure 2.22, in which topological analysis of the electron density and the electron localisation function from scalar relativistic DFT calculations determined this sterically frustrated complex to be a Pd(I)-Pd(I) species with corner sharing interactions.[181]

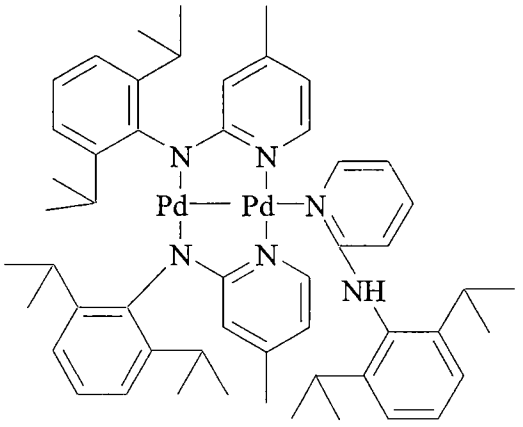
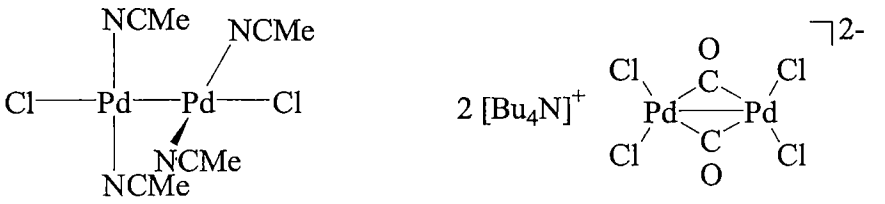


Figure 2.22 Kempe's Pd(I)-Pd(I) bimetallic complex

An example of a mixed valence bimetallic complex was reported by Milstein,[186] where reduction of a PCP pincer type Pd(II) complex led to an unprecedented binuclear Pd(0)-Pd(II) complex. The X-ray structure determination showed the Pd-Pd distance to be 3.0389(11) Å, which is too long to be treated as a Pd-Pd bond, Figure 2.18 (B).

Various combinations of valences, such as Pd(0), Pd(I), Pd(II), Pd(III), and Pd(IV), are possible for dinuclear palladium complexes. Electronic configurations suggests that the Pd(I)-Pd(I) and Pd(III)-Pd(III) combinations are of σ-bonding nature. Many Pd(I)-Pd(I) bonds are known but, very few Pd(III)-Pd(III) interactions known. There are two major different geometries for dinuclear Pd(I)-Pd(I); 'corner-sharing' and 'edge-sharing' geometries.[180] Both geometries are very different in electronic structure. An example of a 'corner-sharing' geometry was studied with extended Hückel calculations on $[Pd_2(NCCH_3)_4Cl_2]$, showing that this type of geometry has *dσ-dσ* bonding that lead to a low barrier rotation surround the Pd-Pd bond when the complex has neither bridging nor bulky ligand substituents.[191] The electronic structure of edge-sharing complexes were studied on $[Pd_2(\mu\text{-}CO)_2Cl_4]^{2-}$, indicating that a molecular orbital involving contribution of a Pd-Pd antibonding interaction is occupied, which makes the nature of Pd-Pd bond complicated and the Pd-Pd interaction was suggested to be through the ligand instead of through space since there was no electron population found between the two Pd atoms.[192] Further MO analysis of the Pd-Pd-H bonding

arrangements of **5a** are pending. Little data has been released at this stage.



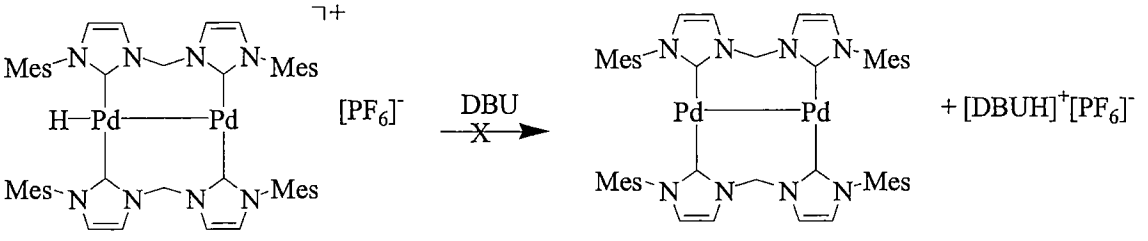
A B

Figure 2.23 Corner and edge sharing Pd(I)-Pd(I) complexes

2.2.5.1.4 Reactivity of $[\{(MesIm)_2CH_2\}_2Pd_2H][PF_6]$ 5a

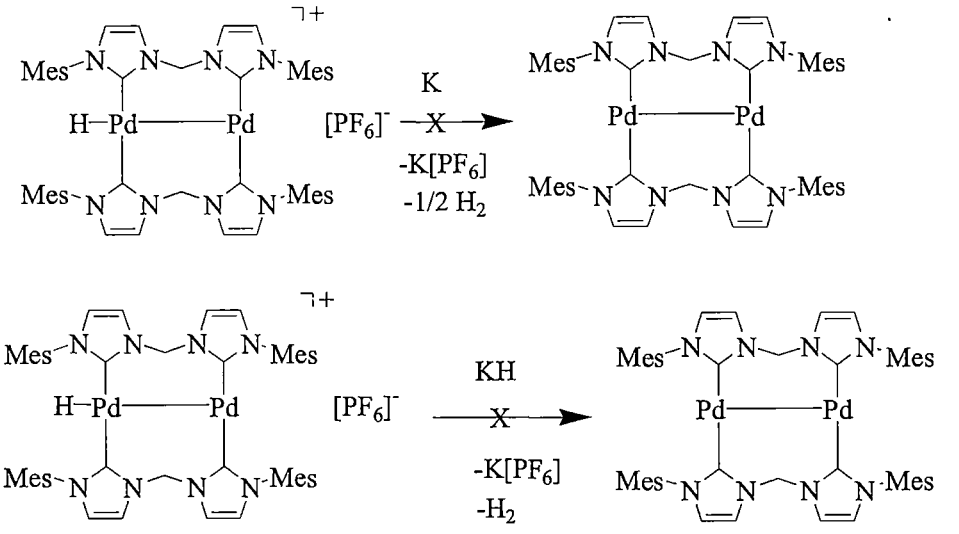
To investigate the reactivity of the dinuclear Pd(I) hydride cation, several reactions were employed. All reactions were performed on NMR scales, typically using anhydrous CD_3OD as solvent. All samples were prepared in the glove box in a nitrogen atmosphere. Reagents investigated were 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), K metal and KH. All reactions were monitored by ^1H NMR spectroscopy and mass spectrometry. Section 2.2.6 will discuss the reactivity of **5a** in relation to catalysis of the Heck reaction, various related cross-coupling reactions and carbon monoxide/ethene copolymerisation.

Reaction of **5a** with (DBU), Scheme 2.22, was intended to reductively deprotonate the cation the hydride ligand of the complex with the organic base in an attempt to give the neutral Pd(0)-Pd(0) complex. No reaction was observed by ^1H NMR spectroscopy, showing only resonances of complex **5a** remaining, which overlapped with DBU resonances. Previously noted deuterium exchange of the hydride occurred here but the retention of the hydride ligand (as D^-) was proven by deuterium NMR spectra that showed the deuteride ligand at *ca.* -16 ppm.



Scheme 2.22 Intended reaction of **5a** with DBU

Potassium hydride and potassium metal were used as alternative reagents for reductive proton abstraction, Scheme 2.23, where in the reduction reaction K metal should give K^+, while KH will abstract the proton to give H_2. These reactions were undertaken in C_6D_6 as solvent. ^1H NMR spectroscopy of the mixtures showed poorly resolvable, weak signals with no hydride resonance. Micro crystals were produced, but were unsuitable for X-ray diffraction. ESI-MS failed to determine the product of the reaction since the presence of the potassium ion disturbed the measurement. When undertaken in THF-d_8 as solvent, no reaction was observed based on ^1H NMR spectroscopy, with the presence of the reactant remaining.



Scheme 2.23 Intended reaction of **5a** with K metal and KH

2.2.5.2 Preparation of [{μ-(*i*Pr$_2$PhIm)$_2$CH$_2$}$_2$Pd$_2$(μ-H)][PF$_6$] 5b

An investigation into the possible effects of various bulky substituents on the reaction outcome and/or subtle structural details of the novel reductive formation of **5a** was undertaken by the attempted preparation of analogues featuring 2,6-diisopropylphenyl, phenyl and *t*-butyl substituents. The use of the bulkiest substituent, 2,6-diisopropylphenyl, was successful in affording a characterised complex described below. However, the less bulky aryl substituent, phenyl, and the *t*-butyl system gave no isolable products. Palladium black formation was observed in these cases. It is possible that the analogues were

formed but were too unstable to allow for isolation or detection.

The cationic complex $[\{\mu\text{-}(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}_2\text{Pd}_2(\mu\text{-H})][\text{PF}_6]$ **5b** was prepared by the reaction of the dicationic chelated bis(NHC) precursor $[\{(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}\text{Pd}(\text{NCMe})_2][\text{PF}_6]_2$ **4b** with excess sodium carbonate in methanol, Figure 2.24. The reaction required eight hours for maximal yields at 50 °C, giving a modest yield of a red crystalline product that precipitated on the walls of the Schlenk flask. Further product could be obtained, again in modest yield, as a second crop from the solution following removal of the first crop of crystals and filtration from the sodium carbonate. Total yields were variable, sometimes as low as 5%, but typically of the order of 10%.

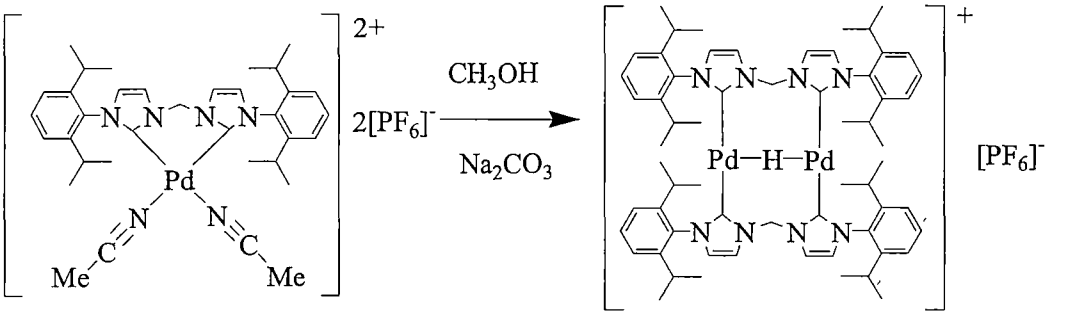


Figure 2.24 Synthesis of $[\{\mu\text{-}(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}_2\text{Pd}_2(\mu\text{-H})][\text{PF}_6]$ **5b**

Similar to what was established to determine the identity of the analogous reaction product featuring the mesityl substituent **5a**, mass spectrometry of **5b** gave initial evidence for the formation of the cationic dipalladium(I) hydride complex. The presence of the hydride was confirmed by ^{1}H NMR spectroscopy and the symmetry of the N-substituents is analogous to **5a** in the room temperature ^{1}H NMR spectrum. Subsequently, an X-ray crystal structure was obtained in which no Pd-Pd bond was observed (Pd··Pd separation 3.3944(12) Å), but the hydride location could not be located. Such a drastic structural change is not unexpected given the crowded nature of **5a** identified in the solid state. At this stage, further study by neutron crystallography has not yet established the hydride location. Given the high fluxionality of **5a**, we also examined the fluxionality of **5b** in solution through variable temperature studies.

In an effort to improve the reaction yield of **5b** the reaction was repeated on an NMR scale in CD_3OD. A complex series of intermediates were observed to form over 6 hours at 50 °C during formation of the red solution. At this point two main species are observed with all of the dicationic starting material $[\{(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}\text{Pd}(\text{NCMe})_2][\text{PF}_6]_2$ **4b** being consumed. At that time period, small amounts of the final cationic dipalladium(I) hydride $[\{\mu\text{-}(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}_2\text{Pd}_2(\mu\text{-H})][\text{PF}_6]$ **5b** was observed (see below for a full description of the ^{1}H NMR spectral details of this complex). It was shown that the conversion of these intermediates to **5b** was not reliant on further reaction with sodium carbonate as filtration at this stage does not reduce yields of **5b**. Thus, after 12 hours, the formation of large prismatic crystals of **5b** suitable for X-ray crystal structure determination were obtained on standing of the red reaction solution that had been decanted from the remaining sodium carbonate. Slightly improved yields were obtained upon further repeats of the reaction on a large scale following this partial mechanistic understanding of the reaction mechanism.

