

**Abnormally bound N-Heterocyclic Carbene
Ligands at Group 10 metal centres:
Synthesis, Structure, Reaction Chemistry and
Catalysis**

by

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Submitted in fulfilment of the requirements of Degree of

Doctor of Philosophy

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Abstract

This thesis describes the synthesis of NHC ligands bound to the C₄ or C₅ atom of imidazolium ring at Pt and Ni metal centres and the study of their reaction chemistry and catalytic behaviour.

In order to prevent deprotonation of the C₂-position novel C₂-blocked imidazolium salts have been synthesised and their behaviour towards C_{4,5}-H oxidative addition to Pt⁰ complexes was investigated. New Pt and Ni hydride complexes bearing NHC ligands coordinated at the C₄- or C₅-position were isolated and characterised. This work demonstrates that blocking the C₂-position of imidazolium salts with alkyl groups does not necessarily prevent such salts interacting with low valent metals, which has implications for catalysis in imidazolium-based ionic liquid solvents. It was also shown that in the presence of alkene, oxidative addition products such as PtHBr(IMes)(1,2-dimethyl-3-propyl-imidazolin-5-ylidene) are susceptible to reductive elimination reactions to give back Pt(IMes)(alkene)₂ complexes and C₂-blocked imidazolium salts.

Novel C₂-blocked picolyl-functionalised imidazolium salts 1,2-dimethyl-3-(2-picolyl)imidazolium tetrafluoroborate and 1,3-di(2-picolyl)-2-methylimidazolium iodide were synthesised. Oxidative addition reaction of these salts to Pt⁰ afforded Pt(H)(IMes)(1,2-dimethyl-3-(2-picolyl)-2-methylimidazolin-5-ylidene) tetrafluoroborate and Pt(H)(IMes)(1,3-di(2-picolyl)-2-methylimidazolin-5-ylidene) iodide, respectively, with C₄-bound abnormal carbene with chelated pyridyl groups isolated exclusively. The picolyl functionalised abnormal NHC Pt-H complexes are not prone to reductive elimination reactions of either the normal or abnormal carbene in presence of alkenes.

Picolyl and aminoethyl functionalised blocked and unblocked imidazolium salts were employed in the hydrosilylation of styrene with triethylsilane by *in situ* generated Pt⁰-catalyst, giving different product selectivity. When using the C₂-blocked imidazolium salt the major product was found to be the dehydrogenative product

triethyl-styryl-silane, while using the C₂-H imidazolium salt the major product was the *anti*-Markovnikov triethyl-(1-phenyl-ethyl)-silane.

Several ultimately unsuccessful strategies to isolate a C₄ free carbene are described. C₂-Blocked 1,3-dimesityl-2-methylimidazolium chloride was synthesised but deprotonation of the C₄-H position failed, with the C₂-Me group deprotonated instead. It seemed necessary designing an imidazolium salt immune to deprotonation at the C₂-position and it is also possible that blocking the C₅ position with a σ -donating alkyl bulky group will protect or stabilise the desired carbenic center.

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Abbreviations used in this thesis

COD	1,5-cyclooctadiene
Cy	cyclohexyl
dba	dibenzylideneacetone
DCM	dichloromethane
DMFU	dimethylfumarate
DMSO	dimethylsulfoxide
Et ₂ O	diethyl ether
GC	gas chromatography
IMes	1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
ⁱ Pr	<i>iso</i> -propyl
M	metal
Me	methyl
MeCN	acetonitrile
Mes	mesityl, 2,4,6-trimethylphenyl
nbe	norbornene
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance
OAc	acetate anion
<i>o</i> -tolyl	<i>ortho</i> -tolyl group
Ph	phenyl
R	alkyl or aryl group
r.t.	room temperature
^t Bu	<i>tertiary</i> -butyl
THF	tetrahydrofuran
TOF	turn over frequency
TMS	trimethylsilane
X	halogen

Table of Contents

Chapter 1. Introduction	1
1.1 Methods for the synthesis of free NHCs	4
1.2 NHC as ligands	5
1.3 Preparation of NHC complexes	7
1.3.1 Deprotonation of an azolium salt by basic ligands on a metal	8
1.3.2 Complexation of preformed free NHCs	9
1.3.3 Oxidative addition of imidazolium salts to low valent metal centres	10
1.3.4 Transmetallation from other metal-NHC complexes	12
1.4 “Abnormal” carbene complexes	13
1.5 Carbene complexes as a catalysts	16
1.6 Aims and thesis Overview	18
1.7 References	19
Chapter 2. C_{4,5}-H oxidative addition of imidazolium salts to Pt⁰ and Ni⁰ complexes	23
2.1. Results and discussion	26
2.1.1 Synthesis of blocked imidazolium salts	26
2.1.2 Syntheses of abnormal Pt-hydride complexes with C _{2,4} blocked Imidazolium Salts	28
2.1.3 Syntheses of abnormal Pt-hydride complexes with C ₂ blocked Imidazolium Salts	30
2.2 Non-Innocent Nature of Imidazolium-Based Ionic Liquids (IL’s)	33
2.3 Reductive Elimination Reactions of C₂-blocked Imidazolium Salt	34
2.4 C_{4,5}-H oxidative addition of Imidazolium Salts to Ni⁰ complexes	38
2.4.1 Results and discussion	39
2.5 Experimental Section	41
2.5.1 Crystal structure solution	48
2.6 References	50

Chapter 3. C_{4,5}-H Oxidative addition of functionalised imidazolium salts to Pt⁰ complexes	52
3.1 Results and discussion	55
3.1.1 Syntheses of C ₂ -blocked picolyl functionalised imidazolium salt	55
3.1.2 Syntheses of abnormal Pt-H complexes from picolyl functionalised imidazolium salts	58
3.2 Experimental section	65
3.3.1 Crystal structure solution	71
3.3 References	74
Chapter 4. Hydrosilylation of styrene catalysed by in situ Pt(0)/Imidazolium salts systems	76
4.1 Results and discussion	79
4.1.2 Imidazolium salts as ligands in the hydrosilylation of styrene with triethylsilane	81
4.3 Experimental Section	85
4.4 References	87
Chapter 5. Attempts to isolate a free ‘abnormal’ carbene	91
5.1 Results and discussion	93
5.2 Experimental Section	95
5.3 References	97
Appendix 1. Publications from this Thesis	98
Appendix 2. Tables of Bond Distances and Angles	99

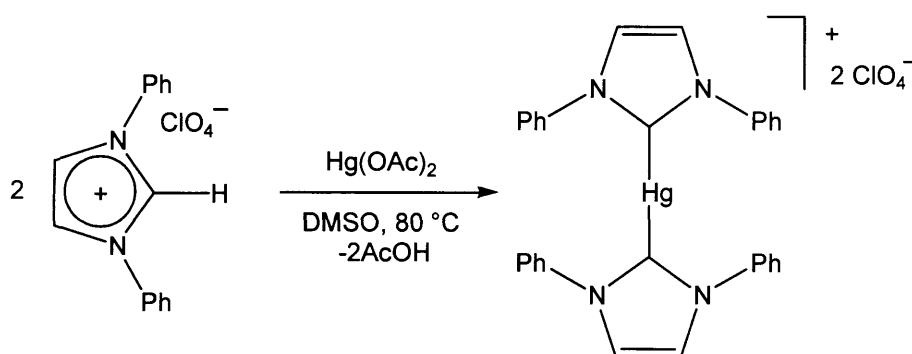
Chapter one. Introduction

Chapter one

INTRODUCTION

Carbenes are neutral compounds featuring a divalent carbon atom (hereafter referred to as the carbenic carbon) with only six electrons in its valence shell. The carbene carbon is linked to two adjacent groups by single covalent bonds, and it possesses two nonbonding electrons.^[1] Carbenes were initially considered to be prototypical reactive intermediates. Carbenes derived from the imidazole system were first studied in the 1960s by Wanzlick *et al.* who demonstrated their existence by trapping experiments but never isolated them (Scheme 1).^[2]

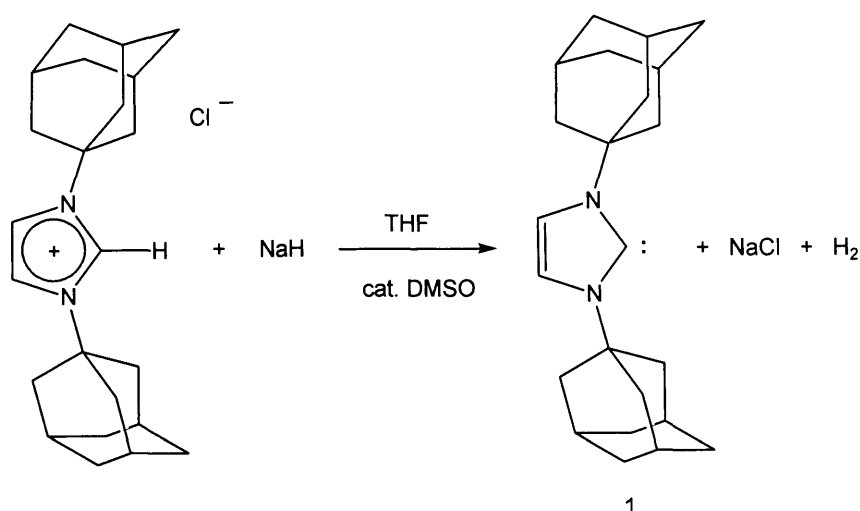
Scheme 1. Preparation of the first transition metal complex of NHCs by Wanzlick.^[2]



It was not until 1991 that Arduengo and co-workers reported the isolation of 1,3-bis(1-admantyl)imidazolin-2-ylidene, the first stable nucleophilic heterocyclic carbene (NHC), by deprotonation of the corresponding imidazolium salt precursor with NaH under anhydrous, oxygen free conditions (Scheme 2).^[3] This isolation of a stable NHC, led to the preparation of metal-NHC complexes by direct reaction of metal precursor with the free carbene.^[4] The success of such direct metal-carbene complexation resulted in an enormous revival in efforts to prepare free carbenes and their complexes. The use of carbenes as ligands has now become widespread.^[5]

Chapter one. Introduction

Scheme 2. The first stable N-heterocyclic carbene (NHC).^[3]

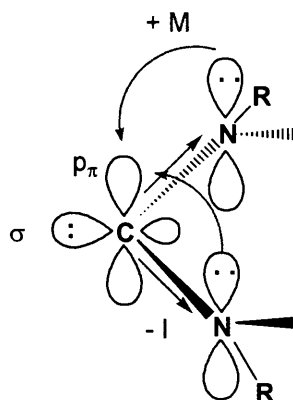


Initially, the stability of 1,3-bis(1-adamantyl)imidazolin-2-ylidene was attributed to a combination of both shielding, due to the bulky adamantyl groups, and the electronic interactions from the electron-rich :N-C=C-N: π -system.^[6] Subsequently, the isolation of a sterically unencumbered carbene, 1,3-bis(1-methyl)imidazolin-2-ylidene carbene, showed that while steric protection of the carbene centre certainly contributed to the observed stability, the electronic character of the N-C-N moiety is crucial.^[6] Two electronic effects deserve consideration, both of which contribute to the carbene stability. Firstly, the electron deficiency of the carbene carbon is reduced by π -electron donation from the two nitrogen lone pairs (the mesomeric effect); and secondly, the electron density of the carbene lone pair is distributed over the neighbouring atoms by the σ -electron attraction of the two adjacent electronegative nitrogen atoms (the inductive effect) (Figure 1).^[1, 7]

In diaminocarbenes (*eg.* NHCs) the increased occupancy of the carbon p_{π} -orbital, resulting from the mesomeric effect, raises its energy level so that the carbon atom's two non-bonding electrons adopt a singlet configuration of paired spins rather than the more reactive triplet arrangement of parallel spins.^[8] Thus, the electronic configuration is critical to the observed stability of NHCs compared to other carbenes and these species exhibit the properties of singlet carbenes.

Chapter one. Introduction

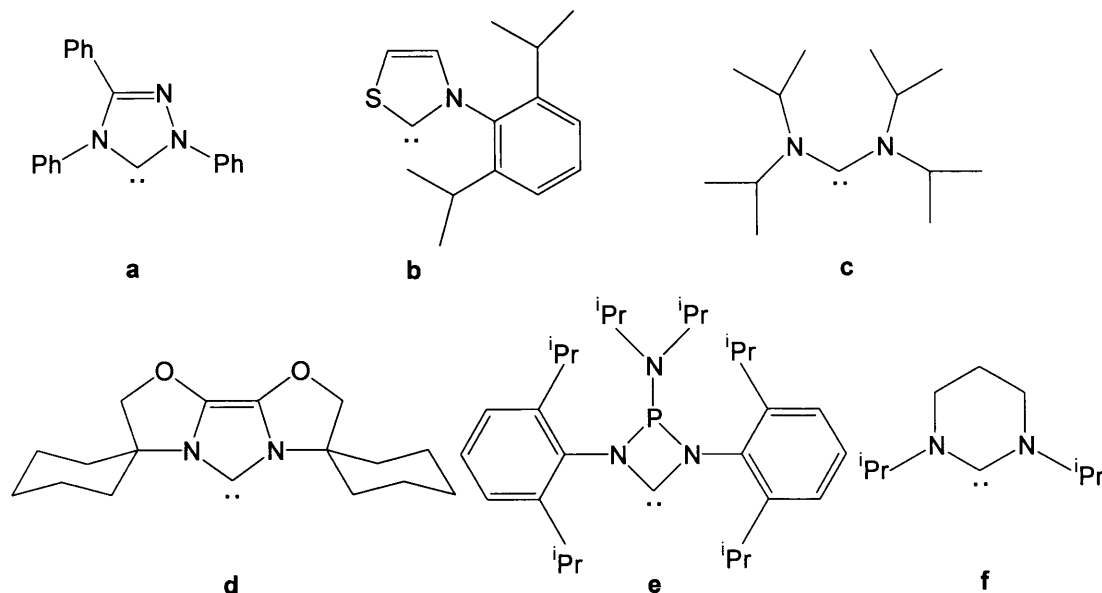
Figure 1. The stabilisation of a free diaminocarbene through mesomeric (+ M) and inductive effects (- I).



Since Arduengo's initial report, many different free carbenes have been isolated with extensive variation to the substituents on the two nitrogen atoms and the other backbone carbon atoms on the imidazolium ring. The availability of isolable NHCs has expanded to the triazolin-2-ylidene^[9] (Figure 2a) and thiazolin-2-ylidene^[10] (Figure 2b) ring systems, acyclic^[11] (Figure 2c), and more recently to other heterocyclic compounds, including large rings and polycyclic fused systems^[12, 13] (Figure 2d). Cyclic diaminocarbenes derived from four- (Figure 2e) and six-membered (Figure 2f) rings are also known.^[14]

Chapter one. Introduction

Figure 2. Representative N-heterocyclic carbene (NHC) ligands.



Although in these examples the substituents on the nitrogen atoms are identical, giving symmetrical NHC ligands, unsymmetrical counterparts are also accessible.^[15, 16]

1.1 Methods for the synthesis of free NHCs

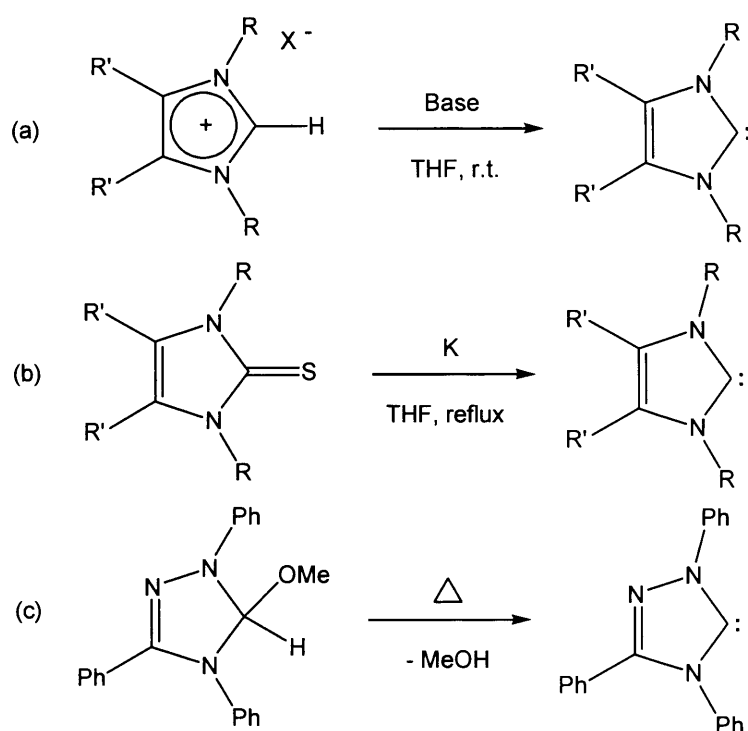
The most common method of generating free NHCs is, as described by Arduengo, via deprotonation of the C₂ position of the precursor azolium salts with a base. Strong bases such as NaH and KO^tBu in THF reaction mixture at room temperature have been used to deprotonate N-alkyl or N-aryl substituted azolium salts. Amides such as Li(NⁱPr₂), LDA or K[N(SiMe₃)₂] have also proven useful to deprotonate some base-sensitive functionalised imidazolium salts with acidic protons (Scheme 3a).^[11, 17]

Another route to generate free NHCs is the reductive desulfurisation of imidazolin-2-thiones with potassium in boiling THF (Scheme 3b).^[18] Thermally stable alkyl-substituted NHCs have been prepared using this method, but it is necessarily limited to thermally stable NHCs.^[19]

Chapter one. Introduction

The thermal elimination of stable small molecules such as methanol or chloroform from 2-substituted imidazolidines,^[20] benzimidazolines^[21] and 1,2,4-triazolines^[9] (Scheme 3c) yields the corresponding NHCs, although the disadvantage of this method is that it is limited to thermally stable NHCs for which an appropriate precursor can be accessed.

Scheme 3. Methods for the preparation of free NHCs.



1.2 NHC as ligands

Carbenes as ligands in metal complexes were known long before free carbenes were isolated,^[22] with the first carbene complex isolated by Fischer in 1964.^[23] Two alternative types of coordinated carbene can be distinguished, the Fischer and the Schrock carbenes (Figure 3). Each represents a different formulation of the bonding of the CR₂ group to the metal. Fischer carbenes have one stabilising heteroatom containing moiety (usually OR

Chapter one. Introduction

or NR_2) attached to the carbene carbon and bind to electronegative metals, most commonly middle to late d -block metals. The carbene ligand in these complexes is usually electrophilic, with the π -electron density concentrated on the metal. Schrock carbenes lack the heteroatom substituent and usually coordinate to a metal of lower electronegativity, generally metals on the left of the d -block. The bonding in these complexes can be described as a covalent double bond between a triplet carbene and a triplet metal fragment. The carbene ligand is considered to be nucleophilic as a result of the greater π -electron density on the carbene.^[24]

In contrast to the double bonds in Fischer and Schrock carbene complexes NHCs involve only a single M-C bond. Crystal structure data confirm that the M-C bond lengths in M(NHC) complexes are very similar to those of standard M-C_{alkyl} single bonds. Computational studies and photoelectron spectroscopy reported for M(NHC)₂ complexes (M = Pd, Pt) revealed that the metal-NHC bond occurs predominantly through σ donation into the metal hybrid ($d_z^2 + s$) orbital from the carbene lone pair.^[25] The fact that heterocyclic carbenes form stable complexes with beryllium and lithium, which have no available electrons to back donate to the carbene, also support this view.^[26] However, the shorter than expected M-C bonds lengths observed in homoleptic Ni⁰ and Pt⁰ (Figure 4) (R = Mes) were attributed to $d_\pi \rightarrow p_\pi$ electron donation from the metal to the NHC ligands.^[27] In a recent work Green and co-workers calculated that the π -donation, for Pt⁰ and Pd⁰ (R = H, Me, Bu^t), contributes 25-30% of the orbital interaction^[28] (Figure 4).

Chapter one. Introduction

Figure 3. Bonding interactions in carbene-metal complexes.

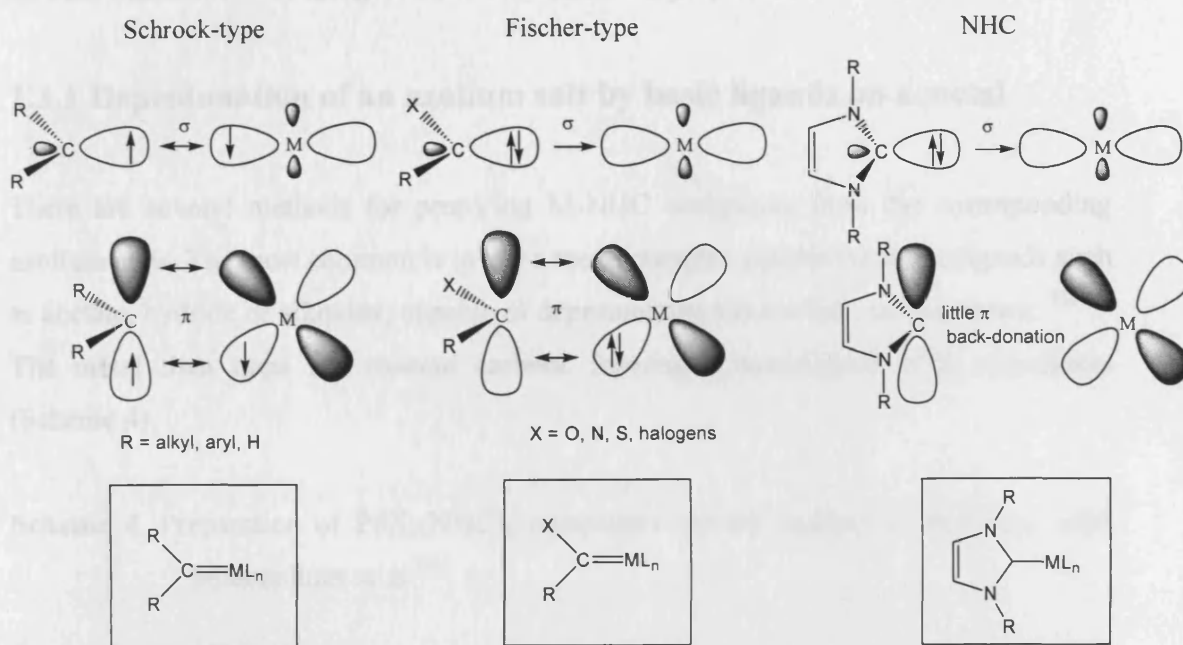
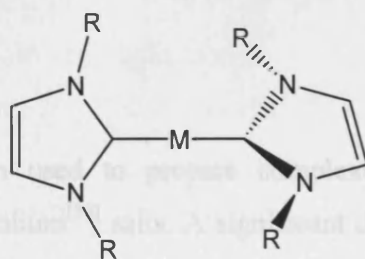


Figure 4. Group 10 $M^0(\text{NHC})_2$ complex.



$M = \text{Ni, Pd, Pt}$

$R = \text{Mes, H, Me, } ^t\text{Bu}$

1.3 Preparation of NHC complexes

Transition-metal complexes containing NHCs have received increased attention, due to their favourable application in homogeneous catalysis. A number of routes for their

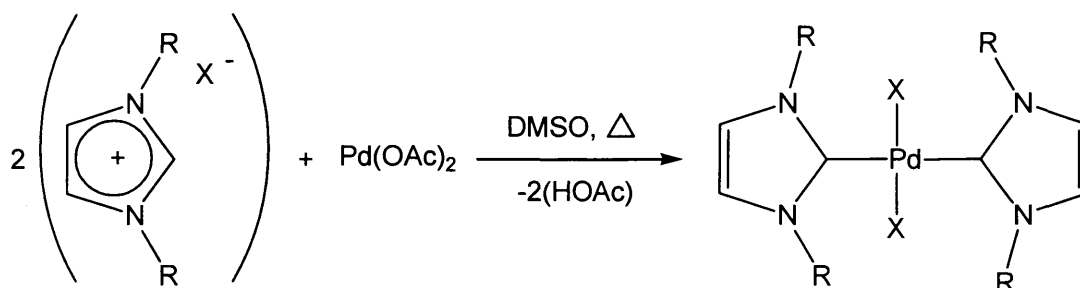
Chapter one. Introduction

synthesis have been developed, and allowing the preparation of complexes bearing carbene ligands with a variety of electronic and steric properties.^[29]

1.3.1 Deprotonation of an azolium salt by basic ligands on a metal

There are several methods for preparing M-NHC complexes from the corresponding azolium salts. The most common is to use a metal complex containing basic ligands such as acetate, hydride or alkoxide, capable of deprotonating the azolium salt precursor.^[30-33] The metal then traps the nascent carbene forming a coordinated NHC complexes (Scheme 4).

Scheme 4. Preparation of $\text{PdX}_2(\text{NHC})_2$ complexes *via* the reaction of $\text{Pd}(\text{OAc})_2$ with imidazolium salts.^[30]

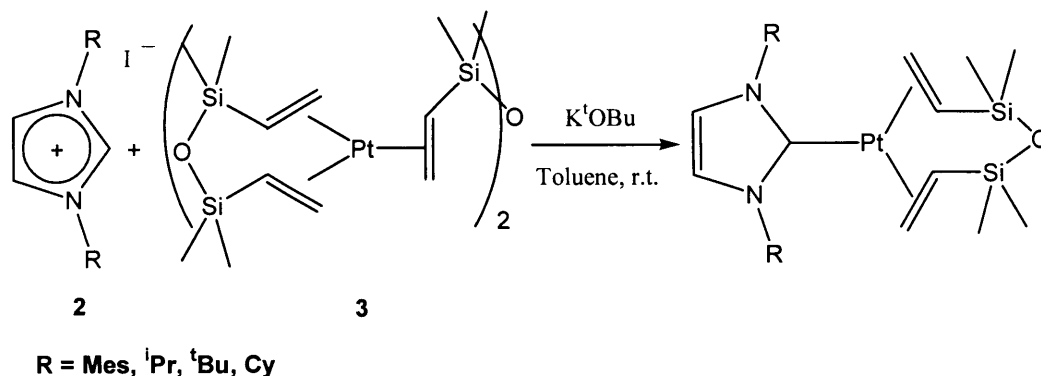


This method has also been used to prepare complexes from benzimidazolium,^[34] triazolium^[35] and benzothiazolium^[36] salts. A significant disadvantage of this method is the limited availability of a suitable metal precursor.

Another method consists of the addition of external base for the in situ deprotonation of the azolium salt in the presence of the metal precursor. The in situ complexation of the ligand has the advantage of not having to handle the potentially unstable free carbene. For example, the use of potassium *tert*-butoxide with imidazolium iodide (**2**) and one equivalent of $\text{Pt}_2[(\eta^2\text{-ViSiMe}_2)_2\text{O}]_3$ (**3**) (Karstedt's catalyst) forms a $\text{Pt}(\text{NHC})(\text{divinyl-tetramethylsiloxane})$ complex (Scheme 5).^[37]

Chapter one. Introduction

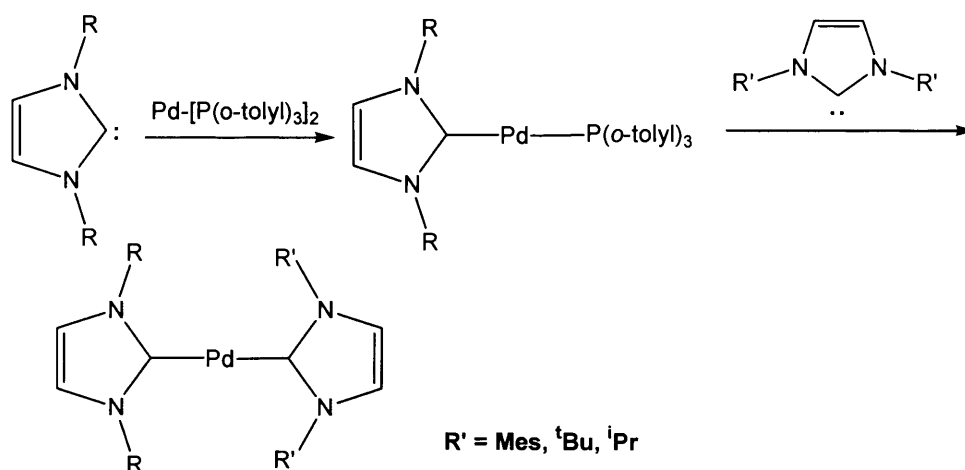
Scheme 5. Preparation of (NHC)Pt(dvtms).^[37]



1.3.2 Complexation of preformed free NHCs

Since the isolation of the stable free NHCs by Arduengo and co-workers, the direct application of these compounds has attracted much attention for the synthesis of metal complexes,^[3, 6, 7] as it was possible to synthesise carbene complexes by the simple addition of the carbene to an appropriate metal precursor.^[38] The strong σ -donor nature of NHC's greatly facilitates displacements of other ligands on the metal centre such as phosphines,^[39-42] carbon monoxide,^[33, 38, 43, 44] solvents^[40, 45] or olefins.^[41, 42, 46, 47] For example in bis(*o*-tolylphosphine)Pd⁰ both phosphine ligands can be replaced by free NHC to form the corresponding Pd⁰(NHC)₂ (Scheme 6).^[42]

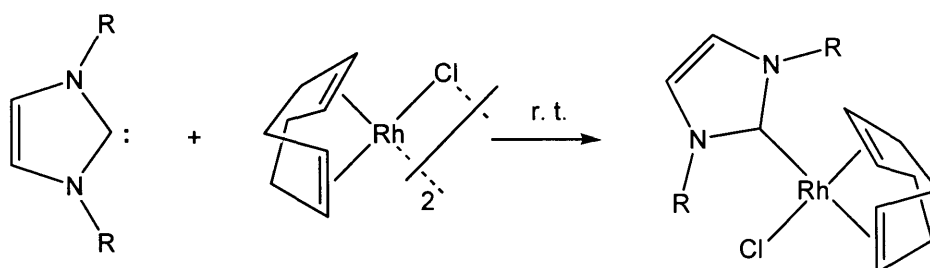
Scheme 6. Preparation of Pd⁰(NHC)₂ complex by phosphine exchange.^[42]



Chapter one. Introduction

NHCs can also cleave dimeric complexes with bridging ligands such as halides, carbon monoxide or acetonitrile.^[7, 48, 49] Examples of this type of complex formation are the reaction of $[(\eta^2, \eta^2\text{-cod})M(\mu\text{-Cl})_2]$ ($M = \text{Rh}, \text{Ir}$) with free NHCs (Scheme 7).^[15, 48, 50]

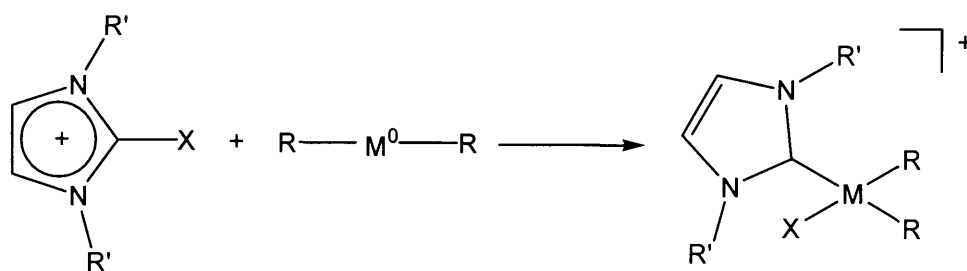
Scheme 7. Cleavage of dimeric complexes by imidazolin-2-ylidenes.^[15]



1.3.3 Oxidative addition of imidazolium salts to low valent metal centres

The acidity of the C_2 proton has been utilised in synthesising carbene complexes from C-H activation of the azolium salts by low-valent metal precursors. While generally restricted to Ni, Pd, Pt, Rh and Ir, these metals are commonly used metals in catalysis and oxidative addition reactions of azolium salts thus provide an easily accessible route to catalytically active carbene complexes (Scheme 8).^[47, 51-54]

Scheme 8. Oxidative addition of imidazolium cations to M^0 complexes.



$\text{X} = \text{H}, \text{halogen}, \text{CH}_3$

$\text{M} = \text{Pt}, \text{Pd}, \text{Ni}, \text{Rh}, \text{Ir}$

$\text{R} = \text{NHC}, \text{PR}''$

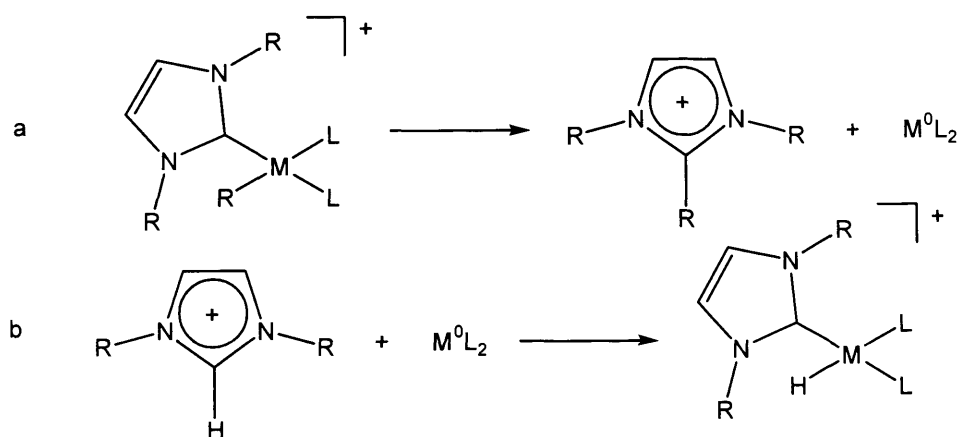
Chapter one. Introduction

Density functional studies have shown that when the imidazolium cation is substituted in the C-2 position by a halogen, hydrogen or a methyl group, the formation of the corresponding carbene M^{II} -halogeno, -hydrido or -hydrocarbyl complex could occur *via* an exothermic process.^[51] The addition of 2-haloimidazoliums is easier and more exothermic than the addition of 2-H imidazoliums and 2-alkylimidazoliums. Oxidative addition is strongly favoured by basic ligands like NHC or PR_3 on the metal, as well as *cis*-chelating ligands, because of the increasing exothermicity of the reaction and the lowering of the activation barrier.^[51]

Despite favouring oxidative addition, the reverse reaction, reductive elimination, is also possible with NHC carbene complexes. A combined kinetic and density functionality study has confirmed that hydrocarbyl-M-carbene complexes (M = group 10 metal) undergo reductive elimination to give M^0 and C_2 -substituted imidazolium salts (Scheme 9a).^[54, 55] Although this elimination reaction presents a potentially serious drawback in the application of complexes of heterocyclic carbenes in catalysis reactions involving hydrocarbon substrates, the likelihood of such a reaction occurring can be reduced. A potentially important method to limit decomposition of M-carbene complexes is to force the reaction in the reverse direction by operating in a large excess of imidazolium cation. Then any M^0 complex that forms as a consequence of reductive elimination may re-form the M-carbene complex through oxidative addition of the imidazolium cation (Scheme 9b).^[56] Furthermore, these results show that the imidazolium cation, which is usually considered an unreactive solvent when used as an ionic liquid, can react with low valent metals to give carbene complexes without the need for added base (Scheme 9b). Oxidative addition reactions are extensively reviewed in the next chapter.

