Zero Valent N-Heterocyclic Carbene Complexes of Nickel, Palladium and Platinum: Synthesis, Structure, Reaction Chemistry and Catalysis

by

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Submitted in fulfilment of the requirements of the Degree of

Doctor of Philosophy

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May 2005

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Abstract

This thesis describes the synthesis of coordinatively unsaturated bis- and mono-N-heterocyclic carbenes of Group 10 metal(0) complexes (Ni, Pd, Pt) and the study of their reaction chemistry and catalytic behaviour.

Novel coordinatively unsaturated mono-NHC-Pd^0 (NHC = N-heterocyclic carbene) complexes stabilised with activated olefin ligands (dimethylfumarate, DMFU and *p*-benzoquinone, BQ) have been synthesised and characterised, including by X-ray crystallography. The Pd^0(NHC)(DMFU)$_2$ complexes were found to be the thermodynamic products of an equilibrium between bis- and mono-NHC-Pd^0(DMFU) species, the equilibrium reaction driven by the formation of an NHC-DMFU coupling product. The Pt^0(NHC)(DMFU)$_2$ complex was also synthesised.

Novel coordinatively unsaturated bis- and mono-NHC-Ni^0 complexes stabilised with DMFU ligands were synthesised and crystallographically characterised. These Ni complexes have a dynamic behaviour in solution, and the same equilibrium observed for palladium between bis- and mono-NHC-M^0(DMFU) species with formation of an NHC-DMFU coupling product was also demonstrated to occur with nickel. Possible mechanisms for this unusual NHC-DMFU coupling process at these nickel and palladium(0) centres are discussed.

The coordinatively unsaturated mono-NHC-Pd^0(DMFU/BQ) complexes, as well a bis-NHC-Pd^0 complex, were tested as precatalysts in the telomerization of butadiene with methanol. All of these well-defined complexes were found to be extremely active and selective catalysts in the telomerization reaction.

The C^2-H oxidative addition of imidazolium salts/ionic liquids to a coordinatively unsaturated mono-NHC-Pt^0 complex and bis-NHC-Ni^0/Pd^0 complexes was studied. These oxidative addition processes occur quickly under mild conditions and produce the corresponding bis- or tris-NHC-M^{II}-H complexes as surprisingly stable compounds. X-Ray crystallographic studies of the two tris-NHC-M^{II}-hydrido complexes (M= Ni, Pd) with the hydride ligands located are reported

The combination of the imidazolium C^2-H oxidative addition and the NHC-hydrocarbyl reductive elimination processes into a catalytic cycle to form a unique Ni^0-catalysed imidazolium-alkene coupling reaction is reported. The scope of this new catalytic transformation that produces 2-alkylimidazolium salts under mild conditions is extended to other types of azolium salts. The implications of these results for NHC chemistry and for the use of imidazolium-based ionic liquids as solvents in transition-metal catalysed reactions is discussed.

Acknowledgments

Many thanks must go to Professor Kingsley Cavell for his excellent supervision and continuous support throughout this PhD. I would also like to thank Kingsley for organising an interesting research stay at the University of Amsterdam, and also allowing me to participate in international conferences in Switzerland and Germany.
I also thank Professor Cornelis Elsevier and particularly Dr. Marcel Duin for their kind welcome and assistance during my stay in Amsterdam.

I wish to extend my appreciation to the all the staff of the chemistry department in Cardiff for their assistance in realising this project. I especially thank Mr. Rob Jenkins for all his help in a number of instrumental techniques. It is certain that without all of you the chemistry department would not look the same.

I must also thank Professor Cameron Jones and Dr. Li-Ling Ooi from Cardiff University for the X-ray structure determinations and their patience in trying to extract crystals from our crystallisation tubes. Thanks also go the skilled staff of the EPSRC National Mass Spectrometry Service Centre in Swansea (UK) and the Warwick Analytical Service Ltd. in Coventry (UK) for the microanalyses.

I also gratefully acknowledge EPRSC for providing me financial support for this work.

I thank all the members and former members of Kingsley's group starting with Dennis, Stuart, Rhian, Maira, Huw, Emyr, Deborha, Mandeep, Gareth, Adrien, Marcello and Emma for providing during these years an entertaining and friendly atmosphere in the lab.
I must especially thank Dr. David Nielsen for originally teaching me how to use a vacuum line and to dry dioxane and finally for helping me to make this thesis read a bit better. Thanks a lot Dave!

Finally, I thank all my friends in Cardiff and the UK and also my family in France for their support during the last past years. Special thanks go to Eli for supporting me during the writing of this thesis. Many thanks also go to Sandrine that supported me for so many years: 'les sentiments partent mais les souvenirs restent...'

Abbreviations used in this thesis

Ad	adamantyl
Ar	aryl group
BQ	1,4-benzoquinone
COD	cycloocta-1,5-diene
Cp	cyclopentadienyl
Cy	cyclohexyl
DAB	diazabuta-1,3-diene
dae	diallyether
dba	dibenzylidene-acetone
DCM	dichloromethane
Dipp	2,6-bis(di-*iso*-propyl)phenyl
DMFU	dimethylfumarate
DMSO	dimethylsulfoxide
Et	ethyl
Et_2O	diethyl ether
EWG	electron withdrawing group
FAB	fast atom bombardment
GC	gas chromatogrphy
i-Pr	*iso*-propyl
IR	infrared
LSIMS	liquid secondary ion mass spectroscopy
M	metal
Me	methyl
Mes	mesityl or 2,4,6-trimethylphenyl
MS	mass spectroscopy
nbe	norbornene
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance
OAc	acetate anion
ORTEP	Oak Ridge Thermal Ellipsoid Program
o-tolyl	*ortho*-tolyl group
Ph	phenyl
RT	room temperature
t-Bu	*tert*-butyl
THF	tetrahydrofuran
TMS	trimethylsilane

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CHAPTER 1

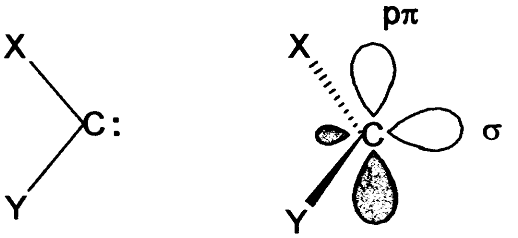
Introduction

1.1. N-Heterocyclic Carbenes (NHC)

1.1.1. Stable Free Carbenes

Free carbenes are neutral compounds featuring a divalent carbon atom having two non-bonding electrons. Because the carbon atom does not possess an octet of electrons, free carbenes are electron deficient and usually highly reactive species.

In terms of structure most free carbenes are bent molecules leading to the carbon atom adopting an sp^2-type hybridization with two non-bonding orbitals. While one orbital retains almost pure p-character and is described as p_π, the other one is stabilised by significant s character and is decribed as σ: [1]



The nature of the substituents X and Y has a great influence on the electronic configurations of free carbenes and their relative thermodynamic stabilities. Heteroatom donor groups on the carbene centre, in particular nitrogen groups render the two non-bonding orbitals σ and p_π unequal in energy through a combination of both inductive (I) and mesomeric (M) effects (Figure 1.1).[1]

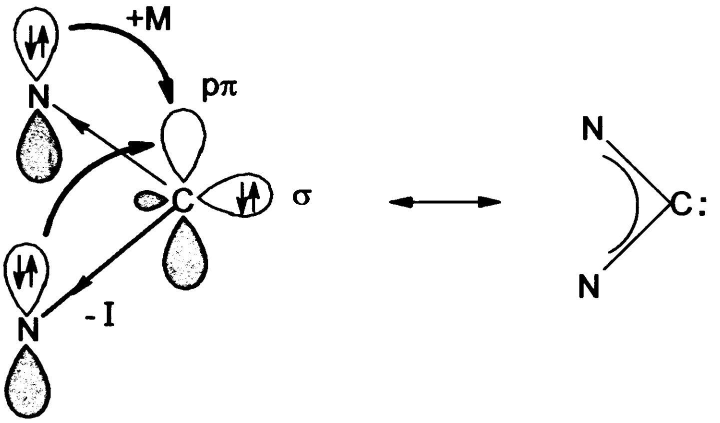
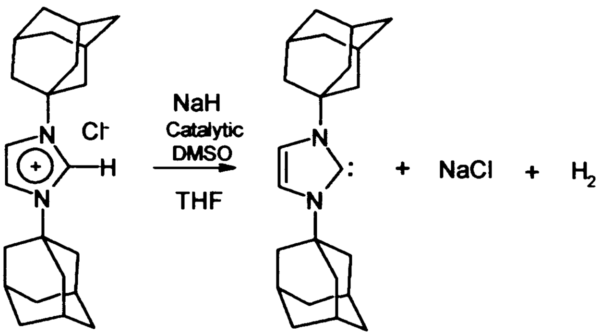


Figure 1.1 Stabilisation of free diamino-carbene through mesomeric and inductive effects.