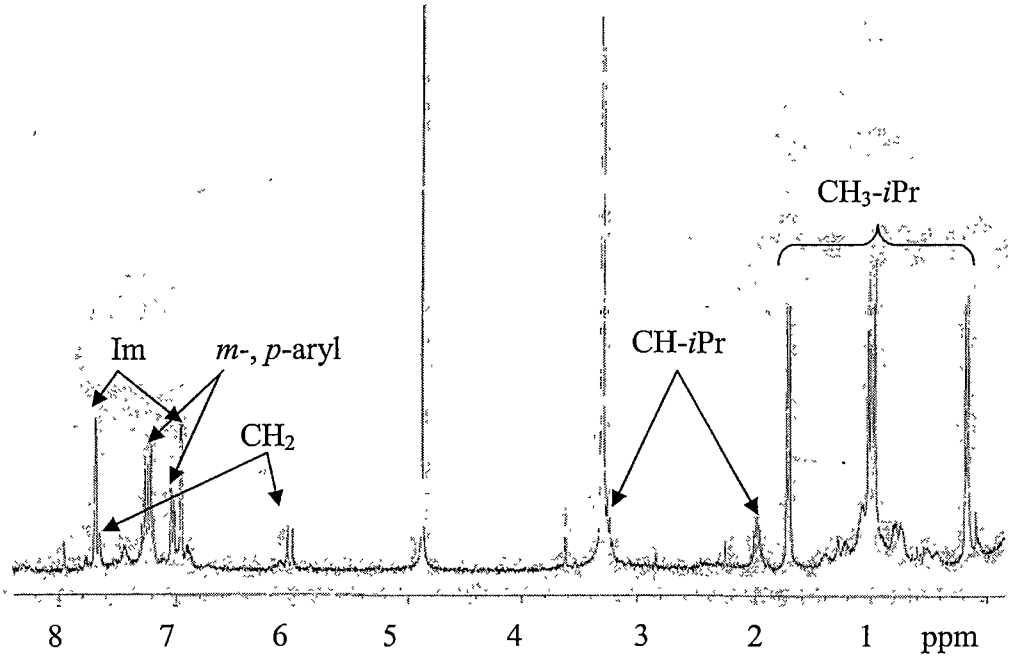


Figure 2.25 ^{1}H NMR spectrum of isolated **5b** at 300 MHz in CD_3OD, hydride resonance at *ca.* -16 ppm is not shown

An NMR scale reaction was undertaken for **5b** and was monitored for several hours by ^{1}H NMR spectroscopy between initial mixing and eight hours of reaction by which time the reaction mixture undergoes no further spectroscopically observable changes. The resonances in the ^{1}H NMR spectrum showed that there are at least four intermediates of the reaction observed at different stages. After 2 hours the starting material **4b** and all intermediates are present, but no product **5b**. All species except for starting material display AB spin systems for the methylene proton resonances. After 3 hours, through to reaction completion, the mixture of resonances simplify, showing starting material, product and two intermediates. Figure 2.26, shows the methylene region, which is the cleanest section with respect to interpreting the number of and identity of the species present. The intermediates remain in approximate 1:1 ratio until they disappear. It is not known why yields are poor, despite the apparent clean transformation of the intermediates of the reaction.

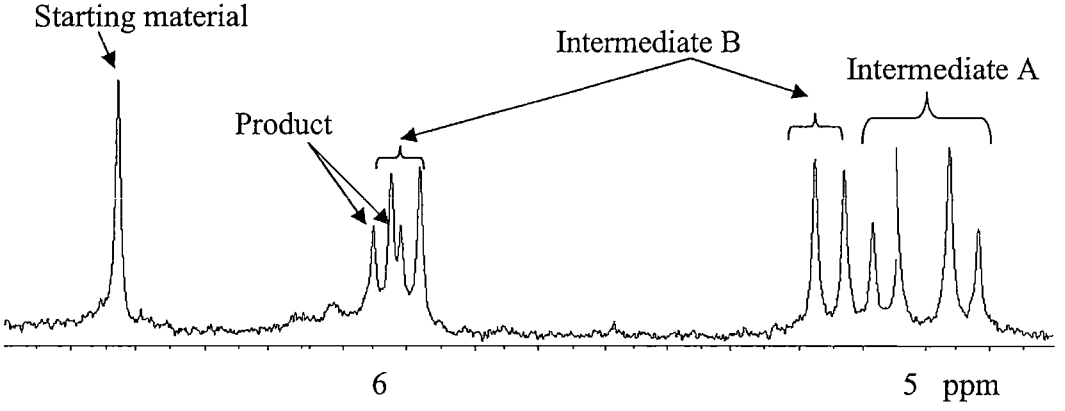


Figure 2.26 ^{1}H NMR spectrum of the reaction mixture for the synthesis of **5b** after 3 hours at 300 MHz in CD_3OD, 5.0-6.4 ppm region

The small scale reaction mentioned above that was monitored by ^{1}H NMR spectroscopy was also simultaneously followed by electrospray ionisation mass spectrometry (ESI-MS). The ESI mass spectrum of the starting material $[\{(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}\text{Pd}(\text{NCMe})_2][\text{PF}_6]_2$ **4b** showed isotopic envelopes at m/z = 573 (cation – 2NCMe) and 619 (cation - NCMe) in which no ion is observed featuring both bound NCMe ligands. There were no additional significant ions up to two hours reaction, despite ^{1}H NMR spectra indicating the emergence of two intermediate species at that stage. During the latter stages, commencing from 3

hours, ions centred around *m/z* = 573 are observed which can be interpreted as a number of species (starting material, $[\{(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}\text{Pd}^0]^+$ or $[\{(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}\text{Pd}^{2+}\text{H}]^+$ species (see below and Scheme 2.26, page 92). At this time the only other significant ions are at *m/z* of 657, 1212, and 1380, with the product ion growing in at *m/z* 1151. On completion of the reaction, ESI-MS shows only ions characteristic of the product, at *m/z* = 1151 (M^+), 573 and 923.

The ions of the intermediate of mass 657 and 1212 are consistent with the dimeric form of the starting material (the ESI-MS of this form from an intentionally prepared sample is unavailable). This is not an unexpected result based on the known thermal conversion of chelated bis(NHC)Pd(II) halide complexes to bridged dinuclear species.[140,145,146] It is noted that the dimer shows a fragmentation ion of 657 for $[\{(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}\text{Pd(NCMe)}_2][\text{PF}_6]_2$ while the starting material only shows $[\{(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}\text{Pd}]^+$ (573) and $[\{(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}\text{Pd(NCMe)}]^+$ (619). In a control study, the monomer to dimer conversion did not occur in methanol without addition of base at 50 °C overnight. Thus, Na_2CO_3 (or more likely *in situ* formed methoxide) seems to promote this conversion. Extended reactions under more forcing conditions at 120 °C in DMSO were also unsuccessful. Presumably the dimeric form observed by ESI-MS accounts for at least one of the early intermediates noted in the NMR spectrum after three hours. It cannot be ruled out that this supposedly very sterically hindered dimer cannot exist in isomeric forms, such as a C_2 or C_i symmetric arrangement which do not interconvert at room temperature. This may account for the observation of two intermediates in approximately equal concentration which disappear at similar rates upon further reaction with base.

At this stage, there are conclusions that can be made on the intermediate with *m/z* =1380. This mass is 229 units greater than **5b**, which is coincident with additional mass equivalent to $i\text{Pr}_2\text{PhIm}$ **1b**, however, no NMR or other ESI-MS data supports this ligand fragmentation occurring. It doesn't represent a stable reaction by-product as it is not present at the completion of the reaction.

ESI-MS of the product **5b** showed various fragmentations having isotopic

envelopes of *m/z* 1151, 923 and 574, Figure 2.27. The M^+ ion can be simulated. The observed *m/z* of 574 cannot be simulated by a single mononuclear complex. This is a possible indication of a mixture of two ions of similar mass, most likely $[\{(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}\text{Pd}]^+$ and $[\{(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}\text{PdH}]^+$ that would arise from an equilibrium of the product **5b** with the two constituent mononuclear species (see Scheme 2.26, page 92, for a further discussion of this). The observed fragment at *m/z* 923 is coincident with the envelope spectrum of **5b** losing one fragment of $i\text{Pr}_2\text{PhIm}$. However this species is thought to be an ESI-MS formed artefact as GC/MS analysis of the hydrolysed reaction mixture shows no indication of such ligand fragmentation. Such ESI-MS fragmentation may relate to hydride attack on the proximal methylene linkage with the complex, according to Scheme 2.24.

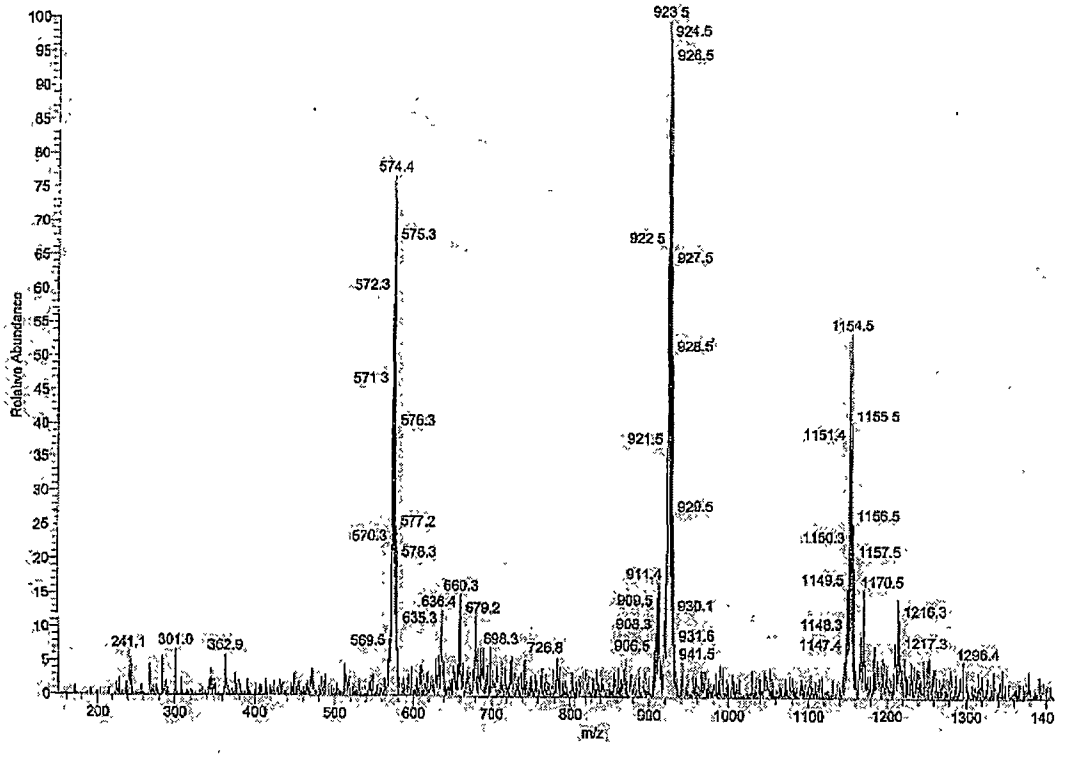
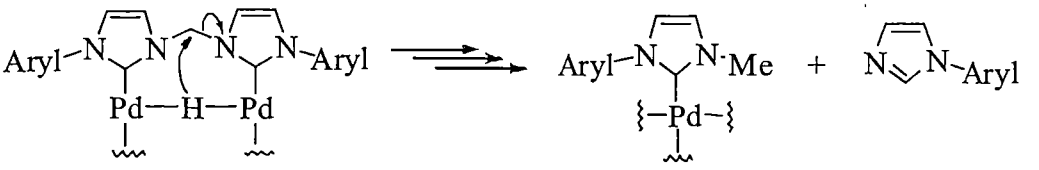


Figure 2.27 ESI-MS of $[\{\mu\text{-}(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}_2\text{Pd}_2(\mu\text{-H})][\text{PF}_6]$ **5b**



Scheme 2.24 Suggested mechanism of hydride attack on the methylene linkage

The occurrence of a minor isomer or impurities in the ^{1}H NMR spectrum of **5b** of consistent intensity were noted on repeated samples of even very highly crystalline samples. ^{1}H and ^{13}C NMR spectroscopy for **5b** was undertaken using CD_3OD solvent, Figure 2.25. ^{1}H NMR resonances for the methyl protons of the major component resonances appear as doublets at 0.17 and 1.72 ppm and overlapping doublets at around 0.99 ppm. The methine protons occur at 1.99 and *ca.* 3.30 ppm (the latter obscured by solvent). The methylene resonances exhibit AB spin systems at 6.00 and 7.68 ppm. The imidazolin-2-ylidene protons occur at 6.95 and 7.68 ppm, while the *m*- and *p*-aryl protons of the 2,6-diisopropylphenyl substituent resonate in the range 7.03-7.21 ppm. A hydride resonance occurs at *ca.* -16.0 ppm. This data are consistent with the solid state structure (see below) where all four 2,6-diisopropylphenyl groups are equivalent and each of these exhibits restricted rotation about the C(*ipso*)-N bonds.

Variable temperature ^{1}H NMR studies has made it apparent that the minor species present in samples of **5b** maybe an isomeric form, though we have no definitive proof of this at this stage. Figure 2.28-2.30 show the various regions of the VT ^{1}H NMR spectra. Considering first the hydride region, at lower temperatures a second hydride becomes observable. Detailed interpretation of the relative concentrations of the species responsible for these resonances is suspect owing to the lowered solubility of the sample at these temperatures. At the temperature region where the second hydride appears, Figure 2.30, there are no concurrent appearances of new resonances in the region of the bis(NHC) ligand. Rather, the appearance of the previously noted minor component become more defined and, perhaps, slightly more relatively intense.