Chapter one. Introduction

Scheme 9. Redox processes undergone by the carbene/imidazolium couple.^[52, 56]

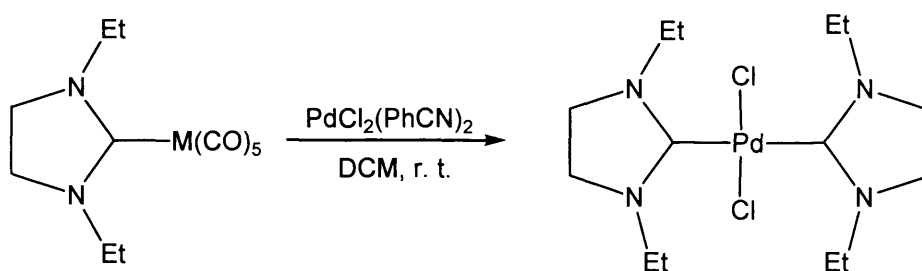


R = alkyl, aryl; M = Ni or Pd

1.3.4 Transmetalation from other metal-NHC complexes

In certain cases, NHC ligands can be transferred intermolecularly from one metal complex to another. Chromium,^[31] molybdenum and tungsten^[57] pentacarbonyl complexes could be used for NHC transfer to a variety of metals including to Pd(II), Pt(II), Rh(I), Cu(I) and Au(I) (Scheme 10).^[12, 58]

Scheme 10. Transmetalation of NHC ligands from group 6 complexes to Pd(II).^[31, 57]



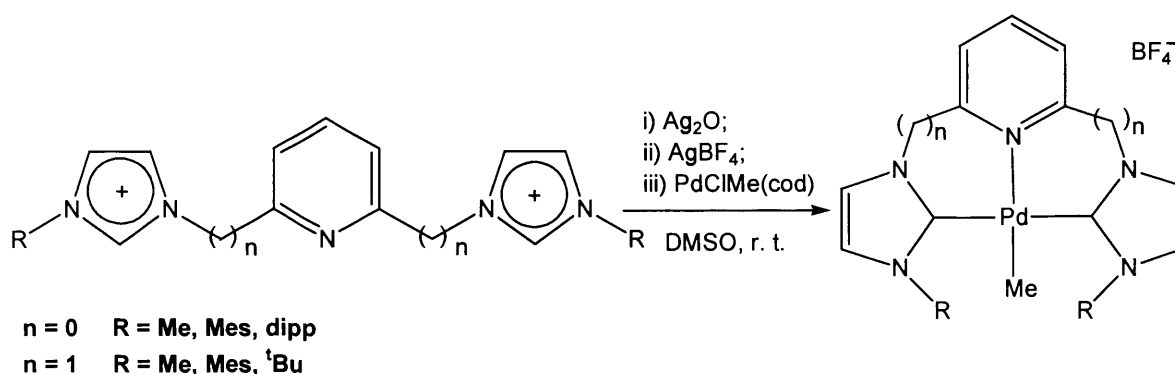
M = Mo, Cr, W

$\text{Ag}^{\text{I}}(\text{NHC})$ complexes have proven to be useful transmetalation reagents for NHC ligands bearing base-sensitive functional groups or activated α -hydrogens,^[59] including pyridine-

Chapter one. Introduction

functionalised *bis*-NHC ligands (Scheme 11).^[60, 61] Transmetalation from $\text{Ag}^{\text{I}}(\text{NHC})$ complexes is an especially useful method of accessing Pd(II)-hydrocarbyl complexes. Formation of a silver carbene using Ag_2O ^[62] can be performed prior to transmetalation or can be formed in situ.

Scheme 11. Preparation of Pd(II) NHC complexes by silver transmetalation.^[61]

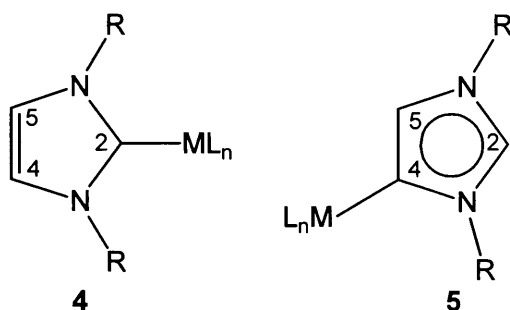


1.4 “Abnormal” carbene complexes

It has recently been discovered that the C_4 and C_5 -H bonds of the imidazolium ring are also susceptible to metallation *via* C-H activation (Figure 5).^[63, 64] C_5 -bound NHCs could potentially offer a useful variant in electronic and steric properties compared to the usual C_2 form. The presence of an easily functionalized nitrogen atom distal to the metal centre also offers new possibilities for the design of multidentate or polymer-bound NHC ligands.

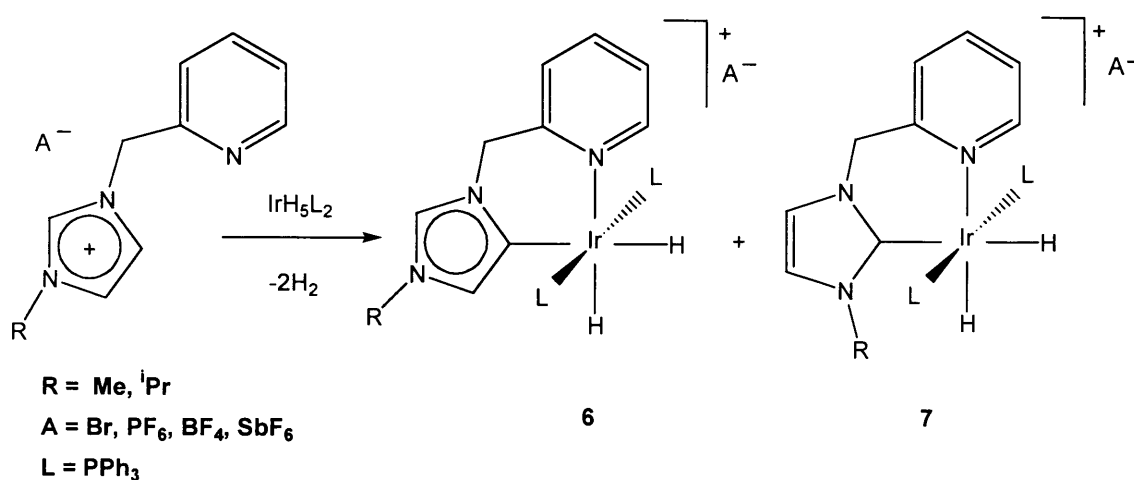
Chapter one. Introduction

Figure 5. Normal (4) and abnormal (5) metal complexes.



Crabtree *et al.* first reported cationic iridium complexes containing bidentate pyridine-functionalized carbene ligands that bind to the metal centre via the C₅ position and pyridyl nitrogen (Scheme 12).^[63] Abnormal NHC complex (6) is favoured by reduced steric strain at the metal center. More recent work demonstrates that binding at C₅ for this system is dependent on the nature of the counter ion.^[65] With anions such as bromide, capable of strong Ion Pairing by C-H \cdots Br hydrogen bonding at C₂, the normal C₂-M binding is obtained. Varying the counter ion A⁻ along the series Br, PF₆, SbF₆, BF₄ progressively switches the kinetic product from the C₂ to the C₅-binding species. Table 1 summarizes the results of NHC binding studies when the anion is varied.^[65, 66]

Scheme 12. First abnormal C₅-NHC.^[63]



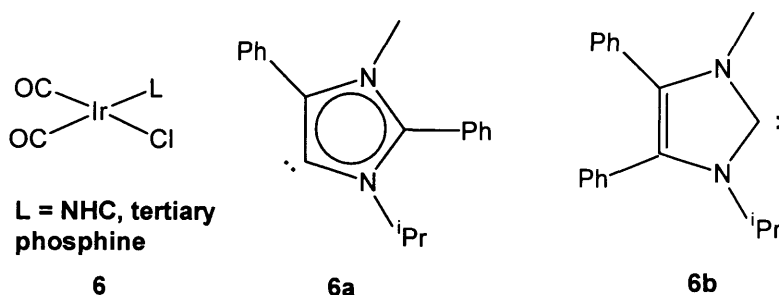
Chapter one. Introduction

Table 1. Ratio (%) of abnormal to normal binding of NHC ligands for various alkyl groups, R and anions A.^[65]

R	A	Abnormal binding at C ₅ centre (6) (% yield)	Normal binding at C ₂ centre (7) (% yield)
Me	Br	9	91
ⁱ Pr	Br	16	84
Me	PF ₆	50	50
Me	BF ₄	55	45
Me	SbF ₆	89	11
ⁱ Pr	BF ₄	100	-

To investigate the nature of abnormal ligand binding Crabtree *et al.* synthesised a series of related normal and abnormal carbene-Ir complexes containing CO ligands (Figure 6). The carbonyl stretching frequencies of IrCl(CO)₂L (L = NHC or phosphine) are recognized as an excellent measure of the σ -donor and π -acceptor properties of the ligand L. The average value of the carbonyl stretching frequencies for complexes **6a** ($\nu_{av}(\text{CO}) = 2003 \text{ cm}^{-1}$) indicates that the donor power of the abnormal carbene is higher than that of electron-rich phosphines (PCy₃: $\nu_{av}(\text{CO}) = 2028 \text{ cm}^{-1}$)^[67] and NHC ligands (**6b**) ($\nu_{av}(\text{CO}) = 2017 \text{ cm}^{-1}$).^[67]

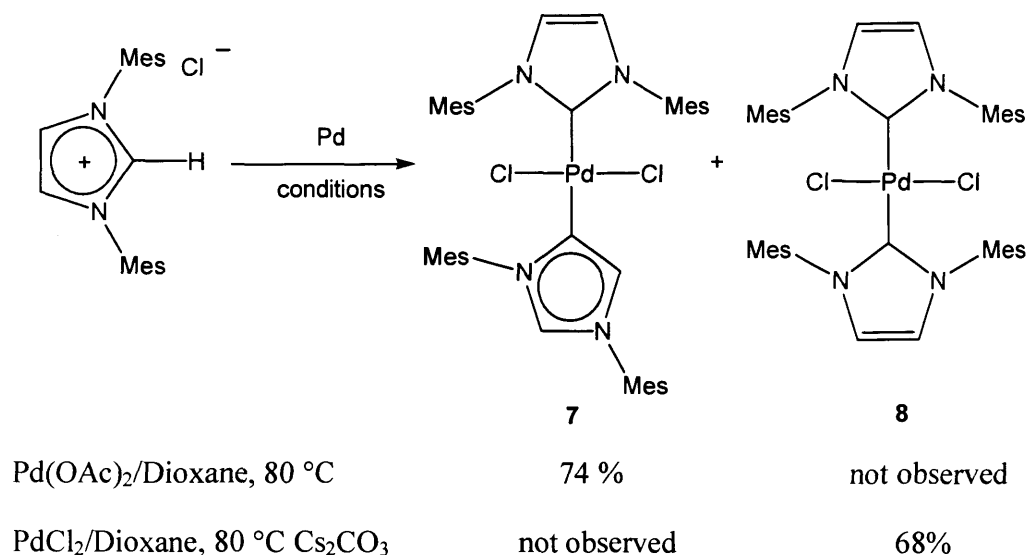
Figure 6. Carbenes used in IR study of ligand donor power.^[67]



Chapter one. Introduction

Nolan *et al.* also reported the synthesis of palladium complexes bearing NHC ligands in normal and abnormal binding modes (**7**). Complex **7** was synthesised from imidazolium salts and Pd(OAc)₂ using a typical preparation for NHC complexes (Scheme 13).^[64] Metal binding at the C₂ position (**2**) was not initially observed, but by adjusting the reaction conditions **8** (using PdCl₂ as a precursor in presence of Cs₂CO₃) could be obtained exclusively. The binding mode of the NHC to Pd was shown to affect the catalytic behaviour of the palladium complexes. Complex **7** was an active catalyst for Suzuki-Miyaura and Heck reactions while complex **8** was inactive for both coupling reactions.^[64]

Scheme 13. Formation of Pd complexes bearing NHC ligands in normal and abnormal binding modes.^[64]



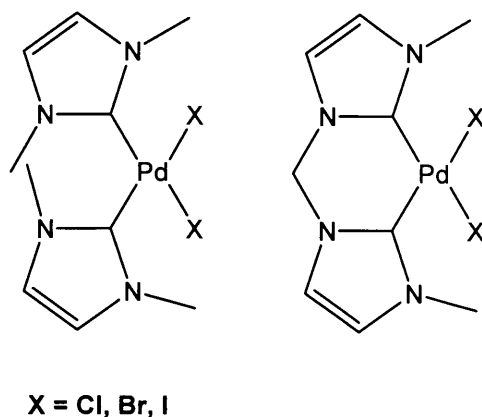
1.5 Carbene complexes as a catalysts

Lappert *et al.* provided early examples of the application of transition metal-carbene complexes in catalysis.^[68,69] However, the need to generate the free carbene ligand *in situ* via electron rich tetra-amino alkenes limited the application of NHCs as ligands and

Chapter one. Introduction

impeded further development.^[69] From 1995, Herrmann *et al.* investigated the use of NHCs as spectator ligands in a range of catalytic processes,^[70] initially reporting that Pd-NHC complexes were active in the Heck coupling reaction (Figure 7). This study revealed several advantages of NHCs as stabilising ligands over the commonly employed phosphines. The major advantage is undoubtedly the NHC stability resulting from the exceptionally stable M-C bond.^[7] Phosphines are known to undergo P-C bond cleavage leading to ligand degradation, while dissociation of the carbene ligand has been observed in very oxidative conditions.^[50] Recently Cloke *et al.* have shown that two coordinate palladium bis-carbene complexes will promote amination of aryl halides and demonstrated an unexpected lability of the palladium-carbene bond.^[71] Given that, as described in the previous section, a wide variety of routes are available to synthesise carbene complexes with different steric and electronic properties.

Figure 7. The first NHC-Pd complexes employed in catalysis.^[50]



Herrmann's work revived interest in the use of NHC-based catalysts in reactions as diverse as asymmetric hydrosilylation (Rh),^[43, 72, 73] furan synthesis (Ru),^[74] CO/ethylene copolymerisation (Pd),^[75] hydroformylation (Rh)^[76] and numerous Group 10 catalysed C-C and C-N coupling reactions.^[72] Particularly notable are the significant achievements obtained for the use of NHCs in a wide variety of the Group 10 metal mediated coupling reactions. Although the Heck^[77] and the Suzuki-Miyaura^[78] couplings are best known, the Sonogashira^[79] and Stille^[80] cross-coupling reactions also represent valuable synthetic

Chapter one. Introduction

tools for the synthesis of aryl-C bonds in organic synthesis, whereby chemoselective and regioselective C-C bonds can be formed. The Buchwald-Hartwig amination of aryl halides has become a powerful method of C-N bond formation.^[81] The hydrosilylation of alkenes enable the production of silicone polymers; this reaction will be more thoroughly reviewed in Chapter 4.^[82] The mechanism for each type of coupling is different but related, and all involve a M^0/M^{II} redox catalytic process in which an initial C-X oxidative addition step to a coordinatively unsaturated M^0 species occurs. The products are then released from the metal either by a reductive elimination process or a base assisted β -H elimination in the case of the Heck reaction.

1.6 Aims and thesis overview

The aim of this work has been to explore the generality of $C_{4,5}$ -H bond activation in blocked imidazolium salts in the presence of Group 10 M^0 complexes. Abnormal carbene ligands could potentially offer a useful variation in electronic and steric properties compared to the usual C_2 -coordinated examples.

Chapter 2 describes the synthesis via an oxidative addition process and characterisation of novel Pt-hydride complexes bearing NHC ligands in an abnormal binding mode. While two examples of abnormal complexes were known at the beginning of this project, these Pt-H species represent the first example of oxidative addition of an imidazolium salt at the $C_{4,5}$ positions of the ring. It was also demonstrated that under certain conditions, these “wrong-way” bound carbenes, in common with their “normal” counterparts, are susceptible to reductive elimination reactions to give back $M(0)$ and imidazolium salt.

Chapter 3 describes the synthesis and characterisation of new abnormal Pt-H complexes with picolyl functionalised imidazolium salts. These complexes have proven to be stable. Reductive elimination reactions of the normal or abnormal carbene and products resulting from alkene insertion into the Pt-H bond were not observed.

Chapter one. Introduction

In Chapter 4 functionalised-imidazolium salts were employed in the hydrosilylation of styrene with triethylsilane by an in situ generated Pt⁰-catalyst. The product selectivity could be varied by the use of imidazolium salts with or without C₂-substituents.

In Chapter five attempts to isolate a abnormal free carbene are described. Although unsuccessful, insights into designing an imidazolium salt immune to deprotonation at undesired sites are offered.

1.8 References

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Chapter one. Introduction

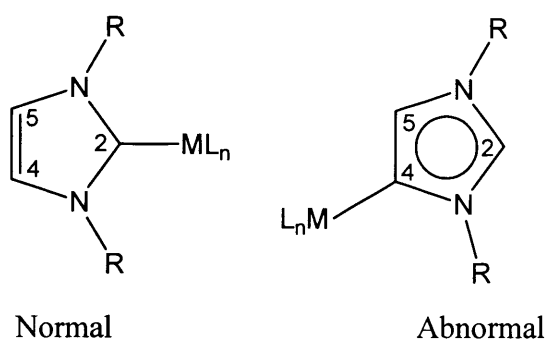
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Chapter two

C_{4,5}-H oxidative addition of imidazolium salts to Pt⁰ and Ni⁰ complexes

Typical transition metal NHC complexes show binding through C₂ due to the acidity of the C₂-proton in the precursor salt. The two adjacent nitrogens also strongly stabilise both the free carbene and the M-C bond as described in chapter 1.^[1-5] However, it has recently been found that the C_{4,5}-H bonds of imidazolium salts are also susceptible to metallation *via* C-H activation in the presence of a base (Figure 1).^[6-8]

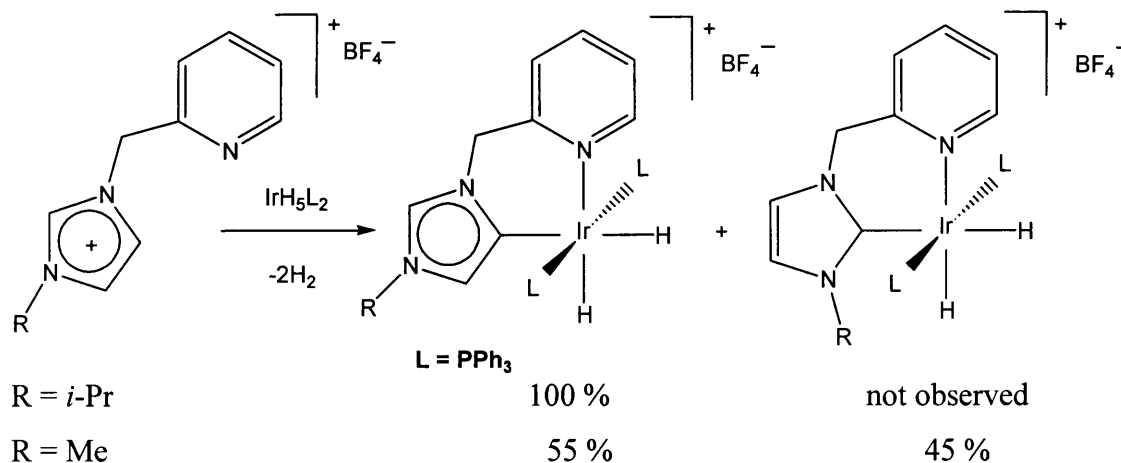
Figure 1. ‘Normal’ and ‘abnormal’ metal-NHC complexes.



R = alkyl, aryl, functional groups

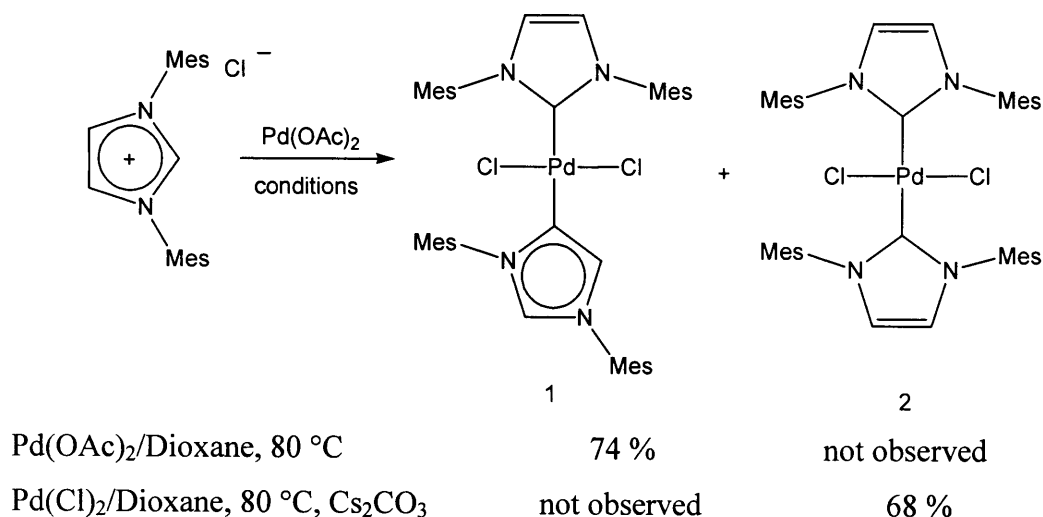
“Abnormal” C₄ metallation of the NHC ring was first reported by Crabtree *et al.* for pyridyl- and picolyl substituted-NHC dihydrides of iridium(III) (Scheme 1).^[6] Activation of the C₄-position was favoured because it results in a lower steric crowding at the metal centre. Large wingtip groups such as *i*-Pr lead to exclusive formation of the abnormal C₄ isomer, while the less sterically demanding Me group led to a mixture of C₂-H (45 %) and C₄-H (55 %) products.

Scheme 1. Synthesis of first abnormal C₅ NHC.



Nolan and co-workers also reported the structure and interesting catalytic reactivity of Pd^{II}Cl₂(NHC)₂ complexes containing “wrong-way” bound NHCs. Complexes were synthesised from imidazolium salts and Pd(OAc)₂ using a typical preparation for NHC complexes (Scheme 2).^[8] Metal binding at the C₂ position (**2**) was not initially observed, but by adjusting the reaction conditions **2** could be obtained exclusively. In both Crabtree’s and Nolan’s studies the C₄ bound carbene was generated by deprotonation reactions (as opposed to oxidative addition), using added base or basic ligands on the metal.

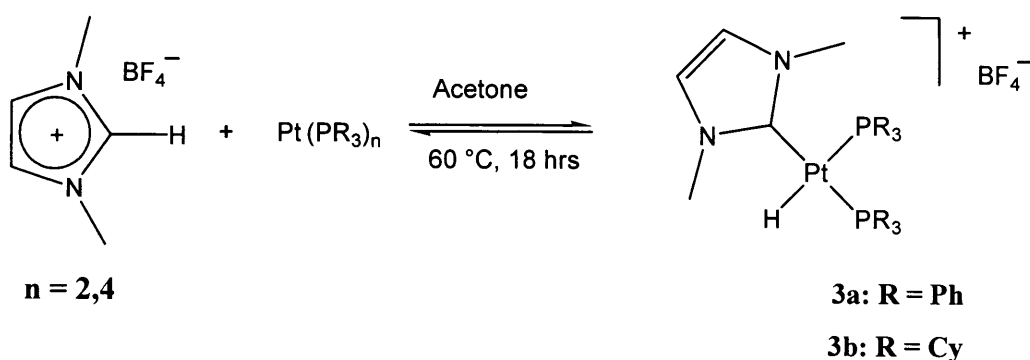
Scheme 2. Formation of Pd complexes bearing NHC ligands in normal and abnormal binding motifs.^[8]



It has been established experimentally, that imidazolium cations can oxidatively add to low valent group 10 metal centers. Theoretical studies confirm that this is a facile reaction with a low activation barrier.^[9] Activation of the C₂-H or C₂-halogen bond gives, respectively, (C₂-Carbene)Metal-(hydrido) or -halide complexes. ^[1, 3, 4, 9] This represents an atom-efficient route to the synthesis of metal-NHC complexes starting directly from an imidazolium salt. The presence of strong σ -donors spectator ligands on the metal also favours the oxidative addition by lowering the activation barrier and increasing the exothermicity of the reaction.^[1, 3, 4, 9]

In 2001, Cavell and co-workers reported the first example of an oxidative addition of a imidazolium C-H bond to a Pt⁰ complex that does not contain a chelating ligand, which was thought to be requisite of this reaction.^[9] Heating equimolar quantities of 1,3-dimethylimidazolium tetrafluoroborate and Pt(PPh₃)₄ in refluxing THF-acetone resulted in the formation of *ca.* 15% (by NMR) of [(NHC)Pt(H)(PPh₃)₂]⁺ (**3a**) (Scheme 3). By eliminating two phosphines from the coordination sphere of Pt, the equilibrium was driven towards formation of the oxidative addition product.^[1, 5, 9] It was concluded that the small amount of product in the former case resulted from an equilibrium between products and reactant. Thus using the unsaturated 14-electron complex Pt(PPh₃)₂ shifted the equilibrium in favour of oxidative addition and gave **3a** in 63% yield.

Scheme 3. Oxidative addition of imidazolium cations to M⁰ complexes.

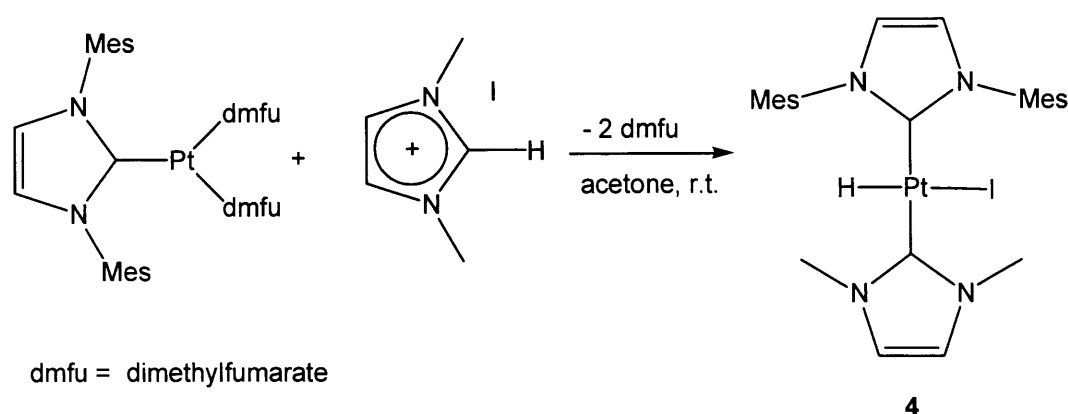


It also was found that C-H activation of the imidazolium cation can be affected under quite mild conditions (r. t.) by using an NHC ancillary ligand on Pt (Scheme 4).^[3] The strongly electron donating carbene increases the ability of the Pt complex to undergo oxidative addition. When an excess of 1,3-dimethylimidazolium iodide was added to

Chapter 2. C_{4,5}-H oxidative addition of imidazolium salts to Pt⁰ and Ni⁰ complexes

Pt(IMes)(η^2 -dimethylfumarate)₂ in acetone, the mono-NHC-Pt⁰ complex was rapidly and completely converted into the thermally stable hydridoplatinum(IMes)(IM) complex (**4**). Although, oxidative addition of imidazolium salts to Pd⁰ and Ni⁰ using ML₂, where L = NHC generated surprisingly stable mixed carbene M-hydride complexes.

Scheme 4. Oxidative addition of imidazolium salts to Pt⁰ complex.



2.1 Results and discussion

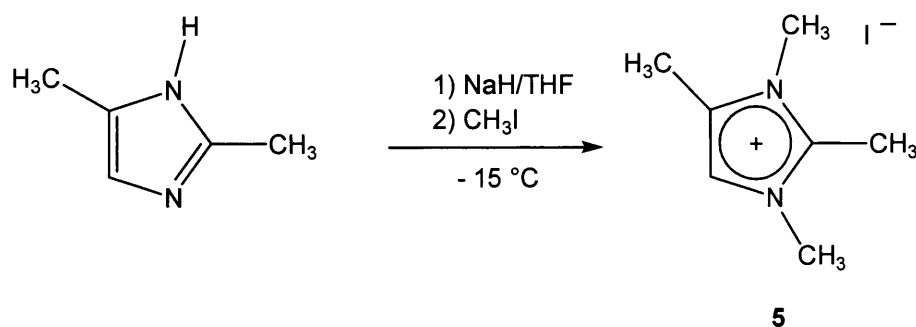
2.1.1 Synthesis of blocked imidazolium salts

It is interesting to observe if C₅-H oxidative addition activation of imidazolium salts would be possible. To promote C₅ activation over C₂ activation, the C₂ position was blocked with a Me group. New C₂-blocked imidazolium salts were synthesised and the behaviour of the imidazolium salts towards C_{4,5}-oxidative addition to Pt⁰ complexes was investigated. This work now demonstrates an elegant method for forming (C_{4,5}-carbene)M(hydrido) compounds, either *in situ* or as isolated complexes, by oxidative addition reactions.

An imidazolium salt with the C₂ position blocked by a methyl group was initially synthesised for oxidative addition studies with Pt⁰. Blocking C₂ prevents the formation of the normal carbene. 1,2,3,4-Tetramethylimidazolium iodide was chosen as a suitable target, and was prepared through the reaction of 2,4-dimethylimidazole with NaH and followed by N-alkylation with CH₃I (Scheme 5). Compound **5** was

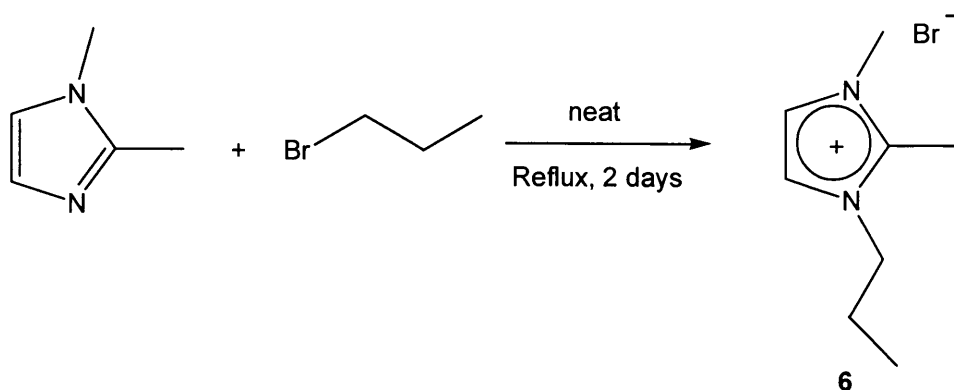
isolated as a colourless crystals in 75% yield and was characterised by ¹H and ¹³C NMR spectroscopy and by high resolution mass spectrometry. In the ¹H NMR spectrum of **5** the C₅-H proton appears as a singlet at 7.08 ppm and the C₂-CH₃ protons appear as a singlet at 2.67 ppm. The ¹³C NMR spectrum showed carbon signals for C₂ and C₅ at 143.5 and 118.5 ppm respectively.

Scheme 5. Synthesis of 1,2,3,4-tetramethylimidazolium iodide.



An unsymmetric C₂ blocked imidazolium salt was also desired for oxidative addition studies with Pt⁰, in particular to study the behaviour of eventual C_{4,5}-Pt isomers. 1,2-Dimethyl-3-propylimidazolium bromide was prepared by refluxing a mixture of 1,2-dimethylimidazole and a large excess of 1-bromopropane (Scheme 6), followed by concentration of the solution resulting in the precipitation of compound **6** as a crystalline solid in 94 % yield. Compound **6** was characterised by ¹H and ¹³C NMR spectroscopy, microanalysis and high resolution mass spectrometry. The ¹H NMR spectrum of **6** displayed two doublets at 7.71 and 7.57 ppm for C₄-H and C₅-H, respectively. The ¹³C NMR spectrum of **6** showed two carbon signals for C₄ and C₅ at 123.71 and 122.17 ppm respectively.

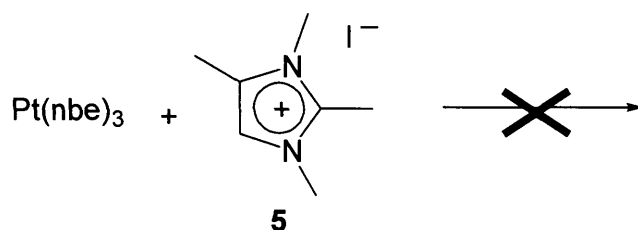
Scheme 6. Syntheses of 1,2-dimethyl-3-propylimidazolium bromide.



2.1.2 Syntheses of abnormal Pt-hydride complexes with C_{2,4} blocked Imidazolium Salts

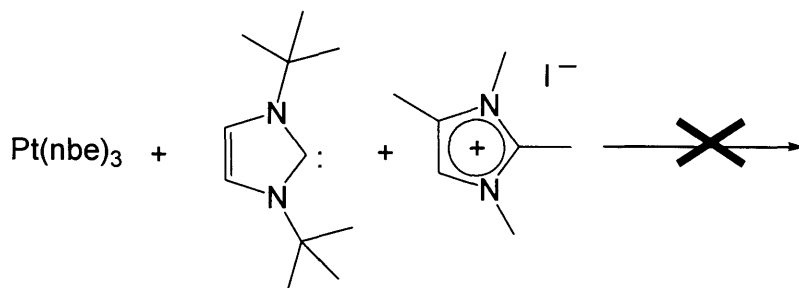
Starting from a Pt⁰ source bearing a easily displaceable ligand the oxidative addition of imidazolium salt **5** would be facilitated. Pt(nbe)₃^[10] (nbe = norbornene) was chosen as a precursor because it contains three labile alkene ligands. When two equivalents of 1,2,3,4-tetramethylimidazolium iodide (**5**) were added to Pt(nbe)₃ in acetone at room temperature no reaction was observed (Scheme 7).

Scheme 7. Attempted reaction of Pt(nbe)₃ with **5**.



To provide a more electron-rich platinum centre one equivalent of 1,3-di-*t*-butylimidazolin-2-ylidene was added but even in this case no reaction was observed (Scheme 8).

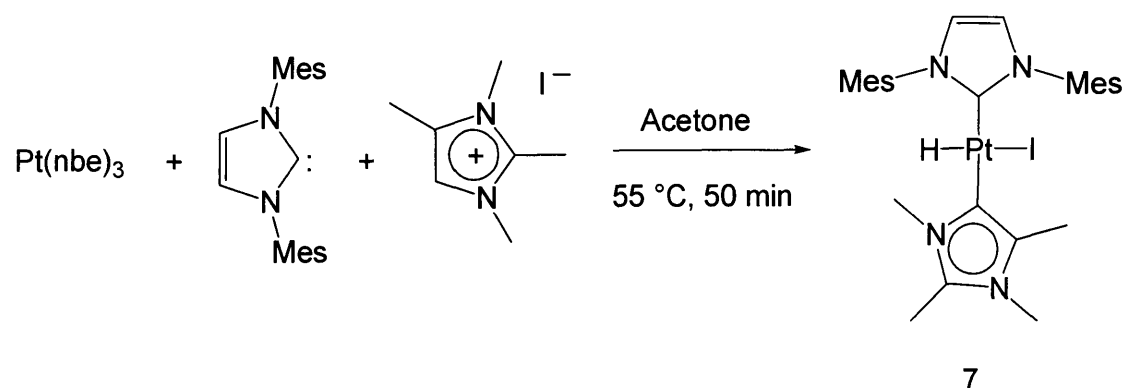
Scheme 8. Attempted reaction of Pt(nbe)₃, **5** and 1,3-di-*t*-butylimidazolin-2-ylidene.



The use of the strong σ -donor and sterically demanding 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes) carbene as spectator ligand resulted in the formation of the first abnormal PtHI(IMes)(ab-NHC) complex (**7**). Mixing Pt(nbe)₃ with IMes in the presence of 1.8 eq of **5** yields complex **7** (50%) (Scheme 9). Compound **7** was

isolated after washing the crude residue with hexane, to remove unreacted IMes, then extracted with THF to leave unreacted salt behind.

Scheme 9. Imidazolium C₅-H oxidative addition to Pt⁰.