Because nitrogen atoms are more electronegative than carbon and are thus σ-withdrawing, they inductively stabilise the σ non-bonding orbital by increasing its s character. Meanwhile, π-donation from the p_π lone pairs on the nitrogens into the carbene empty p_π orbital stabilises the carbene p_π orbital and increases its energy. Carbenes disubstituted by adjacent nitrogens thus benefit from both -I and +M stabilisation effects that result in a large energy gap between the σ and p_π non-bonding orbitals. The increased energy gap favours pairing of the two carbene non-bonding electrons in the σ-orbital in a stable singlet configuration rather than a reactive triplet arrangement of parallel spins in two different orbitals.[1] Nitrogen substituted carbenes are therefore neutral two-electron-donor nucleophiles. Due to the lower electronegativity of carbon, they are stronger nucleophiles than amines.[1b]

The first isolated free N,N-carbene **1**,[2] was obtained from an imidazole ring system where the carbene centre is adjacent to two nitrogens and included in an 6-π-electron, five-menbered ring arrangement that further added to the stabilisation of the carbene centre[3] (Equation 1.1).[2] Although carbenes derived from the imidazole system were first studied in the 1960's by Wanzlick and co-workers,[4,5] who demonstrated their existence by trapping experiments but never isolated them,[5] the isolation of the first free N,N-carbene **1** in 1991 by Arduengo and co-workers by the deprotonation of an imidazolium salt sparked an enormous revival in interest in the preparation of free carbenes.[2] Carbene **1** was isolated as an indefinitively stable colourless crystalline solid when stored under inert atmosphere and with unexpectedly high thermal stability; **1** melts at 240 °C without decomposition.[2]



(1.1)

1

The first isolated stable
free carbene

Since the isolation of **1**, many other nitrogen-stabilised stable free carbenes such as **2**-**8** have been isolated (Figure 1.2). Various cyclic compounds (**2**,[6] **4**,[7] and **7**[8]) and acyclic free carbenes (of the type **3**,[9] **5**,[10] **6**,[10] and **8**[11]) that contain different numbers or types of heteroatoms (S, O) in the molecule have been isolated. Interestingly, the mono-heteroatom-substituted free carbene **8**, recently isolated as a free carbene indefinitively stable at room temperature, demonstrates that one nitrogen is sufficient to stabilise the carbene centre at least in this instance.[11] Finally, very recently the stable free carbene **9** was isolated where, analogous to the imidazole system, the carbene is stabilised by the donation of the electron lone-pairs of the two phophorous atoms to the electron-deficient carbene centre.[12] The recent discoveries of **8** and **9** will certainly extend the range of known stable free carbenes and their potential applications in the future.

This thesis focusses mainly on carbenes derived from the unsaturated imidazole ring (such as 1) and its saturated analogue.These carbenes are defined as imidazolin-2-ylidene (unsaturated ring) and imidazolidin-2-ylidene (saturated ring) type carbenes. These two types of carbene are part of the group commonly called N-heterocyclic carbenes (NHC's) where the carbene is included in a cyclic structure and where at least one nitrogen atom stabilises the carbene centre. In this thesis the common terminology NHC will be used to describe both the imidazolin-2-ylidene and the imidazolidin-2-ylidene type carbenes.

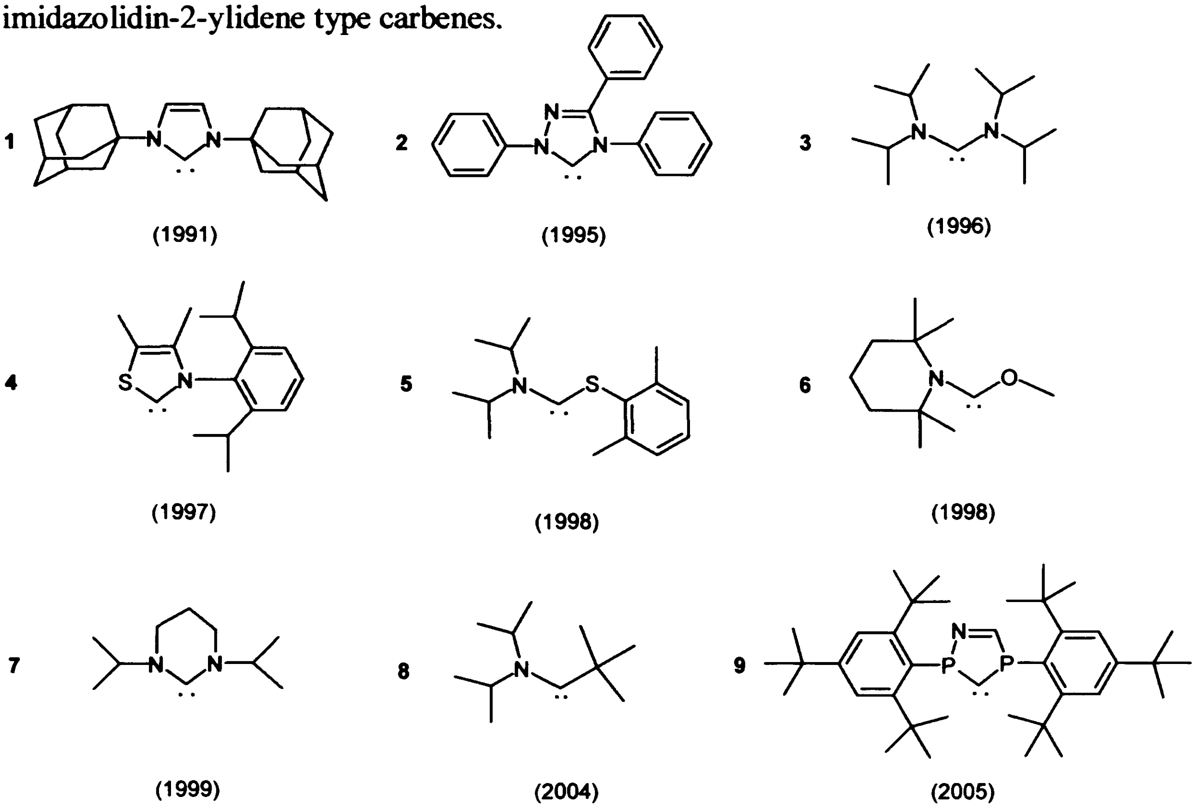


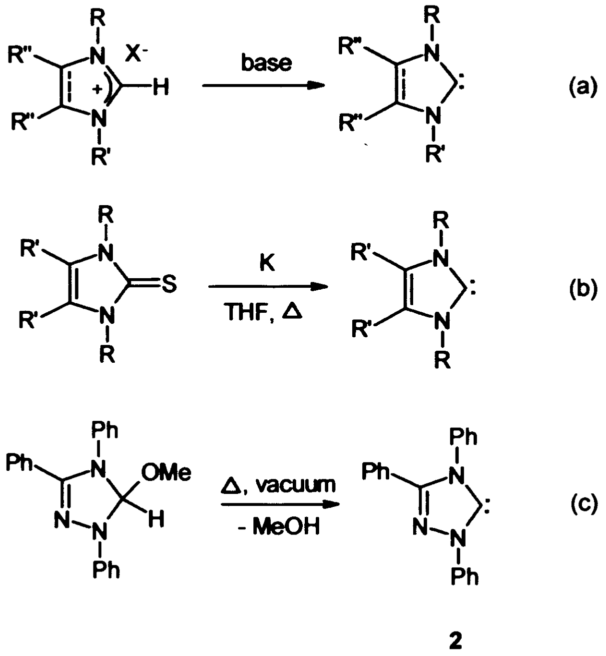
Figure 1.2. Examples of isolated free carbenes (with publication year).