The low temperature appearance of the major species in solution is not significantly different to the room temperature spectrum. This indicates that it

does not appear to undergo an apparent fluxional process. This contrasts with the mesityl analogue $[\{(\mu\text{-MesIm})_2CH_2\}_2Pd_2H][PF_6]$ **5a**, where the low temperature ^1H NMR spectrum is consistent with the Pd-Pd bonded, terminal hydride structure, Section 2.2.5.1.2. In the case of **5b**, this suggests a centrosymmetric structure, as observed in the solid state. Given the Pd···Pd separation at 3.3944(12) Å, the probable complex core is a linear (or near) Pd-H-Pd arrangement.

Attempts to conduct correlation spectroscopy (at both room and low temperature) on **5b** have been difficult, preventing full assignment of even the major component. Thus, at this stage we are unable to offer speculation of the identity or an assigned spectrum of the minor component. The observation of the two hydride resonances at low temperature suggests only two hydridic species being present. If correct, the speculative symmetry of the minor component appears to be reduced relative to the major component. This is most apparent in the tentative assignment of four methylene protons (marked † in Figure 2.29). We are unable to offer further analysis at this stage. A third component also appears to be present, perhaps not a hydridic species.

We note that the overall ligand scaffold symmetry of the mesityl analogue **5a** is C_2, whereas **5b** is crystallographically C_i in the solid state. It would seem unlikely that a C_2 symmetry isomer of **5b** is possible on steric grounds; moreover, such symmetry would not match the observed detail of the minor component (assuming a Pd-H-Pd arrangement). An approximate C_i symmetric ligand with a Pd-Pd-H core (analogous to the mesityl ligand, except for the C_2 symmetric ligand arrangement) is a possible structure that would account for the observed appearance of the minor component. Mitigating against this is the apparent lack of fluxional conversion of the major and minor components.

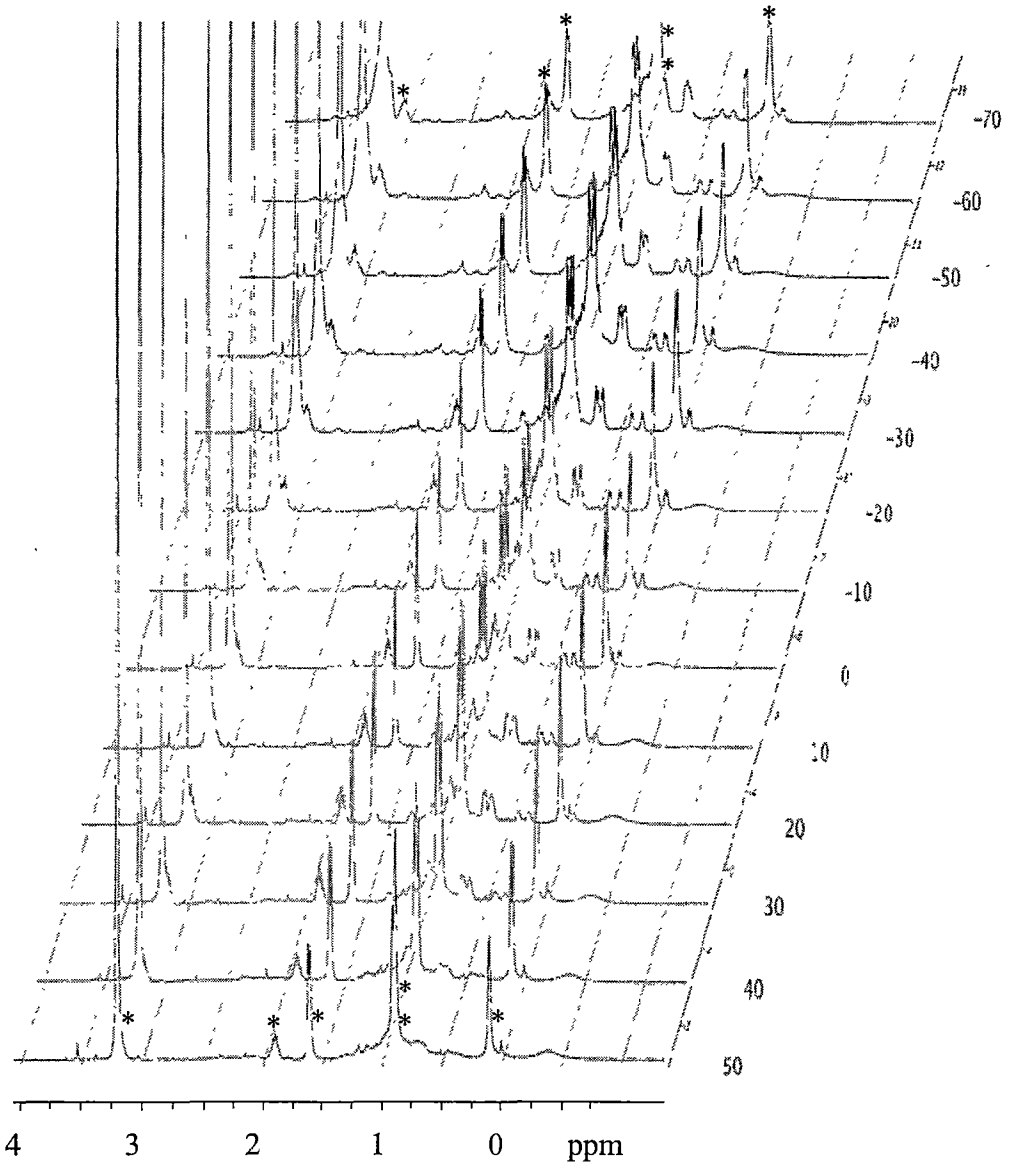


Figure 2.28 ^{1}H NMR spectrum of **5b** at 400 MHz in CD_3OD, in the region 0-4 ppm. Resonances marked with * are the major species in solution

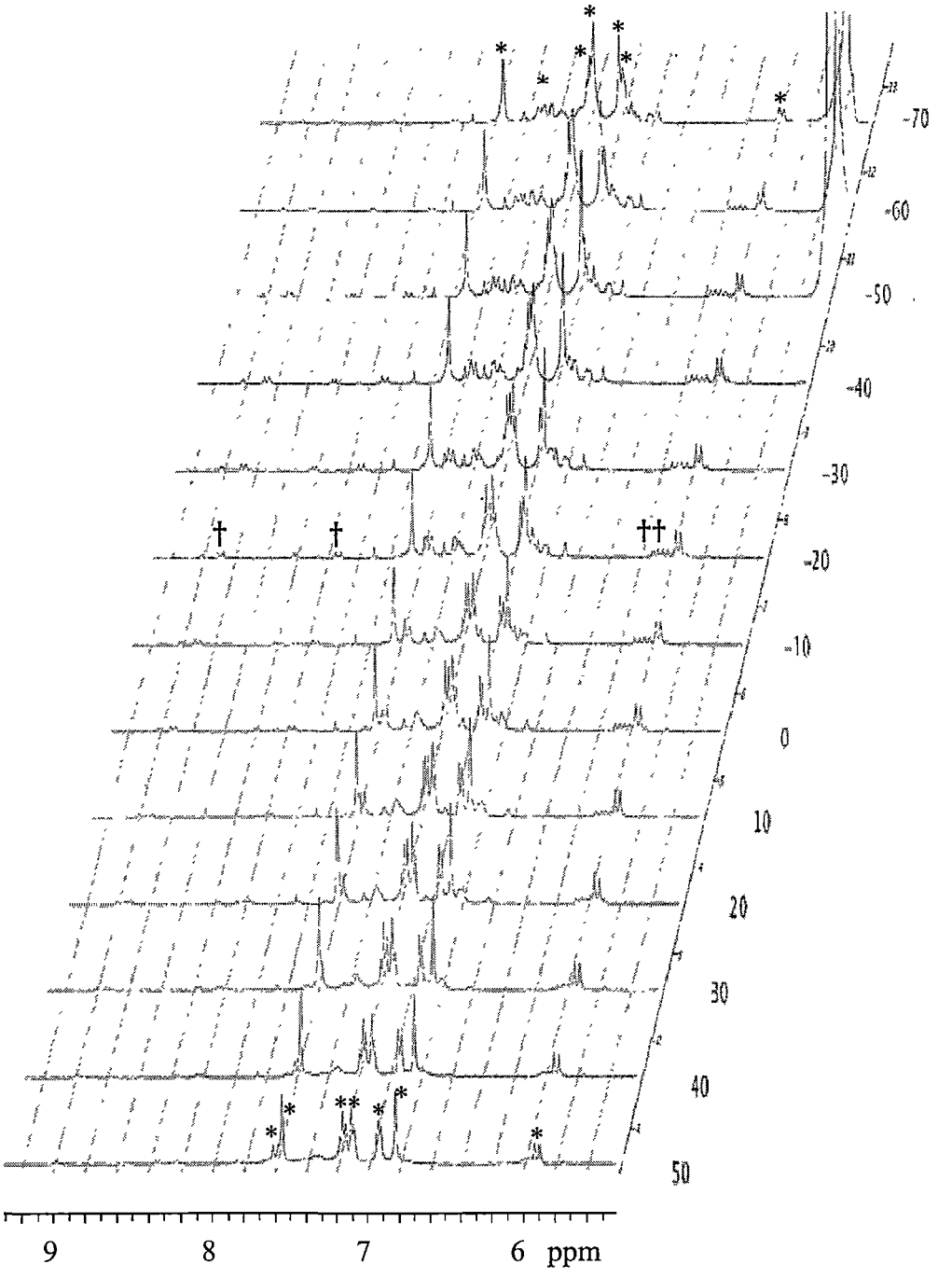


Figure 2.29 ^{1}H NMR spectrum of **5b** at 400 MHz in CD_3OD, in the region 5-9 ppm. Resonances marked with * are the major species in solution. † indicates the tentative assignment of the methylene protons of the most abundant minor components

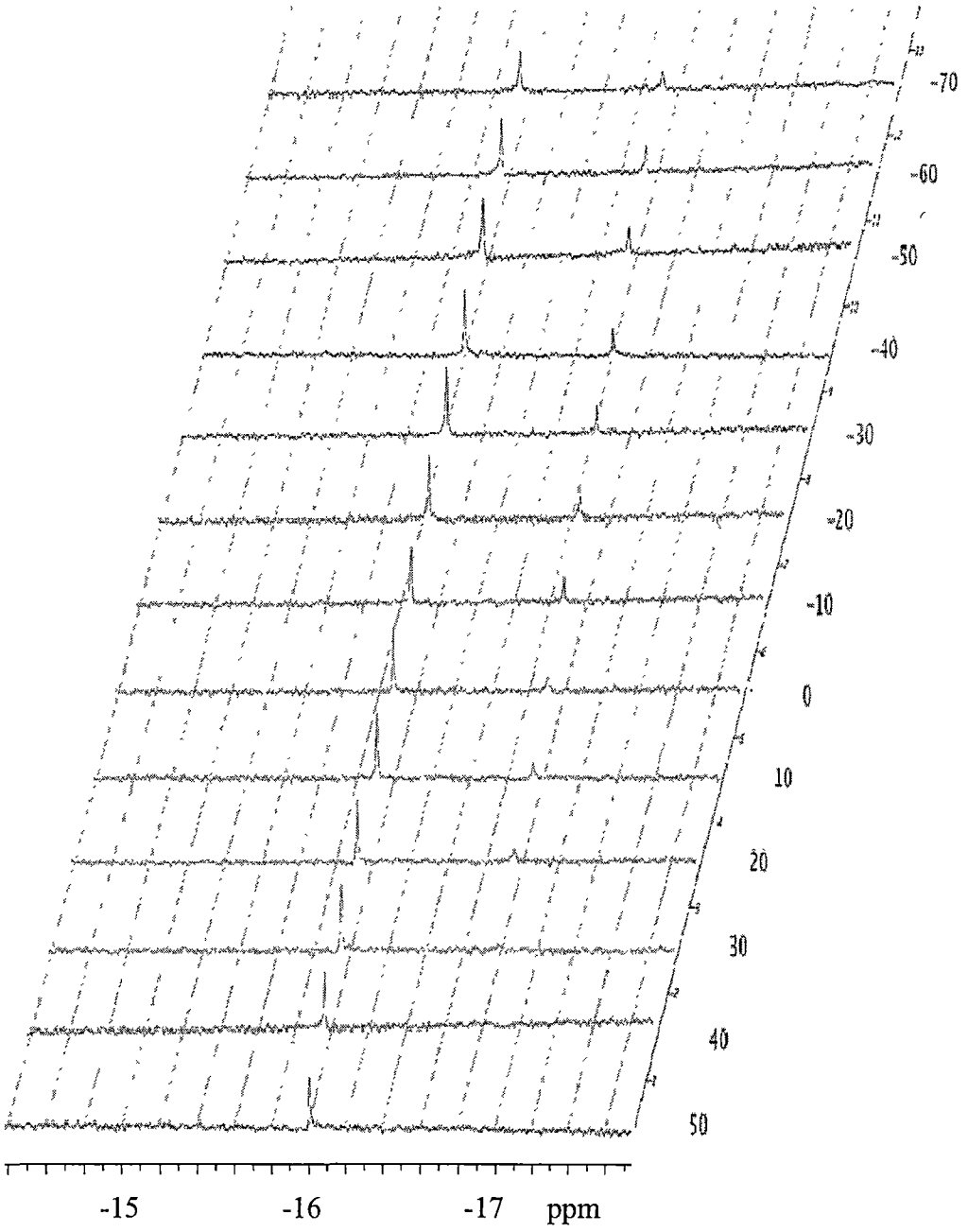


Figure 2.30 ^{1}H NMR spectrum of **5b** at 400 MHz in CD_3OD, metal hydride region

Crystals of $[\{\mu\text{-}(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}_2\text{Pd}_2(\mu\text{-H})][\text{PF}_6]$ **5b** suitable for single crystal X-ray crystal structure determination were grown from the filtered reaction mixture that was allowed to cool slowly to room temperature and let stand overnight. The prismatic crystals of complex **5b** belong to the triclinic space group $P\bar{1}$, a = 11.067(2), b = 12.348(3), c = 13.059(3) Å, α = 71.88(3), β = 74.34(3), γ = 89.94(3) °, with 1 formula unit in the unit cell. The asymmetric unit contains one half of the cation and one half of the hexafluorophosphate anion, both residing on inversion symmetry sites as well as a methanol solvent molecule (disordered with the carbon atom common to both orientations). Figure 2.31 and 2.32 depict the structure of the cationic portion of the complex. Selected bond distances and angles are listed in Table 2.4. The atom numbering given for the structure is not systematic and is for X-ray structural discussion only.