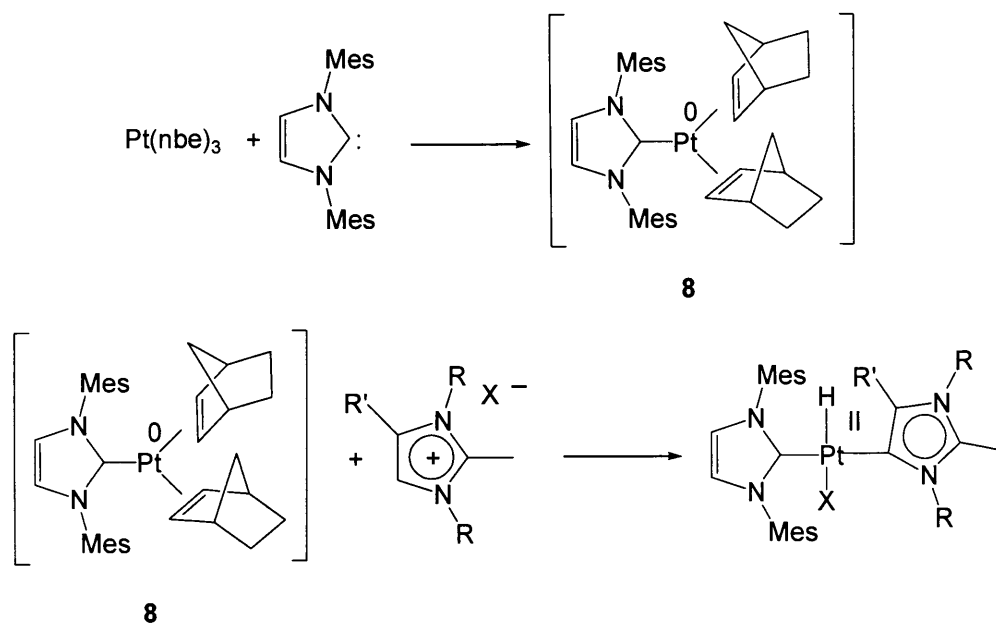
Complex **7** was characterised by ¹H and ¹³C{¹H} NMR spectroscopy. The ¹³C{¹H} NMR spectrum shows characteristic signals due to the IMes C₂ at 180.8 and the C₅ carbon of the abnormal carbene at 145.1 ppm. The presence of a metal-bound abnormal carbene is also indicated by the ¹³C{¹H} NMR spectrum where the C₅ signal for

7 is shifted to low field relative to **5** (δ = 137.27 ppm). The hydride signal for **7** appears in the ¹H NMR spectrum (CD₂Cl₂) at -14.65 ppm (¹J_{Pt-H} = 1749 Hz). This is in agreement with the observed PtHI(IMes)(1,3-dimethylimidazolin-2-ylidene) complex (**4**) (δ = -14.67 ppm, ¹J_{Pt-H} = 1727 Hz). The hydride signal of **7** is at a much higher field than in [(NHC)Pt(H)(PPh₃)₂]⁺ (*cis*-**3a** δ = -5.23 ppm and *trans*-**3a** δ = -6.03 ppm in CD₂Cl₂) or [(NHC)Pt(H)(PCy₃)₂]⁺ (**3b**) (δ = -7.95 ppm in CD₂Cl₂).^[9] Previous studies have shown that in the series of *trans*-PtHX(PR₃)₂ complexes the Pt-H chemical shift is affected by the X group *trans* to the hydride.^[11] The presence of the iodide ligand, with its weaker *trans* influence compared to phosphine or NHC would explain the observed high field shift of the hydride signal in **7** and **4** compared to **3a cis**, *trans* and **3b**.

It is proposed that the reactions of **7** proceed *via* the initial formation of a Pt(nbe)₂(IMes) complex, which then undergoes oxidative addition of the C₅-H bond of the imidazolium salt **5** (Scheme 10). This intermediate Pt(norbornene)₂(IMes) complex (**8**) was observed but not isolated in an NMR experiment. In the ¹H NMR (C₆D₆) spectrum of **8** the C_{4,5}-H signal for the IMes is observed at 6.22 ppm (δ = 6.59

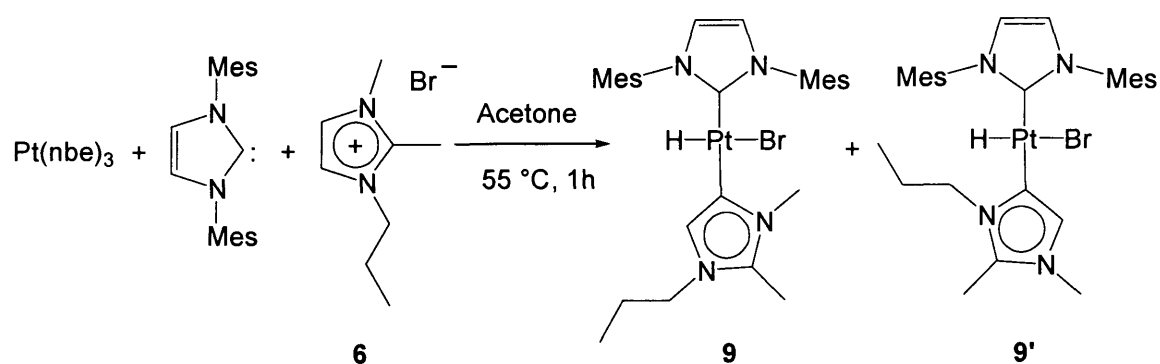
in the free IMes) and the CH protons in the Mes group at 6.47 ppm (also shifted to low field compared to $\delta = 6.92$ ppm in free IMes).

Scheme 10. Proposed scheme for formation of Pt-hydride complexes.



2.1.3 Syntheses of abnormal carbene Pt-hydride complexes with C₂ blocked Imidazolium Salts

Complexes **9** and **9'** were prepared by refluxing $\text{Pt}(\text{nbe})_3$, IMes, and 1.8 equiv of the imidazolium salt 1,2-dimethyl-3-propylimidazolium bromide (**6**) in acetone for one hour. (Scheme 11). The reaction yields the desired products after washing the crude residue with n-hexane and extraction with THF.

Scheme 11. Imidazolium C_{4,5}-H oxidative addition to Pt⁰.

Spectroscopic analysis revealed a mixture of two isomers of PtHBr(IMes)(ab-NHC) in a ratio of 3:1. The minor component **9'** has the Pt connected to the C₄ carbon closest to the N-propyl chain, while the major component **9** has the Pt connected to the C₅ carbon adjacent to the N-methyl group. Steric influences may produce the observed regioselectivity, the preferred isomer **9** shows lower steric crowding at the metal centre.

Complex **9** was characterised by ¹H and ¹³C NMR spectroscopy and by high resolution mass spectrometry. The hydride signal appears in the ¹H NMR spectrum (CD₂Cl₂) at δ = -18.29 (¹J_{Pt-H} = 1714 Hz). The ¹³C NMR spectrum of **8** shows characteristic signals due to the IMes C₂ at δ = 180.9 and the C_{4,5} carbons of the abnormal carbene appears at 124.4 and 151.6 ppm, respectively. In the ¹³C NMR spectrum the C₄ and C₅ signals for **9** are shifted to low field relative to **6**.

Complex **9'** was characterised by ¹H and ¹³C NMR spectroscopy and single crystal X-ray crystallography. In the ¹H NMR spectrum (CD₂Cl₂) the hydride signals appears at δ = -18.31 ppm (¹J_{Pt-H} = 1711 Hz). As with **9**, the ¹³C NMR spectrum of **9'** shows the C₄ (152.4 ppm) and C₅ (126.3 ppm) signals of the abnormal carbene shifted to low field relative to **6**. The ¹³C NMR shifts for C_{4,5} in both **9** and **9'** are comparable with previously reported abnormally bound carbenes.^[12]

Slow diffusion of hexane into a saturated acetone solution of **9** and **9'** afforded a crystalline solid which consisted of two types of crystals, needles and plates. Needles crystals were carefully isolated from the mixture and identified as complex **9'** by ¹H NMR spectrometry. Plate crystals were identified as complex **9** by ¹H NMR spectrometry. The needles were found to be suitable for single-crystal X-ray analysis,

and showed an abnormally bound Pt-NHC carbene complex with Pt bound to C₄ (Figure 2). The crystal contains two identical Pt-carbene molecules and one molecule of acetone in the asymmetric unit. The molecular structure of **9'** shows a slightly distorted square-planar coordination around the platinum(II) centre, with *trans* NHC moieties and hydride and bromide atoms occupying the remaining coordination sites. The normal carbene is oriented perpendicular to the metal plane, which is typical for this type of ligand.^[4, 13] The Br-Pt-C(21)-N torsion angle is -76.8°, close to 90°. The abnormal carbene is nearly co-planar with the metal coordination plane with Br-Pt-C(222)-C(223) torsion angle of 8.6°. Steric crowding from the bulky IMes ligand forces the abnormal carbene to be in *trans* position to it, although electronic effects cannot be excluded. This geometry is similar to that observed by Nolan in his studies on Pd^{II}Cl₂(NHC)₂.^[8] The Pt-C carbene bond lengths of the IMes ligand (Pt(21)-C(21) = 2.018(8) Å) and the C₅ coordinated carbene ligand (Pt(21)-C(223) = 2.041(8) Å) are comparable and consistent with Pt-C single bonds.^[8, 12, 14]

Figure 2. ORTEP projection of **9'** showing the atom labelling scheme. Thermal ellipsoid are drawn at 50% probability level. Hydrogen atoms except for the hydride ligand are omitted for clarity.

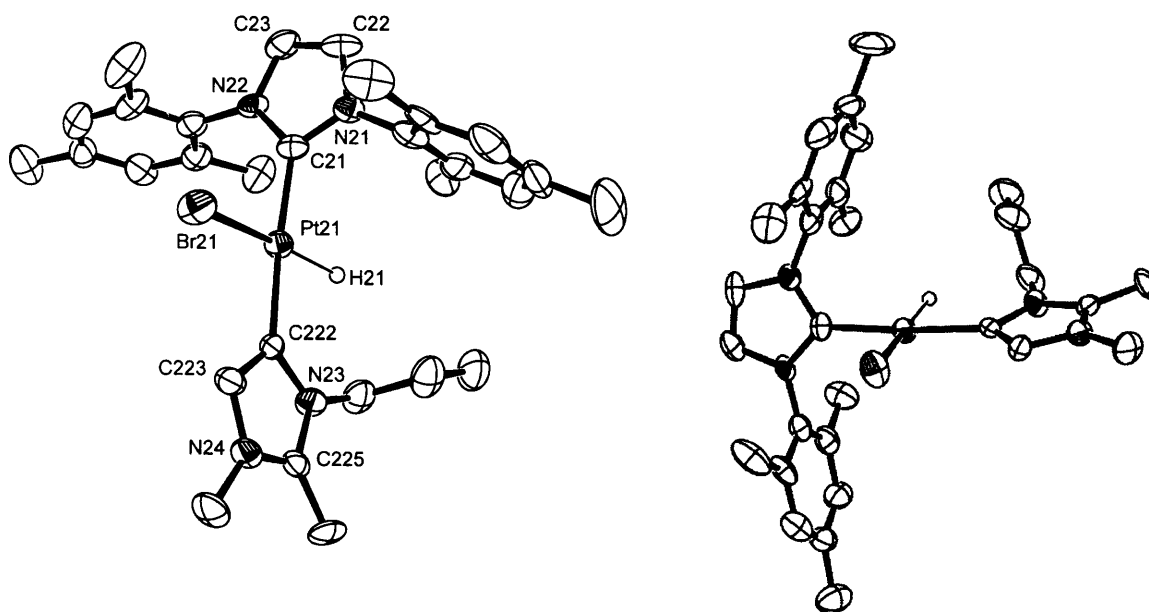


Table 1. Selected Bond Lengths (Å) and Angles (deg) for 9'.

Lengths (Å)			
Pt(21)-C(21)	2.018(8)	Pt(21)-C(222)	2.041(8)
Pt(21)-H(21)	1.8052*	Pt(21)-Br(21)	2.5622(9)
C(21)-N(21)	1.363(11)	C(222)-N(23)	1.432(10)
C(22)-N(21)	1.378(10)	C(225)-N(23)	1.340(10)
C(22)-C(23)	1.323(13)	C(225)-N(24)	1.330(10)
C(23)-N(22)	1.384(11)	C(223)-N(24)	1.377(10)
C(21)-N(22)	1.346(10)	C(222)-C(223)	1.353(11)
Angles (°)			
C(21)-Pt(21)-Br(21)	91.4(2)	C(222)-Pt(21)-Br(21)	90.0(2)
C(21)-Pt(21)-H(21)	93.1*	C(222)-Pt(21)-H(21)	85.2*
C(21)-Pt(21)-C(222)	175.6(3)	Br(21)-Pt(21)-H(21)	173.2

* Calculated, H not found.

2.2 Non-Innocent Nature of Imidazolium-Based Ionic Liquids (IL's)

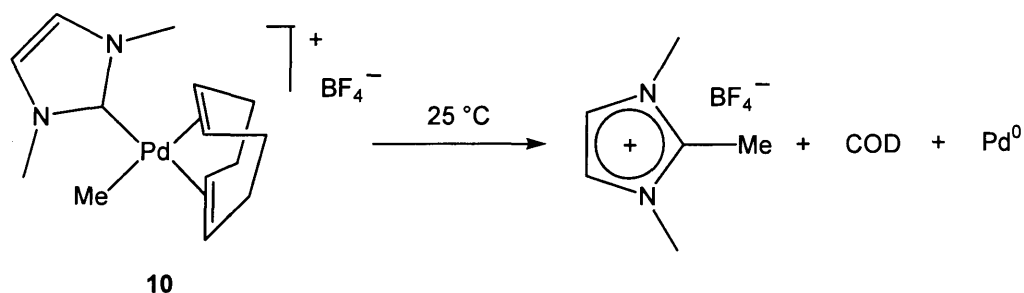
Imidazolium salts have been extensively used as non-aqueous Ionic Liquids (IL's). In particular, those blocked at the C₂ position have been thought to be chemically inert and therefore have been employed as alternatives to non-aqueous solvents for biphasic catalysis.^[15] Improved catalyst stability and, in some examples, improved overall catalytic performance was observed for many reactions conducted in IL's. Examples of reactions carried out in IL's include hydroformylation (Pt, Rh),^[16] Heck-type reactions (Pd)^[17] and hydro-vinylation (Ni)^[18] However the reactivity described in this Chapter clearly demonstrates that C₂-blocked imidazolium salts may also react with low valent group 10 metals, without the need for added base, via an oxidative addition reaction at the imidazolium C₄ or C₅ position. This provides very

clear indication that IL's are not always simple solvents, they may become involved in catalyst generation/activation.

2.3 Reductive Elimination Reactions of C₂-Blocked Imidazolium Salt

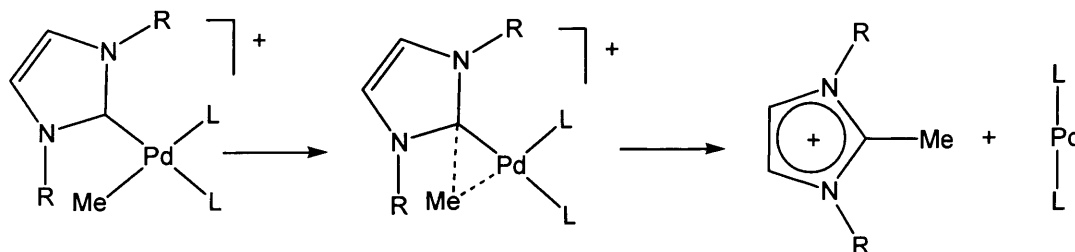
In previous studies on metal carbene complexes Cavell *et al.* identified a facile reductive elimination process, in which an NHC is lost as an imidazolium salt.^[19] The first of these studies was published in 1998, with the synthesis and behaviour of complex **10** examined (Scheme 12). Surprisingly, the complex underwent immediate reductive elimination at room temperature generating 1,2,3-trimethyl-imidazolium tetrafluoroborate, free COD and precipitated Pd⁰.^[20]

Scheme 12. Decomposition of methyl-Pd carbene complexes via reductive elimination.



By exploring the decomposition of complexes in which the Pd⁰ is trapped as a stable bis-phosphine complex, it was demonstrated that reductive elimination proceeds *via* a three centred intermediate (Scheme 13).^[9] During the reductive elimination process, the “bite angle” between the spectator ligands (L) opens up and the attendant angle between the *cis*-methyl group and carbene concurrently closes down, allowing effective orbital overlap for rapid reaction.^[19]

Scheme 13. Decomposition of methyl-Pd carbene complexes via reductive elimination.

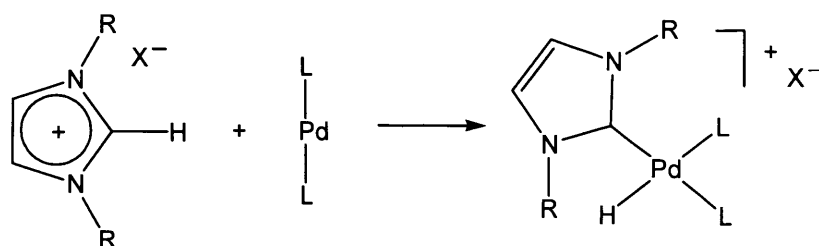


L = P(OPh)₃, PPh₃, PCy₃, PMePh₂

This low energy reductive elimination is a potential deactivation process for NHC-based catalysts, commonly observed where intermediate complexes bearing hydrocarbyl ligands, are formed during a catalytic reaction.

A potentially important method to limit decomposition of M-carbene complexes is to force the reductive elimination reaction in the reverse direction by operating in a large excess of imidazolium cation. Zero valent metal complexes that form as a consequence of reductive elimination may then re-form the M-carbene complex through oxidative addition of the imidazolium cation (Scheme 14).^[21] Combining these redox steps has led to a new atom-efficient catalytic reaction for the substitution of azolium salts at the C₂ position.^[21]

Scheme 14. Oxidative addition of the imidazolium cation to Pd⁰.

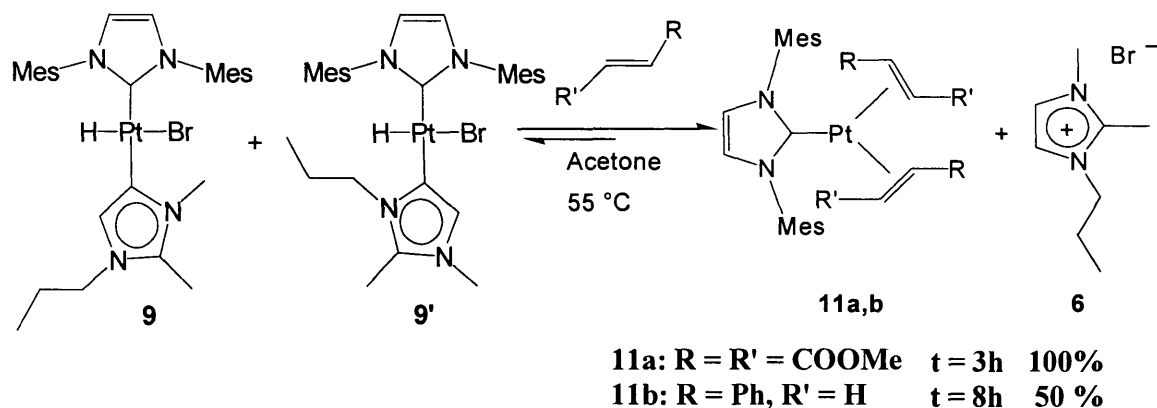


L = P(OPh)₃, PPh₃, PCy₃, PMePh₂ or NHC

It has been now found that “abnormally” bound carbenes, in common with their “normal” counterparts, are susceptible to reductive elimination reactions. In the

presence of alkenes (styrene or dimethylfumarate) a mixture of complexes **9** and **9'** readily eliminate the C₂-blocked imidazolium salt **6** with formation of Pt(IMes)(alkene) complex (**11a,b**) (Scheme 15).^[19, 22]

Scheme 15. Carbene C_{4,5}-H reductive elimination of imidazolium salts.



Stirring a mixture of **9** and **9'** with 5 equivalents of dimethylfumarate in acetone at 55 °C for three hours resulted in quantitative reductive elimination of the C₂-blocked imidazolium salt **6**. The ¹H NMR spectrum of the Pt⁰ product Pt(IMes)(η²-dimethylfumarate)₂ (**11a**) was identical to that observed for a genuine sample.^[3, 23]

The equivalent reaction with styrene resulted in partial (50%) conversion of the abnormally bound Pt-complexes to **11b**. Equilibrium concentrations of **9**, **9'**, **11b**, and **6** were established by ¹H NMR. The ¹H NMR spectrum of **11b** exhibits half the possible proton signals for the styrene, which suggests that complex **11b** contains a mirror plane or a symmetry axis. The vinyl proton (CH_{styrene}) in each coordinated styrene appears as a triplet at 3.16 ppm with the other two protons (CH_{2styrene}) appearing as a double doublet at 2.30 ppm, indicating that the two latter protons are diastereotopic. These vinyl signals appear at a much higher field in the ¹H NMR than in the free styrene (δ = 6.79 CH, δ = 5.86 and 5.27 ppm CH₂). This indicates that there is donation of electron density from the Pt metal into the π* orbitals of the two alkene ligands. Reductive elimination of the “normal” carbene giving IMes·HBr, and products resulting from alkene insertion into the Pt-H bond (e.g. Pt-hydrocarbyl complexes or alkyl C_{4,5}-substituted imidazolium salts) were not observed.

Slow evaporation of acetone from solution of **11b** afforded crystals which were suitable for X-ray diffraction analysis. The solid state structure of **11b** shows one NHC ligand and two styrene molecules coordinated to the platinum centre in a slightly distorted trigonal planar geometry. The C=C double bonds of the coordinated styrenes (1.407 Å) are elongated compared to those of free styrene (1.3245 Å),^[24] due to the reduced electron density of the double bonds caused by back donation of electron density to Pt⁰.

Figure 3. ORTEP projection of Pt(IMes)(η^2 -styrene)₂ (**11b**) showing the atom labelling scheme. Thermal ellipsoid are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

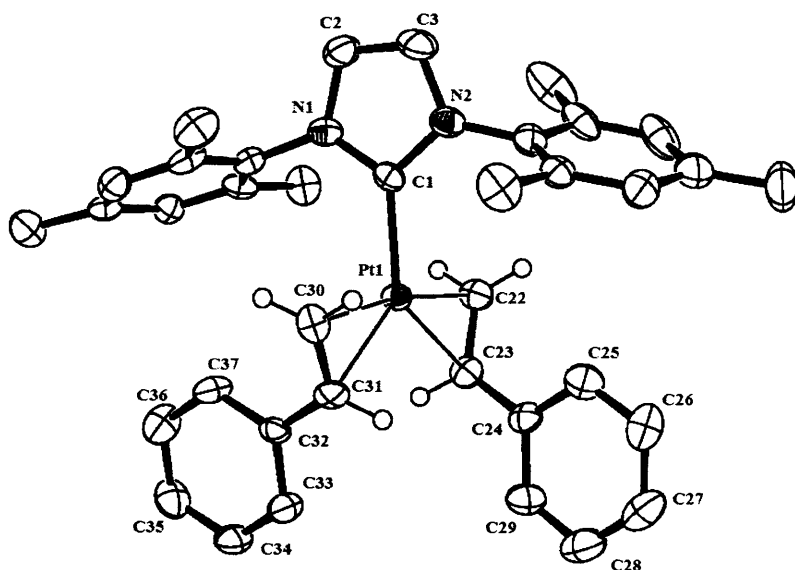


Table 2. Selected Bond Lengths (Å) and Angles (deg) for **11b**.

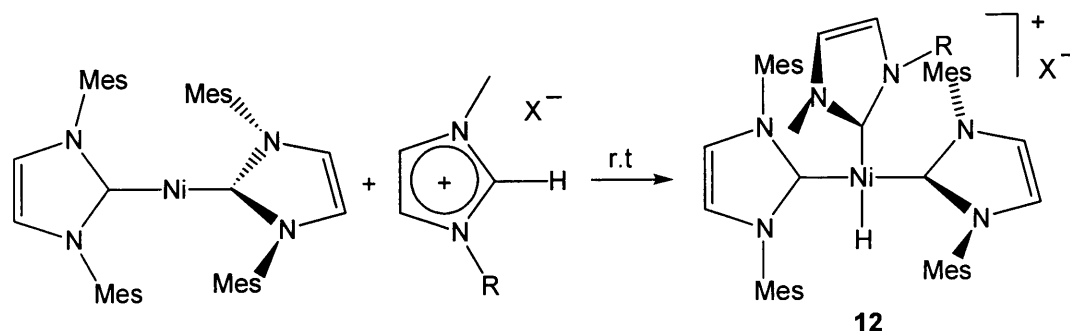
Lengths (Å)			
C(1)-N(1)	1.373(8)	C(23)-Pt(1)	2.130(6)
C(2)-N(1)	1.393(9)	C(30)-Pt(1)	2.109(6)
C(2)-C(3)	1.324(11)	C(31)-Pt(1)	2.140(7)
C(3)-N(2)	1.381(9)	C(22)-C(23)	1.402(10)
C(1)-N(2)	1.351(9)	C(30)-C(31)	1.407(9)
C(1)-Pt(1)	2.039(6)	C(23)-C(24)	1.490(10)
C(22)-Pt(1)	2.121(6)	C(31)-C(32)	1.476(10)
Angles (°)			
C(24)-C(23)-Pt(1)	113.4(4)	C(1)-Pt(1)-C(30)	94.3(3)
C(32)-C(31)-Pt(1)	113.9(5)	C(1)-Pt(1)-C(22)	96.3(3)
C(30)-Pt(1)-C(31)	38.7(3)	C(22)-C(23)-C(24)	121.8(6)
C(22)-Pt(1)-C(23)	38.5(3)	C(30)-C(31)-C(32)	123.4(7)

2.4 C_{4,5}-H oxidative addition of Imidazolium Salts to Ni⁰ complexes

The success of the C_{4,5}-H oxidative addition of C₂ blocked imidazolium salts to Pt⁰ complexes led to attempts to synthesise similar compounds with Ni. Density functional studies have shown that oxidative addition of the imidazolium cation to Ni⁰ species should proceed with a lower activation barrier than Pd⁰ or Pt⁰.^[5, 9]

Recently it has been shown an electron-rich metal centre can promote oxidative addition at room temperature in a one pot reaction (Scheme 16).^[4] The direct generation of a carbene-metal-hydrido species *in situ* may provide an important route to active catalytic species under mild conditions.

Scheme 16. C₂-H oxidative addition of imidazolium salts to Ni⁰ bis (NHC) complex.



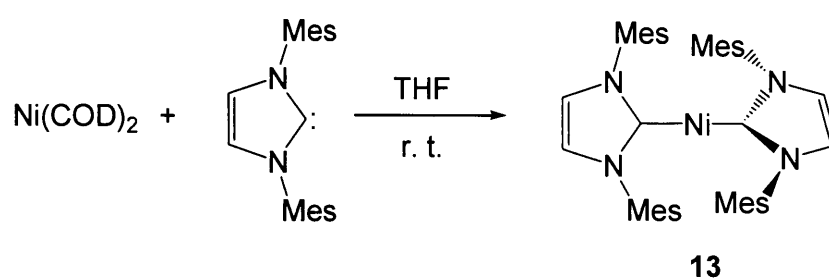
- a) R = Me, X = BF₄ THF, 5 min c) R = Bu, X = PF₆ Toluene, 5 min.
 b) R = Bu, X = BF₄ Toluene, 1 hr

Complexes **12a-c** are rare examples of Ni-H complexes that are stable to air, light and heat. The unexpected stability of such complexes can be rationalised in terms of both steric and electronic effects imparted by the three carbene ligands.^[4] Steric bulk around the metal center and the strong M-NHC bonds give these complexes a rigid structure that could explain their high stability.^[4]

2.4.1 Results and discussion

An electron-rich, coordinative unsaturated L₂M⁰ complex (L = IMes) was employed to facilitate the oxidative addition of C₂-blocked imidazolium salts. The homoleptic (IMes)₂Ni⁰ complex was prepared in situ following a literature report by a ligand displacement reaction starting from Ni(COD)₂ using two equivalents of the IMes free carbene (Scheme 17).

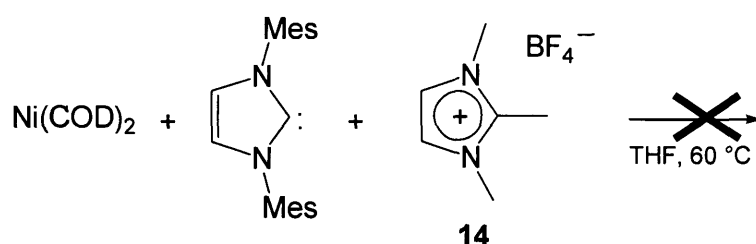
Scheme 17. Synthesis of (IMes)₂Ni⁰.



Chapter 2. C_{4,5}-H oxidative addition of imidazolium salts to Pt⁰ and Ni⁰ complexes

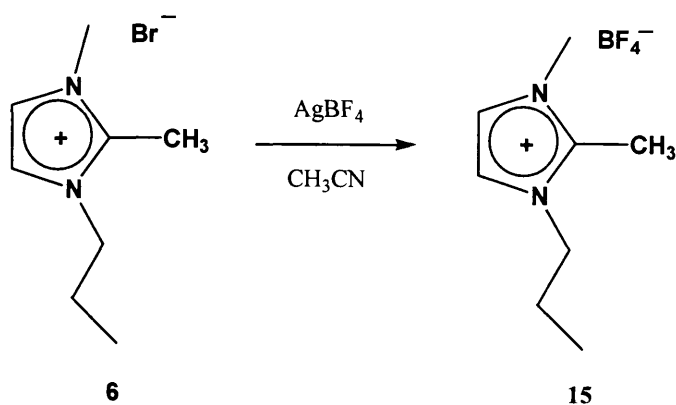
When 1.8 equivalents of 1,2,3-trimethylimidazolium tetrafluoroborate (**14**) was stirred with the *in-situ* generated (IMes)₂Ni no reaction was observed even on increasing the temperature to 60 °C (Scheme 18). It is possible that the imidazolium salt **14** isn't soluble enough in THF. Increasing the bulk of the substituents increases the solubility, blocked imidazolium salt **15** was synthesised to explore solubility and further steric effects.

Scheme 18. Attempted reaction of Ni(COD)₂, IMes and 1,2,3-trimethylimidazolium tetrafluoroborate.



Anion exchange from Br⁻ to BF₄⁻ was accomplished with an excess of AgBF₄. Successful anion exchange was indicated by a diagnostic high-field shift of the C₄-H and C₅-H signals in the ¹H NMR spectrum [$\delta = 7.72$ and 7.57 ppm for Br⁻, $\delta = 7.25$ and 7.19 ppm for BF₄⁻].

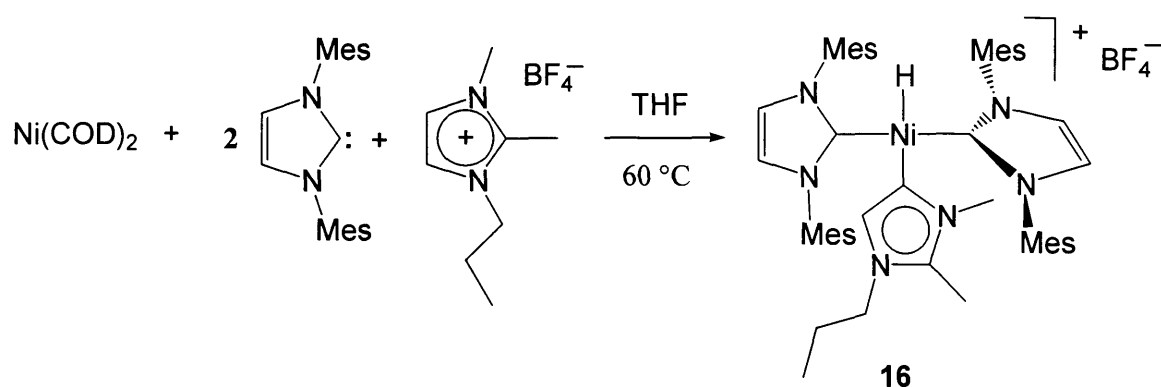
Scheme 19. Synthesis of 1,2-dimethyl-3-propylimidazolium tetrafluoroborate.



When 1.8 equivalents of C₂-blocked imidazolium salt **15** was stirred with generated *in situ* (IMes)₂Ni⁰ (**13**) the deep purple colour of **13** disappeared within 1 hr at 60 °C giving a yellow solution with present traces of Ni⁰. Filtration over celite,

concentration of the solution and addition of hexane led to the isolation of a yellow solid. The Ni-H complex (**16**) was detected but attempts to isolate clean products were unsuccessful even on using different solvents and techniques. The main impurities are the blocked imidazolium salts **15**, which exhibits similar solubility properties to complex **16**.

Scheme 20. Imidazolium C₅-H oxidative addition to Ni⁰.



The ¹H NMR spectrum of **16** shows a Ni-H signal at $\delta = -14.67$ ppm. This value is similar to the hydride signal in **12a-c** ($\delta = -14.96, -15.02$ and -15.02 , respectively (CD₂Cl₂) and in trans-NiHR(PCy₃)₂, (R = Ph, Me; $\delta = -14.8$ and -15.1 , respectively (C₆D₆)), and are consistent with the presence of a ligand with a strong trans influence (e.g. NHC, Ph) trans to the hydride. The ¹³C{¹H} NMR spectrum of **16** shows characteristic signals due to the IMes C₂ at $\delta = 187.85$ and the C₄H in the abnormal carbene at $\delta = 121.81$ ppm.

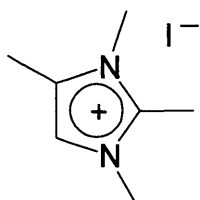
2.5 Experimental Section

All procedures were performed using standard Schlenk techniques, under an atmosphere of dry argon or in a nitrogen glove box. Glassware was dried overnight in an oven at 120 °C or flame dried prior to use. THF, hexane and Et₂O were distilled from sodium benzophenone, toluene from sodium metal, and CH₂Cl₂ from CaH₂, under nitrogen immediately prior to use. Acetone was stirred overnight at room temperature over B₂O₃, and then distilled under argon and stored in a Schlenk bottle. *d*₂-Dichloromethane and *d*₆-benzene were degassed via standard freeze/pump/thaw

Chapter 2. C_{4,5}-H oxidative addition of imidazolium salts to Pt⁰ and Ni⁰ complexes

methods and then dried using the appropriate drying agent. *d*₂-Dichloromethane was dried over 4Å molecular sieves and *d*₆-benzene by reflux over sodium potassium alloy and vacuum transferred into a young Schlenk. NMR spectra were recorded at r.t. on Bruker 400 or 500 MHz Avance spectrometers, with chemical shifts (δ) reported in ppm relative to the residual proton chemical shifts of the internal deuterated solvent (¹H and ¹³C) set relative to external TMS.

Synthesis of 1,2,3,4-tetramethylimidazolium iodide (**5**).

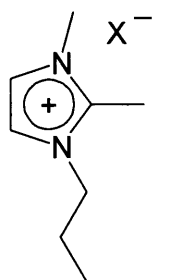


A solution of 2,4-dimethylimidazole (0.500 g, 5.2 mmol) in THF was added dropwise to a cooled (-15 °C) suspension of NaH (0.127 g, 5.2 mmol) in 50 mL of THF. The mixture was allowed to warm to r. t. and stirred for an additional two hrs. 1.72 mL of CH₃I (15.6 mmol) were added dropwise to the mixture that was stirred overnight. The solution was concentrated *in vacuo* upon which a white solid was precipitated. The solid was collected by filtration, dissolved in DCM and filtered to eliminate NaI. The filtrate was evaporated to dryness *in vacuo* and the solid obtained washed with Et₂O. Recrystallisation from CH₃CN-Et₂O afforded colourless crystals of **5** in 75% yield (0.98 g).

HRMS [C₇H₁₃N₂-I]⁺: Found *m/z* 125.1080 Da (+ 1.0 ppm from calculated).

¹H NMR (400 MHz, CD₂Cl₂): δ 7.08 (s, 1H, C₅H), 3.77 (s, 3H, N-CH₃), 3.65 (s, 3H, N-CH₃), 2.67 (s, 3H, C₂-CH₃), 2.24 (s, 3H, C₄-CH₃). ¹³C{¹H} NMR (400 MHz, CD₂Cl₂): δ 143.5 (NC₂N), 129.53 (NC₄C), 118.53 (C₅-H), 35.25 (N₁-CH₃), 32.25 (N₃-CH₃), 11.01 (C₄-CH₃), 8.94 (C₂-CH₃).

Synthesis of **1,2-dimethyl-3-propylimidazolium bromide (6)**.



X = Br, BF₄

A mixture of 1,2-dimethylimidazole (5.07 g, 52.7 mmol) and 1-bromopropane (10.0 mL, 13.5 g, 109.8 mmol) was heated under reflux under a CaCl₂ tube for 2 days. The solution was concentrated *in vacuo* and a white solid collected. The precipitated was washed with Et₂O, giving a white crystalline solid in 94% yield (10.85 g).

Microanalysis: Calc. for C₈H₁₅N₂Br C: 43.85 H: 6.90 N: 12.78% Found C: 43.59 H: 6.88 N: 12.64%. HRMS [C₈H₁₅N₂-Br]⁺: Found *m/z* 139.1238 Da (+ 2.0 ppm from calculated).

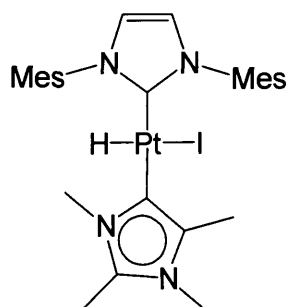
¹H NMR (400 MHz, CD₂Cl₂): δ 7.71 (d, J = 2.09, 1H, C₄-H), 7.57 (d, J = 2.09, 1H, C₅-H), 4.13 (t, J = 7.44, 2H, N-CH₂), 3.92 (s, 3H, N-CH₃), 2.70 (s, 3H, C₂-CH₃), 2.70 (m, 2H, C₇-CH₂), 0.91 (t, J = 7.37, 3H, C₈-CH₃). ¹³C{¹H} NMR (400 MHz, CD₂Cl₂): δ 144.51 (NCN), 123.71 (C₄H), 122.17 (C₅-H), 50.95 (N-CH₂), 36.73 (N-CH₃), 24.07 (C₆-CH₂), 11.48 (C₇-CH₃), 11.39 (C₂-CH₃).