1.1.2. Preparation of Free N-Heterocyclic Carbenes (NHC's)

Most of the common synthetic routes to generate free NHC's are based on deprotonation at the C^2 position of the azolium salts by a base (Scheme 1.1a).[2,13-15] Strong bases such as KO*t*Bu used in stoichiometric amounts or NaH/KH in the presence of a catalytic amount of KO*t*Bu or DMSO as soluble hydride-transfer agents have been used to deprotonate N-alkyl or N-aryl substituted azolium salts in THF at room temperature.[2,13-15] Amides such as $Li(N\textit{i}Pr_2)$ (LDA) or $K[N(SiMe_3)_2]$ have also proven useful to deprotonate some base-sensitive functionalised imidazolium salts.[15,16]

The use of NaH in liquid ammonia-THF solvent mixture at low temperature has allowed the rapid generation of less stable free carbenes, as well as those with oxygen, nitrogen or phosphorus containing N-functionalities, from the corresponding azolium salts.[17,18]

Other routes to generate free NHC's include the reductive desulfurisation of imidazolin-2-thiones with potassium in boiling THF (Scheme 1.1b).[19] Using this method some thermally stable alkyl-substituted NHC have been prepared. Finally, thermal elimination of small molecules such as MeOH from 5-methoxytriazole allowed the isolation of the first triazole based NHC, **2**, that was also the first commercially available free carbene (Scheme 1.1c).[6]



Scheme 1.1. Methods of preparation of free NHC's.

1.1.3. N-Heterocyclic Carbenes as Ligands

Carbene complexes are normally classified according the nature of the formal carbene-metal bond. Until recently carbene complexes were classified as either Fisher- or Schrock-type complexes (Figure 1.3a-b).[20]

In Schrock-type carbene complexes the metal-carbene bond is one of a triplet carbene with a triplet metal fragment, forming essentially a covalent double bond (Figure 1.3a). Highly oxidized early-transition metals and carbenes bearing only alkyl, aryl or hydrogen substituents are generally involved in this type of carbene-metal bond.[20,21]

The metal-carbene bond in Fisher-type carbene complexes results from the σ-donation of the carbene electron lone pair to the metal and π back-bonding from a filled metal *d* orbital into the formally empty p_π carbene orbital (Figure 1.3b). Such complexes usually involve low valent metals of the middle to late transition series and carbene species bearing at least one electronegative π-donor heteroatom for which the singlet state is favoured.[20,21]

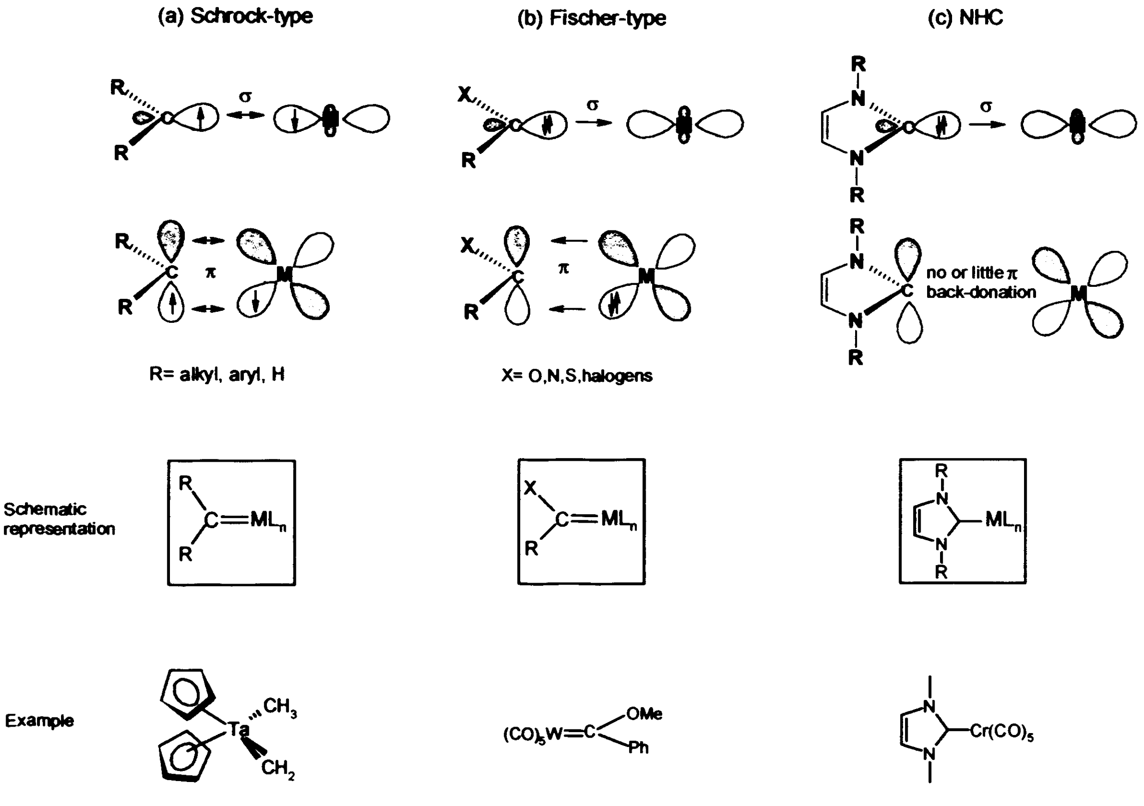


Figure 1.3. Bonding interactions in carbene-metal complexes.