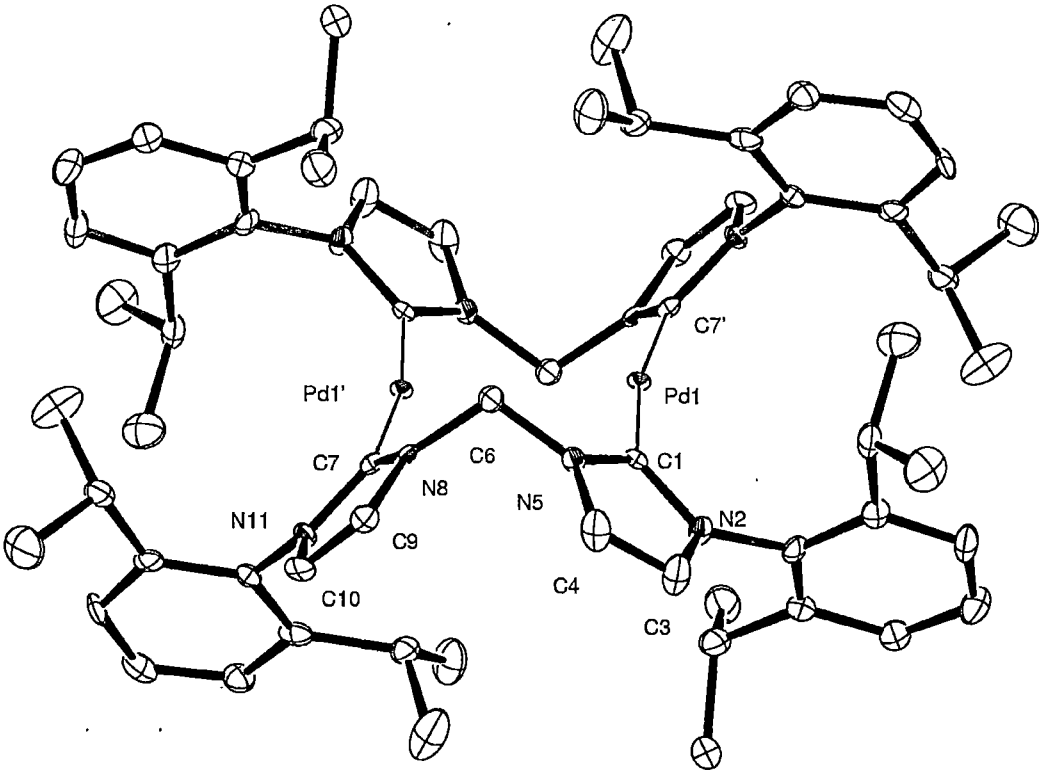


Figure 2.31 ORTEP representation of $[\{\mu\text{-}(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}_2\text{Pd}_2(\mu\text{-H})][\text{PF}_6]$ **5b** with thermal ellipsoids scaled to the 50% probability level. All hydrogen atoms are omitted for clarity.

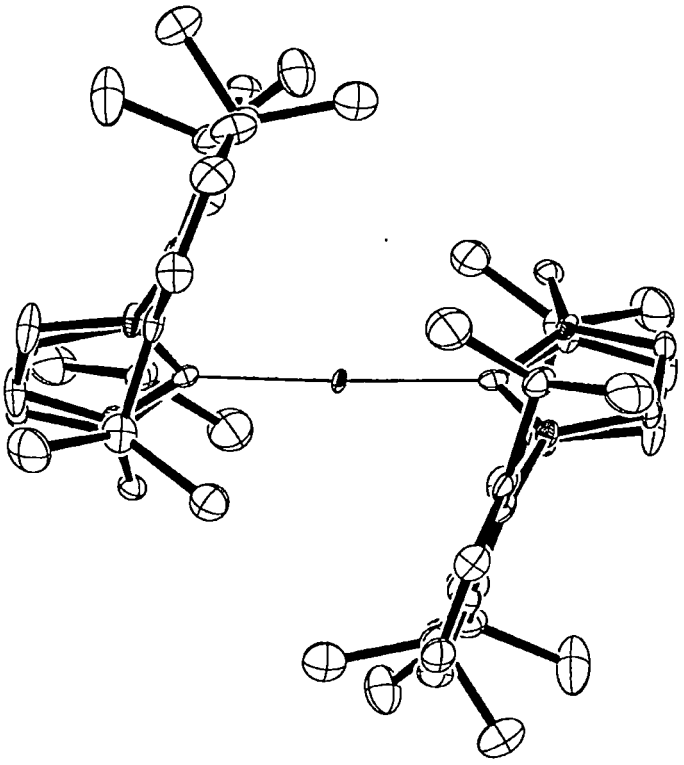


Figure 2.32 ORTEP representation of $[\{\mu\text{-}(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}_2\text{Pd}_2(\mu\text{-H})][\text{PF}_6]$ **5b** with thermal ellipsoids scaled to the 50% probability viewed along the Pd···Pd vector. All hydrogen atoms are omitted for clarity.

Table 2.4 Selected bond lengths (Å) and bond angles (°) for **5b**

Pd1···Pd1'	3.3944(12)
Pd1-C1	2.028(4)
Pd1-C7	2.032(5)
C1-Pd1-C7	169.15(19)
N2-C1-Pd1	125.4(3)
N5-C1-Pd1	131.2(3)
N8-C7-Pd1	131.2(3)
N11-C7-Pd1	126.0(3)

The monocationic dipalladium(I) hydride complex **5b** exhibits no Pd-Pd interaction (Pd···Pd = 3.3944(12) Å) and two bridging methylene-linked imidazolin-2-ylidene ligands. This separation is well beyond that commonly reported for Pd(I)-Pd(I) d^9-d^9 dinuclear species with corner sharing interactions. Interestingly, a sterically frustrated Pd(I)-Pd(I) species reported by Kempe has a surprisingly short Pd-Pd bond distance of 2.429(4) Å.[181] Though in that case the

NCN bridging ligand arrangement would clearly favour a shorter Pd-Pd interaction. The μ-CNCNC arrangement here may well be instrumental in supporting the long Pd···Pd geometry.

Overall, the cation displays crystallographic C_i symmetry, and approximate C_{2h} symmetry, Figure 2.32. Spacefilling representations of [{μ-(MesIm)$_2$CH$_2$}$_2$Pd$_2$H][PF$_6$] **5a**, Figure 2.17, make it apparent that the change in the overall symmetry of the arrangement of the bridging ligands in the cation of **5b** relative to the less bulky mesityl substituted analogue **5a** (C_i versus C_2, respectively) is the direct result of the added steric influence of the 2,6-diisopropylphenyl substituent. Figure 2.33 shows space filling representations of **5b**, highlighting the still congested nature of the cation even with the adopted centrosymmetry. Unlike **5a**, the core Pd$_2$H unit is entirely shrouded by the bridging bis(NHC) ligand set. It is also highly probable that the very significant absence of a Pd-Pd bond in **5b** (in comparison to **5a**) is in response to the increased steric demand of the bis(NHC) ligand.

(a) (b)

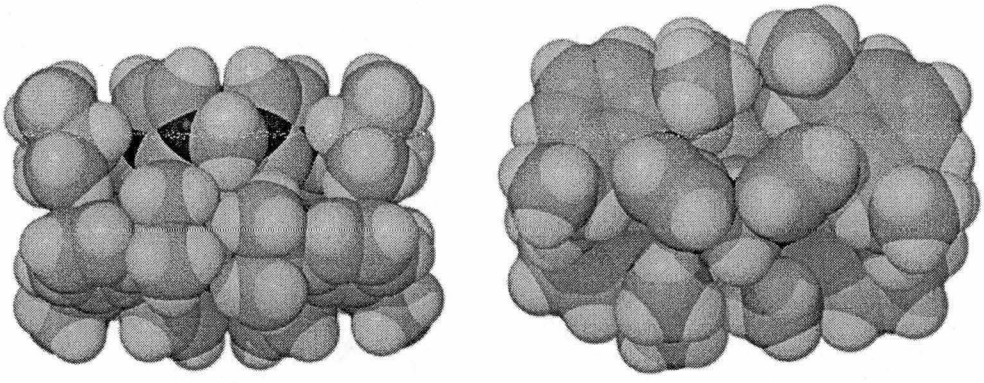


Figure 2.33 Spacefilling representations of [{μ-(*i*Pr$_2$PhIm)$_2$CH$_2$}$_2$Pd$_2$(μ-H)][PF$_6$] **5b**. (a) viewed onto the metal coordination planes, and (b) along the metal coordination planes (along the C-Pd-C direction)

Like in the case of **5a**, the X-ray crystal structure refinement of **5b** also failed to locate the hydride ligand. Crystals of suitable size (*ca.* 0.3 mm^3) have been examined by neutron diffraction in an attempt to resolve this important structural detail but, unfortunately, the refinement details are not available at this point. However, the diamagnetic behaviour of the complex, as well as the Pd···Pd

separation (see below) are very strong indicators of the hydride ligand residing in a linear (or near linear) bridging position between the Pd centres, Figure 2.34 (a). This would represent the first bridging hydride ligand in dinuclear palladium(I) chemistry that is not supported by the presence of a Pd-Pd bond (an example is known for a Pd(II) complex, $[(pincer)Pd(\mu\text{-}H)Pd(pincer)]^+$, pincer = 2,6-$(CH_2PR_2)_2C_6H_3^-$) Figure 2.34 (c).[186]

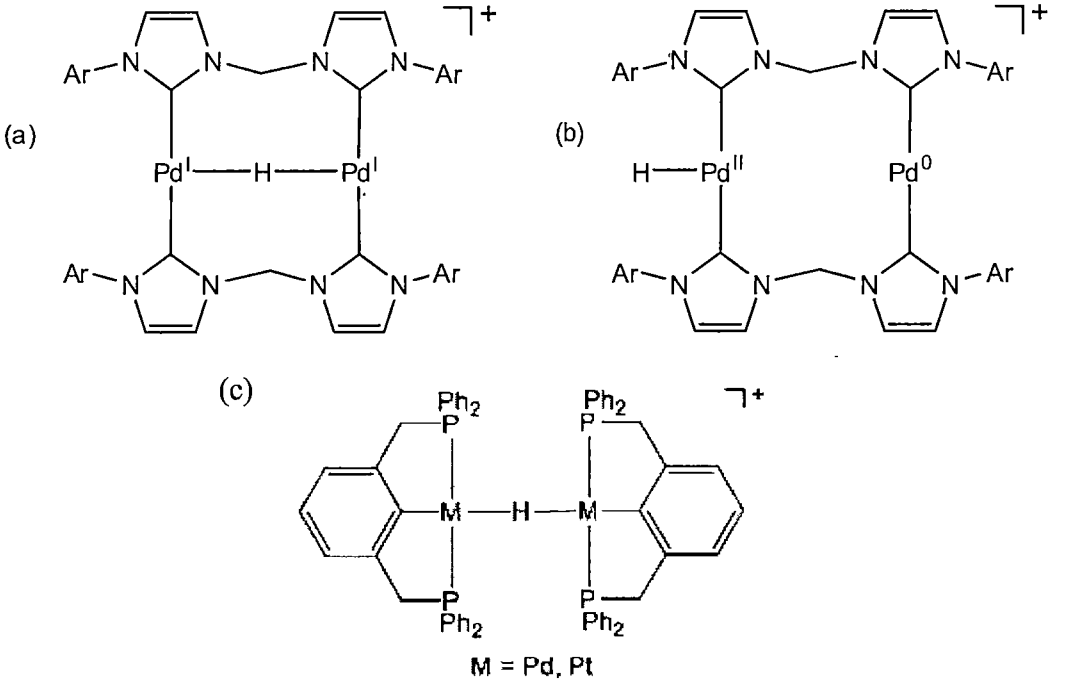


Figure 2.34 (a,b) Speculative locations of the hydride ligand in $[\{\mu\text{-}(i\text{Pr}_2\text{PhIm})_2\text{CH}_2\}_2\text{Pd}_2\text{H}][\text{PF}_6]$ **(5b)**. (c) $[(pincer)Pd(\mu\text{-}H)Pd(pincer)]^+$.