Synthesis of **1,2-dimethyl-3-propylimidazolium tetrafluoroborate (15)**.

1,2-dimethyl-3-propylimidazolium bromide (**6**) (0.200 g 0.91 mmol) was dissolved in CH₃CN and a solution of AgBF₄ (0.195 g, 1 mmol) in CH₃CN was added. After stirring for 3 hrs the precipitated AgBr was removed by filtration under celite and the solvent removed *in vacuo* giving a transparent oil that was washed with Et₂O.

¹H NMR (d₆-DMSO): δ 7.69 (d, J = 2.07, 1H, C₄-H), 7.66 (d, J = 2.07, 1H, C₅-H), 4.13 (t, J = 7.3, 2H, N-CH₂), 3.80 (s, 3H, N-CH₃), 2.63 (s, 3H, C₂-CH₃), 1.78 (m, 2H, C₇-CH₂), 0.86 (t, J = 7.47, 3H, C₈-CH₃).

Synthesis of **PtHI(IMes)(1,2,3,4-tetramethyl-imidazolin-5-ylidene) (7)**.



A mixture of Pt(nbe)₃ (0.500 g, 1.05 mmol), IMes (0.319 g, 1.05 mmol) and 1,2,3,4-tetramethylimidazolium iodide (0.475 g, 1.88 mmol) was heated under reflux in 50 mL of acetone for 50 min, after which time the yellow solution had turned slightly greenish. The solvent was evaporated and the residue washed with 10 mL of hexane. The complex was extracted 2 times with 5 mL of THF and filtrated under celite, the solvent evaporated *in vacuo* to afford **7** as a light yellow solid. (Yield = 50% , 0.395 g).

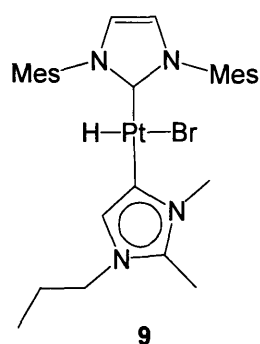
¹H NMR (500 MHz, C₆D₆): δ 6.87 (s, 4H, CH_{mes}), 6.30 (s, 2H, CH_{imid}), 3.07 (s, 3H, N-CH_{3abn}), 2.53 (s, 12H, CH_{3mes}), 2.18 (s, 6H, CH_{3mes}), 2.13 (s, 3H, N-CH_{3abn}), 1.82 (s, 3H, CH_{3abn}), 1.02 (s, 3H, CH_{3abn}), -14.65 (s, 1H, ¹J_{Pt-H} = 1749 Hz). ¹³C{¹H} NMR (500 MHz, CD₂Cl₂): δ 180.8 (NCN), 145.1 (NC₅C_{abn}), 137.27, 137.02, 136.38, 135.10 (C_{arom quat.}), 127.88 (CH_{mes}), 120.38 (CH_{imid}), 35.93 (N-CH₃), 30.34 (N-CH₃), 20.08 (CH_{3mes}), 18.39 (CH_{3mes}), 10.57 (CH_{3abn}), 9.37 (CH_{3abn}).

Synthesis of **PtHBr(IMes)(1,2-dimethyl-3-propyl-imidazolin-5-ylidene) (9)** and **PtHBr(IMes)(1,2-dimethyl-3-propyl-imidazolin-4-ylidene) (9')**.

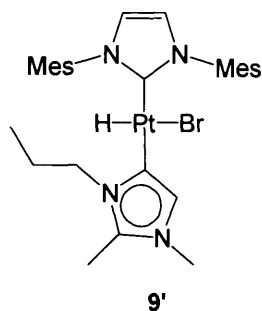
A mixture of Pt(nbe)₃ (0.150 g, 0.31 mmol), IMes (0.096 g, 0.31 mmol) and 1,2-dimethyl-3-propylimidazolium bromide (0.124 g, 0.54 mmol) was refluxed in acetone (25 mL) for 1 hr after which time the yellow solution had turned slightly greenish. The solvent was evaporated *in vacuo* and the residue washed 2 times with 5 mL of hexane at r.t. The complex was extracted 2 times with 4 mL of THF, the solvent evaporated and the product dried *in vacuo* to afford a mixture of **9/9'** as a white solid. (Yield = 44%, 0.098 g).

HRMS [C₂₉H₃₉N₄Pt-K]⁺: Found *m/z* 679.2977 Da (2.8 ppm from calculated).

Chapter 2. C_{4,5}-H oxidative addition of imidazolium salts to Pt⁰ and Ni⁰ complexes

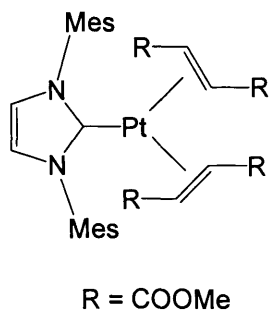


¹H NMR (500 MHz, CD₂Cl₂): δ 6.89 (s, 4H, CH_{mes}), 6.88 (s, 2H, CH_{imid}), 6.45 (s, ³J_{Pt-H} = -14.6 Hz, 1H, CH_{abn}), 3.56 (t, J = 7.52 Hz, 2H, N-CH_{2propyl}) 3.24 (s, 3H, N-CH₃), 2.24 (s, 6H, CH_{3mes}), 2.17 (s, 12H, CH_{3mes}), 2.16 (s, 3H, CH₃), 1.57 (sexet, J = 7.42 Hz 2H, CH_{2propyl}), 0.77 (t, J = 7.41 Hz, 3H, CH_{3propyl}), -18.29 (s, ¹J_{Pt-H} = 1714 Hz, 1 H). ¹³C{¹H} NMR (500 MHz, CD₂Cl₂): δ 180.9 (NCN), 152.4 (NCC), 137.86, 137.06, 135.88 (C_{arom quat.}), 128.59 (CH_{mes}), 126.29 (CH_{abn}), 121.19 (CH_{nml}), 51.70 (N-CH₂), 33.50 (N-CH₃), 22.90 (N-CH_{2prop}), 20.88 (CH_{3ortho}), 18.63 (CH_{3para}), 10.89 (CH_{3prop}), 9.99 (CH_{3abn}).



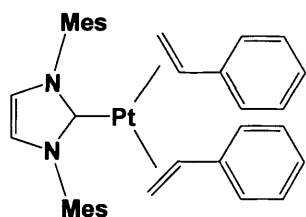
¹H NMR (500 MHz, CD₂Cl₂): δ 6.88 (m, 4H, CH_{mes}), 6.86 (s, 2H, CH_{imid}), 6.48 (s, ³J_{Pt-H} = 14.6Hz, 1H, CH_{abn}), 3.70 (m, 2H, N-CH_{2propyl}) 3.29 (s, 3H, N-CH₃), 2.25 (s, 6H CH_{3mes}), 2.19 (s, 12H, CH_{3mes}), 2.17 (s, 3H, CH₃), 1.40 (sexet, J = 7.69 Hz, 2H, CH_{2propyl}), 0.69 (t, J = 7.72 Hz, 3H, CH_{3propyl}), -18.31 (s, ¹J_{Pt-H} = 1711 Hz, 1H). ¹³C{¹H} NMR (500 MHz, CD₂Cl₂): δ 180.77 (NCN), 151.6 (NCC), 138.04, 137.06, 135.96 (C_{arom quat.}), 128.56 (CH_{aryl}), 124.39 (CH_{abn}), 121.21 (CH_{nml}), 48.59 (N-CH₂), 37.57 (N-CH₃), 23.50 (N-CH_{2prop}), 20.88 (CH_{3ortho}), 18.65 (CH_{3para}), 10.85 (CH_{3prop}), 10.06 (CH_{3abn}).

Synthesis of Pt(IMes)(dmfu)₂ (11a).



A mixture of **9/9'** (0.066 g, 0.09 mmol), and dimethyl fumarate (0.067 g, 0.46 mmol) was refluxed in 3 mL of acetone for 3 h, until the yellow solution darkened slightly. The solvent was evaporated *in vacuo* and the residue washed 2 times with 10 mL of hexane. The product was dried *in vacuo* to afford 0.063 g of a white solid that was spectroscopically identical (¹H NMR) to an authentic sample.^[3] Yield = 100%

Synthesis of Pt(IMes)(sty)₂ (11b).

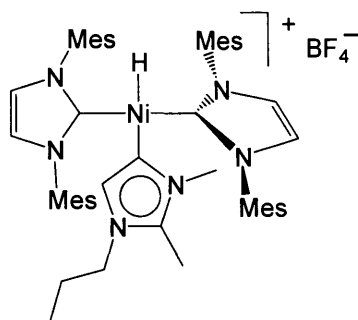


A mixture of **9/9'** (66 mg, 0.09 mmol), and styrene (47.9mg, 0.46 mmol) was heated under reflux in 3 mL of acetone (3 mL) for 8 h, until the yellow solution darkened slightly. The solvent was evaporated *in vacuo* and the residue washed 2 times with 2 mL of hexane. The product was dried *in vacuo* to afford a white solid that was recrystallized from benzene. Yield = 50% (0.036) g. Single crystals were obtained by slow evaporation of C₆D₆ at r.t.

¹H NMR (500 MHz, C₆D₆): δ 6.90 (m, 4H, CH_{arylsty}), 6.86 (s, 2H, CH_{aryl sty}), 6.82 (s, 2H, CH_{mes}), 6.67 (s, 2H, CH_{mes}), 6.43 (m, 4H, CH_{aryl sty}), 6.16 (s, 2H, CH_{imid}), 3.16 (t, J = 24.96, 2H, CH_{sty}), 2.30 (dd, J = 24.66, 4H, CH_{2sty}), 2.06 (s, 6H,

CH_{3mes}), 1.93 (s, 6H, CH_{3mes}), 1.88 (s, 6H, CH_{3mes}). ¹³C{¹H} NMR (500 MHz, CD₂Cl₂): δ 146.89 (NCN), 138.38, 137.21, 135.80, 135.31 (C_{arom quat.}), 128.88, 128.75, 128.16 (CH_{arylstyrene}), 124.09 (CH_{mes}), 123.29 (CH_{sty}), 54.83 (CH_{2styrene}), 20.34 (CH_{3mes}), 17.68 (CH_{3mes}), 17.67 (CH_{3mes}).

Synthesis of NiH(Imes)₂(1,2-dimethyl-3-propyl-imidazolin-5-ylidene)
tetrafluoroborate 16.



A solution of IMes (0.132 g, 0.436 mmol) in 5 mL of THF was added dropwise to a solution of Ni(COD)₂ (0.060 g, 0.218 mmol) in 5 mL of THF and stirred for 20 min. at r. t.. The dark violet solution was then cannulated into a Schlenk flask containing 1-propyl-2,3-methylimidazolium tetrafluoroborate (0.050 g, 0.392 mmol) and stirred for 1 hr at 60 °C. During that time the dark colour disappeared giving a yellow solution that showed traces of Ni⁰. Filtration over Celite, concentration of the solution to 1 mL and addition of 10 mL of hexane led to the isolation of yellow solid. Yield 62%, 0.121 g.

¹H NMR (500 MHz, CD₂Cl₂): δ 6.82 (s, 4H, CH_{mes}), 6.79 (s, 4H, CH_{mes}), 6.65 (s, 8H, CH_{imid}), 6.60 (s, 1H, CH_{abn}), 3.32 (t, 2H, ³J_(HH) = 9 Hz, N-CH_{2propyl}) 2.51 (s, 3H, N-CH₃), 2.31 (s, 6H, CH_{3aryl}), 2.28 (s, 6H, CH_{3mes}), 2.08 (s, 3H, C₂-CH₃) 1.61 (s, 12H, CH_{3mes}), 1.59 (s, 12H, CH_{3mes}), 1.45 (m, 2H, CH_{2propyl}), 0.81 (t, 3H, ³J_(HH) = 7.35 Hz, CH_{3propyl}), -14.67 (s, 1 H, Ni-H). ¹³C{¹H} NMR (500 MHz, CD₂Cl₂): δ 187.85 (NCN), 161.0 (NCC), 137.45, 136.87, 136.33, 137.67 (C_{arom quat.}), 128.12 (CH_{mes}), 127.81 (CH_{mes}), 121.81 (CH_{abn}), 121.22 (CH_{nmi}), 47.70 (N-CH₂), 33.63 (N-CH₃), 22.61 (N-CH_{2prop}), 20.04 (CH_{3ortho}), 17.14 (CH_{3para}), 16.88 (CH_{3para}), 10.21 (CH_{3prop}), 8.30 (CH_{3abn}).

2.4.1 Crystal structure solution

X-ray data collection was carried out at 150K on a Bruker/Nonius Kappa CCD diffractometer using graphite monochromated Mo-K α radiation, equipped with an Oxford Cryostream cooling apparatus. The data was corrected for Lorentz and polarization effects and for absorption using SORTAV^[25]. Structure solution was achieved by direct methods^[26] and refined by full-matrix least-squares on F² with all non-hydrogen atoms assigned anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were placed in idealised positions and allowed to ride on the relevant carbon atom. In the final cycles of refinement a weighting scheme that gave a relatively flat analysis of variance was introduced and refinement continued until convergence was reached. Structure refinement and final geometrical calculations were carried out with the SHELXL-97^[27] program implemented in the WinGX^[28] package.

Table 3. Crystal data and structure refinement for 9'.

Empirical formula	C _{30.50} H ₄₂ Br N ₄ O _{0.50} Pt	
Formula weight	747.68	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	$a = 14.4027(3)$ Å	$\alpha = 75.5820(10)^\circ$.
	$b = 14.4603(3)$ Å	$\beta = 68.7130(10)^\circ$.
	$c = 16.8198(4)$ Å	$\gamma = 75.2790(10)^\circ$.
Volume	3108.76(12) Å ³	
Z	4	
Density (calculated)	1.597 Mg/m ³	
Absorption coefficient	5.825 mm ⁻¹	
F ₀₀₀	1480	
Crystal size	0.25 x 0.08 x 0.08 mm ³	

Chapter 2. C_{4,5}-H oxidative addition of imidazolium salts to Pt⁰ and Ni⁰ complexes

Theta range for data collection	2.92 to 27.52°.
Index ranges	-18<=h<=18, -18<=k<=18, -21<=l<=21
Reflections collected	57703
Independent reflections	14183 [R _{int} = 0.1635]
Completeness to theta = 27.52°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6529 and 0.3237
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	14183 / 24 / 687
Goodness-of-fit on F ²	1.009
Final R indices [I>2sigma(I)]	R1 = 0.0616, wR2 = 0.1112
R indices (all data)	R1 = 0.1321, wR2 = 0.1322
Largest diff. peak and hole	1.066 and -1.653 e.Å ⁻³

Table 4. Crystal data and structure refinement for 11b.

Empirical formula	C ₃₇ H ₄₀ N ₂ Pt	
Formula weight	707.80	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R -3	
Unit cell dimensions	<i>a</i> = 23.300(3) Å	α = 90°.
	<i>b</i> = 23.300(3) Å	β = 90°.
	<i>c</i> = 30.900(6) Å	γ = 120°.
Volume	14528(4) Å ³	
Z	18	
Density (calculated)	1.456 Mg/m ³	
Absorption coefficient	4.372 mm ⁻¹	
F ₀₀₀	6372	
Crystal size	0.25 x 0.15 x 0.15 mm ³	
Theta range for data collection	3.62 to 26.36°.	
Index ranges	-29<=h<=28, -29<=k<=29, -30<=l<=38	

Chapter 2. C_{4,5}-H oxidative addition of imidazolium salts to Pt⁰ and Ni⁰ complexes

Reflections collected	32887
Independent reflections	6547 [$R_{\text{int}} = 0.1251$]
Completeness to $\theta = 26.36^\circ$	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5600 and 0.4078
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6547 / 0 / 367
Goodness-of-fit on F^2	1.032
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0477$, $wR_2 = 0.1077$
R indices (all data)	$R_1 = 0.0714$, $wR_2 = 0.1185$
Largest diff. peak and hole	1.501 and -1.206 e. \AA^{-3}

2.5 References

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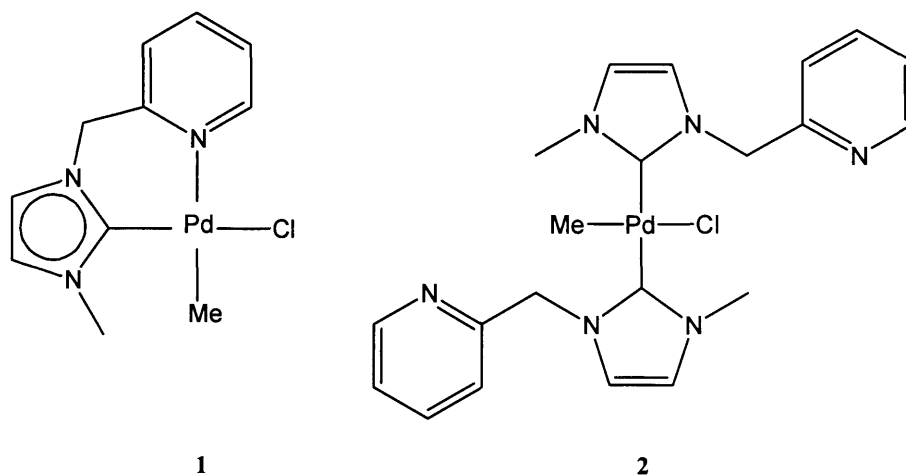
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Chapter Three

C_{4,5}-H Oxidative addition of functionalised imidazolium salts to Pt⁰ complexes

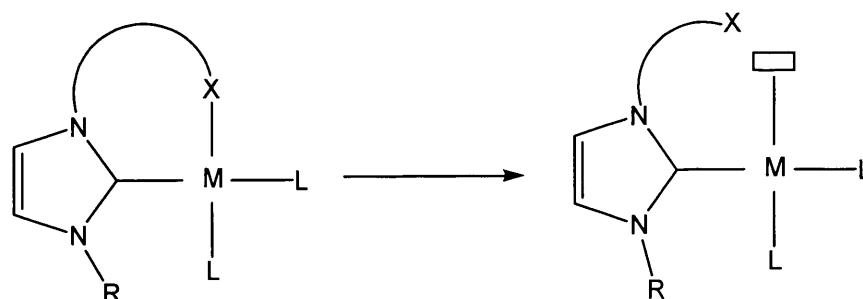
Pyridyl- or picolyl functionalised imidazolium salts have produced a series of interesting transition metal NHC complexes of Pd,^[1, 2] Ni,^[3] Ir,^[4-6] Rh,^[4, 6] Cu,^[7] and Au.^[8] Examples in which the picolyl group is coordinating (**1**) or non coordinating (**2**) to the metal centre have been reported as shown in Figure 1.

Figure 1. Picolyl-substituted NHC metal complexes.



The hemilabile arm in such ligands is capable of reversible dissociation from the metal centre. This dynamic behaviour produces a vacant coordination site that allows for the complexation of substrates (e.g. during a catalytic cycle). At the same time the strong donor moiety remains connected to the metal centre (Scheme 1).

Scheme 1. Hemilabile behaviour of NHC ligands.



X = N, P, O, S

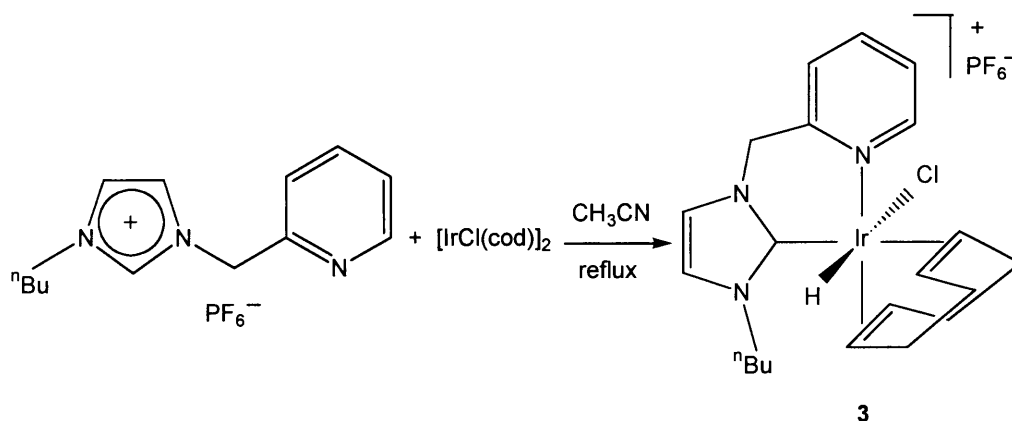
= **vacant coordination site**

L = halogen, alkene

Complexes containing hemilabile ligands have been shown to be active catalysts for hydrogenation,^[9] methanol carbonylation,^[10] hydroformylation,^[11] dimerisation of ethene,^[12] isomerization of alkene,^[13] allylation,^[14] and epoxidation of alkenes, amongst other reaction.^[15] Pyridyl- or picolyl groups are the most common N containing hemilabile moieties on NHC ligands, but O-, S- and P-donor functionalised NHCs have also been reported. Among the functionalised imidazolium salt activation strategies that have been reported, transmetalation from a silver-NHC complex, prepared from the direct reaction of the functionalised imidazolium salt with Ag₂O, is the most common.^[1, 16] A few examples of C-X (X = H, I) oxidative addition by activation of the imidazolium C₂-H or C₄-I bond have been also reported.^[17] In 2005 Peris *et al.* reported the synthesis of [N-n-butyl-N'-(2-pyridylmethyl)imidazolin-2-ylidene](Cl)(H)(1,5-cyclooctadiene)Ir(III) hexafluorophosphate (**3**) (Scheme 2). Complex **3** was synthesised by the oxidative addition reaction of [N-n-butyl-N'-(2-pyridylmethyl)imidazolium hexafluorophosphate to [IrCl(cod)]₂ in refluxing acetonitrile, in the absence of a base.^[6] It is believed that the oxidative addition reaction is favoured by the chelate effect provided by the picolyl group in the resulting complex.

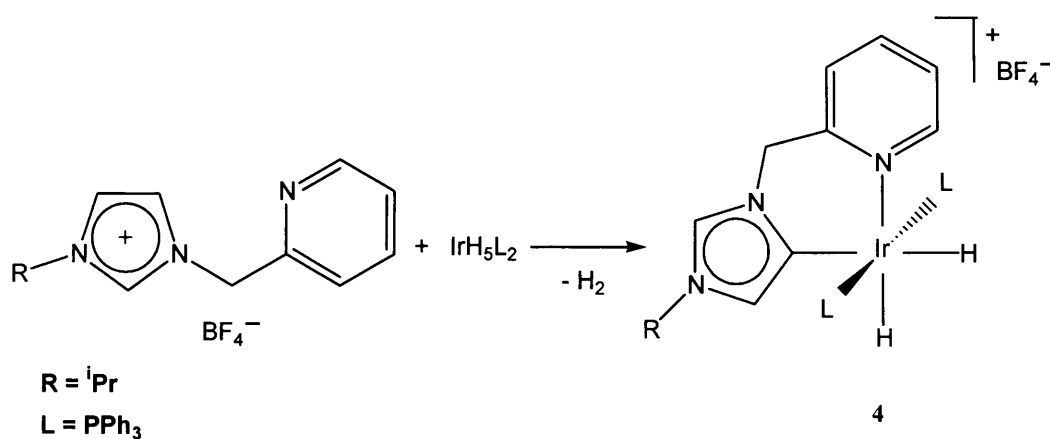
Chapter 3. C_{4,5}-H oxidative addition of functionalised imidazolium salts to Pt⁰ complexes

Scheme 2. Oxidative addition of N-n-butyl-N'-(2-pyridylmethyl)imidazolium hexafluorophosphate to Ir(I) complex.



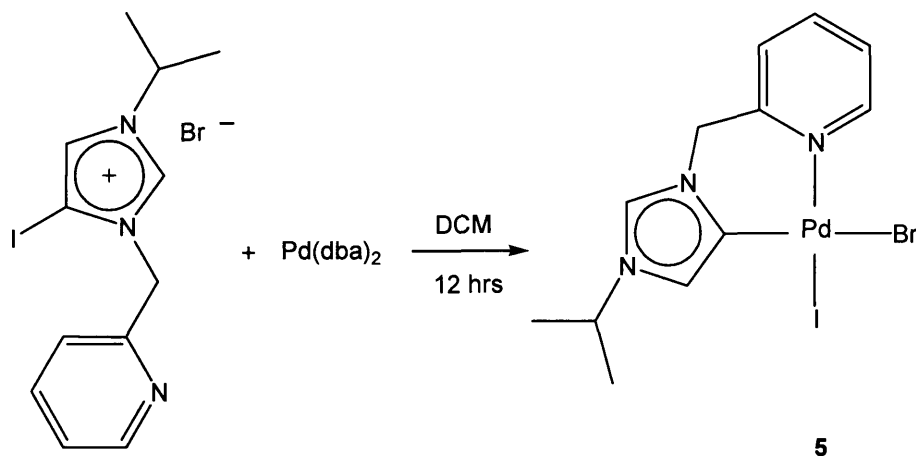
Picolyl functionalised imidazolium salts have also led to examples of abnormal NHC binding. Crabtree *et al.* synthesised iridium complex (**4**) containing picolyl-functionalised NHC carbene ligands that bind the metal centre via the C₄ position and pyridyl nitrogen.

Scheme 3. Abnormal picolyl-substituted NHC iridium complex.



Recently, it has been shown that oxidative addition of pyridyl functionalised 4-iodoimidazolium salt to palladium(0) gives complex **5** in which the NHC is bound to the palladium in an abnormal binding mode (Scheme 4).^[18] Complex **5** showed a catalytic activity in Suzuki cross-coupling reactions that surpasses the analogous C₂-Pd bound.

Scheme 4. Oxidative addition of 4-iodoimidazolium salt.^[18]



This chapter investigates the oxidative additions *via* C₄-H activation of new C₂-blocked picolyl-functionalised imidazolium salts. It is interesting to see if the ligand behaves as a C,N-chelate as observed for the previous abnormal complexes.

3.1 Results and discussion

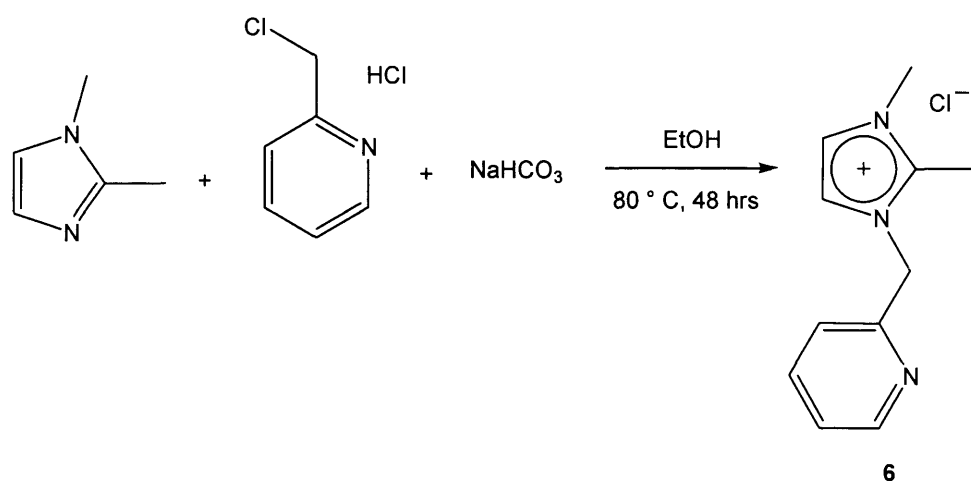
3.1.1 Synthesis of C₂-blocked picolyl functionalised imidazolium salts

The C₂-blocked functionalised imidazolium salt 1,2-dimethyl-3-(2-picolyl)imidazolium chloride (**6**) was synthesized by refluxing 2-picolyl-chloride hydrochloride with 1,2-di-methylimidazole in EtOH in presence of NaHCO₃ for 48 hours (Scheme 5). Compound **6** was isolated as a light brown powder in 72% yield and was characterised by ¹H and ¹³C{¹H} NMR spectroscopy, microanalysis, high resolution mass spectrometry and single crystal X-ray crystallography. The ¹H NMR spectrum (d₆-DMSO) displays two doublets at δ = 7.74 and 7.70 for C₄-H and C₅-H, respectively. The ¹³C{¹H} NMR spectrum shows two carbon signals for C₄ and C₅ at δ = 122.70 and 122.20 ppm, respectively. Anion exchange of chloride to iodide and tetrafluoroborate was accomplished with an excess of NaI and AgBF₄, respectively. Successful anion exchange was indicated by a diagnostic shift to highfield of the ¹H NMR signal of the methylene protons in the picolyl group [δ = 5.53 (Cl⁻), 5.58 (I⁻) and 5.61 ppm (BF₄⁻)]. The ¹H and

Chapter 3. C_{4,5}-H oxidative addition of functionalised imidazolium salts to Pt⁰ complexes

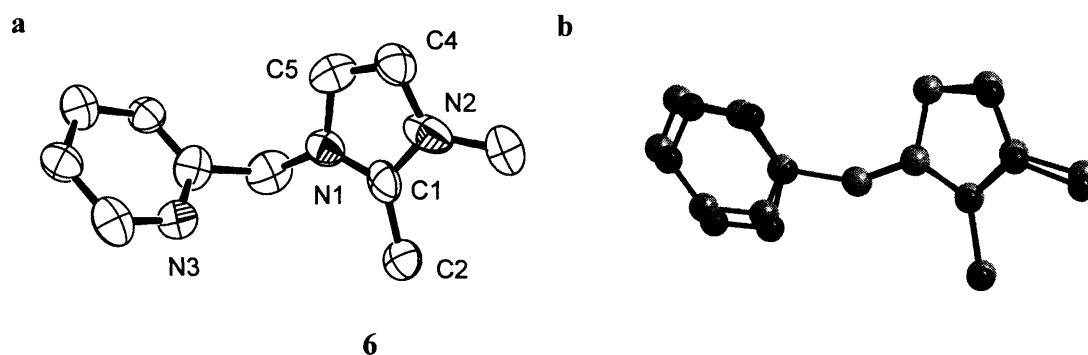
¹³C{¹H} NMR spectra of **6** with iodide and tetrafluoroborate as a counter ions were consistent with the proposed structures, and these results were confirmed by satisfactory high resolution MS measurements and elemental analyses.

Scheme 5. Synthesis of 1,2-dimethyl-3-(2-picolyl)imidazolium chloride.



Diffusion of hexane into a THF solution of **6** yielded crystals suitable for a single crystal X-ray crystallographic determination (Figure 2 a). The asymmetric unit of salt **6** contains two slightly different molecules. Figure 3(b) shows a superposition of the two structures, which differ mainly in rotational conformations and small differences in interatomic distances.

Figure 2. (a) ORTEP projection of **6**; and (b) superposition of two molecules of **6**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms and chloride counter ion are omitted for clarity.



Chapter 3. C_{4,5}-H oxidative addition of functionalised imidazolium salts to Pt⁰ complexes

The C₂-blocked imidazolium salt (**7**) bearing two picolyl substituents was synthesised by refluxing 2-methylimidazole with 2 equivalents of picolylchloride hydrochloride and NaHCO₃ in EtOH for 48 hours (Scheme 6). Compound **7** was isolated as a crystalline solid (85% yield) that was characterised by ¹H and ¹³C NMR, high resolution mass spectroscopy and a single crystal X-ray determination. The ¹H NMR spectrum (d₆-DMSO) displayed a singlet at δ = 7.90 for C_{4,5}-H and a singlet at δ = 5.68 for the two methylene linkers. The ¹³C NMR spectrum shows a signal for C_{4,5} at δ = 122.59. An ORTEP representation of the cation of **7** is shown in Figure 3. The cation is found to be symmetrical in solution but not in the solid state, with an N(1)-C(5)-C(6)-N(3) torsion angle of 79.2° and N(2)-C(11)-C(12)-N(4) of -48.2°.

Scheme 6. Syntheses of 1,3-di(2-picolyl)-2-methylimidazolium chloride.

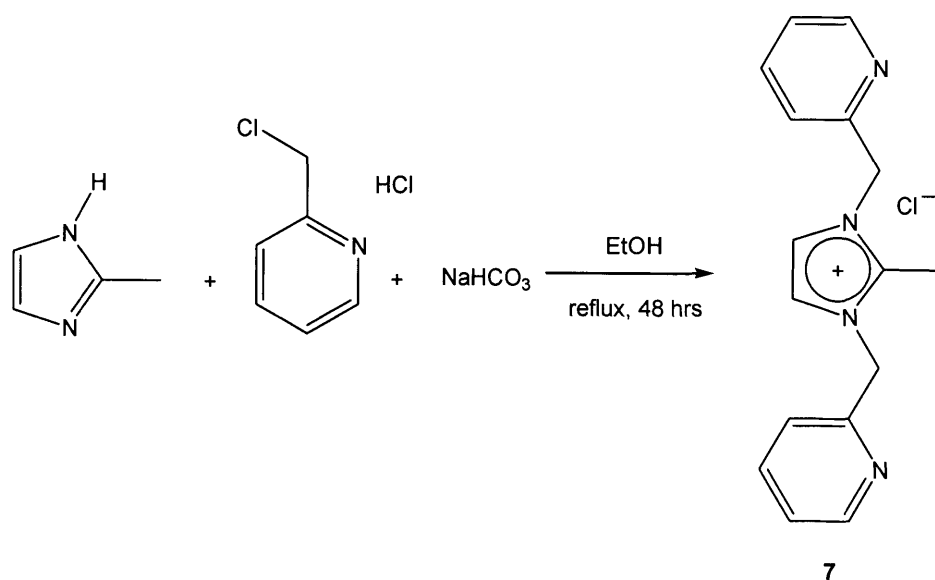
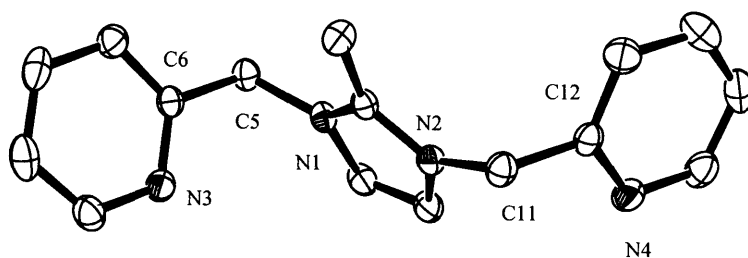


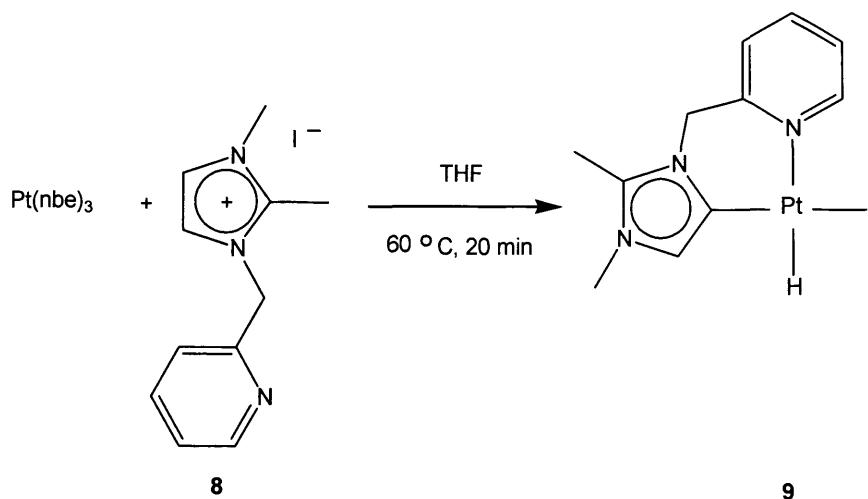
Figure 3. ORTEP projection of the cation of **7** showing thermal ellipsoid at 50% probability level, and the atom labelling scheme. Hydrogen atoms are omitted for clarity.