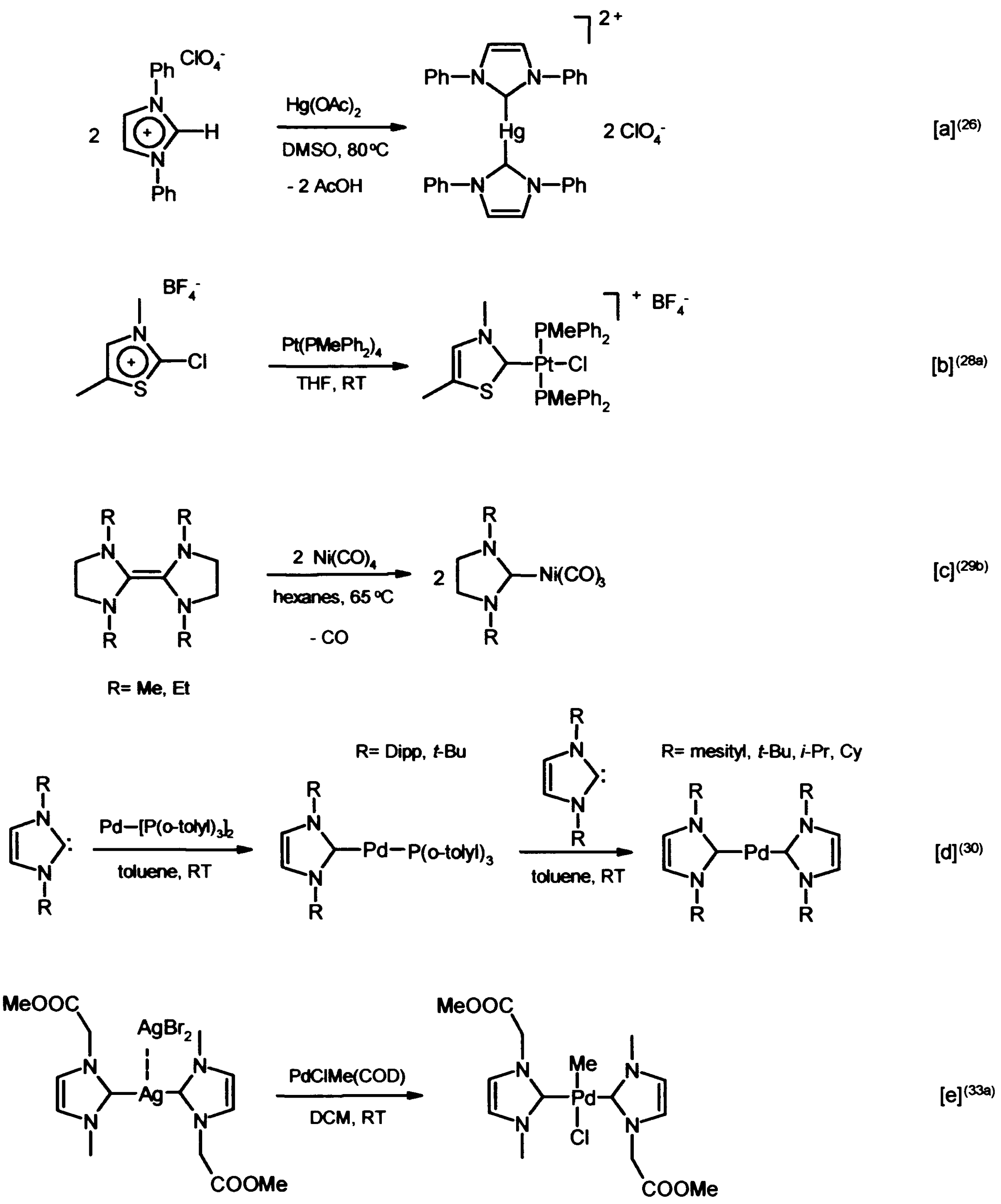
Unlike Fisher-type carbene complexes, NHC's with a stabilised lone pair of electrons and appreciable occupancy of the carbene p_π orbital as a result of π interactions with the two nitrogens atoms, generally bind to metals through σ-donation and show little or no metal to ligand π back-donation (Figure 1.3c). For this reason NHC-M bonds are often regarded as single bonds as opposed to the double bond character of the carbene-metal bond in the Shrock- or Fisher-type complexes (Figure 1.3a-c). Various theoretical[21-23] and experimental studies[22] have confirmed the essentially pure σ-donor nature of NHC ligands in disparate metal complexes. Other experimental studies,[14,24,25] amongst them CO stretching frequency studies on mixed NHC-carbonyl complexes,[14,24] have also revealed that NHC's are, in general, even better σ-donors than trialkylphosphines. Similarly X-ray diffraction studies have shown that M-C bond lengths typical of single bonds are usually observed in NHC complexes, confirming the strong and essentially uniquely σ-donor properties of these ligands.[1a]

Due to these particular binding properties NHC's have been found to form a large range of metal complexes,[1a] as the strong NHC-M σ-bond is sufficient to form stable carbene-metal complexes with most metals, in wide variety of oxidation states. This is opposed to Fisher- or Schrock-type carbenes where π-back bonding is required to stabilise such complexes i.e. only on metals with p- or d-electrons.

NHC's therefore bind to metals as strong σ-donating ligands with no or little π-back donation and are thus more comparable to amines, ethers or phosphines than to classical Fisher- or Schrock- type carbenes with respect to their coordination chemistry.

1.1.4. Preparation of N-Heterocyclic Carbene-Metal Complexes

Although the recent isolation of stable free carbenes has opened new routes for the synthesis of metal-carbene complexes, the first NHC-metal complexes date back to the late 1960's.[26,27] A number of synthetic routes leading to these complexes are now known (Scheme 1.2).[15] NHC complexes can be obtained directly from the *in-situ* deprotonation of an azolium salt in presence of an appropriate metal precursor (Scheme 1.2a). Basic ligands from the metal source, or alternatively an external base, can be used as deprotonating agents.[15] Wanzlick in 1968 used this methodology to synthesise the first reported NHC-M complex from the *in-situ* deprotonation of a imidazolium salt by mercury(II) acetate (Scheme 1.2a).[26] This synthetic route has been used to synthesise a wide variety of carbene complexes of Group 6 to 11 metals,[15] and is particularly valuable in cases where the free carbene is unstable or difficult to handle.



Scheme 1.2. Principal methods of preparation of NHC-metal complexes (with corresponding reference).

It was later found that NHC complexes are also accessible via C^2-X oxidative addition (X = halogen) of azolium salts to low valent metal precursors (Ni^0, Pd^0, Pt^0,

Rh^I, Ir^I, Fe^0, Mn^0, Cr^I) to form the corresponding NHC-M^{+II}-X complexes (Scheme 1.2b).[28a-e] Contrary to the other methods, the oxidation state of the metal precursor changes during the formation of the NHC-M complex. In some cases this methodology can be extended to the C-H oxidative addition of azolium salts to form NHC-M^{II}-H complexes of Group 10 metals[28c,f,g] (*vide infra*).

In the early 1970's Lappert and co-workers discovered that complexes bearing saturated NHC's (imidazolidin-2-ylidene types) could be prepared by thermal cleavage of certain electron rich tetraaminoethylenes in the presence of appropriate metal precursors (Scheme 1.2c). Using this method a range of NHC-M complexes of Group 6, 8 to 10 as well as Mn and Au were synthesised.[29]

The isolation of stable free NHC's has allowed the synthesis of a wide variety of NHC-complexes by simple combination of the free ligand to a metal precursor complex with mininal special requirements for the latter.[1,15] The strong σ-donor nature of NHC's greatly facilitates displacements. For example in bis(tri-ortho-tolylphosphine)palladium(0) both phosphine ligands can be replaced by free NHC to form the corresponding bis-NHC-Pd^0 complexes (Scheme 1.2d).[30] The use of bulky NHC ligands has allowed sequential exchange of the phosphines and the isolation of mixed NHC-phosphine complexes.[31] Free isolated carbene can also cleave dimeric complexes to form monomeric NHC complexes.[15]

Finally, NHC complexes can also be prepared by transfer of the NHC ligands from one metal complex to another.[32] The use of silver(I) NHC complexes in particular, obtained usually from *in-situ* deprotonation of the azolium salt with Ag_2O,[32] has been found to be particularly useful for transferring NHC ligands containing base-sensitive functional groups to palladium(II) complexes (Scheme 1.2e).[33]

1.1.5. N-Heterocyclic Carbene-Metal Complexes in Homogeneous Catalysis.

Due to their strong σ-donor ligand properties, NHC's have application as supporting ligands in various metal catalysed reactions, especially where electron rich spectator ligands are especially required.[1,34] In a number of examples NHC-ligated systems have been shown to equal or even surpass the catalytic performances of traditional systems that use strong σ-donor phosphines as supporting ligands. Although NHC-metal complexes have been known since the late 1960's and a few early reports have demonstrated the catalytic activity of some NHC-Rh complexes in olefin metathesis and hydrosilylation reactions,[35] the real potential of these ligands in homogeneous catalysis has only been realised since the report of Herrmann and co-workers in 1995, relating to the use of NHC-Pd complexes as very active catalysts for the Heck reaction (Figure 1.4).[36]

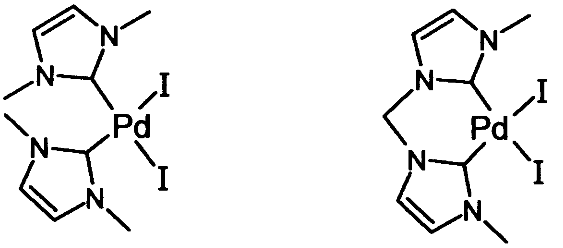


Figure 1.4. First NHC-Pd complexes employed in the Heck reaction

That particular report highlighted several advantages of the NHC-ligated systems. The strong NHC-M bond gives NHC complexes very high thermal stability and resistance to ligand dissociation, allowing NHC-based catalysts to be used in reactions requiring elevated temperatures. It has been observed that neither of the above catalysts degrade to inactive metallic palladium even after 48 hours at 140 °C under the catalytic conditions employed.