However, a plausible Pd(II)/Pd(0) configuration (based on its diamagnetism) featuring a terminal hydride on the cationic Pd(II) centre cannot be ruled out, Figure 2.34(b). The latter would likely feature subtle structural variations at each metal centre and the absence of these features in the solid state could be masked through disorder of the observed centrosymmetric structure. The observed thermal parameters do not appear to indicate this. However, the discussion of the structure of **5a** (Section 2.2.5.1.1) highlighted the fact that Pd-C distances to NHC ligands do not appear to vary greatly with the Pd oxidation state and the presence of the hydride ligand on the Pd centre also did not greatly

influence the geometry about the square planar and T-shaped Pd coordination geometries. The absence of a less symmetrical structure for **5b** to be observed at low temperature by ^{1}H NMR spectroscopy mitigates against a Pd(II)/Pd(0) mixed valence species interpretation such as shown in Figure 2.34 (b) with a speculative terminal hydride ligand located on the cationic Pd(II) centre.

Assuming that the hydride ligand is bridging in complex **5b** from this point in the discussion, to the best of our knowledge, complex **5b** is unique with regard to the absence of a Pd-Pd bond for a dinuclear Pd(I) complex. Dinuclear Pd(I) complexes normally rely on stabilisation by the metal-metal interaction and achieve their diamagnetic behaviour through this interaction. Both Pd centres have distorted T-shaped metal coordination geometries, with the coordination planes being coplanar. Pd-Pd bonds in dinuclear Pd(I) complexes are often supported by bridging ligands, including non linear μ_2-carbonyl and μ_2-hydride arrangements in species derived from reduction products of Pd(II) methoxide complexes which have been structurally authenticated, or at least implied. In the case of **5b**, the putative Pd-H-Pd arrangement implies a Pd-H distance of 1.697 Å, which compares well with terminal Pd-H distances of 1.57(3) Å and 1.77(7) Å in the Pd(II) complexes tris(carbene)palladium(II) hydride complex, Figure 2.12[177] and [(PCP)PdH][PF_6],[193] Figure 2.35, respectively, as well as the bent and linear Pd-H-Pd arrangements in the Pd(II) complexes Pd-H distances are 1.531(11) and 1.540(10) Å for [{(dippp)Pd}$_2$(μ-H)(μ-CO)]Cl, Figure 2.13 (A)[171] and 1.53(5) Å for [Pd_2HMe(μ-Cl)(μ-dppm)$_2$][BPh_4], Figure 2.18 (A).[185]

Initial DFT calculations have shown that **5b** is a Pd(I) containing complex (performed by Prof. Brian F. Yates and Dr. Damien N. Stringer). No detailed analysis is available regarding the nature of Pd-H-Pd bonding arrangement at this stage. The linear Pd-H-Pd arrangement represents a stable structure, with its energy being within 11 kcalmol^{-1} of the Pd-Pd-H arrangement found for the less bulky complex **5a**.

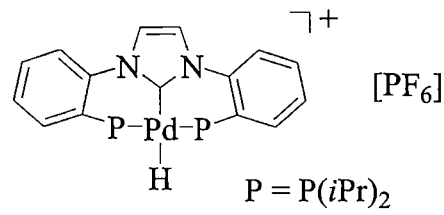


Figure 2.35 [(PCP)PdH][PF_6][193]

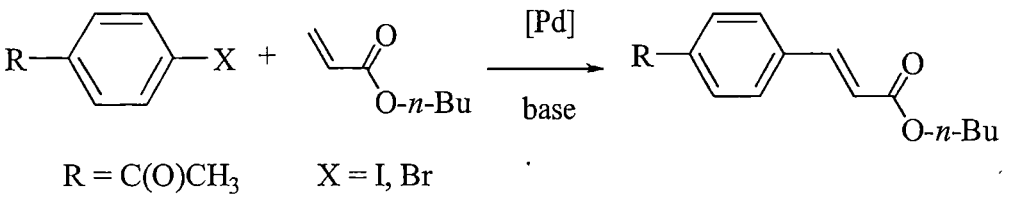
The Pd-C bonds in **5b** are typical for Pd-NHC interactions.[57,70,140] The Pd-C bond distances in **5b** of 2.028(4) and 2.038(5) Å are slightly longer compared to its precursor **4b** of 1.974(3) and 1.988(3) Å and its analogue [{$(MesIm)_2CH_2$}$Pd(NCMe)_2$][PF_6]$_2$ **4a** at 1.965(8) and 1.989(5) Å[137]and [{$(MesIm)_2CH_2$}$Pd(NCMe)_2$][BF_4]$_2$ at 1.966(2) and 1.972(3) Å.[140] Compared to a known tris(carbene)palladium(II) hydride complex at 2.030(2), 2.031(2), and 2.111(2) Å, the Pd-C distances are almost similar for the *trans* disposed NHC ligands. The Pd-C distances are shorter compared to a $(NHC)_2Pd(0)$ complex with the bulky 1,3-bisadamantylimidazolin-2-ylidene ligand with Pd-C distances of 2.076(5) and 2.084(5) Å.[89] The addition of the bulky substituents in **5b** does not seem to affect the Pd-C bond distances relative to **5a**. Again, the distances seem to be slightly affected by the oxidation state of the Pd centres (assuming the structure to be a Pd(I) containing species). The C-Pd-C bond angle of 169.15(19) shows significant distortion from a linear geometry suggesting that the putative bridging hydride leads to a Pd···Pd bond separation less than that preferred by the bridging ligand.

2.2.6 Catalytic studies

This project was aimed at investigating the identity of *in situ* formed palladium *N*-heterocyclic carbene complexes formed under catalytically relevant reaction conditions. In attempted syntheses of the catalytically active species formed under basic methanolic reaction conditions, we did not obtain the envisaged cationic palladium(II) methoxide complexes, instead cationic [{bis(μ-carbene)}$_2Pd_2H]^+$ **5a** and **5b** were obtained. Thus, these complexes were used for further investigations as precatalysts/catalysts in relation to Heck coupling, the related Suzuki and Sonogashira C-C cross-coupling reactions, as well as carbon monoxide/ethene copolymerisation.

2.2.6.1 Heck reaction

Initial catalytic investigation of the Pd NHC complex $[\{\mu\text{-}(MesIm)_2CH_2\}_2Pd_2H][PF_6]$ **5a** as a precatalyst were attempted with the Heck coupling reaction of 4-iodoacetophenone and *n*-butyl acrylate, Scheme 2.25 and Table 2.5.



$R = C(O)CH_3$ $X = I, Br$

Scheme 2.25 Heck reaction

Table 2.5 Heck reactions (120 °C heating, conversions determined by GC)

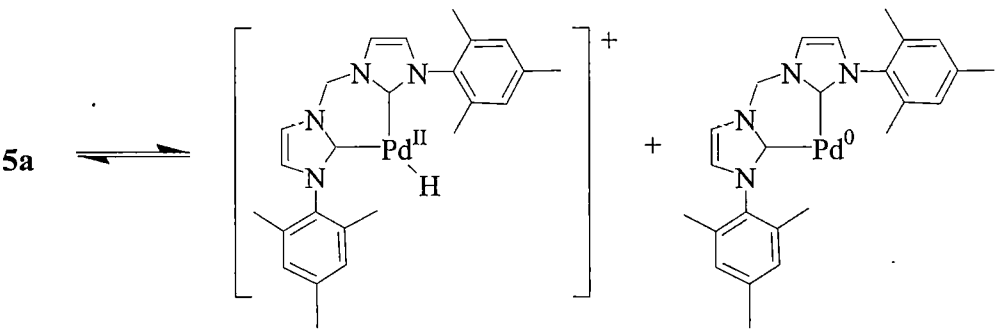
Cat.	Amount (mol%)	Aryl halide	Coupling partner	Time (hr)	Conversion (%)
4a	2.0	4-iodoacetophenone	*n*-butyl acrylate	48	>99
5a	2.0	4-iodoacetophenone	*n*-butyl acrylate	48	>99
3a	2.0	4-bromoacetophenone	*n*-butyl acrylate	48	87
4a	2.0	4-bromoacetophenone	*n*-butyl acrylate	48	90
5a	2.0	4-bromoacetophenone	*n*-butyl acrylate	48	68

Due to low yielding synthesis of the bulkier analogue $[\{\mu\text{-}(iPr_2Ph)_2CH_2\}_2Pd_2(\mu\text{-}H)][PF_6]$ **5b** and the relatively late success in isolating this complex, it was excluded from the catalytic reactions. All reactions were run in *N*,*N*-dimethylacetamide (DMAc) as solvent and Na_2CO_3 as the base with a catalyst loading of 2 mol %. No salt additive was used in this reaction and since the dipalladium(I) hydride complex is in a low oxidation state no reducing agent was used.

Full conversion was achieved with catalyst **5a** at a concentration of 2 mol%, as was also the case with the dicationic Pd(II) complex **4a** used as a comparison employing identical reaction conditions, Table 2.5. In attempting to distinguish the catalytic performance of the Pd(I) species **5a** from the Pd(II)

precursors, the reactions were all attempted using an activated aryl bromide. During the reaction, palladium black was observed for **5a** which was not the case for **4a.** The Heck coupling of the aryl bromide proceeded 68% conversion, lower than when the chelated palladium(II) complex precursors **3a** and **4a** were used, with 87 and 90% conversions, respectively.

The poorer performance of **5a** in the Heck coupling is unsurprising since chelated palladium complexes are expected to have higher thermal stability to cope with the harsh reaction conditions of the Heck reaction, whereas the dinuclear complex **5a** seems to have lower thermal stability. While the traditional Pd(0)/Pd(II) Heck reaction mechanism cycle requiring reduction of the Pd(II) centre is likely adopted by **3a** and **4a,** the mechanism adopted by complex **5a** is unknown. Very few reports of using dinuclear Pd(I) complexes as precatalysts for C-C coupling reactions have appeared.[194] Their performance has suggested that disproportionation to active Pd(II) and/or Pd(0) species occurs and it remains to be demonstrated whether the Pd(I)-Pd(I) interaction has a useful role in promoting this class of reaction. This is in stark contrast to the increasingly topical role that Pd(III)-Pd(III) interactions play in some oxidative addition initiated catalytic processes.[195-198]



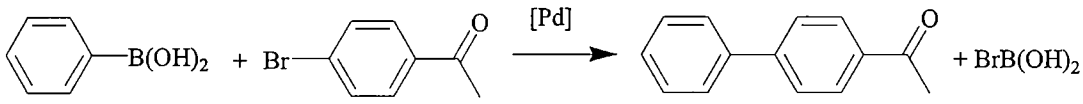
Scheme 2.26 Potential equilibrium of the cationic dipalladium(I) hydride **5a** with the constituent Pd(0) and cationic Pd(II)H species

It was presumed that **5a** was likely formed from the equilibrium reaction of the Pd(0) species $[\{(MesIm)_2CH_2\}_2Pd^0]$ and palladium hydride species $[\{(MesIm)_2CH_2\}_2PdH]^+$, Scheme 2.26. Pd(0) species are typically considered to be the active catalysts for most Heck reactions.[97,111] We attempted the

stoichiometric reaction of **5a** with 4-iodoacetophenone to study the oxidative addition mechanism of the Heck reaction. Pale coloured complex mixtures were observed upon reaction, which are indicative of Pd(II). ^{1}H NMR spectroscopy of this reaction revealed a complex reaction mixture and we could not successfully obtain any valuable information. Mass spectrometric analyses gave ions with *m/z* of 1265 and 1355, which do not indicate $[\{(MesIm)_2CH_2\}_2PdI(C_6H_4\text{-}4\text{-}MeCO)]$ as the likely complex that would form from $[\{(MesIm)_2CH_2\}_2Pd^0]$ in the oxidative addition. This indicated that **5a** likely did not form the Pd(0) species, which was the supposed active catalyst of the Heck reaction. This could be the reason of poor performance of **5a** in the Heck reaction.

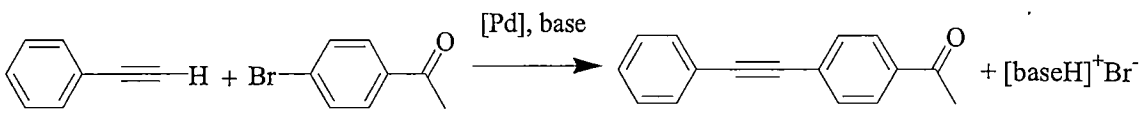
2.2.6.2 Suzuki and Sonogashira reaction

In addition to the Heck reaction, the Suzuki coupling of 4-bromoacetophenone with phenylboronic acid was undertaken with selected complexes with the same catalyst loading in toluene, Scheme 2.27.



Scheme 2.27 Suzuki reaction

Potassium carbonate was used as the base and no reducing agents or additives were again used. Sonogashira coupling of 4-bromoacetophenone and phenylacetylene was also conducted using similar protocols, including without addition of CuI, which is usually needed for this reaction to facilitate the formation of the acetylide anion, Scheme 2.28. Triethylamine was used as the base and solvent. The catalytic performance in both the Suzuki and Sonogashira reactions, particularly in the latter case was again low compared to **4a**, Table 2.6.