3.1.2 Synthesis of abnormal Pt-H complexes from picolyl-functionalised imidazolium salts

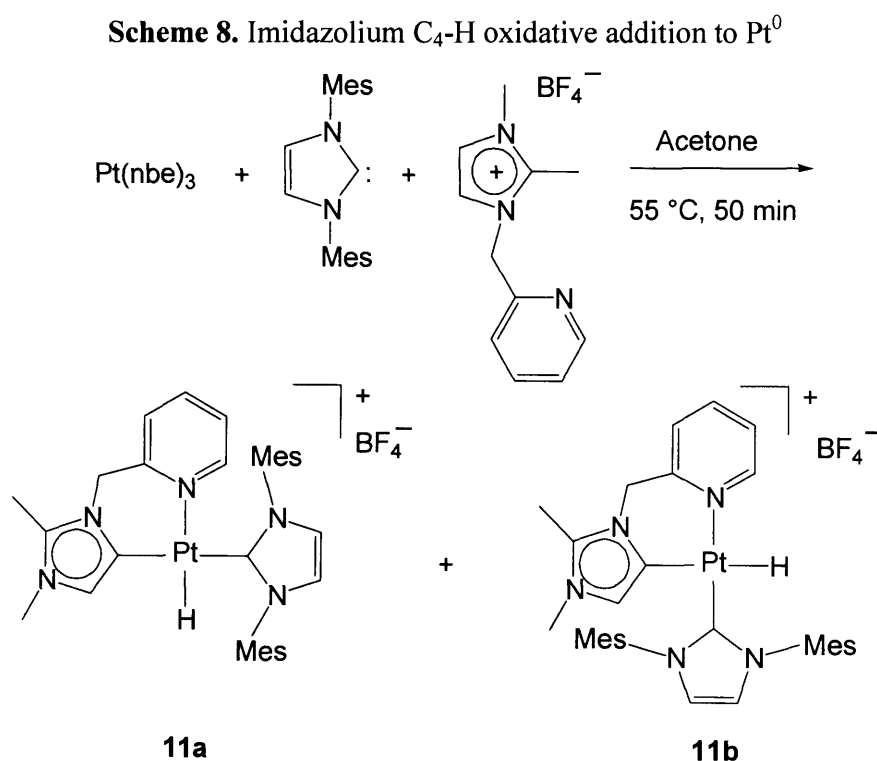
Following the results described in Chapter two, the C₂-H oxidative addition of picolyl-functionalised imidazolium salts to Pt(nbe)₃ was investigated. Attempts to prepare a platinum hydride complex by mixing 1,2-dimethyl-3-(2-picolyl)imidazolium iodide (**8**) and Pt(nbe)₃ enjoyed limited success (Scheme 7). Complex **9** was formed in low yield (10 %) even when using an excess of **8** (1:1.8 molar ratio). The product was contaminated with starting material and repeated recrystallisations with different solvents result in the decomposition of complex **9**. The ¹H NMR of **9** (CD₂Cl₂) showed an hydride signal at – 20.29 ppm (¹J_{Pt-H} = 1316 Hz) and the methylene signal for the picolyl group was shifted to high field (δ = 5.19 compared to δ = 5.67 ppm in the free imidazolium salt **8**).

Scheme 7. Functionalised imidazolium C₄-H oxidative addition to Pt⁰.



To provide a more electron-rich platinum centre the successful strategy used in Chapter 2 was adopted. Thus addition of IMes (1 equivalent) as spectator ligand to Pt(nbe)₃ and 1,2-dimethyl-3-(2-picolyl)imidazolium tetrafluoroborate (**10**) resulted in the isolation of complexes **11a** and **11b** (Scheme 8). Complexes **11a** and **11b** were isolated as a 4:1

mixture in 65 % yield. Complex **11a** was found to be slightly more soluble in THF than complex **11b**, and repeated extraction with small portions of THF resulted in the isolation of **11a** as a pure isomer. The hydride signal for **11a** appears in the ¹H NMR spectrum (d₂-CD₂Cl₂) as a singlet at δ = -18.62 (¹J_{Pt-H} = 1466 Hz), with the C₄-H signal observed as a singlet at 6.30 ppm. The ¹³C NMR spectrum of **11a** shows characteristic signals due to the IMes C₂ at δ = 178.32 ppm and the C₄ carbon of the abnormal carbene at δ = 143.01. Confirmation of the stereochemistry of **11a** came from an NOE experiment. The hydride signal was irradiated and enhancements of the C₅-H signal of the abnormal carbene ligand and one of the CH₃ groups of the mesityl signal were observed. It was concluded from the NOE experiment of **11a** that the Pt-hydride ligand and the imidazolium ring of the abnormal carbene are *cis* to each other and consequently the pyridyl group is bonded to Pt *in trans* position to the hydride.



The two inequivalent protons in the methylene linker of **11a** were expected to give two signals but in the ¹H NMR only a singlet (δ = 4.51 ppm) was observed at room temperature. Danopoulos *et al.* reported Pd complexes with picolyl-functionalised NHC ligands (Figure 4) where the two diastereotopic protons of the methylene bridge were

Chapter 3. C_{4,5}-H oxidative addition of functionalised imidazolium salts to Pt⁰ complexes

observed as separate signals at -20 °C. It is possible that chelate ring flipping renders the two protons indistinguishable on the NMR scale. Variable temperature ¹H NMR studies have been carried out on complex **11a** in d₂-CD₂Cl₂. A gradual decrease of the temperature leads to broadening of the methylene signal indicative that these protons are involved in a dynamic process but separation into two signals was not observed even at 213 K (Figure 5).

Figure 4. Picolyl functionalised NHC complexes of palladium.

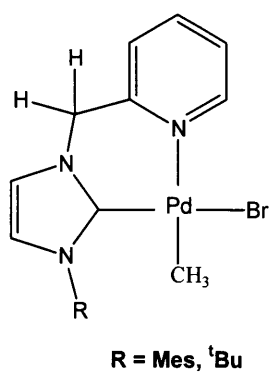
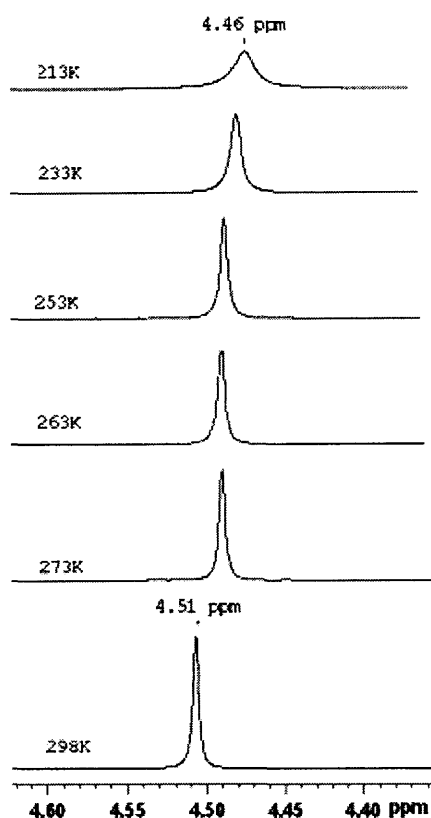


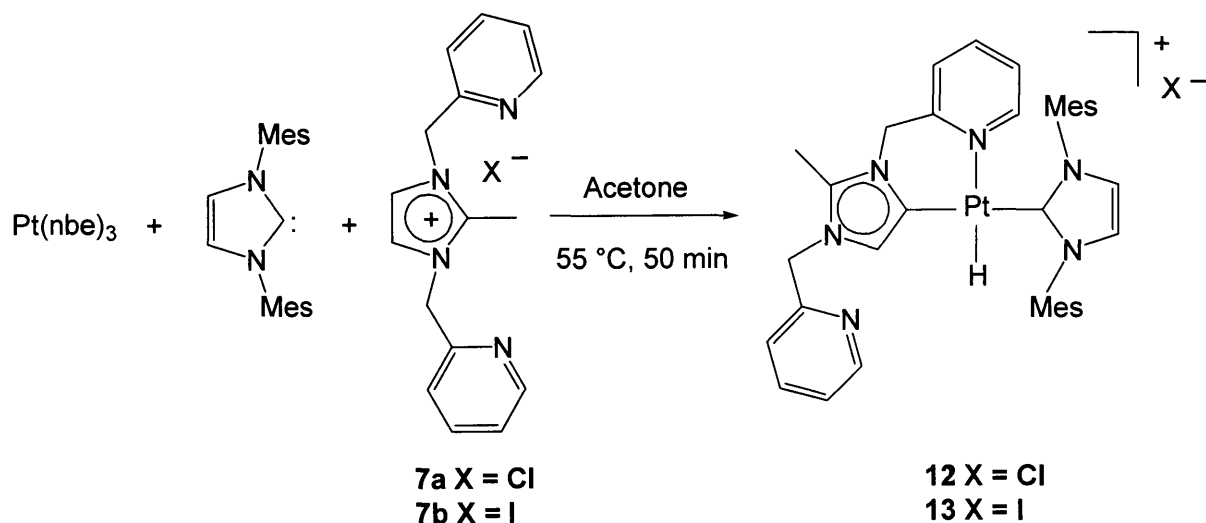
Figure 4. Variable temperature ¹H NMR studies of **11a** in CD₂Cl₂.



Attempts to isolate **11b** as a pure isomer were unsuccessful, the complex was contaminated with complex **11a** (40 %) and C₂-blocked imidazolium **10** (2 %). The Pt-hydride signal for **11b** appears in the ¹H NMR spectrum (CD₂Cl₂) at -15.33 ppm (¹J_{Pt-H} = 1766 Hz). All the signals for **11b** are down field with respect to **11a** complex. The C₄-H signal was observed as a singlet at δ = 6.55 ppm (δ = 6.30 in **11a**).

An analogous procedure starting from bis-picoyl imidazolium salt (**7**) was used to synthesise complexes **12** and **13**. Pt(nbe)₃ was mixed with IMes and 1.8 equivalents of 1,3-di(2-picoyl)-2-methylimidazolium chloride or iodide in acetone. Platinum-hydrides **12** and **13** were isolated after washing the crude with hexane to eliminate unreacted IMes and extraction with THF to leave behind the unreacted imidazolium salt (Scheme 9).

Scheme 9. Imidazolium C₄-H oxidative addition of bis-picolyl imidazolium salt to Pt⁰.



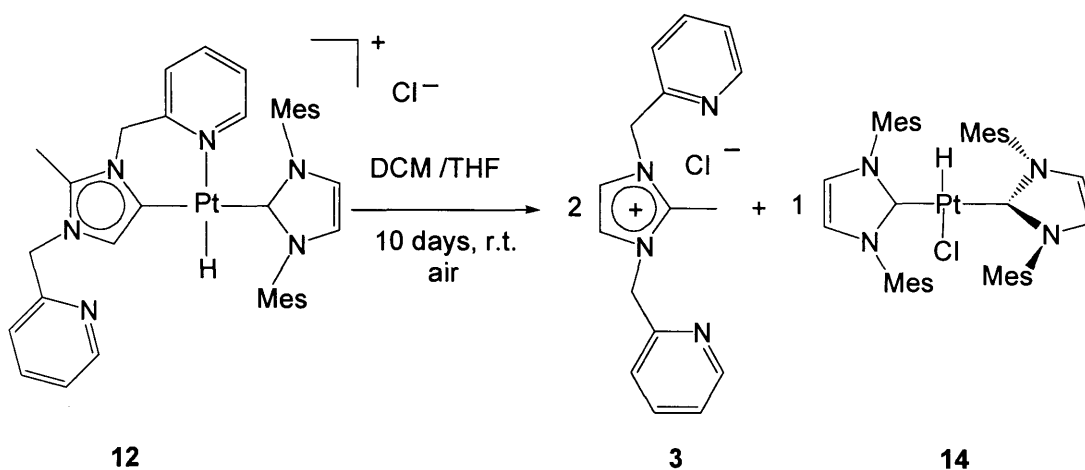
Complex **12** was isolated as a white powder in 55% yield and was characterised by ¹H and ¹³C{¹H} NMR spectroscopy and high resolution mass spectrometry. The hydride signal appear in the ¹H NMR spectrum (d₂-CD₂Cl₂) at δ = -18.59 ppm (¹J_{Pt-H} = 1464.6 Hz) and the C₅-H signal at δ = 6.34 ppm. Both methylene groups are observed as two singlet at δ = 5.03 and 4.87 ppm. Also in this case inequivalent protons were not observed. All signals for the picolyl bound to platinum are shifted to high field with respect to the dangling picolyl group and are comparable to the shifts observed in complex **11a**. Also the ¹J_{Pt-H} are comparable (¹J_{Pt-H} = 1466 Hz for complex **11a**), this is an indication that the chloride doesn't compete with a picolyl group to coordinate to platinum. The ¹³C{¹H} NMR spectrum of **12** shows the C₂-Pt signal for the IMes carbene at δ = 178.44 and the C₄ for the abnormally bound carbon at 143.26 ppm. Complex **13** was isolated as a white powder in 62% yield. Its ¹H NMR spectrum is very similar to that of complex **12**, with the difference that the signals are all shifted to higher field, for example the methylene protons are observed as two singlets at δ = 4.73 and 4.49 ppm (δ = 5.03 and 4.87 in **12**). The Pt-hydride resonance appears as a singlet in the ¹H NMR spectrum (CD₂Cl₂) of **13** at δ = -18.65 (¹J_{Pt-H} = 1469.6 Hz).

For complexes **11a**, **11b**, **12** and **13** reductive elimination reactions of the normal or abnormal carbene was not observed in dry and oxygen free conditions even on

Chapter 3. C_{4,5}-H oxidative addition of functionalised imidazolium salts to Pt⁰ complexes

increasing the temperature. It is interesting to note however, that a dichloromethane:THF (1:3) solution of complex **12** progressively decomposed over 10 days under air (Scheme 10). Slow evaporation of the resulting mixture afforded a crystalline solid and a light yellow oil. Analysis of the oil by ¹H NMR revealed the formation of 1,3-di(2-picolyl)-2-methylimidazolium chloride, Pt(IMes)₂HCl and Pt⁰ black. Crystals of the solid were carefully isolated from the oil, and X-ray analysis showed the Pt-H complex, PtH(Cl)(IMes)₂ (**14**).

Scheme 10. Decomposition of **12**.



The mechanism by which Pt(IMes)₂HCl was formed is not known; it is possible that it is the result of the oxidative addition of IMesH⁺ to an Pt⁰ intermediate formed after reductive elimination of 1,3-di(2-picolyl)-2-methylimidazolium chloride. In the ¹H NMR spectrum (CD₂Cl₂) of **14** the hydride signal appears as singlet at $\delta = -19.1$ (¹J_{Pt-H} = 1746 Hz). The molecular structure of **14** is depicted in Figure 3; some selected bond lengths and angles are presented in table 1. The C(1)-Pt(1)-Cl(1) angle and the C(22)-Pt(1)-Cl(1) angle are 92.31° and 90.11°, C(1)-Pt(1)-C(22) is 177°, indicative of a square planar environment about Pt with *trans* NHC moieties and hydride and chloride atoms occupying the remaining coordination sites. The torsion angle N(3)-C(22)-C(1)-N(1) is found to be 50.3°. The dihedral angle between planes N(3)N(4)C(22) and N(1)N(2)C(1) is 48.6° and the distance between the centroids of planes N(3)N(4)C(22) and

Chapter 3. C_{4,5}-H oxidative addition of functionalised imidazolium salts to Pt⁰ complexes

N(1)N(2)C(1) is 6.393 Å. As expected from theoretical calculations the two carbene are in trans disposition and the NHC are not co-planar, this is possibly due to steric crowding from the two bulky IMes.

Figure 6. ORTEP projection of **14** showing the atom labelling scheme. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms (except Pt-H) are omitted for clarity.

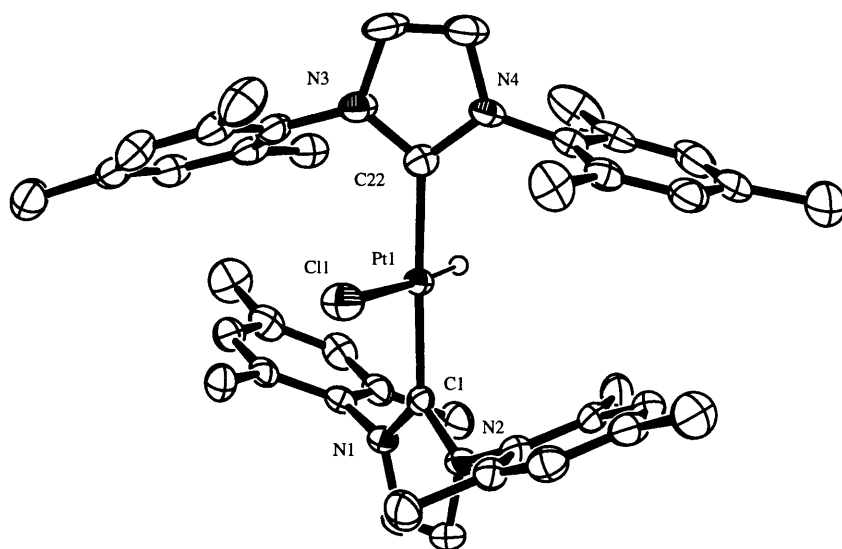


Table 1. Selected Bond Lengths (Å) and Angles (deg) for **14**.

Lengths Å			
Pt(1)-C(1)	1.997(4)	Pt(1)-C(22)	2.007(4)
Pt(1)-H(1)	1.40 *	Pt(1)-Cl(1)	2.4187(12)
C(1)-N(1)	1.367(5)	C(22)-N(3)	1.357(5)
C(1)-N(2)	1.362(4)	C(22)-N(4)	1.355(5)
Angles °			
C(1)-Pt(1)-Cl(1)	92.31(11)	C(22)-Pt(1)-Cl(1)	90.11(12)
C(1)-Pt(1)-C(22)	177.42(15)	C(22)-N(3)-C(25)	124.1(3)
C(1)-N(1)-C(4)	124.7(3)		

*Calculated, H not found

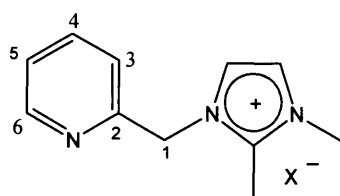
Compound **14** is found to be an unknown complex, although a similar compound was reported by Cavell *et al.* in 2003, and was synthesised by C-H activation of 1,3-dimethylimidazolium iodide by Pt(IMes)(η^2 -dimethylfumarate) as described in chapter 2 Scheme 4.^[19]

In conclusion new abnormal carbene Pt-H complexes with picolyl functionalised imidazolium salts were synthesised via oxidative addition reactions. C₂-blocked picolyl functionalised imidazolium salt were found to behave as C-N-chelate ligands.

3.2 Experimental section

All procedures were performed using standard Schlenk techniques, under an atmosphere of dry argon or in a nitrogen glove box. Glassware was dried overnight in an oven at 120 °C or flame dried prior to use. THF, hexane and Et₂O were distilled from sodium benzophenone, toluene from sodium metal, and CH₂Cl₂ from CaH₂, under nitrogen immediately prior to use. Acetone was stirred overnight at room temperature over B₂O₃, and then distilled under argon and stored in a Schlenk bottle. *d*₂-Dichloromethane and *d*₆-benzene were degassed via standard freeze/pump/thaw methods and then dried using the appropriate drying agent. *d*₂-Dichloromethane was dried over 4Å molecular sieves and *d*₆-benzene by reflux over sodium potassium alloy and vacuum transferred into a young Schlenk. NMR spectra were recorded at r.t. on Bruker 400 or 500 MHz Avance spectrometers, with chemical shifts (δ) reported in ppm relative to the residual proton chemical shifts of the internal deuterated solvent (¹H and ¹³C) set relative to external TMS.

Synthesis of 1,2-dimethyl-3-(2-picoly)imidazolium chloride (6).



2- Picolychloride hydrochloride (2.00 g, 12.19 mmol), 1,2-methylimidazole (1.33 g, 13.84 mmol) and NaHCO₃ (1.54g, 18.28 mmol) were taken up in 20 mL of ethanol and refluxed for 2 days. The solvent was removed *in vacuo*, the residue taken up in DCM and the solution filtered. Removal of the DCM *in vacuo* gave an oil that was triturated with THF and Et₂O to give a brown powder, that was further washed with THF, Et₂O and dried *in vacuo*. Yield: 2.22 g, 72% . Single crystals were obtained by slow diffusion of hexane in a acetonic solution of the salt.

Chapter 3. C_{4,5}-H oxidative addition of functionalised imidazolium salts to Pt⁰ complexes

¹H NMR (500 MHz, d₆-DMSO): δ 8.43 (m, 1H, H_{6pyridyl}), 7.80 (m, 1H, H_{4pyridyl}), 7.74 (d, J = 2.03 Hz, 1H, CH), 7.70 (d, J = 2.03 Hz, 1H, CH), 7.41 (m, 1H, H_{3pyridyl}), 7.30 (m, 1H, H_{5pyridyl}), 5.53 (s, 2H, N-CH₂), 3.74 (s, 3H, NCH₃), 2.53 (s, 3H, CH₃).

¹³C{¹H} NMR (500 MHz, d₆-DMSO): δ 154.02 (C_{2pyridyl}), 149.91 (C_{6pyridyl}), 145.55 (NCN), 137.84 (C_{4pyridyl}), 123.85 (C_{5pyridyl}), 122.79 (C_{3pyridyl}), 122.70 (CH), 122.20 (CH), 52.06 (CH₂), 35.20 (N-CH₃), 9.96 (CH₃).

Synthesis of **1,2-dimethyl-3-(2-picoly)imidazolium iodide (8)**.

1,2-Dimethyl-3-(2-picoly)imidazolium chloride (1.0 g, 4.47 mmol) was dissolved in 10 mL of acetonitrile and a solution of NaI (0.81 g, 5.36 mmol) in 10 mL of acetonitrile was added dropwise. The mixture was stirring for 24 hrs at room temperature. The solvent was removed *in vacuo* and the residue was extracted with DCM leaving behind NaI. After evaporation of the solvent, compound **2a** was obtained as a light brown powder. Recrystallisation from THF-Et₂O give 1.28 g of a white solid in 90% yield.

Anal. Calc. for C₁₁N₃H₁₄I; C: 41.92 H: 4.48 N: 13.33% Found; C: 41.72 H: 4.38 N: 13.33%.

¹H NMR (500 MHz, CD₂Cl₂): δ 8.42 (m, 1H, H_{6pyridyl}), 7.71 (m, 1H, H_{4pyridyl}), 7.57 (d, 1H, CH), 7.55 (d, 1H, CH), 7.36 (m, 1H, H_{3pyridyl}), 7.23 (m 1H, H_{5pyridyl}), 5.55 (s, 2H, N-CH₂), 3.84 (s, 3H, NCH₃) 2.72 (s, 3H, CH₃).

¹³C{¹H} NMR (500 MHz, CD₂Cl₂): δ 152.67 (C_{2pyridyl}), 150.32 (C_{6pyridyl}), 145.69 (NCN), 137.91 (C_{4pyridyl}), 124.26 (CH), 123.41 (C_{3pyridyl}), 122.74 (C_{5pyridyl}), 53.86 (CH₂), 36.62 (N-CH₃), 11.89 (CH₃).

Synthesis of **1,2-dimethyl-3-(2-picoly)imidazolium tetrafluoroborate (10)**.

1,2-Dimethyl-3-(2-picoly)imidazolium chloride (1.20 g, 5.36 mmol) was dissolved in 15 mL of acetone and a solution of NaBF₄ (0.707 g, 6.44 mmol) in 10 mL of acetone was added dropwise. The mixture was stirred for 24 hrs at room temperature. The solvent was removed and the residue was extracted with DCM leaving behind NaCl. After

Chapter 3. C_{4,5}-H oxidative addition of functionalised imidazolium salts to Pt⁰ complexes

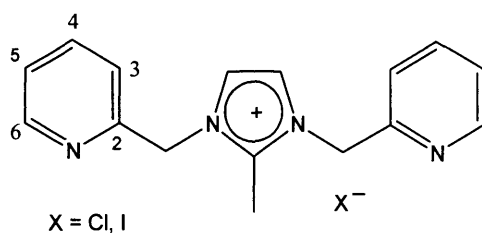
evaporation of the solvent, compound **2b** was obtained as an orange oil that was triturated with THF to give a white powder. This was further washed with THF, Et₂O and dried *in vacuo*. Yield: 1.4g, 95%.

HRMS [C₁₁H₁₄N₃-BF₄]⁺; Found *m/z* 188.1179 Da (-4.6 ppm from calculated).

¹H NMR (500 MHz, DMSO): δ 8.58 (m, 1H, H_{6pyridyl}), 7.95 (m, 1H, H_{4pyridyl}), 7.74 (d, J = 2 Hz, 1H, CH), 7.70 (d, J = 2 Hz, 1H, CH), 7.52 (m, 1H, H_{3pyridyl}), 7.45 (m 1H, H_{5pyridyl}), 5.61 (s, 2H, N-CH₂), 3.85 (s, 3H, NCH₃) 2.65 (s, 3H, CH₃).

¹³C{¹H} NMR (500 MHz, DMSO): δ 153.53 (C_{2pyridyl}), 149.57 (C_{6pyridyl}), 145.19 (NCN), 137.49 (C_{4pyridyl}), 123.51 (C_{5pyridyl}), 122.41 (C_{3pyridyl}), 122.25 (CH), 121.79 (CH), 51.75 (CH₂), 34.81 (N-CH₃), 9.48 (CH₃).

Synthesis of 1,3-di(2-picoly)l-2-methylimidazolium chloride (7).



2-Picolylchloride hydrochloride (2.03 g, 13.40 mmol), 2-methylimidazole (0.50 g 6.10 mmol) and NaHCO₃ (1.56 g, 18.53 mmol) were taken up in 20 mL of ethanol and refluxed for 2 days. The solvent was removed *in vacuo*, the residue taken up in 10 mL of DCM, dried over MgSO₄ and the solution filtered. Removal of DCM *in vacuo* gave an oil that was triturated with THF to give a light brown powder that was further washed with THF, Et₂O and dried *in vacuo*. Yield: 1.56 g, 85%. Single crystals were obtained by slow diffusion of hexane in a THF solution of the salt.

Anal. Calc. for C₁₆H₁₇N₄Cl; C: 63.89 H: 5.70 N: 18.63%, Found; C: 63.53 H: 5.66 N: 18.39%. HRMS [C₁₆H₁₇N₄-Cl]⁺: Found *m/z* 265.1457 Da (1.4 ppm from calculated).

¹H NMR (500 MHz, d₆-DMSO): δ 8.56 (m, 2H, H_{6pyridyl}), 7.90 (m, 4H, H_{4pyridyl}) 7.81(s, 2 H, CH), 7.52 (m, 2H, H_{3pyridyl}), 7.41 (m 2H, H_{5pyridyl}), 5.68 (s, 4H, N-CH₂), 2.66 (s, 3H, CH₃). ¹³C{¹H} NMR (500 MHz, d₆-DMSO): δ 153.88 (C_{2pyridyl}), 149.97 (C_{6pyridyl}), 146.23 (NCN), 137.90 (C_{4pyridyl}), 123.89 (C_{5pyridyl}), 122.69 (C_{3pyridyl}), 122.59 (CH), 52.23 (CH₂), 10.36 (CH₃).

Synthesis of **1,3-di(2-picolyl)-2-methylimidazolium iodide (7b)**.

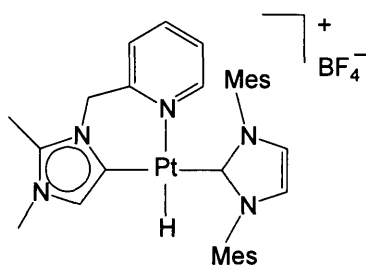
1,3-di(2-picolyl)-2-methylimidazolium chloride (1.5g, 4.99 mmol) was dissolved in 10 mL of acetonitrile and a solution of NaI (0.898 g, 5.99 mmol) in 10 mL of acetonitrile was added dropwise. The mixture was stirred for 24 hrs at room temperature. The solvent was removed *in vacuo* and the residue was extracted with DCM leaving behind NaI. After evaporation of the solvent, compound **2a** was obtained as a light brown powder. Recrystallisation from THF-Et₂O gave 1.86 g of a white solid in 95% yield.

¹H NMR (400 MHz, CD₂Cl₂): δ 8.45 (m, 2H, H_{6pyridyl}), 7.74 (m, 4H, H_{4pyridyl}), 7.57 (s, 2H, CH_{imid}), 7.52 (m, 2H, H_{3pyridyl}), 7.21 (m, 2H, H_{5pyridyl}), 5.54 (s, 4H, N-CH₂), 2.76 (s, 3H, CH₃).

¹³C{¹H} NMR (400 MHz, CD₂Cl₂): δ 153.07 (C_{2pyridyl}), 150.64 (C_{6pyridyl}), 146.79 (NCN), 138.31 (C_{4pyridyl}), 124.66 (CH), 123.64 (C_{3pyridyl}), 122.96 (C_{5pyridyl}), 53.86 (CH₂), 12.42 (CH₃).

Syntheses of **PtH (IMes)(1,2-dimethyl-3-(2-picolyl)imidazolin-4-ylidene) BF₄ (11a)**

and **PtH (IMes)(1,2-dimethyl-3-(2-picolyl)imidazolin-5-ylidene) BF₄ (11b)**



A mixture of Pt(nbe)₃ (0.150 g, 0.31 mmol), IMes (0.096 g, 0.31 mmol) and 1,2-dimethyl-3-(2-picolyl)imidazolium tetrafluoroborate (0.155 g, 0.56 mmol) was refluxed in 25 mL of acetone for 1 hr after which time the yellow solution had lightened slightly. The solvent was concentrated to 1 mL *in vacuo* and addition of 10 mL of hexane led to the isolation of white solid that was further washed 2 times with 5 mL of hexane. The products were extracted with 4 mL of THF and the solvent concentrated *in vacuo*. Addition of 10 mL of hexane led to the precipitation of a white solid that was dried under

Chapter 3. C_{4,5}-H oxidative addition of functionalised imidazolium salts to Pt⁰ complexes

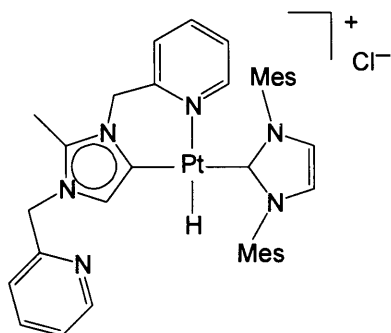
vacuum and found to be a mixture of **11a/11b** (4:1). Yield: 0.161g 67 %. Complex **11a** was isolated pure after extraction with 1 mL of THF from the mixture.

HRMS [C₃₂H₃₈N₅Pt-BF₄]⁺: Found *m/z* 687.2775 Da (3.8 ppm from calculated).

¹H NMR (500 MHz, CD₂Cl₂): δ 8.32 (m, 1H, H_{6pyridyl}), 7.75 (m, 1H, H_{4pyridyl}), 7.43 (m, 1H, H_{3pyridyl}), 7.17 (m 1H, H_{5pyridyl}), 7.12 (s, 2H, CH_{imid}), 6.82 (s, 4H, CH_{mes}), 6.30 (s, 1H, CH_{abn}), 4.50 (s, 2H, N-CH₂), 3.39 (s, 3H, N-CH₃), 2.43 (s, 3H, CH₃), 2.24 (s, 6H, CH_{3mes}), 2.04 (s, 12H, CH_{3mes}) -18.65 (s, ¹J_{Pt-H} = 1468 Hz, 1 H).

¹³C{¹H} NMR (500 MHz, CD₂Cl₂): δ 178.32 (s, Pt-NCN) 152.24 (s, C_{2pyridyl}), 151.72 (s, C_{6pyridyl}), 143.01 (s, Pt-CCN), 139.65, 133.48, 129.11, 126.39 (s, C_{arom quat}), 138.31 (s, C_{4pyridyl}), 135.40 (s, C_{3pyridyl}), 128.14 (s, CH_{mes}), 126.39 (s, CH_{abn}), 125.38 (s, C_{5pyridyl}), 121.48 (s, CH_{imid}), 52.01 (s, CH₂), 33.22 (s, N-CH₃), 20.06 (s, CH_{3mes}), 17.69 (s, CH_{3mes}), 8.53 (s, CH_{3abn}).

Synthesis of PtH(IMes)(1,3-di(2-picoly)-2-methylimidazolin-4-ylidene) chloride (**12**)



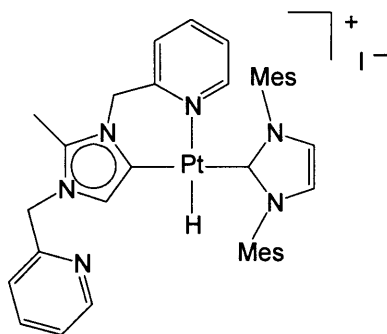
A mixture of Pt(nbe)₃ (0.166 g, 0.35 mmol), IMes (0.106 g, 0.35 mmol) and 1,3-di(2-picoly)-2-methylimidazolium chloride (0.158 g, 0.52 mmol) was refluxed in 25 mL of acetone for 1 hr, after which time the yellow solution had lightened slightly. The solvent was concentrated *in vacuo* (1 mL) and addition of 10 mL of hexane led to the isolation of white solid that was further washed two times with 5 mL of hexane. The complex was extracted with 5 mL of THF, the solvent concentrated *in vacuo*, and addition of 10 mL of hexane led to the precipitation of 0.154 g of **12** as a white solid in 55% yield.

Chapter 3. C_{4,5}-H oxidative addition of functionalised imidazolium salts to Pt⁰ complexes

¹H NMR (500 MHz, CD₂Cl₂): δ 8.41 (m, 1H, H_{6pyridyl}), 8.28 (m, 1H, H_{4pyridyl}), 8.16 (m, 1H, H_{4'pyridyl}), 7.76 (m, 1H, H_{3pyridyl}), 7.14 (m, 1H, H_{3'pyridyl}), 7.09 (m, 1H, H_{5pyridyl}), 7.06 (s, 2H, CH_{imid}), 6.87 (s, 4H, CH_{mes}), 6.34 (s, 1H, CH_{abn}), 5.03 (s, 2H, N-CH₂), 4.87 (s, 2H, N-CH₂), 2.78 (s, 3H, CH₃) 2.28 (s, 6H, CH_{3mes}), 2.04 (s, 6H, CH_{3mes}), -18.59 (s, ¹J_{Pt-H} = 1464.6 Hz, 1 H) .

¹³C{¹H} NMR (500 MHz, CD₂Cl₂): δ 178.44(Pt-NCN) 152.74 (C_{2pyridyl}), 152.17 (C_{2pyridyl}), 151.81 (C_{6pyridyl}), 149.20 (C_{6pyridyl}), 143.26 (Pt-CCN), 140.42, 136.73, 135.40 (C_{arom quat}), 138.30 (C_{4pyridyl}), 137.81 (C_{4pyridyl}), 136.47 (C_{3pyridyl}), 135.38 (C_{3pyridyl}), 128.15 (CH_{mes}), 125.76 (CH_{abn}), 125.11 (C_{5pyridyl}), 124.10 (C_{5pyridyl}), 121.37 (CH_{imid}), 51.72 (CH₂), 51.68 (CH₂), 20.05 (CH_{3mes}), 17.69 (CH_{3mes}), 9.92 (CH_{3abn}).

Synthesis of PtH(IMes)(1,3-di(2-picolyl)-2-methylimidazolin-4-ylidene) iodide (**13**)



A mixture of Pt(nbe)₃ (0.150 g, 0.32 mmol), IMes (0.096 g, 0.32 mmol) and 1,3-di(2-picolyl)-2-methylimidazolium iodide (0.152 g, 0.48 mmol) was refluxed in 25 mL of acetone for 1 hr, after which time the yellow solution had lightened slightly. The solvent was concentrated *in vacuo* (1 mL) and addition of 10 mL of hexane led to the isolation of white solid that was further washed two times with 5 mL of hexane. The complex was extracted with 5 mL of THF, the solvent concentrated *in vacuo*, and addition of 10 mL of hexane led to the precipitation of 0.171 g of **13** as a white solid in 60% yield.

HRMS [C₃₇H₄₁N₆Pt-I]⁺: *m/z* 764.3064 Da (3.0 ppm from calculated).