It has also been pointed out that NHC's are generally simple to prepare from the readily accessible, tuneable and stable imidazolium salt precursors. This permits an easy access to a wide range of ligands with different steric and electronic properties.[15,34]

Following the work of Herrmann[36] a large number of reports have emerged on the use of NHC-based catalysts in reactions as diverse as asymmetric hydrosilylation (Rh),[18,34,37] furan synthesis (Ru),[38] CO/ethylene copolymerisation (Pd),[39] hydroformylation (Rh),[40] atom transfer radical polymerisation (Fe),[41] ethylene oligomerization [42] and numerous Group 10 C-C and C-N coupling reactions (*vide infra*).[34]

Particularly notable are the significant achievements obtained from the use of NHC's in Ru-mediated metathesis reactions, where the replacement of one phosphine ligand with an NHC ligand in the Ru alkylidene complexes (Grubbs catalysts) led to a dramatic improvement in activity for the methathesis of a wide range of olefins (Figure 1.5).[43]

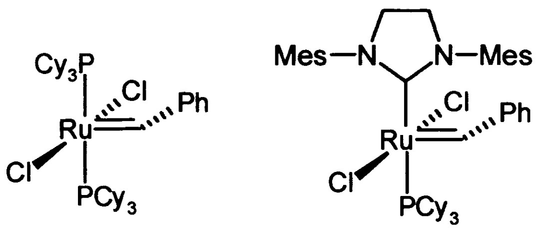
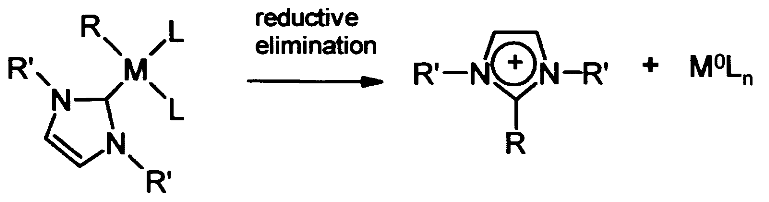


Figure 1.5. Grubbs's first and second generation metathesis catalysts.

However, even though NHC's have found applications as supporting ligands in various catalysed reactions due to their strong σ-donor properties and highly stable $M-C_{Carbene}$ bond, a number of reports have highlighted that NHC ligands can in fact be prone to a facile reductive elimination process to give 2-hydrocarbyl imidazolium salts (Equation 1.2).[44,45,46]



(1.2)

R = alkyl, aryl; M = Ni or Pd

This low energy decomposition pathway represents a serious potential deactivation process for NHC-based catalysts and can potentially directly affect the catalytic performance of NHC-based systems when intermediate complexes bearing hydrocarbyl ligands are formed during a catalytic reaction. This has been observed for example during the catalytic dimerization of 1-butene with Ni^{II}-NHC complexes in toluene,[46a] or the ethylene polymerization with Fe^{II}-NHC complexes,[46b] where in both cases the catalyst was found to quickly decompose to give various 2-hydrocarbyl imidazolium salts.[46]

1.1.6. N-Heterocyclic Carbene-Group 10 Metal(0) Catalysed Coupling Reactions.

Since the initial report by Herrmann[36] NHC ligands have found particularly important applications as supporting ligands in a wide variety of the Group 10 metal(0) mediated coupling reactions (Figure 1.6).[30,33,47-62]

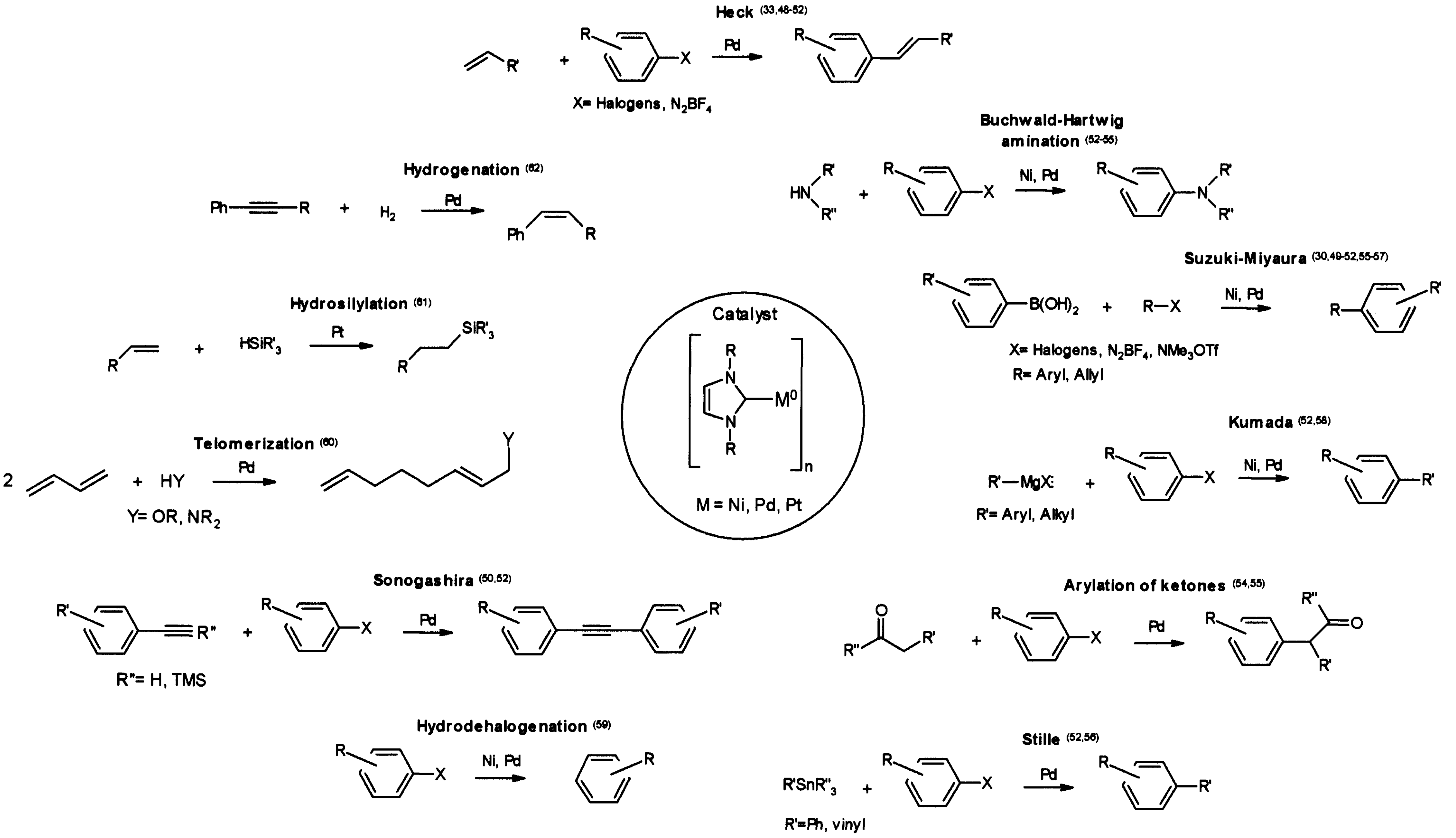


Figure 1.6. Examples of NHC-Group 10 metal(0) catalysed reactions (with corresponding reference).

Importantly these metal catalysed reactions have major synthetic interest. The Heck and the Suzuki-Miyaura couplings especially, but also the Kumada, Stille and Sonogashira cross-coupling reactions, are extremely valuable tools for the formation of aryl-C bonds in organic synthesis, especially when inexpensive aryl chlorides can be used as substrates.[63] The Buchwald-Hartwig amination is a powerful method for the formation C-N bonds.[64] The telomerization reaction can assemble simple and cheap starting materials to give valuable functionalized octadienes in a 100% atom-efficient manner (see Chapter 4).[65] Similarly, the hydrosilylation of alkenes enable the production of silicon polymers with total atom efficiency.[66]

While the exact mechanism of each type of coupling is different, all the aforementioned reactions proceed according a M^0/M^{II} redox catalytic process in which an initial oxidative addition step to a coordinatively unsaturated M^0 species occurs (Figure 1.7). The products are then released from the metal either by a reductive elimination process or a β-H elimination (Heck).