Scheme 2.28 Sonogashira reaction

Table 2.6 Suzuki and Sonogashira reactions (Suzuki reaction: 120 °C heating, Sonogashira reaction: 90 °C heating, conversions determined by GC)

Cat.	Amount (mol%)	Aryl halide	Coupling partner	Time (hr)	Conversion (%)
4a	2.0	4-bromoacetophenone	$C_6H_5B(OH)_2$	24	86
5a	2.0	4-bromoacetophenone	$C_6H_5B(OH)_2$	24	60
4a	2.0	4-bromoacetophenone	phenylacetylene	48	75
5a	2.0	4-bromoacetophenone	phenylacetylene	48	10

2.2.6.3 Carbon monoxide/ethene copolymerisation

The carbon monoxide/ethene copolymerisation system using the dicationic chelated bis(NHC)Pd(II) complex **4a** as the precatalyst was of significant interest to us. The chelated bis(NHC)Pd(II) complex **4a** shows relatively poor activity (g copolymer/g Pd), but produced copolymer with very high molecular weight.[140] This possibly indicates poor *in situ* precatalyst conversion into the actual catalyst. Thus, direct synthetic access to the catalytically active species offers great promise in producing a highly active catalyst. The dipalladium(I) hydride complexes **5a** and **5b** were tested for activity in carbon monoxide/ethene copolymerisation, and compared to the performance of the dicationic palladium(II) precursors **4a** and **4b**.

Table 2.7 Carbon monoxide/ethene copolymerisation reactions

Cat.	Temp. (°C)	Pressure C_2H_4/CO (bar)	Solvent	Vol. (mL)	Time (hr)	Yield (g polymer/ g Pd)
5a	r.t.	10/10	CH_3OH	50	0.5	0
5a	50	45/45	CH_3OH	50	24	0
4a	50	20/20	CH_3OH	20	24	3.47
4a	50	40/40	CH_3OH	50	24	1.04
4a+Na_2CO_3	50	20/20	CH_3OH	20	24	0
4b	50	45/45	CH_3OH	50	24	1.86
4b+Na_2CO_3	50	45/45	CH_3OH	50	24	0
5b	50	45/45	CH_3OH	50	24	0

Solutions of the complexes were pre-prepared in anhydrous methanol and no additives were used for the reaction. At first, complex **5a** was tested at room temperature for 30 minutes. The complex had decomposed, with palladium black deposited and no polymer resulted. GC-MS revealed that no formylation products were formed. Complex **4a** was used as comparison, and the reaction was undertaken at 50 °C overnight. It yielded 3.47 g polymer/g Pd of polymer product, Table 2.7. Similar results were also observed when their analogues $[\{(i\text{Pr}_2\text{Ph})_2\text{CH}_2\}\text{Pd(NCMe)}_2][\text{PF}_6]_2$ **4b** and $[\{\mu\text{-}(i\text{Pr}_2\text{Ph})_2\text{CH}_2\}_2\text{Pd}_2\text{H}][\text{PF}_6]$ **5b** were used as the precatalyst. Complex **5b** had decomposed and no polymer resulted, while **4b** resulted in 1.86 g polymer/g Pd.

We envisaged the formation of the cationic chelated $\text{Pd}^{\text{II}}\text{OMe}$ complex in our base assisted reaction of **4a** and **4b**, but the Pd(I) species **5a** and **5b** formed. To study the possibility of the *in situ* formation of active cationic $\text{Pd}^{\text{II}}\text{OMe}$ or $\text{Pd}^{\text{II}}\text{H}$ species (as possible intermediates in the synthesis of **5a** and **5b**), further copolymerisation reactions were undertaken using complex **4a** and **4b** with added Na_2CO_3. These reactions did not yield polymer. As the synthesis of **5b** was shown to proceed over several hours via a number intermediates (possibly $\text{Pd}^{\text{II}}\text{OMe}$ or $\text{Pd}^{\text{II}}\text{H}$ species), further runs were conducted where carbon monoxide and ethene were added in delayed fashion. However, these also did not result in any polymer. As the dipalladium(I) hydride complexes **5a** and **5b** are inactive in C_2H_4/CO copolymerisation, this possibly suggests that a palladium methoxide species is needed as the actual catalyst of this reaction instead of palladium hydride species. This is still an unsolved issue of the copolymerisation mechanism described by Drent, as explained in Chapter 1, at least in the case of NHC based systems.

Previous reported copolymerisation using **4a** with similar reaction conditions: 50 °C heating, 40/40 bar ethene/CO pressure and just 60 minutes reaction time yielded 135 g polymer/g Pd, while for our reactions only 1.04 g polymer/g Pd was obtained.[140] This low polymer yield for **4a** compared to the previous report cannot be explained, but is likely due to gas quality and reactor variations. Nevertheless, it is clear that **5a** and **5b** perform worse or have no activity relative to **4a** and **4b**. The implication of complex **4b** is a potential

catalyst for CO/C_2H_4 copolymerisation stands. The bulkier substituent on **4b** does not seem to have a major influence on the catalysis performance; slightly worse relative performance is noted. Formylation or C_2H_4 oligomerisation products were not observed. As the performance of **4b** was not improved relative to **4a**, we did not characterise the polymer in detail. Facile decomposition of the dinuclear complex during the initiation phase by a CO insertion process could be another factor influencing the observed poor performance.

In order to study the decomposition of **5a** in CO/C_2H_4 copolymerisation, LSI-MS and ^1H NMR spectroscopic analyses on the reaction of **5a** and CO, as well as **5a** with C_2H_4 were undertaken. Reaction with CO resulted in a dark red solid that was unable to be crystallised and rapidly decomposed into palladium black. The ^1H NMR spectra in CD_3OD were not informative. LSI-MS showed ion envelopes at *m/z* 489 and 935 which were not assignable. Reactions with ethene resulted in pale yellow solutions. The ^1H NMR spectrum in CD_3OD gave very low intensity resonances devoid of aromatic/alkenyl protons. There are no conclusions that can be drawn as a result from the reaction of **5a** with carbon monoxide and ethene.

3: Conclusion

3.1 Concluding Statement

The aim of this project was to investigate *in situ* formed palladium *N*-heterocyclic carbene complexes under catalytically relevant reaction conditions from palladium(II) precatalysts. This aim is underpinned by the importance of neutral and cationic palladium(II) complexes as precatalysts for carbon monoxide/ethene copolymerisation as well as various related C-C coupling reactions. Complexes with the bulky substituents, 2,4,6-mesityl and 2,6-diisopropylphenyl were able to be synthesised through to the complete envisaged synthetic schemes, while analogous complexes with less bulky phenyl and *tert*-butyl substituents were not able to be prepared. The complexes synthesised have been characterised in most cases by NMR spectroscopy, microanalysis and X-ray structure determinations.

The envisaged putative carbon monoxide/ethene copolymerisation catalysts, the cationic palladium(II) methoxide complexes, which were to be synthesised by reaction of the dicationic palladium(II) precursors with sodium carbonate in methanol unexpectedly afforded stable dipalladium(I) hydride complexes $[\{\mu\text{-}(MesIm)_2CH_2\}_2Pd_2H][PF_6]$ **5a** and $[\{\mu\text{-}(i Pr_2Ph)_2CH_2\}_2Pd_2(\mu\text{-}H)][PF_6]$ **5b**. These complexes were presumably formed from the *in situ* formed methoxide complex, which decomposes *via* β-hydride elimination and reduction processes. These complexes are novel, having different bonding characteristics in comparison to other reported dinuclear palladium(I) hydride complexes. They are the first Pd(I) NHC complexes and, respectively, the first terminal Pd(I)-Pd(I)-H and linear Pd(I)-H-Pd(I) complexes without a Pd-Pd bond.

The monocationic dipalladium(I) hydride **5a** exhibits a Pd-Pd interaction (2.7527(7) Å) and two bridging methylene-linked imidazolin-2-ylidene ligands with approximate non-crystallographic C_2 symmetry. The hydride occupies a terminal position attached in an approximately linear Pd-Pd-H arrangement, which was unambiguously located by neutron crystal structure determination. The

synthesis of **5a** was monitored by ^{1}H NMR spectroscopy at room temperature and shown to proceed without any detectable reaction intermediates. In solution **5a** is fluxional, with the ^{1}H NMR spectrum exhibiting a relatively simple appearance at room temperature as a result of a number of fluxional processes that increase the time averaged molecular symmetry beyond that seen in the solid state determined structure. At low temperature the spectrum exhibits the same symmetry as that seen in the solid state. Reactivity investigations of **5a** with 1,8-diazabicyclo[5.4.0]undec-7-ene, K metal, KH, ethene and carbon monoxide were all inconclusive.

In stark contrast, complex **5b** still maintains two bridging methylene-linked imidazolin-2-ylidene ligands, but no Pd-Pd bond is observed. The cation displays overall crystallographic C_i symmetry (approximately C_{2h} symmetry). The X-ray crystal structure refinement of **5b** also failed to locate the hydride ligand. Crystals have been examined by neutron diffraction in an attempt to resolve this important structural detail but, unfortunately, the refinement details are not available at this point. The diamagnetic behaviour of **5b**, however, as well as the Pd···Pd separation (3.3944(12) Å) are very strong indicators of the hydride ligand residing in a linear bridging position between the Pd centres. Assuming this is the case, this would represent the first bridging hydride ligand in a palladium(I) complex that is not supported by the presence of a Pd-Pd bond. The synthesis of **5b** was monitored by ^{1}H NMR spectroscopy and mass spectrometry showing the formation of a number of intermediates. In solution **5b** is also fluxional. But, unlike for **5a**, at low temperature the palladium centres did not become inequivalent, which is consistent with the proposed bridging hydride structure.

The dipalladium(I) hydride **5a** was shown to be an effective catalyst for the Heck reaction of an aryl iodide. However, it was less effective compared to its dicationic Pd(II) precursor in catalysing Heck, Suzuki and Sonogashira reactions with aryl bromides. The stoichiometric reaction between **5a** and 4-iodoacetophenone did not indicate the formation of the corresponding $[\{(MesIm)_2CH_2\}_2PdI(aryl)]$ complex which is likely the species to be formed as a result of oxidative addition to Pd(0) species as the active catalyst under the

traditional Heck reaction mechanism. The behaviour of **5b** in Heck type reactions and C-C coupling reactions remains unknown.

Both of the dipalladium(I) hydride complexes **5a** and **5b** were not effective catalysts for carbon monoxide/ethene copolymerisation. This failure to catalyse the reaction may suggest that a palladium methoxide species are the actual catalysts. Facile decomposition of the dinuclear complex during the initiation phase by a CO insertion process could be another factor influencing the observed poor performance.

3.2 Future Work

Further study into the mechanism of dicationic chelated NHC Pd complexes as precatalysts in carbon monoxide/ethene copolymerisation is justified. Since there was no catalytic activity shown from both **5a** and **5b**, access to the palladium methoxide would be of major significance. According to the mechanistic proposals of Drent, this distinction remains unknown for the case of NHC catalysed systems at least. The novel outcomes of the synthesis of the low valent complexes **5a** and **5b** and their unique structures warrant further investigations. Subtle variations in steric bulk in the [{1,1'-di(aryl)-3,3'-methylenediimidazolin-2,2'-diylidene}palladium(II)bis(acetonitrile)][PF_6]$_2$ system, or indeed through a wider examination of ligand effects, could lead to further extension of this class of dinuclear system, or indeed metal clusters of higher nuclearity or mononuclear species.

4: Experimental

4.1 General Considerations

All reactions involving organometallic reagents were carried out under an inert atmosphere of high purity argon using standard Schlenk techniques unless stated otherwise. Handling of air-sensitive solids was carried out in a dry glove box (Innovative Technologies) under a nitrogen atmosphere with Schlenk type glassware. Glassware was heated under vacuum and refilled with nitrogen to ensure oxygen and moisture was excluded from the reactions. Solvents used were of analytical grade and were dried by passing through columns on an Innovative Technologies Solvent Purifier. All reagents were purchased from Sigma-Aldrich and used as received unless stated otherwise. Anhydrous methanol ($\geq$ 99.8 % purity) was purchased from Sigma-Aldrich and stored in an ampoule over 3Å molecular sieves. Palladium acetate were purchased from Precious Metal Online and used as received. 1-Phenylimidazole was purchased from Sigma-Aldrich and used without further purification. For the other non-air sensitive syntheses, solvents were of analytical grade and were used as received.

4.2 Instrumentation

NMR studies were carried out on a 300 MHz Varian Gemini Mercury Plus spectrometer at room temperature (293 K) in $CDCl_3$, DMSO-d_6, CD_3OD or THF-d_8. THF-d_8 was dried over Na prior to use and stored in an inert atmosphere glove box. VT-NMR studies were performed by Dr. James Horne at the Central Science laboratory using a 400 MHz Varian Inova wide bore spectrometer with 1D-PFG-5 mm z-axis gradient probe. CD_3OD was purchased as an anhydrous solvent and used without further purification. ^1H NMR spectra were recorded at 299.89 MHz while ^{13}C NMR spectra were recorded at 75.41 MHz. ^1H NMR and ^{13}C NMR spectra were referenced to the residual ^1H resonance of the solvent residual peaks, while ^{13}C NMR spectra were referenced to the deuterated ^{13}C resonance.