¹H NMR (500 MHz, CD₂Cl₂): δ 8.39 (m, 1H, H_{6pyridyl}), 8.30 (m, 1H, H_{6'pyridyl}), 7.87 (m, 1H, H_{4pyridyl}), 7.78 (m, 1H, H_{4'pyridyl}), 7.60 (m, 1H, H_{3pyridyl}), 7.57 (m, 1H, H_{3'pyridyl}), 7.12 (m 1H, H_{5pyridyl}), 7.08 (m 1H, H_{5pyridyl}), 7.04 (s, 2H, CH_{imid}), 6.81(s, 4H, CH_{mes}), 6.38 (s,

Chapter 3. C_{4,5}-H oxidative addition of functionalised imidazolium salts to Pt⁰ complexes

1H, CH_{abn}), 4.73 (s, 2H, N-CH₂), 4.49 (s, 2H, N-CH₂), 2.78(s, 3H, CH₃), 2.58 (s, 3H, CH₃), 2.25 (s, 6H, CH_{3mes}), 2.04(s, 6H, CH_{3mes}), -18.65 (s, ¹J_{Pt-H} = 1469.6 Hz, 1 H).

¹³C{¹H} NMR (500 MHz, CD₂Cl₂): δ 178.44 (Pt-NCN) 152.74 (C_{2pyridyl}), 152.17 (C_{2pyridyl}), 151.81 (C_{6pyridyl}), 149.20 (C_{6pyridyl}), 143.26 (Pt-CCN), 140.42, 136.73, 135.40 (C_{arom quat}), 138.29 (C_{4pyridyl}), 137.79 (C_{4pyridyl}), 136.50 (C_{3pyridyl}), 135.39 (C_{3pyridyl}), 127.11 (CH_{Mes}), 125.76 (CH_{abn}), 125.11 (C_{5pyridyl}), 124.10 (C_{5pyridyl}), 121.46 (CH_{imid}), 66.99 (CH₂), 51.82 (CH₂), 20.16 (CH_{3mes}), 18.21 (CH_{3mes}), 10.86 (CH_{3abn}).

3.4 Crystal structure solution

X-ray data collection was carried out at 150K on a Bruker/Nonius Kappa CCD diffractometer using graphite monochromated Mo-Ka radiation, equipped with an Oxford Cryostream cooling apparatus. The data was corrected for Lorentz and polarization effects and for absorption using SORTAV^[20]. Structure solution was achieved by direct methods^[21] and refined by full-matrix least-squares on F² with all non-hydrogen atoms assigned anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were placed in idealised positions and allowed to ride on the relevant carbon atom. In the final cycles of refinement a weighting scheme that gave a relatively flat analysis of variance was introduced and refinement continued until convergence was reached. Structure refinement and final geometrical calculations were carried out with the SHELXL-97^[22] program implemented in the WinGX^[23] package.

Table 1. Crystal data and structure refinement for 7.

Empirical formula	C ₁₆ H ₁₇ Cl N ₄
Formula weight	300.79
Temperature	150(2) K
Wavelength	0.71069 Å
Crystal system, space group	Monoclinic, P2 ₁ /c

Chapter 3. C_{4,5}-H oxidative addition of functionalised imidazolium salts to Pt⁰ complexes

Unit cell dimensions	$a = 8.592(5) \text{ \AA}$ $b = 19.683(5) \text{ \AA}$ $c = 9.010(5) \text{ \AA}$	$\alpha = 90.000(5) \text{ deg.}$ $\beta = 102.760(5) \text{ deg.}$ $\gamma = 90.000(5) \text{ deg.}$
Volume	1486.1(13) Å ³	
Z, Calculated density	4, 1.344 Mg/m ³	
Absorption coefficient	0.256 mm ⁻¹	
F ₀₀₀	632	
Crystal size	0.30 x 0.20 x 0.08 mm	
Theta range for data collection	3.11 to 27.00 deg.	
Limiting indices	-10 ≤ h ≤ 10, -25 ≤ k ≤ 25, -11 ≤ l ≤ 11	
Reflections collected / unique	6291 / 3232 [R _{int} = 0.0258]	
Completeness to theta = 27.00	99.5 %	
Absorption correction	Multi scan	
Max. and min. transmission	sortav 0.583 and 0.337	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3232 / 0 / 192	
Goodness-of-fit on F ²	1.039	
Final R indices [I > 2σ(I)]	R1 = 0.0345, wR2 = 0.0804	
R indices (all data)	R1 = 0.0464, wR2 = 0.0860	
Extinction coefficient	0.0084(19)	
Largest diff. peak and hole	0.255 and -0.265 e.Å ⁻³	

Chapter 3. C_{4,5}-H oxidative addition of functionalised imidazolium salts to Pt⁰ complexes

Table 2. Crystal data and structure refinement for 13.

Empirical formula	C ₄₂ H ₄₉ Cl N ₄ Pt	
Formula weight	840.39	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	orthorhombic, Pbc _a	
Unit cell dimensions	<i>a</i> = 17.024(3) Å <i>b</i> = 19.114(4) Å <i>c</i> = 23.094(5) Å	α = 90 deg. β = 90 deg. γ = 90 deg.
Volume	7514(3) Å ³	
Z, Calculated density	8, 1.486 Mg/m ³	
Absorption coefficient	3.840 mm ⁻¹	
F ₀₀₀	3392	
Crystal size	0.50 x 0.25 x 0.15 mm	
Theta range for data collection	2.97 to 27.00 deg.	
Limiting indices	-21 ≤ <i>h</i> ≤ 21, -24 ≤ <i>k</i> ≤ 24, -29 ≤ <i>l</i> ≤ 29	
Reflections collected / unique	15638 / 8188 [R _{int} = 0.0309]	
Completeness to theta = 27.00	99.8 %	
Max. and min. transmission	sortav 0.581 and 0.375	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8188 / 0 / 449	
Goodness-of-fit on F ²	1.020	
Final R indices [I > 2σ(I)]	R1 = 0.0329, wR2 = 0.0785	
R indices (all data)	R1 = 0.0466, wR2 = 0.0844	
Largest diff. peak and hole	1.466 and -1.743 e.Å ⁻³	

3.3 References

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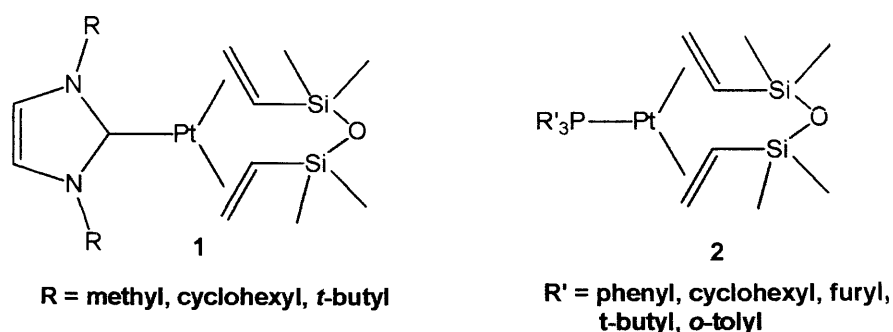
Chapter Four

Hydrosilylation of styrene catalysed by *in situ* Pt(0)/Imidazolium salt systems

The catalytic hydrosilylation of unsaturated carbon-carbon compounds is one of the most important methods for the synthesis of organosilicon compounds.^[1, 2] Numerous transition metal based catalysts for this reaction have been reported, including metals of Groups 8,^[3] 9^[4] and 10.^[5, 6] Platinum catalysts, in particular, are very active. For example, the Speier catalyst,^[1, 7] H₂PtCl₆ dissolved in *iso*-propanol, and the Karstedt catalyst, H₂PtCl₆ dissolved in divinyltetramethyldisiloxane, show high activity and are widely used.^[8] Unfortunately, these catalysts exhibit poor stabilities and the formation of colloidal Pt species often results in undesired side reactions. Development of new hydrosilylation catalysts has been the focus of active research for several decades, due to the utility of the resulting organosilanes in applications ranging from the preparation of silicon-containing polymers to the synthesis of bioactive compounds.^[1, 9]

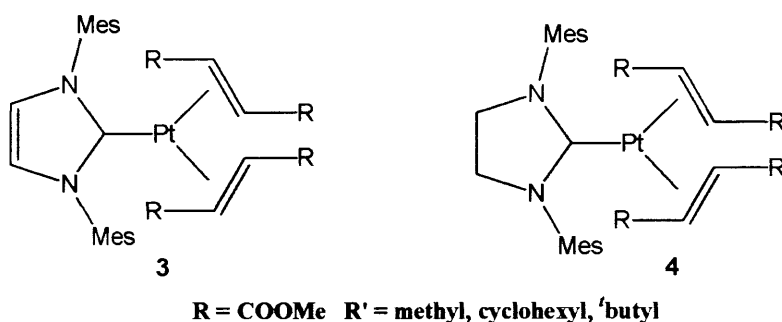
Platinum-NHC complexes that catalyze hydrosilylation reaction of alkenes with remarkable efficiency and selectivity have been reported by Markò *et al.* who used Pt(0)-catalysts with unsaturated NHC-containing alkyl-substituents (**1**) for the efficient hydrosilylation of 1-octene and 1,1,1,3,5,5,5,-heptamethyl trisiloxane (Figure 1).^[10] With these catalysts side reactions such as isomerization and dehydrogenative silylation were significantly suppressed. The Pt-NHC catalysts (**1**) were more efficient, in terms of both activity and selectivity, than the analogous Pt- phosphine complexes (**2**).

Figure 1. Hydrosilylation catalysts of Markò *et al.*



Elsevier *et al.* reported the use of new platinum(0) complexes (**3** and **4**) derived from bulky unsaturated and saturated NHCs in the hydrosilylation of styrene with triethylsilane. Using **3** and **4** the reaction proceeds with unprecedented selectivity, yielding exclusively products **I** and **II** (Scheme 1).^[6]

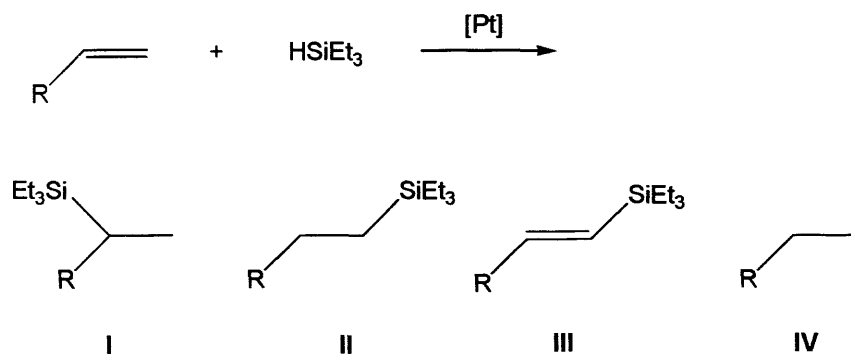
Figure 2. Elsevier *et al.* hydrosilylation catalysts.



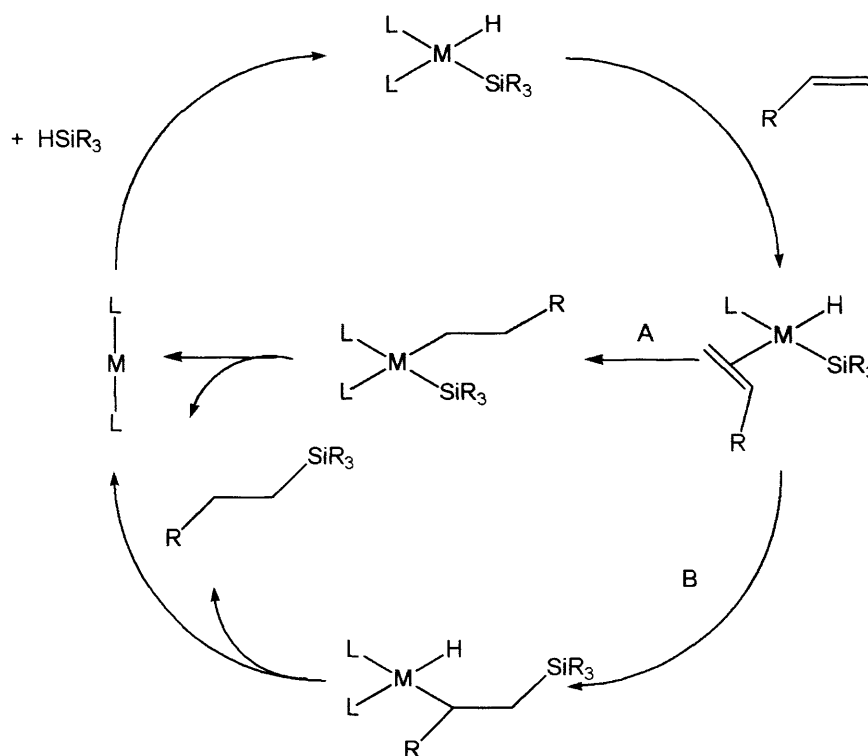
The Pt-catalysed hydrosilylation of alkenes generally leads to *anti*-Markovnikov products with high selectivity (**I**), although the Markovnikov products (**II**) are also observed (Scheme 1).^[6] The hydrosilylation of alkenes is often accompanied by side-reactions such as dehydrogenative silylation leading to product **III** and **IV**.^[11] In 1965, Chalk and Harrod proposed a mechanism for the hydrosilylation of alkenes catalyzed by Group 8 metal complexes.^[11] The first step of this mechanism is the oxidative addition of the hydrosilane to the transition metal complex. The alkene then inserts into the M-H bond, followed by reductive elimination of the Si-C bond to release the product (Scheme 2, route A). Later, in order to explain vinylsilane products **III**, a modified mechanism was proposed (Scheme 2, route B). In route B the alkene inserts into the M-SiR₃ bond, followed by C-H reductive elimination giving **II**. The intermediate [M(H)(CH₂CH₂SiR₃)L_n] is formed in this mechanism, from which β-H abstraction yields vinylsilane **III** which dissociates giving a M-hydride species that can subsequently hydrogenate one equivalent of alkene giving **IV** (Scheme 3).

In this Chapter the use of blocked functionalised imidazolium salts as ligands using an *in situ* protocol in the Pt-catalysed hydrosilylation of styrene with triethylsilane is investigated.

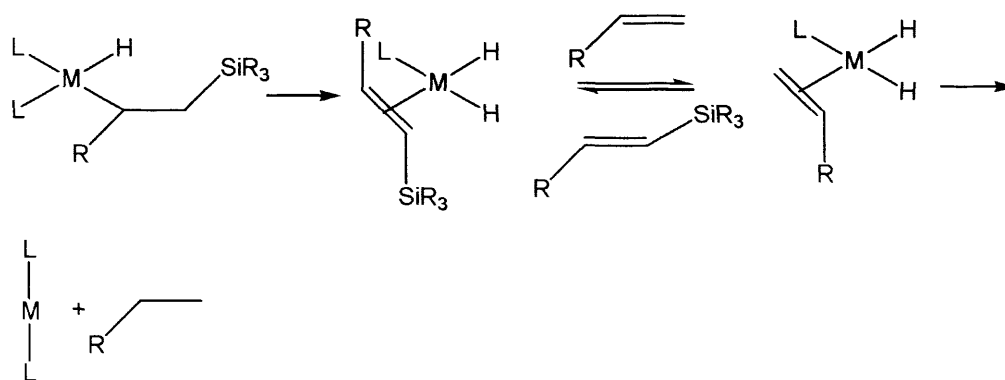
Scheme 1. Hydrosilylation and dehydrogenative silylation of alkene with triethylsilane.



Scheme 2. Chalk-Harrod (Route A) and modified Chalk-Harrod (Route B) mechanism for the hydrosilylation of alkenes.



Scheme 3. Formation of dehydrogenative silylation products.



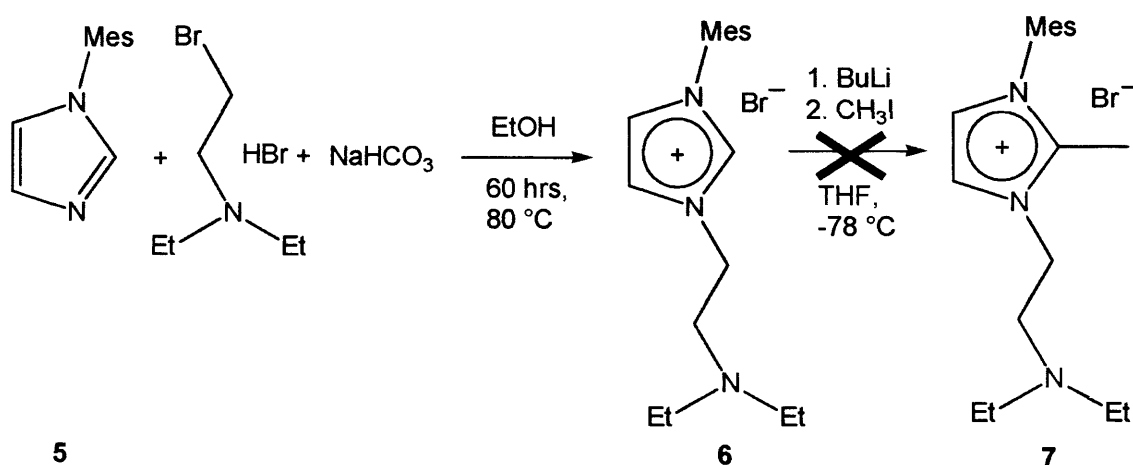
4.1 Results and Discussion

4.1.1 Synthesis of imidazolium salts functionalised with a diethylamino group

Functionalisation of NHC ligands with additional donor functionalities has led to efficient catalysts in alkylation,^[12] hydrogenation,^[13] hydrosilylation^[14] and olefin metathesis reactions.^[15] C₂-Blocked imidazolium salts have not been reported in hydrosilylation. A new C₂-blocked imidazolium salt with a donor functionalised side chain on one nitrogen and a bulky group on the other was desired for testing in catalytic hydrosilylation. It was also interesting to compare the catalytic behaviour toward hydrosilylation with the C₂-H analogues.

Reaction of 1-(2,4,6-trimethylphenyl)imidazole with 2-diethylaminoethyl bromide hydrobromide in the presence of NaHCO₃ in EtOH yielded 1-(2-diethylaminoethyl)-3-(2,4,6-trimethylphenyl)-2*H*-imidazolium bromide (**6**) as a pale yellow powder in 80% yield (Scheme 4). The ¹H NMR spectrum of **6** (d₆-DMSO) shows the C₂-H proton as a singlet at δ 9.77 and the C_{4,5}-H protons were observed as doublets at δ 8.08 and 7.91, respectively. The ¹³C{¹H} NMR spectrum showed signals for C₄, C₅ and C₂ at δ 129.58, 123.76 and 140.57, respectively.

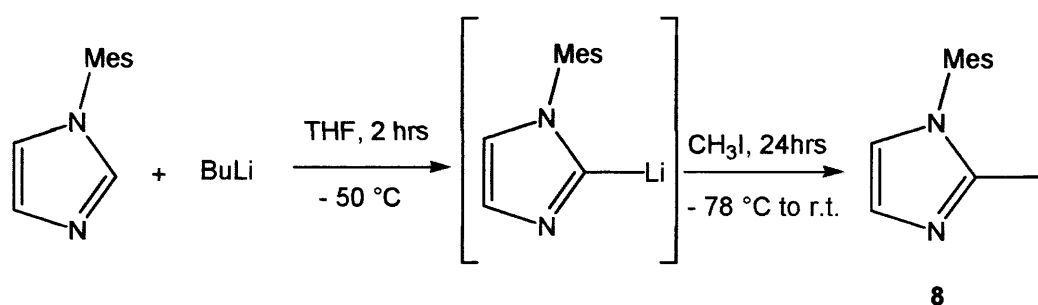
Scheme 4. Attempted synthesis of 1-(2,4,6-trimethylphenyl)-2-methyl-3-(2-diethylaminoethyl)imidazolium bromide from the 2-H salt.



Attempts to block the C₂-position by the further reaction of **6** with *n*-butyllithium and CH₃I failed (Scheme 5) as the diethylamino group nitrogen was also methylated. A strategy based

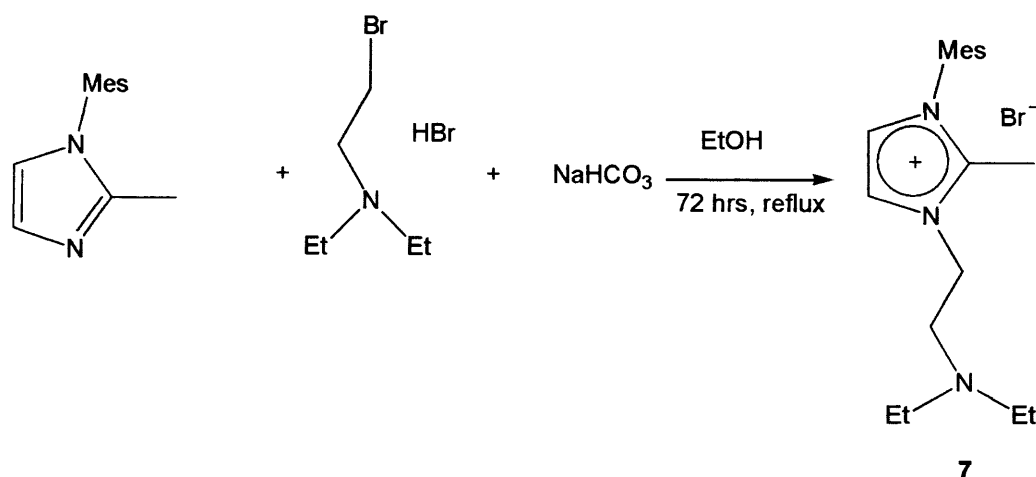
on blocking the C₂-position in the precursor (**5**) was thus adopted. The reaction of **5** with n-butyllithium at -50 °C for 2 hours followed by C₂-alkylation with a stoichiometric quantity of CH₃I at -78 °C resulted in the isolation of 1-(2,4,6-trimethylphenyl)-2-methylimidazole (**8**) in high yield (Scheme 5). The ¹H NMR spectrum (d₂-CD₂Cl₂) of **8** shows the C₂-CH₃ signal as a singlet at δ 2.25 with the C_{4,5}-H protons appearing as doublets at δ 7.10 and 6.74, respectively.

Scheme 5. Synthesis of 1-(2,4,6-trimethylphenyl)-2-methylimidazole.



Refluxing 1-(2,4,6-trimethylphenyl)-2-methylimidazole with 2-diethylaminoethyl bromide hydrobromide and NaHCO₃ in EtOH for 72 hours (Scheme 6) resulted in the isolation of imidazolium salt **7** as white powder in 78% yield. Compound **7** was characterised by ¹H and ¹³C NMR spectroscopy and gave a satisfactory high resolution mass determination.

Scheme 6. Synthesis of 1-(2,4,6-trimethylphenyl)-2-methyl-3-(2-diethylaminoethyl)imidazolium bromide.



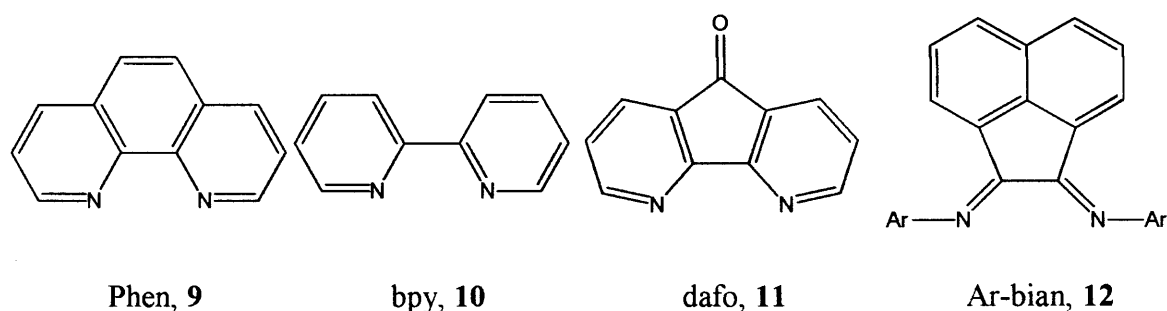
The ¹H NMR spectrum (d₆-DMSO) of **7** shows two doublets due to the C_{4,5}-H protons at δ 8.06 and 8.09, respectively. The ¹³C{¹H} NMR spectrum (d₂-CD₂Cl₂) of **7** showed two

signals for C₄ and C₅ at δ 124.37 and 122.33, respectively. The methylene carbon signals in the diethylamino-ethyl chain appear at δ 47.72 and 47.62.

4.1.2 Imidazolium salts as ligands in the hydrosilylation of styrene with triethylsilane

An *in situ* approach to obtain a Pt-imidazolium salt catalyst from Pt(nbe)₃ (nbe = norbornene) was followed. The weakly bound nbe ligands readily dissociate from the Pt⁰ centre generating active, coordinatively unsaturated Pt(0)-species. Pt(nbe)₃ has also been used as a precursor for hydrosilylation reactions with bidentate nitrogen-donor ligands such as 1,10-phenanthroline (**9**), 2,2'-bipyridyl (**10**), 4,5-diazafluoren-9-one (**11**) and bis(arylimino)acenaphthene (**12**) (Figure 3).^[16]

Figure 3. Cis-coordinating dinitrogen ligands.



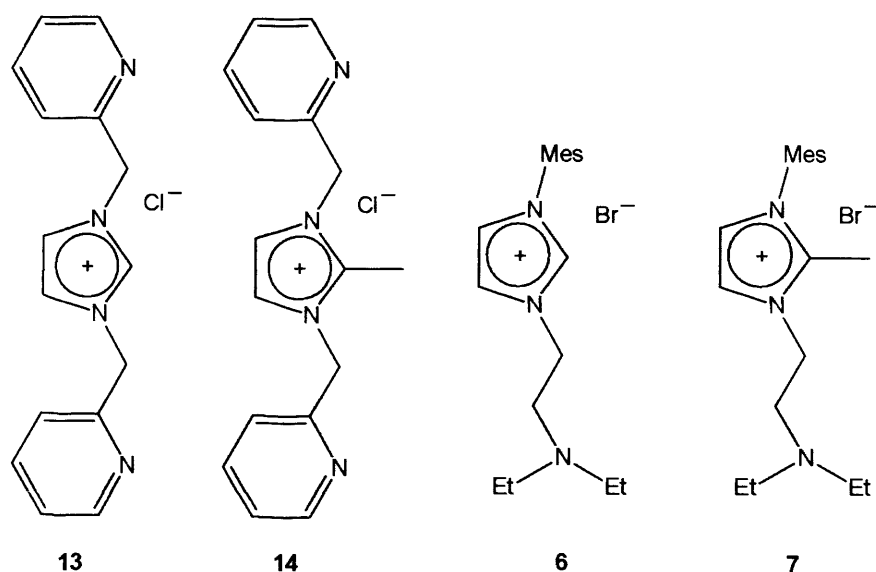
Nitrogen-donor ligands **9-12** are known to stabilise Pt(0) compounds when coordinated in a bidentate manner^[17] but ligands **11** and **12** can give rise to free coordination sites due to their hemilability.^[18, 19] For example, crystal structures of [Pd(η^3 -C₃H₈C(O)Me)(Cl)(*p*-MeO-C₆H₄-bian)]^[18] and [Pd(dafo)(η^2 -naphthoquinone)]^[19] have been obtained in which both α -diimine ligands adopt the η^1 -coordinated structure. In general, ligands that form more stable Pt(0) complexes result in a lower catalytic activity and generate somewhat more dehydrogenative silylation products compared to ligands which form less stable complexes. For example, **9** promotes hydrosilylation slowly at 100 °C, while **11** shows high catalytic activity at 30 °C, with the amount of dehydrogenative silylation product correspondingly decreasing for the latter ligand.^[16]

In light of this result, N-functionalised C₂-H and C₂-blocked imidazolium salts **6**, **7**, **13** and **14** (see chapter 3) were tested in the hydrosilylation of styrene by triethylsilane using an *in*

Chapter 4. Hydrosilylation of styrene catalysed by *in situ* Pt(0)/Imidazolium salts

situ formed catalyst with $\text{Pt}(\text{nbe})_3$ as Pt source (Figure 4). The limited solubility of the imidazolium salts in toluene necessitated a premixing time of 60 min in the presence of base, prior to start the catalysis, to allow for the formation of the catalytically active complex. The catalytic hydrosilylation of styrene with triethylsilane using blocked and unblocked imidazolium salts yielded products **I**, **III** and **IV** (Scheme 7), results are given in Table 1.

Figure 4. Imidazolium salts tested in the hydrosilylation of styrene with triethylsilane.



Scheme 7. Hydrosilylation and dehydrogenative silylation products of styrene with triethylsilane

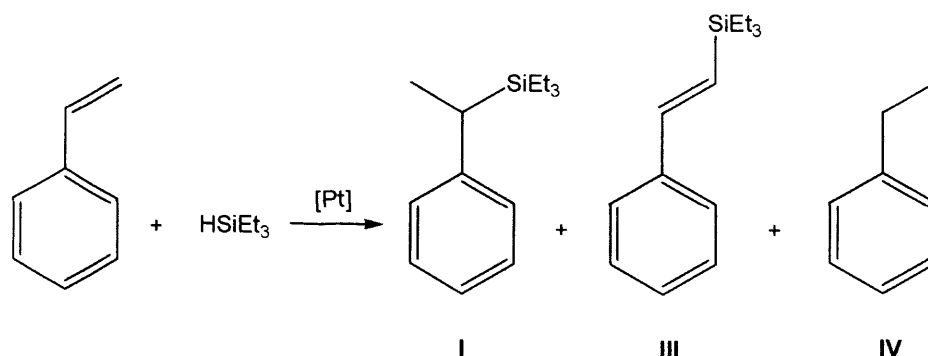


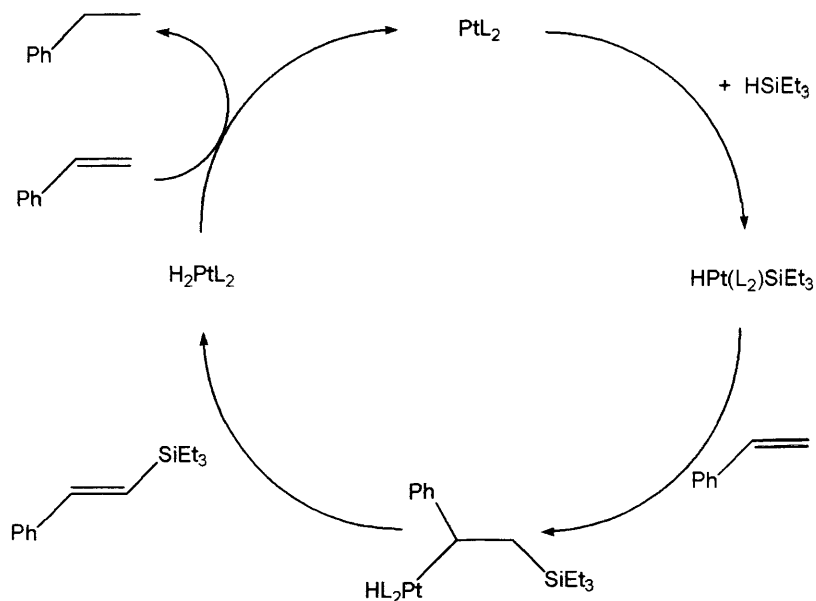
Table 1. Hydrosilylation of styrene with triethylsilane

Entry	Ligand	C-Si bond Yield [%] I + III	Selectivity [%] I : III:IV
1*	6	40	82 : 8 : 10
2	7	85	5 : 83 : 12
3	13	1	32 : 8 : 60
4	14	4	32 : 50 : 18

Conditions: 1% mol catalyst. *0.1% mol catalyst, styrene/triethylsilane ratio 1.0, 120 °C, toluene. Combined GC-MS yield of products, based on consumed styrene, I, III and IV after 12* and 24 hrs using *n*-decane as internal standard.

When one equivalent of 1-(2-diethylaminoethyl)-3-(2,4,6-trimethyl-phenyl)-2*H*-imidazolium bromide (**6**) (Table 1, entry 1) was used as ligand with 0.1 mol % of Pt(*n*be)₃, hydrosilylation yielded the *anti*-Markovnikov product (**I**) and the dehydrogenative silylation product (**II**); selectivity 10 : 1. Ethylbenzene (**III**) was also formed in similar proportion to the unsaturated silyl product (**II**) by hydrogenation of styrene (Scheme 8). No significant catalyst decomposition (formation of colloidal Pt) was observed.

Completely different catalytic behaviour was observed when C₂-blocked imidazolium salt **7** (Table 1, entry 2) was used as ligand with 1 mol % of Pt(*n*be)₃, hydrosilylation yielded the dehydrogenative silylation product (**II**) as major product, together with the *anti*-Markovnikov product (**I**); selectivity 16.6 : 1. The increased amount of dehydrogenative silylation for entry 2, ligand **7** (Table 1) might be explained by invoking the C₅-coordination to the Pt center. The catalyst was generated by stirring ligand **7**, Pt(*n*be)₃ and 2 equivalent of KO^tBu. It is possible that the base deprotonated the C₅-H position and the resulting catalytic active species favour the synthesis of compound **II**. It has been proposed that dehydrogenative silylation is initiated by β-hydride elimination after the insertion of the styrene into the platinum–silicon bond (Scheme 8).

Scheme 8. Dehydrogenative silylation of styrene.

For comparison, 1,3-di(2-picolyl)-2-imidazolium chloride (**13**) (Table 1, entry 3) and 1,3-di(2-picolyl)-2-methylimidazolium chloride (**14**) (Table 1, entry 4), potentially strong chelating ligands to platinum, were also tested in hydrosilylation of styrene with triethylsilane, using 1 mol % of $Pt(nbe)_3$. Compounds **13** and **14** show a reduced activity with respect to compounds **6** and **7** (Table 1, entries 1 and 2, respectively), perhaps because the catalytic active species results in a complex that is coordinatively saturated. Compounds **13** and **14** are tridentate ligands that may block sites on the Pt-NHC active catalyst required for substrate binding. The predominant product for **13** is the ethylbenzene.

The dehydrogenative silylation product (**III**) is the major product observed when using the C_2 -blocked imidazolium salt **14**, while the *anti*-Markovnikov product (**I**) is the major one in the presence of **13** considering the C-Si bond products formed. The difference in efficiency between compounds **7** and **14** (entry 2 and 4, Table 1) and **6** and **13** (entry 1 and 3, Table 1) can be rationalised in terms of differences in coordination characteristics of the 1-(2-diethylamino-ethyl)group and pyridyl groups, the 1-(2-diethylamino-ethyl)group is more flexible and less nucleophilic and can readily dissociate from Pt to adopt the η^1 -coordinate structure.

Elsevier *et al* reported the use of Pt(0) complexes derived from bulky unsaturated and saturated non functionalised carbenes in the hydrosilylation of styrene with triethylsilane, and found the reaction to proceed with high selectivity yielding products **II** and **I**, only a

small amounts of products **III** was formed (Scheme 9) Table 2 (entry 1 and 2).^[6] The improved activity of Pt complexes derived from SIMes·HCl (1,3-dimesityl-4,5-dihydroimidazolium chloride) relative to its unsaturated analogue IMes·HCl (1,3-dimesitylimidazolium chloride) was explained by the difference in σ -donor strength between these two ligands. Interestingly, the main product formed **II** was not observed using ligands **6**, **7**, **13** and **14** (Table 1). Using [Pt(IMes)₂] (entry 3, table 2) as catalyst, low activity was observed (< 2 %), together with a high degree of dehydrogenative silylation (**III** = 53.1 %). Apparently, two bulky and strong σ -donor carbene ligands coordinated to the Pt center results in a complex that is too stable for effective catalytic hydrosilylation.

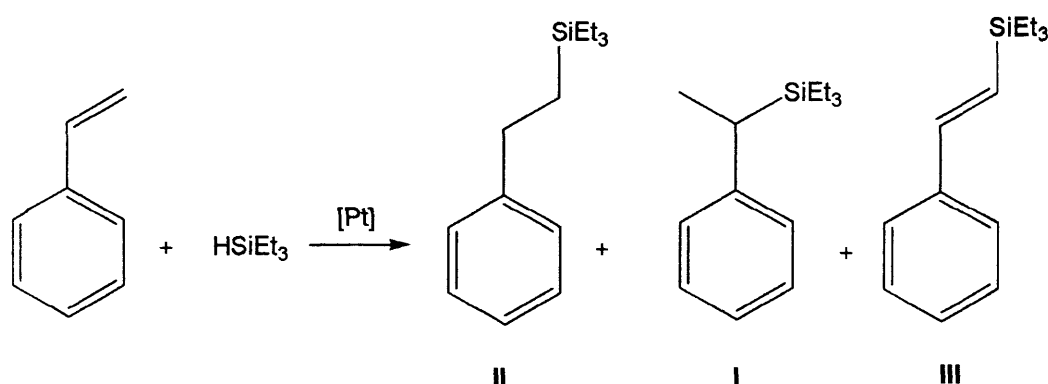


Table 2. Hydrosilylation of styrene with triethylsilane with *in situ* generated Pt-NHC catalysts.^[6]

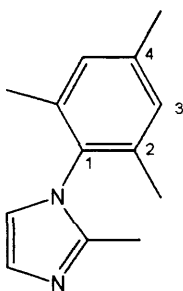
Entry	Ligand	Yield [%] (II + I + III)	Selectivity [%] II : I : III
1	[Pt(nbe) ₃] + SIMes·HCl	> 99	82.5 : 17.2 : 0.3
2	[Pt(nbe) ₃] + IMes·HCl	31.2	78.3 : 15.9 : 5.8
3	[Pt(IMes) ₂]	< 2	35.3 : 11.6 : 53.1

Conditions: 1% mol catalyst, styrene/triethylsilane ratio 1.0, 100 °C, toluene. Pt complex stirred with 1 equivalent of imidazolium salt and 2 equivalents of K^tOBu for 1 hr prior to catalysis. Total GC-yield after 3 hrs using *n*-decane as internal standard.