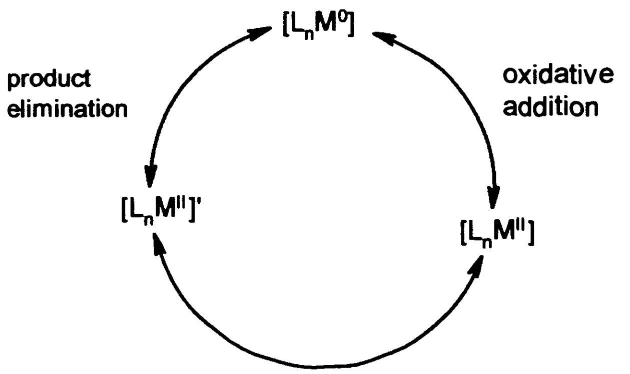
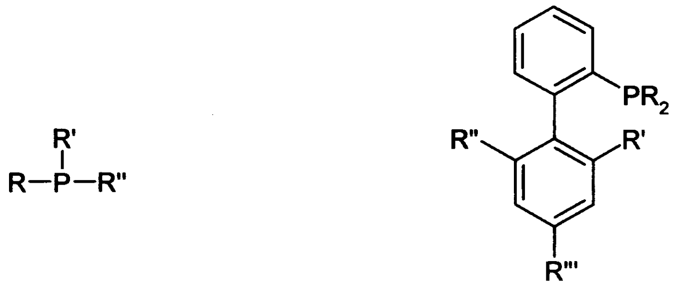


Figure 1.7. General catalytic cycle for Group 10 metal(0) catalysed reactions.

Interestingly, in most cases higher catalyst performances were observed when using NHC ligands that bear bulky N-substituents (such as mesityl or 2,6-diisopropylphenyl groups) and when using a low ligand to metal ratio (typically L/M = 1-2).[30,47-62] This low ligand to metal ratio suggests that coordinatively unsaturated M^0 species bearing one or two supporting ligands might be the active catalysts in these reactions.

In fact these NHC-based catalytic systems are closely related to systems developed by several research groups in the late 1990's that used bulky, electron rich phosphines as supporting ligands in similar C-C and C-N coupling reactions,[67] as well as in Pd^0 catalysed C-O bond forming reactions[68] (Figure 1.8).



R, R', R'' = Cy, *t*-Bu
R, R'= *t*-Bu, Ad; R''= Fc, Ad, *n*-Bu

Ad= adamantyl
Fc= ferrocenyl

R= Cy, *t*-Bu
R'= H, Me, Et, *i*-Pr, NMe$_2$, OMe
R''= H, *i*-Pr, OMe
R'''= H, *i*-Pr

Figure 1.8. Bulky and electron rich phosphines employed in Pd^0 catalysed coupling reactions.

Several mechanistic studies with the phosphine systems[69-71] have demonstrated that the strong σ-donor properties of the phosphine ligands favour the oxidative addition process by increasing the electron density at the metal centre, while the steric bulk of the ligands help to generate[70] and stabilise key reactive low-ligated metal intermediates such as mono-ligated metal species.[71] Both of these elements (steric bulk and strong σ-donation of the phosphine ligand) are believed to be key factors for the production of extremely active catalyst in these carbon-carbon and carbon-heteroatom bond formation reactions.

Since experimental evidence suggests that bulky ligands are usually required in NHC based systems to generate effective catalysts, it may be supposed that similar catalytic intermediates might be formed in both the NHC and phosphine systems. However, while both systems present some similarities, NHC ligands differ quite significantly from phosphine ligands not only in terms of σ-donor abilities but also in terms of steric properties, moreover the chemical behaviour of the coordinated ligand itself is different (*vide supra* hydrocarbyl-NHC reductive elimination process).

Thus outside of phosphine systems, little is still understood about the true nature of the intermediates involve in these NHC-Group 10 metal(0) catalysed coupling reactions.[45,49,72] The availability of mechanistic information and the study of individual catalytic steps of these reactions is essential for further development.

Moreover, the generation of active M^0 catalytic species in NHC systems has been achieved in different ways. In a number of reactions an '*in-situ* method' has been employed, whereby the active catalyst is generated by *in-situ* deprotonation of the azolium salt by a basic component followed by (assumed) coordination of the generated NHC to an appropriate metal source.[52] Often, the best catalytic results have been obtained by keeping a low azolium salt to metal precursor ratio. However, the *in-situ* method can suffer from incomplete conversion of azolium salt to NHC, or from possible side reactions during the generation of the active catalyst. Such side reactions include; formation of multi-coordinated neutral or charged metal species, interaction of the active catalyst with the products of the deprotonation process (such as the resulting salt), addition of free NHC to activated double bonds or reaction of the carbene with other functional groups present on the metal source or in the substrate used in the reaction.[1a,6,73] These side reactions will impact on the activity and/or selectivity of the catalyst. Therefore even though this *in-situ* methodology presents major practical advantages since it requires in most cases the use of stable and simple catalyst precursors, it is essential to compare results of this method with those derived from the use of a well-defined coordinatively unsaturated M^0 catalyst that minimises these possible side reactions.

1.2. Aims and Thesis Overview

The aim of this project was to synthesise and study the reaction chemistry of coordinatively unsaturated $(NHC)_n$-M^0 Group 10 complexes (n = 1, 2) that bear bulky substituents on the nitrogens. These complexes could find use as potential new catalysts for various M^0 catalysed coupling reactions, and could also be useful complexes for use in mechanistic studies. Furthermore the study of the interaction of these coordinatively unsaturated M^0 complexes with imidazolium salts, often used as ionic liquids, is also of particular interest from the point of view of using such complexes as catalysts in reactions performed in imidazolium based ionic liquid solvents.

Finally from a synthetic point of view no mono-NHC-Group 10 metal(0) complexes not bearing additional phosphine ligands were known at the start of this project.

Chapter 2 describes the synthesis and characterisation of two novel types of mono-NHC-Pd^0-olefin complexes with dimethylfumarate (DMFU) and 1,4-benzoquinone (BQ) as the olefinic ligands. While the former is monomeric and is stabilised by two olefinic units, the latter is a dimeric compound both in solution and in the solid state and bears only one olefin per palladium. Interestingly, the $Pd^0(NHC)(DMFU)_2$ type complexes are the thermodynamic product resulting from the interaction of a $Pd^0(NHC)_2$ species with DMFU ligands, driven by the formation of an organic side product formed from an NHC-DMFU coupling process. The platinum version of the dimethylfumarate palladium complex is also presented in Chapter 2. The $Pt^0(NHC)(DMFU)_2$ complex is readily synthesised from $Pt(COD)_2$ and exhibits similar spectroscopic data to its palladium counterpart.

Chapter 3 describes the synthesis and characterisation of a novel $Ni^0(NHC)_2$ (DMFU) complex as well as two novel of mono-NHC-Ni^0 complexes bearing one or two DMFU units. While the $Ni^0(NHC)(DMFU)_2$ complex is monomeric like its palladium and platinium counterparts, the $Ni^0(NHC)(DMFU)$ complex is dimeric both in solution and in the solid state. The thermodynamic equilibrium between bis- and mono-NHC-M^0 species in the presence of DMFU ligands observed for palladium is also demonstrated to occur with nickel, leading to the formation of a NHC-DMFU coupling product. Possible mechanisms for such a coupling process will be discussed.

In Chapter 4, results of the catalytic testing of two mono-NHC-Pd^0-olefin complexes described in Chapter 2, in the telomerization of butadiene with methanol is presented. Comparison is made with a known $Pd^0(NHC)_2$ complex as well as with a NHC-Pd^0 catalyst generated using the *in-situ* method.

Chapter 5 describes the stoichiometric C^2-H oxidative addition of imidazolium salts/ionic liquids to the $Pt^0(NHC)(DMFU)_2$ complex described in Chapter 2 as well as to known $M^0(NHC)_2$ complexes of nickel and palladium. These oxidative addition processes occur quickly under mild conditions and produce the corresponding bis- or tris-NHC-M^{II}-H complexes as surprisingly stable compounds .