Elemental and GC-MS analyses were carried by the Central Science Laboratory at the University of Tasmania using a Carlo Erba EA1108 Elemental Analyser, and a Varian 3800 GC coupled to a Varian 1200 triple quadrupole MS, respectively. The liquid products resulting from C-C coupling reactions and CO/C_2H_4 copolymerisation were analysed on a Hewlett Packard Series II 5890 instrument utilising a nitrogen carrier gas and FID detector with HP-1 cross-linked methyl siloxane (25 x 0.35 x 0.52 mm film thickness) column and then verified by GC-MS. Initial oven temperature was set at 40 °C for four minutes, increasing at 20 °C per minutes to a final temperature of 300 °C.

X-ray crystallography studies were conducted by Dr. Michael Gardiner and Adam James at School of Chemistry University of Tasmania using CAD4, -80 °C, Mo-Kα radiation or at the Australian Synchrotron using the PX1 beamline, -173 °C, $\lambda = 0.77501$ Å. Neutron X-ray diffraction was performed by Dr. Marie-Hélène Lemée-Cailleau, ILL, Grenoble France, and Dr. Alison Edwards at Bragg Institute ANSTO, New South Wales.

ESI-MS and LSIMS were performed by Dr. Noel Davies and Mr. Marshall Hughes, respectively, and microanalyses were performed by Dr. Thomas Rodemann at the Central Science Laboratory, University of Tasmania.

4.3 Ligand Synthesis

4.3.1 Preparation of 1-(2,4,6-mesityl)imidazole, MesIm 1a

Method I (modified literature procedure of Herrmann[140]): A solution of methanol (200 mL) and H_2O (200 mL) containing paraformaldehyde (6.0 g, 0.20 mol), mesitylammonium salt (prepared from the addition of phosphoric acid (10 mL, 85 %) to mesitylamine (27.0 g, 0.20 mol) in 100 mL H_2O until a pH of *ca.* 2 was reached) and glyoxal (23 mL of 40 % aqueous solution, 0.20 mol) was refluxed for 3 hours giving a yellowish coloured solution. An ammonium chloride solution (10.7 g, 0.20 mol and 40 mL H_2O) was added dropwise over 30 minutes. During the addition the solution turns yellow and then rapidly black. Reflux was continued for a further one hour and then cooled in an ice bath. Solid NaOH was added at 0 °C until a pH $>$ 12 was obtained and a dark organic layer separated.

H_2O (300 mL) was added to the reaction mixture and the product was extracted with hexane (3 x 500 mL). The combined hexane extracts were dried over $MgSO_4$, filtered and the hexane evaporated to yield the product as a light brown solid which was recrystallised from ethyl acetate as a colourless crystalline solid (3.0 g, 13 %).

Method II (modified literature procedure of Gridnev)[165]: Glyoxal 40 % aq. (8.2 mL, 72.0 mmol) was added to a methanol solution (40 mL) of mesitylamine (10.1 mL, 72.0 mmol) and the mixture was stirred overnight at room temperature until yellowish precipitate formed. Ammonium chloride (3.80 g, 72.0 mmol) was added followed by paraformaldehyde (2.16 g, 72.0 mmol). The mixture was diluted in methanol (300 mL) and the resulting mixture refluxed for an hour. Afterward, phosphoric acid (10 mL, 85 %) was added dropwise over 30 minutes. The resulting mixture was refluxed for further 4 hours. The mixture was then cooled and methanol removed by rotary evaporation. The mixture was basified with 40 % aq. potassium hydroxide until pH > 9. The resulting mixture (solution and precipitate) was extracted with dichloromethane (3x 250 mL) and washed with H_2O. The mixture was then dried over anhydrous magnesium sulphate, filtered and the dichloromethane was removed and the resulting yellow solid was purified by soxhlet extraction giving a yellow solid that was subsequently crystallised by slow evaporation of a hexane solution. The product was shown to be spectroscopically identical to that reported in the literature (9.87 g, 74 %).

^{1}H NMR (299.89 MHz, $CDCl_3$): δ 1.98 (6 H, s, *o*-Me), 2.33 (3 H, s, *p*-Me), 6.89 (1 H, s, CH(imidazole)), 6.97 (2 H, s, *m*-CH(mesityl)), 7.24, 7.42 (2 x 1 H, bs, CH(imidazole)).

4.3.2 Preparation of 1-(2,6-diisopropylphenyl)imidazole, *i*Pr$_2$PhIm 1b

Method I (modified literature procedure of US Patent 3,637,731[167]): Thiophosgene (29.8 g, 0.26 mol) was suspended in water (300 mL) and 2,6-diisopropyphenylamine (45 mL, 0.24 mol) was added slowly. The solution was stirred for 2 hours and then extracted in dichloromethane, filtered and the solvent was removed *in vacuo* giving the isothiocyanate intermediate. Aminoacetaldehyde

diethyl acetal (50.1 g, 0.23 mol) in ethanol (260 mL) was added to the isothiocyanate solution and the mixture refluxed for 2 hours. Ethanol was removed *in vacuo* and the residue was suspended in HCl (250 mL, 10 %) and the mixture refluxed. After one hour, the solution was cooled in an ice bath and the solid that formed was collected by filtration, washed with water and left to air dry. The product was suspended in HNO_3 (200 mL, 20%) and warmed for 10 minutes creating a vigorous reaction which was then cooled. The product was basified with ammonia solution (25 %) and was extracted in dichloromethane at room temperature. The mixture was then dried over anhydrous magnesium sulphate, filtered and the solvent was removed. The resulting yellow solid was purified by recrystallisation from dichloromethane (3.90 g, 7%).

Method II (modified literature procedure of Gridnev[165]): 2,6-diisopropylaniline (8.86 g, 0.050 mol) was diluted in methanol (25 mL) and added glyoxal 40 % aq. (5.7 mL, 0.050 mol) and the mixture was stirred overnight at room temperature until a yellowish precipitate was formed. Ammonium chloride (2.68 g, 0.050 mol) was added followed by paraformaldehyde (1.50 g, 0.050 mol). The mixture was diluted with methanol (200 mL) and the resulting mixture refluxed for an hour. Afterward, phosphoric acid (10 mL) was added dropwise over 10 minutes. The resulting mixture was refluxed for further 4 hour. The mixture was then cooled and methanol removed by rotary evaporation. The mixture was basified with aq. potassium hydroxide until pH > 9. The resulting mixture (solution and precipitate) was extracted with dichloromethane (3x 250 mL) and washed with H_2O. The mixture was then dried over anhydrous magnesium sulphate, filtered and the dichloromethane was removed and the resulting yellow solid was subsequently purified by vacuum sublimation as colourless crystals. The product was shown to be spectroscopically identical to that reported in the literature (1.07 g, 11%).

^{1}H NMR (299.89 MHz, $CDCl_3$): δ 1.13 (12 H, d, $^3J_{HH}$ = 6.75 Hz, CH_3 (*i*Pr)), 2.38 (2 H, sept., $^3J_{HH}$ = 6.65 Hz, CH(*i*Pr), 6.97 (1 H, bs, CH(imidazole)), 7.28 (2 H, d, $^3J_{HH}$ = 7.91 Hz, *m*-CH(aryl)), 7.30 (1 H, bs, CH(imidazole)), 7.46 (1 H, m, *p*-CH(aryl)), 7.60 (1 H, bs , CH(imidazole)).

4.3.4 Preparation of $[(MesImH)_2CH_2]Br_2$ 2a

Synthesis followed a modified literature procedure of Herrmann.[140] A stirred toluene solution (20 mL) of MesIm **1a** (3.00 g, 16.1 mmol) and dibromomethane (2.80 g, 16.1 mmol) was heated at 150 °C for 2 days to yield a white powder of the product which was collected by filtration and dried *in vacuo*. The product was shown to be spectroscopically identical to that reported in the literature (3.07 g, 36 %).

^{1}H NMR (299.89 MHz, DMSO-d_6): δ 2.04 (12 H, s, *o*-Me), 2.31 (6 H, s, *p*-Me), 7.01 (2 H, s, CH_2), 7.15 (4 H, s, *m*-CH(mesityl)), 8.11 (2 H, s, CH(imidazolium)), 8.61 (2H, s, CH(imidazolium)), 10.19 (2 H, s, CH(imidazolium)).

4.3.5 Preparation of $[(iPr_2PhImH)_2CH_2]Br_2$ 2b

Synthesis followed a modified literature procedure of Herrmann.[140] A stirred toluene solution (5 mL) of iPr_2PhIm **1b** (2.28 g, 10.0 mmol) and dibromomethane (1.74 g, 10.0 mmol) was heated at 120 °C for 24 hours to yield a white powder of the product which was collected by filtration and dried *in vacuo*. The product was shown to be spectroscopically identical to that reported in the literature (2.91 g, 46 %).

^{1}H NMR (299.89 MHz, DMSO-d_6): δ 1.12 (24 H, d, $^3J_{HH}$ = 6.29 Hz, CH_3(*i*Pr)), 2.25 (4 H, sept., $^3J_{HH}$ = 6.69 Hz, CH(*i*Pr)), 7.00 (2 H, s, CH_2), 7.47 (4 H, d, $^3J_{HH}$ = 7.71 Hz, *m*-CH(aryl)), 7.65 (2 H, t, $^3J_{HH}$ = 7.68 Hz, *p*-CH(aryl)), 8.28 (2 H, s, CH(imidazolium)), 8.51 (2 H, s, CH(imidazolium)), 10.14 (2 H, s, CH(imidazolium)).

4.3.6 Preparation of $[(PhImH)_2CH_2]Br_2$ 2c

Synthesis followed a modified literature procedure of Herrmann.[140] A stirred toluene solution (10 mL) of 1-phenylimidazole **1c** (0.25 g, 1.8 mmol) and dibromomethane (0.30 g, 1.8 mmol) was heated at 120 °C for 24 hours to yield a white powder of the product which was collected by filtration and dried *in vacuo*.

The product was shown to be spectroscopically identical to that reported in the literature (0.22 g, 28 %).

^{1}H NMR (299.89 MHz, DMSO-d_6): δ 6.97 (2 H, s, CH_2), 7.68-7.73 (10 H, m, CH(phenyl)), 7.83 (2 H, s, CH(imidazolium)), 7.86 (2 H, s, CH(imidazolium)), 10.15 (2 H, s, CH(imidazolium)).

4.4 Metal Complex Synthesis

4.4.1 Preparation of [{(MesIm$_2$)CH$_2$}PdBr$_2$] 3a

Synthesis followed literature procedure of Herrmann.[140] A stirred dimethyl sulfoxide solution (15 mL) of [(MesImH)$_2$CH$_2$]Br$_2$ **2a** (1.01 g, 1.85 mmol) and Pd(OAc)$_2$ (624 mg, 1.85 mol) was heated at 50 °C for 3 hours and then at 110 °C for a further 2 hours, during which time the reaction solution had turned to a pale yellow solution from being initially orange. The remaining dimethyl sulfoxide was then removed *in vacuo* to give a yellow solid which was washed with dichloromethane to give the product as a very pale yellow solid. Recrystallisation from acetonitrile gave the product as very fine pale yellow needles. The product was shown to be spectroscopically identical to that reported in the literature (0.89 g, 74 %).

^{1}H NMR (299.89 MHz, DMSO-d_6): δ 2.06 (12 H, bs, *o*-Me), 2.54 (6 H, bs, p-Me), 5.89 (2 H, s, CH_2), 6.59 (4 H, bs, *m*-CH(mesityl)), 7.35 (2 H, bs, CH(imidazolin-2-ylidene)), 7.82 (2 H, bs, CH(imidazolin-2-ylidene)).

4.4.2 Preparation of [{(*i*Pr$_2$PhIm)$_2$CH$_2$}PdBr$_2$] 3b

Synthesis followed a patent by Straβner.[168] Prior to the addition of dimethyl sulfoxide, the imidazolium salt and palladium acetate were dried by heating *ca.* 70 °C for 15 minutes *in vacuo*. A stirred dimethyl sulfoxide solution (5 mL) of [(*i*Pr$_2$PhImH)$_2$CH$_2$]Br$_2$ **2b** (1.60 g, 2.5 mmol) and Pd(OAc)$_2$ (0.57 g, 2.5 mmol) was gradually heated for an hour at 40 °C, one hour at 60 °C, two hours at 80 °C, two hours at 100 °C and another hour at 130 °C. At the end of the reaction the solvent was removed *in vacuo* and the product rinsed in dichloromethane giving a pale yellow solid in excellent yield. The product can be

purified by recrystallisation from acetonitrile. The product was shown to be spectroscopically identical to that reported in the literature (1.87 g, 99 %).

^{1}H NMR (299.89 MHz, DMSO-d_6): δ 1.00 (12 H, d, $^3J_{HH}$ = 6.00 Hz, CH_3(*i*Pr)), 1.30 (12 H, d, $^3J_{HH}$ = 6.45 Hz, CH_3(*i*Pr)), 1.89 (4 H, d, $^3J_{HH}$ = 6.00 Hz, CH(*i*Pr)), 6.53 (2 H, s, CH_2), 7.00-7.70 (8 H, bs, 4 x *m*-CH(aryl), 2 x *p*-CH(aryl), 2 x CH(imidazolin-2-ylidene)), 7.85 (2 H, s, CH(imidazolin-2-ylidene)).