4.3 Experimental Section

All procedures were performed using standard Schlenk techniques, under an atmosphere of dry argon or in a nitrogen glove box. Glassware was dried overnight in an oven at 120°C or flame dried prior to use. THF, hexane and Et₂O were distilled from sodium benzophenone, toluene from sodium metal and CH₂Cl₂ from CaH₂. The solvents were freshly distilled under nitrogen immediately prior to use. Acetone was dried over activated B₂O₃, stirred overnight at room temperature and then distilled under argon and stored in a Schlenk bottle. *d*₂-Dichloromethane and *d*₆-benzene were degassed via standard freeze/pump/thaw methods and then dried using the appropriate drying agent. *d*₂-Dichloromethane was dried over 4Å molecular sieves and *d*₆-benzene by reflux over sodium potassium alloy and vacuum transferred into a young Schlenk flask. NMR spectra were recorded at 295 K on a Bruker 400 or 500 MHz spectrometers, with chemical shifts (δ) reported in ppm relative to the residual proton chemical shifts of the internal deuterated solvent (¹H and ¹³C) set relative to external TMS. GC-MS analyses were carried out with a Agilent 5973N apparatus equipped with a column HP5-MS (30 m x 0.55 mm x 25mm) with n-decane as internal standard.

Synthesis of 1-(2,4,6-trimethylphenyl)-2-methylimidazole (8).



To 1.00 g (5.37 mmol) of 1-(2,4,6-trimethylphenyl)-2-methylimidazole was added 20 mL of THF. The solution was cooled to -50 °C, after which 2.6 mL (5.9 mmol) of *n*-butyllithium (2.25 M in Et₂O) was added dropwise. The mixture was stirred for 3 hours, after which it was cooled to -78 °C and CH₃I (0.38 mL, 5.37 mmol) added dropwise. The mixture was stirred until the temperature reached 15 °C, then the solvent was evaporated *in vacuo* giving a transparent oil. The oil was dissolved in DCM and filtered over Celite, the solvent was evaporated *in vacuo* and the white powder obtained washed with hexane and dried *in vacuo* giving 0.989 g of a white solid. (Yield: 92%).

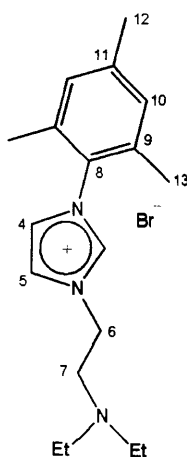
Chapter 4. Hydrosilylation of styrene catalysed by *in situ* Pt(0)/Imidazolium salts

HRMS [$C_{13}H_{17}N_2$]: Found m/z 201.1392 Da (0.5 ppm from calculated)

1H NMR (400 MHz, CD_2Cl_2): δ 7.10 (d, $J = 1.42$ Hz, 1H, CH_{imid}), 6.92 (s, 2H, CH_{mes}), 6.74 (d, $J = 1.42$ Hz, 1H, CH_{imid}), 2.25 (s, 3H, CH_{3imid}), 2.10 (s, 3H, CH_{3mes}), 1.84 (s, 6H, CH_{3mes}).

$^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2): δ 146.39 (NCN), 139.62 ($C_{(4)mes}$), 135.71 ($C_{(1)mes}$), 133.19 ($C_{(2)mes}$), 129.51 ($C_{(3)mes}$), 128.25 (C_{4imid}), 120.13 (C_{5imid}), 21.16 (CH_{3mes}), 17.47 (CH_{3mes}), 13.19 (CH_{3imid}).

Synthesis of 1-(2,4,6-trimethylphenyl)-3-(2-diethylaminoethyl)imidazolium bromide (6).



2-Diethylaminoethyl bromide hydrobromide (0.70 g, 2.68 mmol), 1-(2,4,6-trimethylphenyl)imidazole (0.50 g, 2.68 mmol) and $NaHCO_3$ (0.343 g, 4.1 mmol) were taken up in 15 mL of ethanol and the mixture refluxed for 4 days. The solvent was then removed *in vacuo*, the residue taken up in 10 mL of DCM and the solution filtered over Celite. Removal of the solvent *in vacuo* gave an oil that was washed two times with 10 mL of Et_2O and triturated with THF to give 0.785 g of a pale yellow powder that was washed with THF and Et_2O and dried *in vacuo*. Yield: 80%

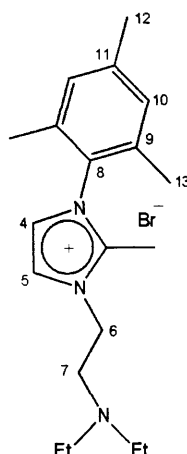
Anal. Calc. for $C_{18}H_{28}N_3Br$; C: 59.01 H: 7.70 N: 11.47% Found; C: 58.86 H: 7.64 N: 11.23%. HRMS [$C_{18}H_{28}N_3-Br$] $^+$: Found m/z 286.2283 Da (0.0 ppm from calculated).

1H NMR (400 MHz, d_6 -DMSO): δ 9.77 (s, 1H, CH_{2imid}), 8.08 (d, $J = 1.48$ Hz, 1H, CH_{4imid}), 7.91 (d, $J = 1.48$ Hz, 1H, CH_{5imid}), 7.21 (s, 2H, CH_{Mes}), 4.32 (t, $J = 5.31$ Hz, 2H, $CH_{2(6)}$), 2.79 (t, $J = 5.31$ Hz, 2H, $CH_{2(7)}$), 2.50 (q, $J = 7.08$ Hz, 4H, CH_{2Et}), 2.34 (s, 3H, CH_{3mes}), 2.02 (s, 6H, CH_{3mes}), 0.86 (t, $J = 7.08$ Hz, 6H, CH_{3Et}).

Chapter 4. Hydrosilylation of styrene catalysed by *in situ* Pt(0)/Imidazolium salts

$^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, d_6 -DMSO): δ 140.57 (NCN), 137.99 ($\text{C}_{11\text{mes}}$), 134.65 ($\text{C}_{8\text{mes}}$), 131.55 ($\text{C}_{9\text{mes}}$), 129.59 ($\text{CH}_{10\text{mes}}$), 129.58 ($\text{C}_{4\text{imid}}$), 123.76 ($\text{C}_{5\text{imid}}$), 52.07 ($\text{CH}_{2(6)}$), 48.12 ($\text{CH}_{2(7)}$), 46.38 ($\text{CH}_{2\text{Et}}$), 20.93 ($\text{CH}_{3(12\text{mes})}$), 17.15 ($\text{CH}_{3(13\text{mes})}$), 12.18 ($\text{CH}_{3\text{Et}}$)

Synthesis of 1-(2,4,6-trimethylphenyl)-2-methyl-3-(2-diethylaminoethyl)imidazolium bromide (7).



2-Diethylaminoethyl bromide hydrobromide (0.75 g, 2.75 mmol), 1-(2,4,6-trimethylphenyl)2-methylimidazole (0.50 g, 2.5 mmol) and NaHCO_3 (0.361 g, 4.3 mmol) were taken up in 15 mL of ethanol and the mixture refluxed for 2.5 days. The solvent was removed *in vacuo*, the residue taken up in 10 mL of DCM and the solution filtered over celite. Removal of the solvent *in vacuo* gave an oil that was washed two times with 10 mL of Et_2O and triturated with THF to give a white powder that was further washed with THF and Et_2O and dried *in vacuo*. Yield: 78%, 0.742 g.

Anal. Calc. for $\text{C}_{19}\text{H}_{30}\text{N}_3\text{Br}$; C: 60 H: 7.95 N: 11.053% Found; C: 50.31 H: 7.08 N: 8.99%.

HRMS [$\text{C}_{19}\text{H}_{30}\text{N}_3\text{Br}$] $^+$: Found m/z 300.2426 Da (-4.7 ppm from calculated).

^1H NMR (400 MHz, CD_2Cl_2): δ 7.86 (d, $J = 1.94$ Hz, 1H, $\text{CH}_{4\text{imid}}$), 7.29 (d, $J = 1.94$ Hz, 1H, $\text{CH}_{5\text{imid}}$), 7.11 (s, 2H, CH_{mes}), 4.44 (t, $J = 5.07$ Hz, 2H, $\text{CH}_{2(6)}$), 2.86 (t, $J = 5.07$ Hz, 2H, $\text{CH}_{2(7)}$), 2.49 (q, $J = 6.99$ Hz, 4H, $\text{CH}_{2\text{Et}}$), 2.42 (s, 3H, $\text{CH}_{3\text{imid}}$), 2.29 (s, 3H, $\text{CH}_{3\text{mes}}$), 1.92 (s, 6H, $\text{CH}_{3\text{mes}}$), 0.86 (t, $J = 6.99$ Hz, 6H, $\text{CH}_{3\text{Et}}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (400 MHz, CD_2Cl_2): δ 145.87 (s, NCN), 142.43 ($\text{C}_{11\text{mes}}$), 135.50 ($\text{C}_{8\text{mes}}$), 130.80 ($\text{C}_{9\text{mes}}$), 130.73 ($\text{CH}_{10\text{mes}}$), 124.37 ($\text{C}_{4\text{imid}}$), 122.33 ($\text{C}_{5\text{imid}}$), 53.95 ($\text{CH}_{2(6)}$), 47.72 ($\text{CH}_{2(7)}$), 47.62 ($\text{CH}_{2\text{Et}}$), 21.68 ($\text{CH}_{3(12\text{mes})}$), 18.20 ($\text{CH}_{3(13\text{mes})}$), 12.35 ($\text{CH}_{3\text{Et}}$), 9.05 ($\text{CH}_{3\text{imid}}$).

General procedure for the hydrosilylation of styrene with triethylsilane.

0.05 mmol of Pt(nbe)₃, 1 equivalent of the desired imidazolium salt and 2 equivalents of KO^tBu were stirred for 1 hr. at r.t in 20 mL of toluene. Then 0.58 mL of styrene (5 mmol), 0.58 mL of dioxane (3 mmol) as internal standard and 0.80 mL of triethylsilane (5 mmol) were syringed in. The schlenk was immediately immersed in a 120 °C oil bath. Samples were taken periodically for GC-MS analysis.

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Chapter 4. Hydrosilylation of styrene catalysed by *in situ* Pt(0)/Imidazolium salts

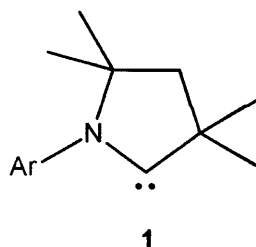
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Chapter Five

Attempts to isolate a free 'abnormal' NHC

Free imidazolin-4(5)-ylidene ligands have not yet been reported. However, Bertrand *et al.* recently succeeded in preparing the first stable cyclic alkylaminocarbenes (CAACs) (**1**) (Figure 1).^[1] The replacement of one electronegative amino substituent of imidazolidin-2-ylidene by a σ -donating alkyl group makes the CAAC ligands more electron rich than phosphines or even the parent NHC ligands.^[1] Furthermore the presence of the tertiary carbon next to the carbene centre offers the possibility of constructing ligands with different steric environments compared to NHCs. Similarly, for free imidazolin-4-ylidene ligands the presence of an easy functionalised nitrogen atom distal to the carbenic centre could offer new possibilities for the design of multidentate or polymer bound imidazolin-4-ylidene ligands.

Figure 1. First reported stable cyclic alkylaminocarbene.^[1]



Ar = 2,6-diisopropylphenyl

Recent studies by Crabtree *et al.* on the electronic and steric properties of Ir(NHC) complexes showing the $C_{4,5}$ coordination mode for a series of NHCs (including one case in which the C_2 position had been blocked) confirmed the stronger electron-donor properties of C_4 -NHC ligands compared to phosphines and C_2 -NHCs.^[2] The carbonyl stretching frequencies [$\nu(\text{CO})$] of selected $\text{IrCl}(\text{NHC})(\text{CO})_2$ complexes was determined to be an indirect measure of the electron density transferred from the NHC ligand to the carbonyl through the metal. Thus, a transmetalation reaction from the corresponding silver-NHC salt to $[\text{Ir}(\mu\text{-Cl})(\text{COD})]_2$ afforded complexes **2** and **4**

(Scheme 1). The COD was easily displaced from these complexes by CO at 1 atm to give the corresponding dicarbonyl compounds **3** and **5** (Scheme 1). A plot of the IR $\nu(\text{CO})$ stretching frequencies for $\text{IrCl}(\text{L})(\text{CO})_2$ (L = NHC or phosphine) indicates that the donor power of the abnormal carbene in complex **3** ($\nu_{\text{av}}(\text{CO}) = 2003 \text{ cm}^{-1}$) is higher than that of electron-rich phosphines (e.g. PCy_3 ; $\nu_{\text{av}}(\text{CO}) = 2028 \text{ cm}^{-1}$) and the 'normal' NHC in complex **5** ($\nu_{\text{av}}(\text{CO}) = 2017 \text{ cm}^{-1}$).^[2] Bertrand *et al.* have also reported the carbonyl stretching frequencies for analogous complex **6** ($\nu_{\text{av}}(\text{CO}) = 2013 \text{ cm}^{-1}$) bearing a CAAC ligand (Figure 2).^[1] These studies indicate that the abnormally bound NHC ligand is a substantially stronger electron-donor to late transition metals than even the CAACs.

Scheme 1. Synthesis of $(\text{NHC})\text{Ir}(\text{CO})_2\text{Cl}$.^[2]

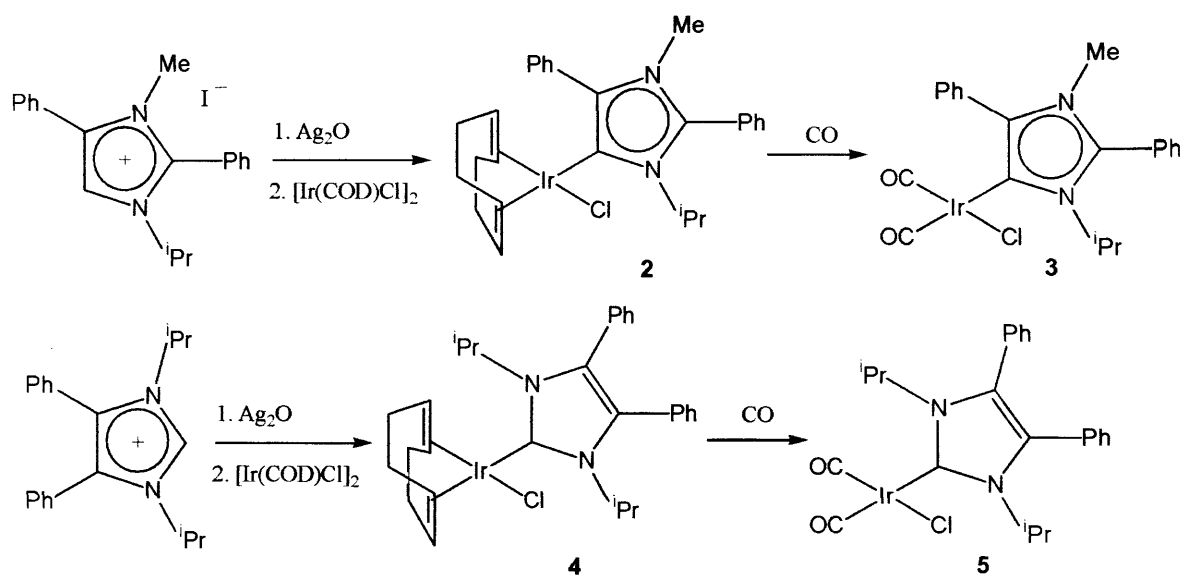
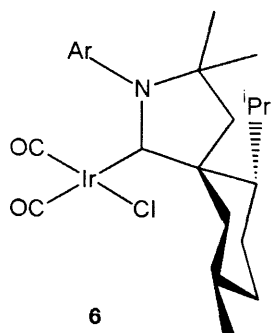


Figure 2. $\text{IrCl}(\text{CAAC})(\text{CO})_2$ used in IR study of ligand donor ability.^[1]

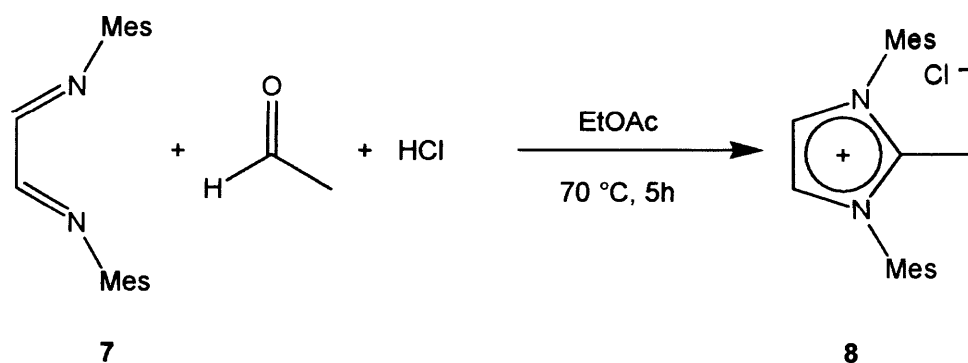


The C₄-Ir site in complex **2** likely has more electron density at the carbenic carbon than the C₂-NHC due to one nitrogen being replaced by a C-Ph group with a reduced electron withdrawing inductive effect. This may account for the greater donating ability of the abnormal carbene and the fact that free C_{4,5}-NHCs have not yet been reported. However, in Bertrand's CAACs the replacement of one of the electronegative amino substituents of NHCs by σ -donating alkyl group does not prevent the CAAC ligands being stable enough to be isolated.

5.1 Results and discussion

A C₂-blocked imidazolium salt with two mesityl groups at the nitrogens was considered a suitable substrate to study if the resulting free abnormal carbene could be isolated. C₂-Blocked imidazolium **8** was therefore synthesised from the corresponding diimine **7** using acetaldehyde to close the ring in the presence of HCl at 70 °C (Scheme 2). Compound **8** was isolated as a white solid in 73% yield and was characterised by ¹H and ¹³C{¹H} NMR spectroscopy, microanalysis and high resolution mass spectrometry. The ¹H NMR spectrum of **8** displayed a singlet due to C_{4,5}-H protons at δ 7.67 and the C₂-CH₃ singlet at δ 2.11. The ¹³C{¹H} NMR spectrum of **8** showed a signal due to C_{4,5} at δ 124.65.

Scheme 2. Synthesis of 1,3-dimesityl-2-methylimidazolium chloride.

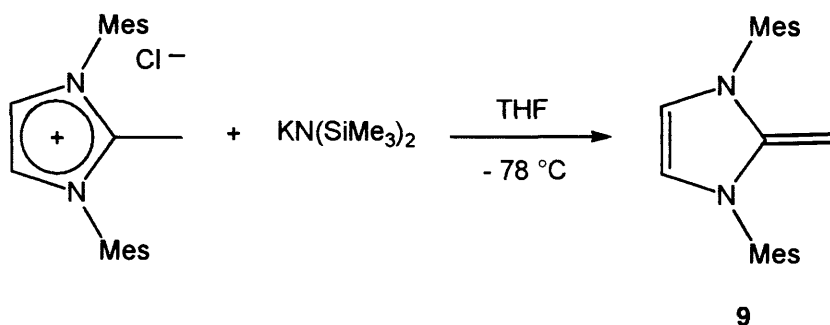


The strategy adopted to isolate the abnormal free carbene was to use a base to deprotonate the C₄-position in the blocked imidazolium salt **8**. The reaction was performed at -78 °C in THF using KN(SiMe₃)₂ as base, concentration of the solution

Chapter 5. Attempts to isolate a free abnormal NHC

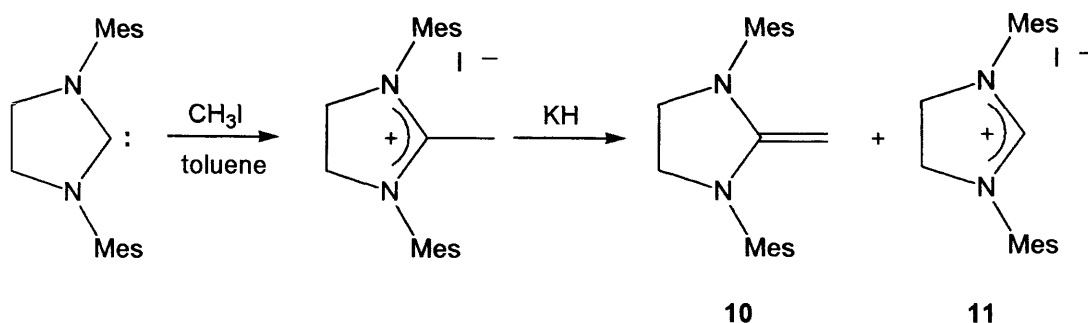
and extraction with toluene resulted in the isolation of a pale light yellow powder in 80% yield. Surprisingly, spectroscopic analyses revealed the formation of 2-methylene-1,3-dimesityl-2,3-dihydro-1H-imidazole (**9**) resulting from deprotonation at the C₂-methyl group, instead of the desired C₄-H position (Scheme 3). Compound **9** was characterised by ¹H and ¹³C{¹H} NMR spectroscopy and high resolution mass spectrometry. The ¹H NMR spectrum of **9** displayed a singlet at δ 5.83 due to the methylene protons, and a singlet due to C_{4,5}-H protons at δ 7.27. The ¹³C{¹H} NMR spectrum of **9** showed signals at δ 113.46 due to C_{4,5} and δ 41.48 ppm due to the new methylene carbon.

Scheme 3. Attempt to isolate a free abnormal carbene, giving instead **9**.



Arduengo *et al.* reported the synthesis of 2-methylene-1,3-bis(2,4,6-trimethylphenyl)-imidazolidine (**10**), the saturated version of **9** (Scheme 4).^[3] Reaction of SIMes with CH₃I proceeds rapidly to alkylate the carbene centre and produce a 2-methylimidazolium ion that in the presence of a base affords olefins **10** and the corresponding imidazolium salt **11**.^[3]

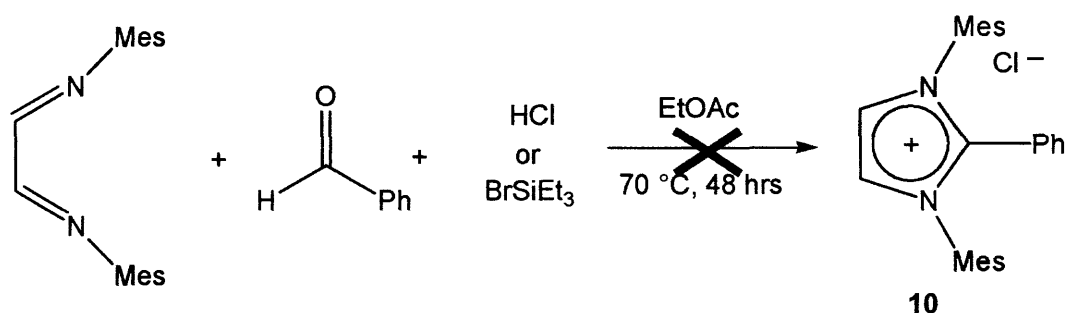
Scheme 4. Synthesis of 2-methylene-1,3-bis(2,4,6-trimethylphenyl)-imidazolidine.^[3]



Chapter 5. Attempts to isolate a free abnormal NHC

As blocking the C₂-position with a methyl group was found to be ineffective an imidazolium salt immune to deprotonation at the C₂-substituent was desired to give a chance of deprotonation at the C₄-H position. Starting from diimine **7**, benzaldehyde was substituted for acetaldehyde, using the same reaction conditions that gave **8**. However, closure was not observed, perhaps for steric reasons. Also, no reaction was observed on using HCl instead of bromotrimethylsilane as an acid source.

Scheme 4. Attempts to synthesise 1,3-dimesityl-2-phenylimidazolium chloride.



In conclusion, although the attempts to isolate the free abnormal carbene were unsuccessful, a better understanding of the blocking group requirements for the C₂-position was achieved. Further work could also consider blocking the C₅ position with a σ -donating alkyl bulky group, as observed for Bertrands CAACs, in order to protect or stabilise the desired carbenic centre.

5.2 Experimental section

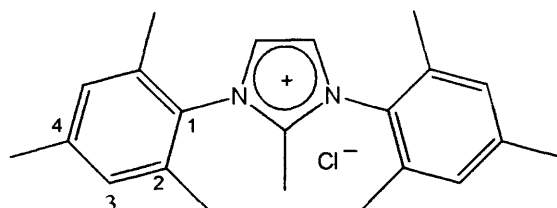
All procedures were performed using standard Schlenk techniques, under an atmosphere of dry argon or in a nitrogen glove box. Glassware was dried overnight in an oven at 120 °C or flame dried prior to use. THF, hexane and Et₂O were distilled from sodium benzophenone, toluene from sodium metal, and CH₂Cl₂ from CaH₂, under nitrogen immediately prior to use. Acetone was stirred overnight at room temperature over B₂O₃, and then distilled under argon and stored in a Schlenk bottle. *d*₂-Dichloromethane and *d*₆-benzene were degassed via standard freeze/pump/thaw methods and then dried using the appropriate drying agent. *d*₂-Dichloromethane was dried over 4Å molecular sieves and *d*₆-benzene by reflux over sodium potassium alloy and vacuum transferred into a young Schlenk flask. NMR spectra were recorded at r.t.



Chapter 5. Attempts to isolate a free abnormal NHC

on Bruker 400 or 500 MHz Avance spectrometers, with chemical shifts (δ) reported in ppm relative to the residual proton chemical shifts of the internal deuterated solvent (^1H and ^{13}C) set relative to external TMS.

Synthesis of 1,3-dimesityl-2-methylimidazolium chloride (8).

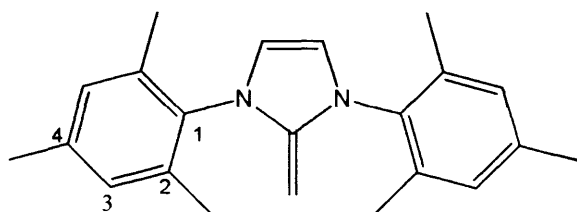


To a solution of 1,4 mesityl dimine (1.00 g, 3.42 mmol) in 30 ml of EtOAc was added a solution of acetaldehyde (0.151 g, 3.96 mmol) and HCl 2M in Et₂O (1.5 ml, 3.4 mmol) in 10 mL of EtOAc. The solution was heated to 70°C for 5hrs, during which time the colour of the reaction turned brown and a light brown precipitate was formed. The mixture was filtrate and the solid recrystallised from DCM-Et₂O. Yield 0.886 g, 73%.

Anal. Calc. for C₂₂H₂₇N₂Cl; C: 74.45 H: 7.67 N: 7.89%, Found; C: 69.98 H: 7.49 N: 7.39% HRMS [C₂₂H₂₇N₂-Cl]⁺: Found *m/z* 319.2161 Da (-4.1 ppm from calculated). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.67 (s, 2H, CH_{imid}), 7.09 (s, 4H, CH_{mes}), 2.32 (s, 6H, CH_{3mes}), 2.11 (s, 3H, CH_{3imid}), 2.02 (s, 12H, CH_{3mes}).

¹³C{¹H} NMR (400 MHz, CD₂Cl₂): δ 142.65 (NCN), 134.61 (C_{(1)mes}), 134.58 (C_{(4)mes}), 130.69 (C_{(2)mes}), 129.97 (C_{(3)mes}), 124.65 (C_{4,5-H}), 21.35 (CH_{3mes}), 17.74 (CH_{3mes}), 10.45 (CH₃).

Synthesis of 2-methylene-1,3-dimesityl-2,3-dihydro-1H-imidazole (9).



Chapter 5. Attempts to isolate a free abnormal NHC

A solution of KN(SiMe₃) (0.124 g, 6.19 mmol) in 10 mL of THF was added at -78 °C to a stirred solution of 1,3-dimesityl-2-methylimidazolium chloride (0.200 g, 5.63 mmol) in 10 mL of THF. The solution was warmed to -10 °C and the solvent evaporated *in vacuo*. Extraction of the residue with toluene afforded 0.143 g of compound **9** in 80% yield.

¹H NMR (400 MHz, C₆D₆): δ 7.27(s, 2H, CH_{imid}), 6.89 (s, 4H, CH_{mes}), 5.83 (s, 2H, CH₂), 2.32 (s, 12H, CH_{3mes}), 2.23 (s, 6H, CH_{3mes}).

¹³C{¹H} NMR (400 MHz, C₆D₆): δ 148.99 (NCN), 138.10 (C_{(1)mes}), 135.17 (C_{(4)mes}), 130.26 (C_{(2)mes}), 129.69 (C_{(3)mes}), 113.46 (CH_{imi}), 41.48 (CH₂), 21.45 (CH_{3mes}), 18.67 (CH_{3mes}).

5.3 References

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Tables of Bond Distances and Angles

Table A.1. Bond lengths [Å] and angles[°] for

Pt(IMes)(1,2-dimethyl-3-propyl-imidazolin-4-ylidene)HBr complex 9' (See chapter 2).

O(1)-C(2)	1.239(13)	C(110)-H(11A)	0.9800
C(1)-C(2)	1.477(18)	C(110)-H(11B)	0.9800
C(1)-H(1A)	0.9800	C(110)-H(11C)	0.9800
C(1)-H(1B)	0.9800	C(111)-H(11D)	0.9800
C(1)-H(1C)	0.9800	C(111)-H(11E)	0.9800
C(2)-C(3)	1.419(16)	C(111)-H(11F)	0.9800
C(3)-H(3A)	0.9800	C(112)-H(11G)	0.9800
C(3)-H(3B)	0.9800	C(112)-H(11H)	0.9800
C(3)-H(3C)	0.9800	C(112)-H(11I)	0.9800
C(11)-N(12)	1.368(10)	C(113)-C(118)	1.362(12)
C(11)-N(11)	1.391(10)	C(113)-C(114)	1.400(12)
C(11)-Pt(11)	1.987(8)	C(113)-N(11)	1.446(11)
C(12)-C(13)	1.360(12)	C(114)-C(115)	1.391(13)
C(12)-N(11)	1.383(11)	C(114)-C(119)	1.478(12)
C(12)-H(12)	0.9500	C(115)-C(116)	1.386(13)
C(13)-N(12)	1.364(10)	C(115)-H(115)	0.9500
C(13)-H(13)	0.9500	C(116)-C(117)	1.390(12)
C(14)-C(19)	1.385(12)	C(116)-C(120)	1.519(13)
C(14)-C(15)	1.405(12)	C(117)-C(118)	1.385(12)
C(14)-N(12)	1.438(11)	C(117)-H(117)	0.9500
C(15)-C(16)	1.376(12)	C(118)-C(121)	1.529(12)
C(15)-C(110)	1.528(13)	C(119)-H(11J)	0.9800
C(16)-C(17)	1.400(14)	C(119)-H(11K)	0.9800
C(16)-H(16)	0.9500	C(119)-H(11L)	0.9800
C(17)-C(18)	1.385(14)	C(120)-H(12A)	0.9800
C(17)-C(111)	1.518(13)	C(120)-H(12B)	0.9800
C(18)-C(19)	1.379(12)	C(120)-H(12C)	0.9800
C(18)-H(18)	0.9500	C(121)-H(12D)	0.9800
C(19)-C(112)	1.512(13)	C(121)-H(12E)	0.9800

Appendix 2. Tables of Bond Distances and Angles

C(121)-H(12F)	0.9800	C(24)-C(29)	1.395(12)
C(122)-C(123)	1.377(11)	C(24)-N(21)	1.452(11)
C(122)-N(14)	1.425(11)	C(25)-C(26)	1.394(13)
C(122)-Pt(11)	2.041(8)	C(25)-C(210)	1.521(13)
C(123)-N(13)	1.392(10)	C(26)-C(27)	1.370(15)
C(123)-H(123)	0.9500	C(26)-H(26)	0.9500
C(124)-N(13)	1.466(10)	C(27)-C(28)	1.392(15)
C(124)-H(12G)	0.9800	C(27)-C(211)	1.518(14)
C(124)-H(12H)	0.9800	C(28)-C(29)	1.413(13)
C(124)-H(12I)	0.9800	C(28)-H(28)	0.9500
C(125)-N(13)	1.312(11)	C(29)-C(212)	1.499(13)
C(125)-N(14)	1.327(10)	C(210)-H(21A)	0.9800
C(125)-C(126)	1.496(12)	C(210)-H(21B)	0.9800
C(126)-H(12J)	0.9800	C(210)-H(21C)	0.9800
C(126)-H(12K)	0.9800	C(211)-H(21D)	0.9800
C(126)-H(12L)	0.9800	C(211)-H(21E)	0.9800
C(127)-N(14)	1.455(10)	C(211)-H(21F)	0.9800
C(127)-C(128)	1.502(12)	C(212)-H(21G)	0.9800
C(127)-H(12M)	0.9900	C(212)-H(21H)	0.9800
C(127)-H(12N)	0.9900	C(212)-H(21I)	0.9800
C(128)-C(129)	1.527(12)	C(213)-C(218)	1.389(12)
C(128)-H(12O)	0.9900	C(213)-C(214)	1.390(12)
C(128)-H(12P)	0.9900	C(213)-N(22)	1.454(11)
C(129)-H(12Q)	0.9800	C(214)-C(215)	1.387(13)
C(129)-H(12R)	0.9800	C(214)-C(219)	1.504(12)
C(129)-H(12S)	0.9800	C(215)-C(216)	1.368(12)
Br(11)-Pt(11)	2.5512(10)	C(215)-H(215)	0.9500
C(21)-N(22)	1.346(10)	C(216)-C(217)	1.383(13)
C(21)-N(21)	1.363(11)	C(216)-C(220)	1.501(13)
C(21)-Pt(21)	2.018(8)	C(217)-C(218)	1.377(13)
C(22)-C(23)	1.323(13)	C(217)-H(217)	0.9500
C(22)-N(21)	1.378(10)	C(218)-C(221)	1.490(13)
C(22)-H(22)	0.9500	C(219)-H(21J)	0.9800
C(23)-N(22)	1.384(11)	C(219)-H(21K)	0.9800
C(23)-H(23)	0.9500	C(219)-H(21L)	0.9800
C(24)-C(25)	1.379(12)	C(220)-H(22A)	0.9800