Finally, Chapter 6 describes the combination of the imidazolium C^2-H oxidative addition and the NHC-hydrocarbyl reductive elimination processes into a catalytic cycle to form a unique Ni^0-catalysed imidazolium-alkene coupling reaction. The scope of this new catalytic transformation may be extended to other types of azolium salts. The implications for the results described in Chapters 5 and 6 for NHC chemistry and for the use of imidazolium-based ionic liquids as solvents in transition-metal catalysed reactions is discussed.

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CHAPTER 2

N-Heterocyclic Carbene Complexes of Pd^0 and Pt^0

2.1. N-Heterocyclic Carbene Palladium(0) Complexes

2.1.1. Introduction

On starting this project the well-defined, coordinatively unsaturated NHC-Pd^0 complexes **1-6** were known in the literature (Figure 2.1).

Complexes **1** and **2** were the first bis-NHC-Pd^0 to be reported and used in stoichiometric oxidative addition studies of Ar-X and X_2 (X= I, Br). Complexes **1** and **2** were synthesised by ligand displacement reactions from the respective Pd(COD)(alkene) complexes using the free NHC.[1]

Soon after, a series of homoleptic bis-NHC-Pd^0 complexes **3a-d** was synthesised using different methods. Complex **3a** was obtained by metal vapor synthesis,[2] complexe **3b** by ligand displacement reactions from $Pd[P(o\text{-tolyl})_3]_2$,[3,4] **3c** and **3d** by reduction of $[Pd(allyl)_2(\mu\text{-Cl})_2]$ with sodium dimethylmalonate in presence of the corresponding free NHC.[5,6] Complexes **3b** have been used as catalysts in the Suzuki-Miyaura coupling, **3c** and **3d** in the Buchwald-Hartwig amination reaction as well as in ligand exchange studies. Complexes **4-6** were also obtained by ligand displacement reactions.[6]

While this project was undertaken a series of mono-NHC-Pd^0(alkene) complexes **7-9** appeared in the literature. Complexes **7**, synthesised from $[Pd_2(dae)_3]$ (dae = diallylether) using the free NHC's,[7,8] were found to be highly selective catalysts for the telomerization[7,8] and the dimerization of butadiene.[9] Complexes **8-9**,[10] synthesised by ligand displacement reactions from the corresponding Pd(COD)(quinone) complexes using the free NHC, were found to be highly active catalysts for the Heck reaction of aryl chlorides,[11] the Heck and Suzuki coupling of aryldiazonium salts,[12] and the Kumada reaction with alkyl chlorides.[13]

Recently, complex **10**, obtained by ligand displacement from Pd(nbd)(MA)- (nbd = norbornadiene, MA = maleic anhydride) with the free NHC, has been found to be a highly selective catalyst for the semihydrogenation of alkynes Z-alkenes.[14]

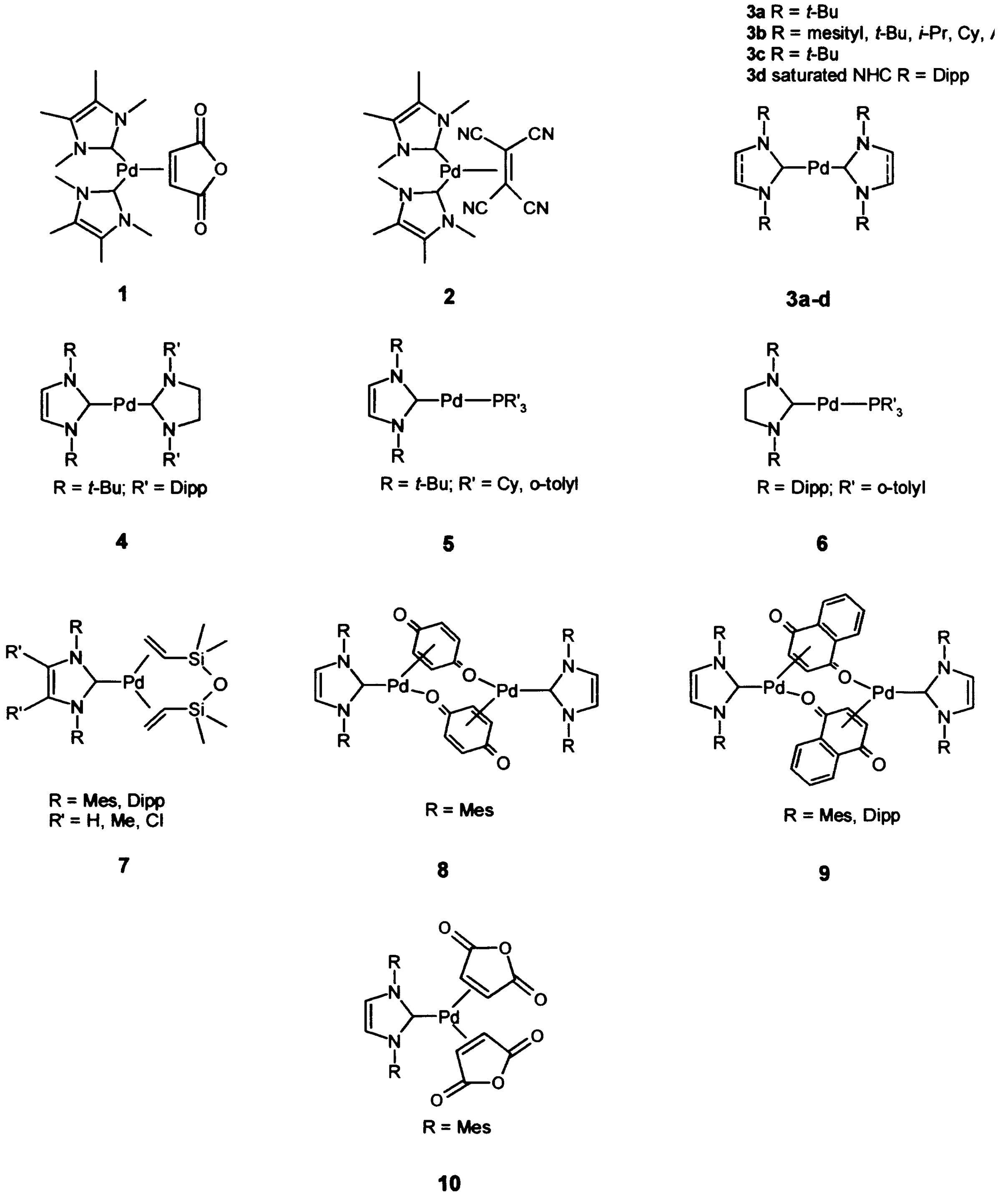
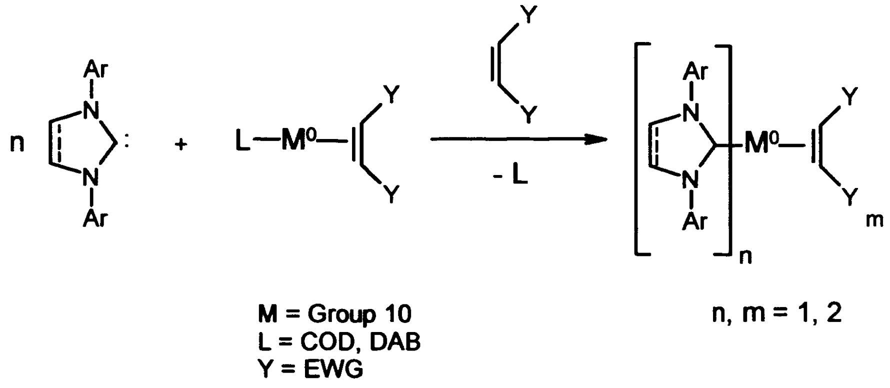


Figure 2.1. Known coordinatively unsaturated NHC-Pd^0 complexes.