4.4.3 Preparation of [{(PhIm)$_2$CH$_2$}PdBr$_2$] 3c

Method I followed literature procedure of Okuyama[170]: A stirred dimethyl sulfoxide solution (5 mL) of [(PhImH)$_2$CH$_2$]Br$_2$ **2c** (0.22 g, 0.5 mmol) and Pd(OAc)$_2$ (0.10 g, 0.5 mmol) was gradually heated in dimethyl sulfoxide for an hour at 40 °C and 10 minutes at 110 °C. At the end of the reaction the solvent was removed, the product rinsed dichloromethane and then dried *in vacuo*.

Method II followed a modified literature procedure of Herrmann[140]: same amount of the precursor and Pd(OAc)$_2$ was heated at 50 °C for 3 hours and then at 110 °C for a further 2 hours.

Both methods give substantial amounts of palladium black that cannot be removed by purification. Attempts to recrystallise the product were unsuccessful. ^{1}H NMR spectra of each reaction mixture did not match with literature data and mass spectrometric methods showed the possible presence of various reaction intermediates in accordance with mechanistic studies by Herrmann[146] and Albrecht.[144]

4.4.4 Preparation of [{(MesIm)$_2$CH$_2$}Pd(NCMe)$_2$][PF$_6$]$_2$ 4a

Synthesis followed a modified literature procedure of Herrmann.[140] [{(MesIm)$_2$CH$_2$}PdBr$_2$] **3a** (0.80 g, 1.2 mmol) was suspended in an acetonitrile : water solution (120 mL : 120 mL) with sodium hexafluorophosphate (4.00 g, 238.0 mmol) and the mixture was heated at 80 °C for 90 minutes before removing the acetonitrile *in vacuo* to precipitate the product as a white solid. The product was collected by filtration, washed with water, dried *in vacuo* and recrystallised

by vapour diffusion of diethyl ether into a saturated acetonitrile solution. The product was shown to be spectroscopically identical to that reported in the literature (0.50 g, 47 %).

^{1}H NMR (299.89 MHz, DMSO-d_6): δ 2.05 (12 H, s, *o*-Me), 2.31 (6 H, s, *p*-Me), 2.49 (6 H, s, MeCN), 6.61 (2 H, s, CH_2), 7.09, (4 H, s, *m*-CH(mesityl)), 7.57 (2 H, s, CH(imidazolin-2-ylidene), 7.99 (2 H, s, CH(imidazolin-2-ylidene)).

4.4.5 Preparation of [{(*i*Pr$_2$PhIm)$_2$CH$_2$}Pd(NCMe)$_2$][PF$_6$]$_2$ 4b

An acetonitrile : water solution (240:240 mL) of [{(*i*Pr$_2$PhIm)$_2$CH$_2$}PdBr$_2$] **3b** (1.88 g, 3.0 mmol) and sodium hexafluorophosphate (18.8 g, 112.0 mmol) was heated at 80 °C for 90 minutes before removing the acetonitrile *in vacuo* to precipitate the product. The product was collected by filtration as a white solid, washed with water, dried *in vacuo* and recrystallised by vapour diffusion of diethyl ether into a saturated acetonitrile solution (1.39 g, 50%).

^{1}H NMR (299.89 MHz, DMSO-d_6): δ 1.02 (12 H, d, $^3J_{HH}$ = 6.60 Hz, CH_3(*i*Pr)), 1.28 (12 H, d, $^3J_{HH}$ = 6.60 Hz, CH_3(*i*Pr)), 2.05 (6 H, s, MeCN), 2.51 (4 H, sept., $^3J_{HH}$ = 6.60 Hz, CH(*i*Pr)), 6.61 (2 H, s, CH_2), 7.36 (4 H, d, $^3J_{HH}$ = 7.79 Hz, *m*-CH(aryl)), 7.52 (2 H, t, $^3J_{HH}$ = 7.50 Hz, *p*-CH(aryl)), 7.68 (2 H, s, CH(imidazolin-2-ylidene)), 8.00 (2 H, s, CH(imidazolin-2-ylidene)).

^{13}C NMR (75.41 MHz, DMSO-d_6): δ 1.9 (CH_3(MeCN)), 23.6 (CH_3(*i*Pr)), 26.0 (CH_3(*i*Pr)), 28.9 (CH(*i*Pr)), 62.8 (CH_2), 119.0 (CN(MeCN)), 123.1 (CH(imidazolin-2-ylidene)), 124.6 (*m*-CH(aryl)), 128.7 (CH(imidazolin-2-ylidene)), 131.1 (*p*-CH(aryl)), 135.3 (C(*ipso*-aryl)), 143.6 (carbene), 145.7 (CH(*o*-aryl)).

LSI-MS *m/z* 801 [{(*i*Pr$_2$PhIm)$_2$CH$_2$}Pd(NCMe)$_2$][PF$_6$]$^+$.

ESI-MS *m/z* 573 [{(*i*Pr$_2$PhIm)$_2$CH$_2$}Pd]$^+$, 619 [{(*i*Pr$_2$PhIm)$_2$CH$_2$}Pd(NCMe)]$^+$.

Found C 44.95, H 5.06, N 9.72%, calc. (for $C_{35}H_{46}N_6F_{12}P_2Pd$) C 44.38, H 4.90, N 8.87%.

4.4.6 Preparation of [{μ-(MesIm)$_2$CH$_2$}$_2$Pd$_2$H][PF$_6$] 5a

A methanol solution (5 mL) of [{(MesIm)$_2$CH$_2$}Pd(NCMe)$_2$][PF$_6$]$_2$ **4a** (0.20 g, 0.23 mmol) and sodium carbonate (0.060 g, 0.6 mmol) was heated for two hours at 50 °C giving a red solution. The solution was filtered from the excess sodium carbonate and the product crystallised upon concentration *in vacuo* to *ca.* 10 mL. Red crystals were obtained via recrystallisation by slow cooling in an acetone bath in the freezer at -20 °C, afforded a mixture of red needle and prismatic crystals that were isolated by removal of the methanolic mother liquor, which could be cropped for further product yield. Crystal isolation could also be conducted using tetrahydrofuran with the same procedure, producing block crystals. The crystals were dried *in vacuo* and stored in the glove box (110 mg, 84%).

^{1}H NMR (299.89 MHz, CD_3OD): δ -16.21 (1 H, s, hydride) 1.48 (12 H, s, *o*-Me), 1.64 (12 H, s, *o*-Me), 2.41 (12 H, bs, *p*-Me), 5.97 (2 H, d, $^2J_{HH}$ = 12.00 Hz, CH_2), 6.82 (4 H, s, CH(imidazolin-2-ylidene)), 6.87 (4 H, s, *m*-CH(aryl)), 6.93 (4 H, s, *m*-CH(aryl)) 7.48 (8 H, s, CH(imidazolin-2-ylidene)), (6 H, s, *o*-Me), 7.88 (2 H, bd, $^2J_{HH}$ = 12.60 Hz, CH_2).

^{13}C-NMR (75.41 MHz, CD_3OD): δ 16.8 (*o*-Me), 17.4 (*o*-Me), 20.1 (*p*-Me), 64.1 (CH_2), 119.4 (CH(imidazolin-2-ylidene), 122.4 (CH(imidazolin-2-ylidene)), 128.5 (*m*-CH(aryl)), 129.0 (*m*-CH(aryl)), 134.83, 135.45, 137.1, 138.12 (2 x *o*-CH(aryl), *p*-CH(aryl), carbene).

LSI-MS *m/z* 983 M, [{μ-(MesIm)$_2$CH$_2$}$_2$Pd$_2$H]$^+$.

Found C 52.78, H 5.17, N 9.55% calc. (for $C_{50}H_{57}N_8Pd_2PF_6$) C 53.25, H 5.09, N 9.94%.

4.4.7 Preparation of [{μ-(*i*Pr$_2$PhIm)CH$_2$}$_2$Pd$_2$(μ-H)][PF$_6$] 5b

A methanol solution (5 mL) of [{(*i*Pr$_2$PhIm)$_2$CH$_2$}Pd(NCMe)$_2$][PF$_6$]$_2$ **4b** (0.20 g, 0.21 mmol) and sodium carbonate (0.060 g, 0.6 mmol) was heated for

eight hours at 50 °C giving a red solution. The solution was filtered from the excess sodium carbonate and the product crystallised upon concentration *in vacuo* to *ca.* 10 mL. Red crystals were obtained via recrystallisation by slow cooling at room temperature, affording red prismatic crystals that were isolated by removal of the methanolic mother liquor. The crystals were dried *in vacuo* and stored in the glove box (17 mg, 13 %).

^{1}H NMR (299.89 MHz, CD_3OD): δ –16.0 (s, hydride), 0.17 (12 H, d, $^3J_{HH}$ = 6.90 Hz, CH_3(iPr)), 0.98 (12 H, d, $^3J_{HH}$ = 6.90 Hz, CH_3(iPr)), 1.02 (12 H, d, $^3J_{HH}$ = 6.90 Hz, CH_3(iPr)), 1.72 (12 H, d, $^3J_{HH}$ = 6.90 Hz, CH_3(iPr)), 1.98 (2 H, d, $^3J_{HH}$ = 6.90 Hz, CH(iPr)), 3.30 (2 H, m, CH(iPr)), 6.00 (2 H, d, $^2J_{HH}$ = 12.66 Hz, CH_2), 6.95 (4 H, d, $^3J_{HH}$ = 1.50 Hz, CH(imidazolin-2-ylidene)), 7.03 (4 H, d, $^3J_{HH}$ = 5.89 Hz, *m*-CH(aryl)), 7.19 (4 H, d, $^3J_{HH}$ = 7.12 Hz, *m*-CH(aryl)), 7.21 (4 H, t, $^3J_{HH}$ = 7.12 Hz, *p*-CH(aryl)), 7.68 (4 H, s, CH(imidazolin-2-ylidene)), 7.69 (2 H, m, CH_2).

^{13}C NMR (75.41 MHz, CD_3OD): δ 16.9 (CH_3(iPr)), 17.2 (CH_3(iPr)), 18.3 (CH(iPr)), 20.1 (2 x CH_3(iPr)), 21.6 (CH(iPr)), 64.1 (CH_2), 119.4 (CH(imidazolin-2-ylidene)), 122.44 (CH(imidazolin-2-ylidene)), 128.52 (*m*-CH(aryl)), 129.03 (*m*-CH(aryl)), 134.83 (*o*-CH(aryl)), 135.45 (*o*-CH(aryl)), 138.1 (*m*-CH(aryl)), carbene resonance could not be assigned.

ESI-MS *m/z* 1151 $[\{\mu\text{-}(i\text{PrPh}_2\text{Im})\text{CH}_2\}_2\text{Pd}_2\text{H}]^+$.

Found C 57.12, H 6.33, N 8.49% calc. ($C_{62}H_{81}N_8Pd_2PF_6$) C 57.18, H 6.23, N 8.67%.

4.5 General Procedure for C-C coupling Reactions

4.5.1 Heck reactions

In a typical run, a 100 mL Schlenk flask was prepared under nitrogen and charged with 2 mol% catalyst (0.030 mmol) and sodium carbonate (0.24 mg, 2.3 mmol). Aryl halide (0.30 g, 1.5 mmol), *N,N*-dimethylacetamide (5 mL) and *n*-butyl acrylate (600 μL, 4.2 mmol) were then injected and the solution heated to

120 °C. After the desired time, the solution was cooled and analysed by gas chromatography.

4.5.2 Suzuki reactions

A 100 mL Schlenk flask was prepared under nitrogen and filled with 2 mol % catalyst (0.030 mmol) and potassium carbonate (0.42 g, 3.0 mmol). 4-bromoacetophenone (0.30 g, 1.5 mmol), phenylboronic acid (0.20 g, 1.7 mmol), and toluene (5 mL) were injected through a septum and the solution heated at 120 °C for 24 hours in an oil bath with vigorous stirring, after which time it was cooled and analysed by gas chromatography.

4.5.3 Sonogashira reactions

A 100 mL Schlenk flask was prepared under nitrogen and charged with 4-bromoacetophenone (0.30 g, 1.5 mmol) and 2 mol % of catalyst (0.030 mmol). Phenylacetylene (0.20 mL, 1.8 mmol) were injected along with triethylamine (5 mL) through a septum and the mixture heated at 90 °C for 48 hours. After the desired time the solution was cooled and analysed by gas chromatography.

4.6 General Procedure for CO/C_2H_4 Copolymerisation Reactions

Method I: the solutions for carbon monoxide/ethene copolymerisation studies were prepared by dissolving the catalyst in methanol (50 mL) which was transferred directly under a flow of argon into a vacuum dried Parr autoclave equipped with a stirring bar. The stirred solutions were charged with ethene and then CO and heated to 50 °C. The copolymerisation rates were monitored by the reducing pressure of the autoclave which usually commenced at the start of the reaction. The vessel was cooled to room temperature and the powders were collected, washed with methanol, dried *in vacuo* and weighed. Soluble products were analysed by GC-MS prior to any significant evaporation of any expected formylation products.

Method II: Particularly for NMR studies, NMR tubes fitted with Youngs 24/40 type stopcocks were prepared in a glove box under an inert atmosphere and

filled with the complexes and CD_3OD. Afterwards it was purged with ethene and CO.

4.7 General Procedure for NMR Scale Reactions

The compounds used for NMR scale reaction were prepared in a glove box under a nitrogen atmosphere. Anhydrous deuterated solvents and the compound were put in the NMR tubes fitted with Youngs type 24/40 stopcocks, and the reactant added. The chemical reagent or reactants used in the reaction were used as received or dried by standard procedures.

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