Appendix 2. Tables of Bond Distances and Angles

C(220)-H(22B)	0.9800	H(1A)-C(1)-H(1B)	109.5
C(220)-H(22C)	0.9800	C(2)-C(1)-H(1C)	109.5
C(221)-H(22D)	0.9800	H(1A)-C(1)-H(1C)	109.5
C(221)-H(22E)	0.9800	H(1B)-C(1)-H(1C)	109.5
C(221)-H(22F)	0.9800	O(1)-C(2)-C(3)	120.4(14)
C(222)-C(223)	1.353(11)	O(1)-C(2)-C(1)	118.9(13)
C(222)-N(23)	1.432(10)	C(3)-C(2)-C(1)	120.7(12)
C(222)-Pt(21)	2.041(8)	C(2)-C(3)-H(3A)	109.5
C(223)-N(24)	1.377(10)	C(2)-C(3)-H(3B)	109.5
C(223)-H(223)	0.9500	H(3A)-C(3)-H(3B)	109.5
C(224)-N(24)	1.450(10)	C(2)-C(3)-H(3C)	109.5
C(224)-H(22G)	0.9800	H(3A)-C(3)-H(3C)	109.5
C(224)-H(22H)	0.9800	H(3B)-C(3)-H(3C)	109.5
C(224)-H(22I)	0.9800	N(12)-C(11)-N(11)	101.9(7)
C(225)-N(24)	1.330(10)	N(12)-C(11)-Pt(11)	127.0(6)
C(225)-N(23)	1.340(10)	N(11)-C(11)-Pt(11)	131.2(6)
C(225)-C(226)	1.495(11)	C(13)-C(12)-N(11)	106.0(8)
C(226)-H(22J)	0.9800	C(13)-C(12)-H(12)	127.0
C(226)-H(22K)	0.9800	N(11)-C(12)-H(12)	127.0
C(226)-H(22L)	0.9800	C(12)-C(13)-N(12)	107.0(8)
C(227)-N(23)	1.462(11)	C(12)-C(13)-H(13)	126.5
C(227)-C(228)	1.508(13)	N(12)-C(13)-H(13)	126.5
C(227)-H(22M)	0.9900	C(19)-C(14)-C(15)	121.6(9)
C(227)-H(22N)	0.9900	C(19)-C(14)-N(12)	118.7(8)
C(228)-C(229)	1.544(13)	C(15)-C(14)-N(12)	119.7(8)
C(228)-H(22O)	0.9900	C(16)-C(15)-C(14)	118.3(9)
C(228)-H(22P)	0.9900	C(16)-C(15)-C(110)	120.8(9)
C(229)-H(22Q)	0.9800	C(14)-C(15)-C(110)	120.9(8)
C(229)-H(22R)	0.9800	C(15)-C(16)-C(17)	121.4(10)
C(229)-H(22S)	0.9800	C(15)-C(16)-H(16)	119.3
Br(21)-Pt(21)	2.5622(9)	C(17)-C(16)-H(16)	119.3
Pt(11)-H(11)	2.1003	C(18)-C(17)-C(16)	118.3(10)
Pt(21)-H(21)	1.8052	C(18)-C(17)-C(111)	120.3(10)
		C(16)-C(17)-C(111)	121.2(10)
C(2)-C(1)-H(1A)	109.5	C(19)-C(18)-C(17)	122.2(10)
C(2)-C(1)-H(1B)	109.5	C(19)-C(18)-H(18)	118.9

Appendix 2. Tables of Bond Distances and Angles

C(17)-C(18)-H(18)	118.9	C(116)-C(117)-H(117)	119.0
C(18)-C(19)-C(14)	118.2(9)	C(113)-C(118)-C(117)	118.3(9)
C(18)-C(19)-C(112)	120.0(9)	C(113)-C(118)-C(121)	121.7(9)
C(14)-C(19)-C(112)	121.9(8)	C(117)-C(118)-C(121)	119.9(9)
C(15)-C(110)-H(11A)	109.5	C(114)-C(119)-H(11J)	109.5
C(15)-C(110)-H(11B)	109.5	C(114)-C(119)-H(11K)	109.5
H(11A)-C(110)-H(11B)	109.5	H(11J)-C(119)-H(11K)	109.5
C(15)-C(110)-H(11C)	109.5	C(114)-C(119)-H(11L)	109.5
H(11A)-C(110)-H(11C)	109.5	H(11J)-C(119)-H(11L)	109.5
H(11B)-C(110)-H(11C)	109.5	H(11K)-C(119)-H(11L)	109.5
C(17)-C(111)-H(11D)	109.5	C(116)-C(120)-H(12A)	109.5
C(17)-C(111)-H(11E)	109.5	C(116)-C(120)-H(12B)	109.5
H(11D)-C(111)-H(11E)	109.5	H(12A)-C(120)-H(12B)	109.5
C(17)-C(111)-H(11F)	109.5	C(116)-C(120)-H(12C)	109.5
H(11D)-C(111)-H(11F)	109.5	H(12A)-C(120)-H(12C)	109.5
H(11E)-C(111)-H(11F)	109.5	H(12B)-C(120)-H(12C)	109.5
C(19)-C(112)-H(11G)	109.5	C(118)-C(121)-H(12D)	109.5
C(19)-C(112)-H(11H)	109.5	C(118)-C(121)-H(12E)	109.5
H(11G)-C(112)-H(11H)	109.5	H(12D)-C(121)-H(12E)	109.5
C(19)-C(112)-H(11I)	109.5	C(118)-C(121)-H(12F)	109.5
H(11G)-C(112)-H(11I)	109.5	H(12D)-C(121)-H(12F)	109.5
H(11H)-C(112)-H(11I)	109.5	H(12E)-C(121)-H(12F)	109.5
C(118)-C(113)-C(114)	123.0(9)	C(123)-C(122)-N(14)	102.3(7)
C(118)-C(113)-N(11)	119.4(8)	C(123)-C(122)-Pt(11)	128.5(7)
C(114)-C(113)-N(11)	117.4(8)	N(14)-C(122)-Pt(11)	128.8(6)
C(115)-C(114)-C(113)	116.2(9)	C(122)-C(123)-N(13)	108.9(8)
C(115)-C(114)-C(119)	120.9(9)	C(122)-C(123)-H(123)	125.5
C(113)-C(114)-C(119)	122.9(9)	N(13)-C(123)-H(123)	125.5
C(116)-C(115)-C(114)	123.1(9)	N(13)-C(124)-H(12G)	109.5
C(116)-C(115)-H(115)	118.4	N(13)-C(124)-H(12H)	109.5
C(114)-C(115)-H(115)	118.4	H(12G)-C(124)-H(12H)	109.5
C(115)-C(116)-C(117)	117.2(9)	N(13)-C(124)-H(12I)	109.5
C(115)-C(116)-C(120)	120.4(9)	H(12G)-C(124)-H(12I)	109.5
C(117)-C(116)-C(120)	122.3(10)	H(12H)-C(124)-H(12I)	109.5
C(118)-C(117)-C(116)	122.0(9)	N(13)-C(125)-N(14)	107.9(8)
C(118)-C(117)-H(117)	119.0	N(13)-C(125)-C(126)	124.1(8)

Appendix 2. Tables of Bond Distances and Angles

N(14)-C(125)-C(126)	127.9(8)	C(122)-N(14)-C(127)	123.5(7)
C(125)-C(126)-H(12J)	109.5	N(22)-C(21)-N(21)	103.7(7)
C(125)-C(126)-H(12K)	109.5	N(22)-C(21)-Pt(21)	131.1(6)
H(12J)-C(126)-H(12K)	109.5	N(21)-C(21)-Pt(21)	125.2(6)
C(125)-C(126)-H(12L)	109.5	C(23)-C(22)-N(21)	107.3(9)
H(12J)-C(126)-H(12L)	109.5	C(23)-C(22)-H(22)	126.3
H(12K)-C(126)-H(12L)	109.5	N(21)-C(22)-H(22)	126.3
N(14)-C(127)-C(128)	112.3(7)	C(22)-C(23)-N(22)	106.6(8)
N(14)-C(127)-H(12M)	109.1	C(22)-C(23)-H(23)	126.7
C(128)-C(127)-H(12M)	109.1	N(22)-C(23)-H(23)	126.7
N(14)-C(127)-H(12N)	109.1	C(25)-C(24)-C(29)	123.3(9)
C(128)-C(127)-H(12N)	109.1	C(25)-C(24)-N(21)	118.1(8)
H(12M)-C(127)-H(12N)	107.9	C(29)-C(24)-N(21)	118.3(8)
C(127)-C(128)-C(129)	111.3(8)	C(24)-C(25)-C(26)	116.9(10)
C(127)-C(128)-H(12O)	109.4	C(24)-C(25)-C(210)	122.1(9)
C(129)-C(128)-H(12O)	109.4	C(26)-C(25)-C(210)	121.0(9)
C(127)-C(128)-H(12P)	109.4	C(27)-C(26)-C(25)	122.8(10)
C(129)-C(128)-H(12P)	109.4	C(27)-C(26)-H(26)	118.6
H(12O)-C(128)-H(12P)	108.0	C(25)-C(26)-H(26)	118.6
C(128)-C(129)-H(12Q)	109.5	C(26)-C(27)-C(28)	119.1(10)
C(128)-C(129)-H(12R)	109.5	C(26)-C(27)-C(211)	122.0(12)
H(12Q)-C(129)-H(12R)	109.5	C(28)-C(27)-C(211)	118.9(12)
C(128)-C(129)-H(12S)	109.5	C(27)-C(28)-C(29)	120.6(10)
H(12Q)-C(129)-H(12S)	109.5	C(27)-C(28)-H(28)	119.7
H(12R)-C(129)-H(12S)	109.5	C(29)-C(28)-H(28)	119.7
C(12)-N(11)-C(11)	112.0(7)	C(24)-C(29)-C(28)	117.2(9)
C(12)-N(11)-C(113)	121.7(7)	C(24)-C(29)-C(212)	122.5(9)
C(11)-N(11)-C(113)	126.1(6)	C(28)-C(29)-C(212)	120.3(9)
C(13)-N(12)-C(11)	113.1(7)	C(25)-C(210)-H(21A)	109.5
C(13)-N(12)-C(14)	123.4(7)	C(25)-C(210)-H(21B)	109.5
C(11)-N(12)-C(14)	123.4(7)	H(21A)-C(210)-H(21B)	109.5
C(125)-N(13)-C(123)	109.3(7)	C(25)-C(210)-H(21C)	109.5
C(125)-N(13)-C(124)	126.9(8)	H(21A)-C(210)-H(21C)	109.5
C(123)-N(13)-C(124)	123.7(8)	H(21B)-C(210)-H(21C)	109.5
C(125)-N(14)-C(122)	111.5(7)	C(27)-C(211)-H(21D)	109.5
C(125)-N(14)-C(127)	125.0(7)	C(27)-C(211)-H(21E)	109.5

Appendix 2. Tables of Bond Distances and Angles

H(21D)-C(211)-H(21E)	109.5	H(22A)-C(220)-H(22B)	109.5
C(27)-C(211)-H(21F)	109.5	C(216)-C(220)-H(22C)	109.5
H(21D)-C(211)-H(21F)	109.5	H(22A)-C(220)-H(22C)	109.5
H(21E)-C(211)-H(21F)	109.5	H(22B)-C(220)-H(22C)	109.5
C(29)-C(212)-H(21G)	109.5	C(218)-C(221)-H(22D)	109.5
C(29)-C(212)-H(21H)	109.5	C(218)-C(221)-H(22E)	109.5
H(21G)-C(212)-H(21H)	109.5	H(22D)-C(221)-H(22E)	109.5
C(29)-C(212)-H(21I)	109.5	C(218)-C(221)-H(22F)	109.5
H(21G)-C(212)-H(21I)	109.5	H(22D)-C(221)-H(22F)	109.5
H(21H)-C(212)-H(21I)	109.5	H(22E)-C(221)-H(22F)	109.5
C(218)-C(213)-C(214)	122.5(9)	C(223)-C(222)-N(23)	102.2(7)
C(218)-C(213)-N(22)	119.1(8)	C(223)-C(222)-Pt(21)	131.2(6)
C(214)-C(213)-N(22)	118.2(8)	N(23)-C(222)-Pt(21)	126.6(6)
C(215)-C(214)-C(213)	117.2(8)	C(222)-C(223)-N(24)	111.1(8)
C(215)-C(214)-C(219)	121.2(9)	C(222)-C(223)-H(223)	124.5
C(213)-C(214)-C(219)	121.6(9)	N(24)-C(223)-H(223)	124.5
C(216)-C(215)-C(214)	122.7(9)	N(24)-C(224)-H(22G)	109.5
C(216)-C(215)-H(215)	118.7	N(24)-C(224)-H(22H)	109.5
C(214)-C(215)-H(215)	118.7	H(22G)-C(224)-H(22H)	109.5
C(215)-C(216)-C(217)	117.6(9)	N(24)-C(224)-H(22I)	109.5
C(215)-C(216)-C(220)	121.2(9)	H(22G)-C(224)-H(22I)	109.5
C(217)-C(216)-C(220)	121.2(9)	H(22H)-C(224)-H(22I)	109.5
C(218)-C(217)-C(216)	123.2(8)	N(24)-C(225)-N(23)	107.6(7)
C(218)-C(217)-H(217)	118.4	N(24)-C(225)-C(226)	125.1(8)
C(216)-C(217)-H(217)	118.4	N(23)-C(225)-C(226)	127.3(8)
C(217)-C(218)-C(213)	116.8(8)	C(225)-C(226)-H(22J)	109.5
C(217)-C(218)-C(221)	120.9(8)	C(225)-C(226)-H(22K)	109.5
C(213)-C(218)-C(221)	122.3(9)	H(22J)-C(226)-H(22K)	109.5
C(214)-C(219)-H(21J)	109.5	C(225)-C(226)-H(22L)	109.5
C(214)-C(219)-H(21K)	109.5	H(22J)-C(226)-H(22L)	109.5
H(21J)-C(219)-H(21K)	109.5	H(22K)-C(226)-H(22L)	109.5
C(214)-C(219)-H(21L)	109.5	N(23)-C(227)-C(228)	110.7(8)
H(21J)-C(219)-H(21L)	109.5	N(23)-C(227)-H(22M)	109.5
H(21K)-C(219)-H(21L)	109.5	C(228)-C(227)-H(22M)	109.5
C(216)-C(220)-H(22A)	109.5	N(23)-C(227)-H(22N)	109.5
C(216)-C(220)-H(22B)	109.5	C(228)-C(227)-H(22N)	109.5

Appendix 2. Tables of Bond Distances and Angles

H(22M)-C(227)-H(22N)	108.1	Br(21)-Pt(21)-H(21)	173.2
C(227)-C(228)-C(229)	110.0(9)		
C(227)-C(228)-H(22O)	109.7		
C(229)-C(228)-H(22O)	109.7		
C(227)-C(228)-H(22P)	109.7		
C(229)-C(228)-H(22P)	109.7		
H(22O)-C(228)-H(22P)	108.2		
C(228)-C(229)-H(22Q)	109.5		
C(228)-C(229)-H(22R)	109.5		
H(22Q)-C(229)-H(22R)	109.5		
C(228)-C(229)-H(22S)	109.5		
H(22Q)-C(229)-H(22S)	109.5		
H(22R)-C(229)-H(22S)	109.5		
C(21)-N(21)-C(22)	110.8(8)		
C(21)-N(21)-C(24)	123.8(7)		
C(22)-N(21)-C(24)	125.3(8)		
C(21)-N(22)-C(23)	111.5(7)		
C(21)-N(22)-C(213)	125.3(7)		
C(23)-N(22)-C(213)	122.7(7)		
C(225)-N(23)-C(222)	110.8(7)		
C(225)-N(23)-C(227)	122.0(7)		
C(222)-N(23)-C(227)	127.2(7)		
C(225)-N(24)-C(223)	108.2(7)		
C(225)-N(24)-C(224)	125.3(8)		
C(223)-N(24)-C(224)	126.3(8)		
C(11)-Pt(11)-C(122)	174.2(3)		
C(11)-Pt(11)-Br(11)	90.9(2)		
C(122)-Pt(11)-Br(11)	90.2(2)		
C(11)-Pt(11)-H(11)	92.4		
C(122)-Pt(11)-H(11)	85.5		
Br(11)-Pt(11)-H(11)	169.6		
C(21)-Pt(21)-C(222)	175.6(3)		
C(21)-Pt(21)-Br(21)	91.4(2)		
C(222)-Pt(21)-Br(21)	90.0(2)		
C(21)-Pt(21)-H(21)	93.1		
C(222)-Pt(21)-H(21)	85.2		

Appendix 2. Tables of Bond Distances and Angles

Table A. 2. Bond lengths [Å] and angles[°] for Pt(IMes)(Sty)₂ complex 11b (See chapter 2).

C(1)-N(2)	1.351(9)	C(14)-C(15)	1.371(10)
C(1)-N(1)	1.373(8)	C(14)-C(19)	1.516(10)
C(1)-Pt(1)	2.039(6)	C(15)-C(16)	1.416(10)
C(2)-C(3)	1.324(11)	C(15)-H(15)	0.9500
C(2)-N(1)	1.393(9)	C(16)-C(17)	1.381(10)
C(2)-H(2)	0.9500	C(16)-C(20)	1.480(10)
C(3)-N(2)	1.381(9)	C(17)-C(18)	1.394(10)
C(3)-H(3)	0.9500	C(17)-H(17)	0.9500
C(4)-C(9)	1.392(10)	C(18)-C(21)	1.506(10)
C(4)-C(5)	1.399(10)	C(19)-H(19A)	0.9800
C(4)-N(1)	1.435(9)	C(19)-H(19B)	0.9800
C(5)-C(6)	1.383(10)	C(19)-H(19C)	0.9800
C(5)-C(10)	1.499(10)	C(20)-H(20A)	0.9800
C(6)-C(7)	1.378(11)	C(20)-H(20B)	0.9800
C(6)-H(6)	0.9500	C(20)-H(20C)	0.9800
C(7)-C(8)	1.393(13)	C(21)-H(21A)	0.9800
C(7)-C(11)	1.478(13)	C(21)-H(21B)	0.9800
C(8)-C(9)	1.380(12)	C(21)-H(21C)	0.9800
C(8)-H(8)	0.9500	C(22)-C(23)	1.402(10)
C(9)-C(12)	1.510(12)	C(22)-Pt(1)	2.121(6)
C(10)-H(10A)	0.9800	C(22)-H(22A)	0.9500
C(10)-H(10B)	0.9800	C(22)-H(22B)	0.9500
C(10)-H(10C)	0.9800	C(23)-C(24)	1.490(10)
C(11)-H(11A)	0.9800	C(23)-Pt(1)	2.130(6)
C(11)-H(11B)	0.9800	C(23)-H(23A)	0.9500
C(11)-H(11C)	0.9800	C(24)-C(25)	1.382(10)
C(12)-H(12A)	0.9800	C(24)-C(29)	1.403(9)
C(12)-H(12B)	0.9800	C(25)-C(26)	1.383(11)
C(12)-H(12C)	0.9800	C(25)-H(25)	0.9500
C(13)-C(14)	1.389(10)	C(26)-C(27)	1.368(11)
C(13)-C(18)	1.389(9)	C(26)-H(26)	0.9500
C(13)-N(2)	1.443(9)	C(27)-C(28)	1.375(12)

Appendix 2. Tables of Bond Distances and Angles

C(27)-H(27)	0.9500	C(6)-C(5)-C(10)	121.4(7)
C(28)-C(29)	1.362(11)	C(4)-C(5)-C(10)	120.7(7)
C(28)-H(28)	0.9500	C(7)-C(6)-C(5)	123.2(8)
C(29)-H(29)	0.9500	C(7)-C(6)-H(6)	118.4
C(30)-C(31)	1.407(9)	C(5)-C(6)-H(6)	118.4
C(30)-Pt(1)	2.109(6)	C(6)-C(7)-C(8)	116.4(8)
C(30)-H(30A)	0.9500	C(6)-C(7)-C(11)	120.7(9)
C(30)-H(30B)	0.9500	C(8)-C(7)-C(11)	122.9(8)
C(31)-C(32)	1.476(10)	C(9)-C(8)-C(7)	123.7(7)
C(31)-Pt(1)	2.140(7)	C(9)-C(8)-H(8)	118.1
C(31)-H(31A)	0.9500	C(7)-C(8)-H(8)	118.1
C(32)-C(37)	1.376(10)	C(8)-C(9)-C(4)	117.4(7)
C(32)-C(33)	1.385(10)	C(8)-C(9)-C(12)	121.7(7)
C(33)-C(34)	1.381(12)	C(4)-C(9)-C(12)	120.9(8)
C(33)-H(33)	0.9500	C(5)-C(10)-H(10A)	109.5
C(34)-C(35)	1.355(13)	C(5)-C(10)-H(10B)	109.5
C(34)-H(34)	0.9500	H(10A)-C(10)-H(10B)	109.5
C(35)-C(36)	1.376(12)	C(5)-C(10)-H(10C)	109.5
C(35)-H(35)	0.9500	H(10A)-C(10)-H(10C)	109.5
C(36)-C(37)	1.391(11)	H(10B)-C(10)-H(10C)	109.5
C(36)-H(36)	0.9500	C(7)-C(11)-H(11A)	109.5
C(37)-H(37)	0.9500	C(7)-C(11)-H(11B)	109.5
		H(11A)-C(11)-H(11B)	109.5
N(2)-C(1)-N(1)	103.7(5)	C(7)-C(11)-H(11C)	109.5
N(2)-C(1)-Pt(1)	127.7(5)	H(11A)-C(11)-H(11C)	109.5
N(1)-C(1)-Pt(1)	128.6(5)	H(11B)-C(11)-H(11C)	109.5
C(3)-C(2)-N(1)	107.5(6)	C(9)-C(12)-H(12A)	109.5
C(3)-C(2)-H(2)	126.3	C(9)-C(12)-H(12B)	109.5
N(1)-C(2)-H(2)	126.3	H(12A)-C(12)-H(12B)	109.5
C(2)-C(3)-N(2)	106.8(7)	C(9)-C(12)-H(12C)	109.5
C(2)-C(3)-H(3)	126.6	H(12A)-C(12)-H(12C)	109.5
N(2)-C(3)-H(3)	126.6	H(12B)-C(12)-H(12C)	109.5
C(9)-C(4)-C(5)	121.3(7)	C(14)-C(13)-C(18)	121.5(7)
C(9)-C(4)-N(1)	118.8(7)	C(14)-C(13)-N(2)	119.1(6)
C(5)-C(4)-N(1)	119.8(6)	C(18)-C(13)-N(2)	119.4(6)
C(6)-C(5)-C(4)	117.9(7)	C(15)-C(14)-C(13)	119.1(7)

Appendix 2. Tables of Bond Distances and Angles

C(15)-C(14)-C(19)	119.8(7)	Pt(1)-C(22)-H(22B)	86.4
C(13)-C(14)-C(19)	121.1(7)	H(22A)-C(22)-H(22B)	120.0
C(14)-C(15)-C(16)	121.6(6)	C(22)-C(23)-C(24)	121.8(6)
C(14)-C(15)-H(15)	119.2	C(22)-C(23)-Pt(1)	70.4(4)
C(16)-C(15)-H(15)	119.2	C(24)-C(23)-Pt(1)	113.4(4)
C(17)-C(16)-C(15)	117.3(7)	C(22)-C(23)-H(23A)	119.1
C(17)-C(16)-C(20)	122.5(7)	C(24)-C(23)-H(23A)	119.1
C(15)-C(16)-C(20)	120.2(7)	Pt(1)-C(23)-H(23A)	86.4
C(16)-C(17)-C(18)	122.5(7)	C(25)-C(24)-C(29)	116.9(7)
C(16)-C(17)-H(17)	118.7	C(25)-C(24)-C(23)	122.9(6)
C(18)-C(17)-H(17)	118.7	C(29)-C(24)-C(23)	120.1(6)
C(13)-C(18)-C(17)	118.0(6)	C(24)-C(25)-C(26)	122.1(7)
C(13)-C(18)-C(21)	121.6(6)	C(24)-C(25)-H(25)	119.0
C(17)-C(18)-C(21)	120.3(6)	C(26)-C(25)-H(25)	119.0
C(14)-C(19)-H(19A)	109.5	C(27)-C(26)-C(25)	119.9(8)
C(14)-C(19)-H(19B)	109.5	C(27)-C(26)-H(26)	120.1
H(19A)-C(19)-H(19B)	109.5	C(25)-C(26)-H(26)	120.1
C(14)-C(19)-H(19C)	109.5	C(26)-C(27)-C(28)	118.7(8)
H(19A)-C(19)-H(19C)	109.5	C(26)-C(27)-H(27)	120.6
H(19B)-C(19)-H(19C)	109.5	C(28)-C(27)-H(27)	120.6
C(16)-C(20)-H(20A)	109.5	C(29)-C(28)-C(27)	121.9(7)
C(16)-C(20)-H(20B)	109.5	C(29)-C(28)-H(28)	119.0
H(20A)-C(20)-H(20B)	109.5	C(27)-C(28)-H(28)	119.0
C(16)-C(20)-H(20C)	109.5	C(28)-C(29)-C(24)	120.4(7)
H(20A)-C(20)-H(20C)	109.5	C(28)-C(29)-H(29)	119.8
H(20B)-C(20)-H(20C)	109.5	C(24)-C(29)-H(29)	119.8
C(18)-C(21)-H(21A)	109.5	C(31)-C(30)-Pt(1)	71.9(4)
C(18)-C(21)-H(21B)	109.5	C(31)-C(30)-H(30A)	120.0
H(21A)-C(21)-H(21B)	109.5	Pt(1)-C(30)-H(30A)	112.3
C(18)-C(21)-H(21C)	109.5	C(31)-C(30)-H(30B)	120.0
H(21A)-C(21)-H(21C)	109.5	Pt(1)-C(30)-H(30B)	86.1
H(21B)-C(21)-H(21C)	109.5	H(30A)-C(30)-H(30B)	120.0
C(23)-C(22)-Pt(1)	71.1(4)	C(30)-C(31)-C(32)	123.4(7)
C(23)-C(22)-H(22A)	120.0	C(30)-C(31)-Pt(1)	69.4(4)
Pt(1)-C(22)-H(22A)	112.8	C(32)-C(31)-Pt(1)	113.9(5)
C(23)-C(22)-H(22B)	120.0	C(30)-C(31)-H(31A)	118.3

Appendix 2. Tables of Bond Distances and Angles

C(32)-C(31)-H(31A)	118.3
Pt(1)-C(31)-H(31A)	86.7
C(37)-C(32)-C(33)	117.6(7)
C(37)-C(32)-C(31)	121.6(6)
C(33)-C(32)-C(31)	120.7(7)
C(34)-C(33)-C(32)	121.5(8)
C(34)-C(33)-H(33)	119.3
C(32)-C(33)-H(33)	119.3
C(35)-C(34)-C(33)	120.1(8)
C(35)-C(34)-H(34)	120.0
C(33)-C(34)-H(34)	120.0
C(34)-C(35)-C(36)	120.0(8)
C(34)-C(35)-H(35)	120.0
C(36)-C(35)-H(35)	120.0
C(35)-C(36)-C(37)	119.8(8)
C(35)-C(36)-H(36)	120.1
C(37)-C(36)-H(36)	120.1
C(32)-C(37)-C(36)	121.0(8)
C(32)-C(37)-H(37)	119.5
C(36)-C(37)-H(37)	119.5
C(1)-N(1)-C(2)	110.1(6)
C(1)-N(1)-C(4)	125.7(6)
C(2)-N(1)-C(4)	123.8(6)
C(1)-N(2)-C(3)	111.8(6)
C(1)-N(2)-C(13)	125.5(5)
C(3)-N(2)-C(13)	122.7(6)
C(1)-Pt(1)-C(30)	94.3(3)
C(1)-Pt(1)-C(22)	96.3(3)
C(30)-Pt(1)-C(22)	169.3(3)
C(1)-Pt(1)-C(23)	134.0(3)
C(30)-Pt(1)-C(23)	131.1(3)
C(22)-Pt(1)-C(23)	38.5(3)
C(1)-Pt(1)-C(31)	132.8(2)
C(30)-Pt(1)-C(31)	38.7(3)
C(22)-Pt(1)-C(31)	130.7(3)
C(23)-Pt(1)-C(31)	93.1(3)

Appendix 2. Tables of Bond Distances and Angles

Table A. 3. Bond lengths [Å] and angles[°] for 1,3-di(2-picolyl)-2-methylimidazolium chloride (7).

(See chapter 3)

N(1)-C(1)	1.3444(19)	C(16)-N(4)-C(12)	116.95(14)
N(1)-C(3)	1.3813(19)	C(3)-C(4)-N(2)	107.26(13)
N(1)-C(5)	1.4718(19)	N(1)-C(5)-C(6)	111.88(12)
C(1)-N(2)	1.3452(19)	N(3)-C(6)-C(7)	123.24(14)
C(1)-C(2)	1.475(2)	N(3)-C(6)-C(5)	116.29(12)
N(2)-C(4)	1.3822(19)	C(7)-C(6)-C(5)	120.43(13)
N(2)-C(11)	1.4789(19)	C(6)-C(7)-C(8)	118.79(15)
N(3)-C(6)	1.3395(19)	C(9)-C(8)-C(7)	118.66(14)
N(3)-C(10)	1.342(2)	C(9)-C(8)-C(7)	118.66(14)
C(3)-C(4)	1.347(2)	C(8)-C(9)-C(10)	118.69(15)
N(4)-C(16)	1.339(2)	N(3)-C(10)-C(9)	123.76(15)
N(4)-C(12)	1.3439(19)	N(2)-C(11)-C(12)	110.55(11)
C(5)-C(6)	1.510(2)	N(4)-C(12)-C(13)	122.84(14)
C(6)-C(7)	1.384(2)	N(4)-C(12)-C(11)	115.76(13)
C(7)-C(8)	1.387(2)	C(13)-C(12)-C(11)	121.40(13)
C(8)-C(9)	1.376(2)	C(12)-C(13)-C(14)	118.92(15)
C(9)-C(10)	1.380(2)	C(15)-C(14)-C(13)	118.84(15)
C(11)-C(12)	1.511(2)	C(14)-C(15)-C(16)	118.48(16)
C(12)-C(13)	1.381(2)	N(4)-C(16)-C(15)	123.98(15)
C(13)-C(14)	1.391(2)		
C(14)-C(15)	1.371(2)		
C(15)-C(16)	1.381(2)		
C(1)-N(1)-C(3)	109.64(12)		
C(1)-N(1)-C(5)	124.68(12)		
C(3)-N(1)-C(5)	125.51(12)		
N(1)-C(1)-N(2)	106.81(12)		
N(1)-C(1)-C(2)	124.50(13)		
N(2)-C(1)-C(2)	128.69(13)		
C(1)-N(2)-C(4)	109.36(12)		
C(1)-N(2)-C(11)	126.98(12)		
C(4)-N(2)-C(11)	123.63(12)		
C(6)-N(3)-C(10)	116.86(13)		

Appendix 2. Tables of Bond Distances and Angles

Table A. 4. Bond lengths [Å] and angles[°] for Pt(IMes)₂HCl (14). (See chapter 3)

Pt(1)-C(1)	1.997(4)	C(26)-C(27)	1.392(6)
Pt(1)-C(22)	2.007(4)	C(26)-C(31)	1.520(6)
Pt(1)-Cl(1)	2.4187(12)	C(27)-C(28)	1.388(6)
N(1)-C(1)	1.367(5)	C(28)-C(29)	1.385(6)
N(1)-C(2)	1.387(5)	C(28)-C(32)	1.512(6)
N(1)-C(4)	1.442(5)	C(29)-C(30)	1.384(6)
C(1)-N(2)	1.362(4)	C(30)-C(33)	1.502(6)
N(2)-C(3)	1.393(4)	C(34)-C(35)	1.384(6)
N(2)-C(13)	1.440(4)	C(34)-C(39)	1.398(5)
C(2)-C(3)	1.335(6)	C(35)-C(36)	1.394(6)
N(3)-C(22)	1.357(5)	C(35)-C(40)	1.510(6)
N(3)-C(23)	1.391(5)	C(36)-C(37)	1.388(7)
N(3)-C(25)	1.441(5)	C(37)-C(38)	1.378(7)
N(4)-C(22)	1.355(5)	C(37)-C(41)	1.515(6)
N(4)-C(24)	1.380(5)	C(38)-C(39)	1.391(6)
N(4)-C(34)	1.446(5)	C(39)-C(42)	1.484(6)
C(4)-C(9)	1.387(6)	Pt(1)-H(1)	is ca. 1.40
C(4)-C(5)	1.409(5)	C(1)-Pt(1)-C(22)	177.42(15)
C(5)-C(6)	1.390(5)	C(1)-Pt(1)-Cl(1)	92.31(11)
C(5)-C(10)	1.503(6)	C(22)-Pt(1)-Cl(1)	90.11(12)
C(6)-C(7)	1.381(6)	C(1)-N(1)-C(2)	111.2(3)
C(7)-C(8)	1.399(6)	C(1)-N(1)-C(4)	124.1(3)
C(7)-C(11)	1.515(6)	C(2)-N(1)-C(4)	124.4(3)
C(8)-C(9)	1.384(6)	N(2)-C(1)-N(1)	103.7(3)
C(9)-C(12)	1.509(5)	N(2)-C(1)-Pt(1)	127.6(3)
C(13)-C(18)	1.387(5)	N(1)-C(1)-Pt(1)	128.7(3)
C(13)-C(14)	1.394(5)	C(1)-N(2)-C(3)	111.3(3)
C(14)-C(15)	1.398(5)	C(1)-N(2)-C(13)	124.5(3)
C(14)-C(19)	1.506(5)	C(3)-N(2)-C(13)	124.2(3)
C(15)-C(16)	1.388(6)	C(3)-C(2)-N(1)	107.2(4)
C(16)-C(17)	1.374(6)	C(22)-N(3)-C(23)	110.3(3)
C(16)-C(20)	1.520(5)	C(22)-N(3)-C(25)	124.7(3)
C(17)-C(18)	1.404(5)	C(23)-N(3)-C(25)	124.9(3)
C(18)-C(21)	1.494(6)	C(2)-C(3)-N(2)	106.7(3)
C(23)-C(24)	1.327(6)	C(22)-N(4)-C(24)	111.4(3)
C(25)-C(26)	1.386(6)	C(22)-N(4)-C(34)	125.1(3)

Appendix 2. Tables of Bond Distances and Angles

C(25)-C(30)	1.402(5)	C(24)-N(4)-C(34)	123.5(3)
C(9)-C(4)-C(5)	122.3(4)	C(28)-C(27)-C(26)	121.6(4)
C(9)-C(4)-N(1)	118.3(3)	(29)-C(28)-C(27)	118.0(4)
C(5)-C(4)-N(1)	119.4(3)	C(29)-C(28)-C(32)	120.9(4)
C(6)-C(5)-C(4)	116.8(4)	C(27)-C(28)-C(32)	121.0(4)
C(6)-C(5)-C(10)	121.6(3)	C(30)-C(29)-C(28)	122.8(4)
C(4)-C(5)-C(10)	121.6(3)	C(29)-C(30)-C(25)	117.4(4)
C(7)-C(6)-C(5)	123.0(4)	C(29)-C(30)-C(33)	121.0(4)
C(6)-C(7)-C(8)	117.8(4)	C(25)-C(30)-C(33)	121.6(4)
C(6)-C(7)-C(11)	121.8(4)	C(35)-C(34)-C(39)	122.5(4)
C(8)-C(7)-C(11)	120.4(4)	C(35)-C(34)-N(4)	118.8(4)
C(9)-C(8)-C(7)	122.0(4)	C(39)-C(34)-N(4)	118.6(4)
C(8)-C(9)-C(4)	118.1(4)	C(34)-C(35)-C(36)	118.5(4)
C(8)-C(9)-C(12)	121.5(4)	C(34)-C(35)-C(40)	121.3(4)
C(4)-C(9)-C(12)	120.4(4)	C(36)-C(35)-C(40)	120.2(5)
C(18)-C(13)-C(14)	123.0(4)	C(37)-C(36)-C(35)	120.6(5)
C(18)-C(13)-N(2)	118.5(4)	C(38)-C(37)-C(36)	119.1(4)
C(14)-C(13)-N(2)	118.4(3)	C(38)-C(37)-C(41)	120.8(5)
C(13)-C(14)-C(15)	117.7(4)	C(36)-C(37)-C(41)	120.1(5)
C(13)-C(14)-C(19)	121.7(4)	C(37)-C(38)-C(39)	122.5(4)
C(15)-C(14)-C(19)	120.6(4)	C(38)-C(39)-C(34)	116.7(4)
C(16)-C(15)-C(14)	121.1(4)	C(38)-C(39)-C(42)	122.2(4)
C(17)-C(16)-C(15)	119.0(4)	C(34)-C(39)-C(42)	121.1(4)
C(17)-C(16)-C(20)	121.1(4)	C(25)-C(26)-C(31)	121.3(4)
C(15)-C(16)-C(20)	119.9(4)	C(27)-C(26)-C(31)	120.3(4)
C(16)-C(17)-C(18)	122.5(4)		
C(13)-C(18)-C(17)	116.7(4)		
C(13)-C(18)-C(21)	122.6(3)		
C(17)-C(18)-C(21)	120.8(3)		
N(4)-C(22)-N(3)	104.2(3)		
N(4)-C(22)-Pt(1)	127.0(3)		
N(3)-C(22)-Pt(1)	128.8(3)		
C(24)-C(23)-N(3)	107.4(3)		
C(23)-C(24)-N(4)	106.7(4)		
C(26)-C(25)-C(30)	121.7(4)		
C(26)-C(25)-N(3)	119.8(4)		
C(30)-C(25)-N(3)	118.5(4)		
C(25)-C(26)-C(27)	118.4(4)		