2.1.2. Results and discussion

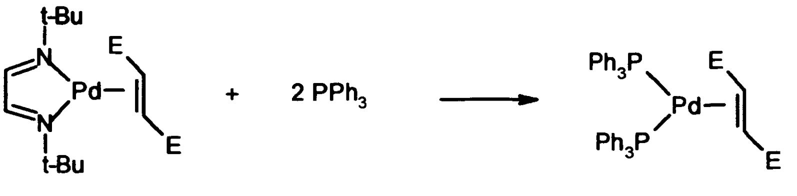
2.1.2.1. Synthesis Strategy

Because of the strong σ-donor properties of NHC ligands, one way to stabilise coordinatively unsaturated NHC-M^0 complexes of Group 10 is to have a π-acceptor ligand that will accept the electron density from the metal centre, such as an activated alkene, in a *trans* position to the NHC ligand. Starting from a M^0 source bearing an easily displaceable ligand (COD or DAB) and an activated alkene, the addition of the free NHC should give the required stablised NHC complex through a ligand displacement reaction:



2.1.2.2. Synthesis of the Complexes $Pd^0(NHC)_n(DMFU)_m$ (where n, m = 1, 2)

The complex Pd(^{t}BuDAB)(DMFU) (**11**) [^{t}BuDAB = 1,4-di-(*tert*-butyl) diazabuta-1, 3-diene and DMFU = dimethylfumarate], which is readily prepared from $Pd(dba)_2$,[15] was chosen as the starting palladium(0) source. Complex **11** has been shown to undergo facile displacement of the ^{t}BuDAB ligand with σ-donor ligands such as PPh_3 (Equation 2.1),[15] so the assumption was made that a stronger σ-donor ligand such as an NHC would also displace the DAB ligand to form complexes of the type $Pd^0(NHC)_n(DMFU)_m$ where n, m = 1, 2.

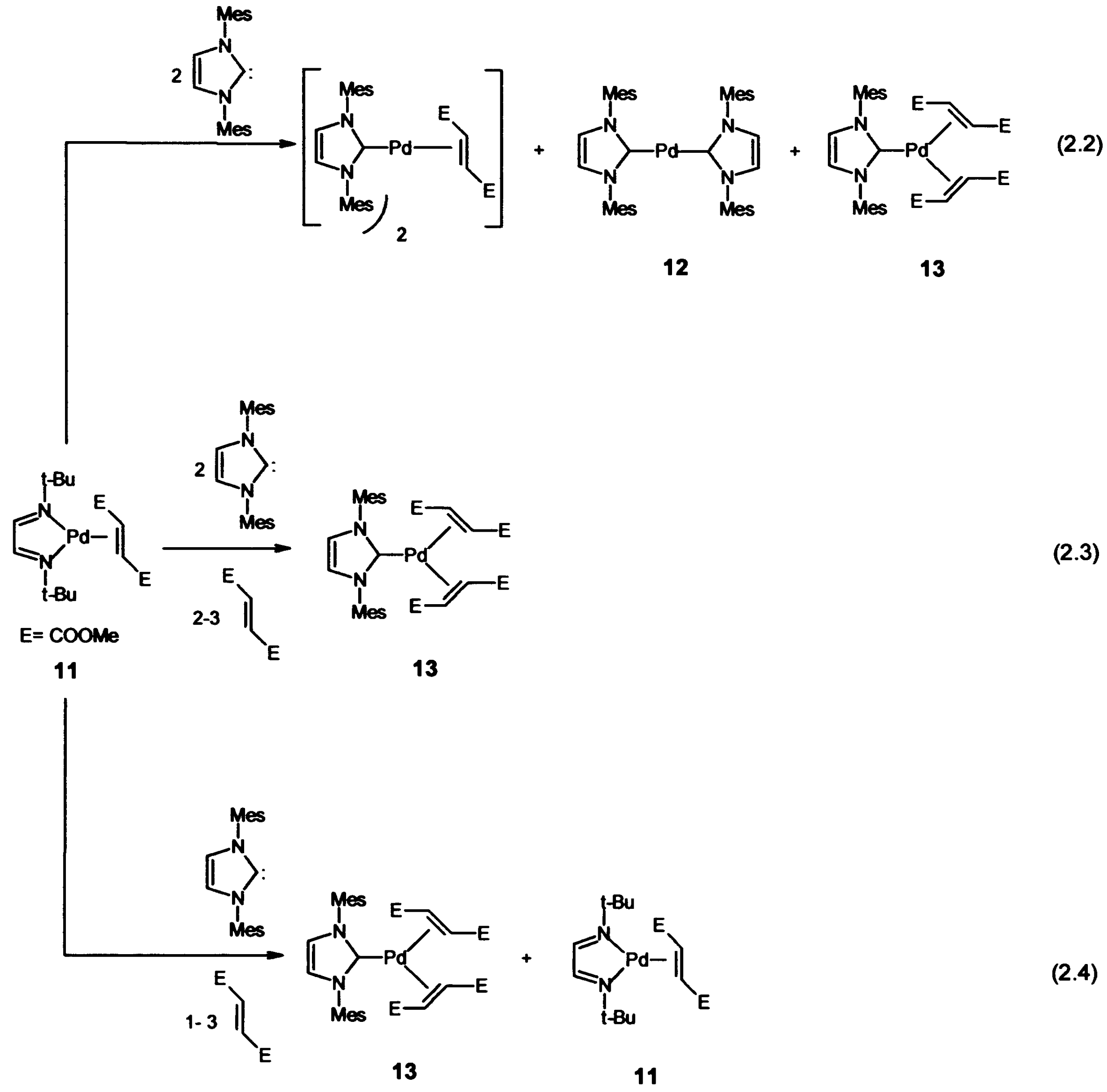


(2.1)

E= COOMe

11

When two equivalents of NHC were added to **11** in THF at room temperature a mixture of different compounds (Equation 2.2) was obtained. After evaporation of the solvent, the bis-carbene olefin complex [Pd(NHC)$_2$(DMFU)] precipitated immediately as a yellow solid from the dark etheral washings. This complex readily dissociates in solution to give Pd(NHC)$_2$, **12**, and free DMFU, as confirmed by ^{1}H and ^{13}C NMR spectroscopy (C$_6$D$_6$).[16] Complex **13** precipitates as a colourless crystalline material from the etheral washings on standing at room temperature. It seems likely that the products obtained from the reaction mixture probably all originate from the intermediate [Pd(NHC)$_2$(DMFU)], formed initially after displacement of the DAB ligand.

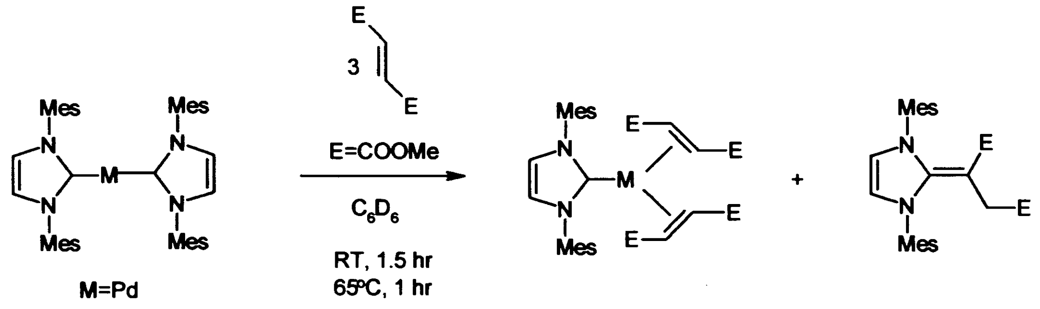


Surprisingly, when two equivalents of NHC were added to **11** in THF, followed by addition of two to three equivalents of DMFU, **13** was the only product obtained

(Equation 2.3). Complex **13** could thus be isolated as an analytically pure compound following this synthetic route (*vide infra* synthesis of complex **13**).

Attempts were made to synthetise **13** by adding only one equivalent or a slight excess of NHC to **11**, followed by the addition of one to three equivalents of DMFU (Equation 2.4). However this synthetic route did not permit the isolation of pure **13** due to the presence of traces of starting material, **11** in the product (10-15 mol%). Separation of the two compounds using normal methods proved difficult due to similar solubility properties of the two complexes.

These DAB/NHC ligand displacement reactions (Equations 2.2 and 2.3) suggest that **13** is the thermodynamic product whereas [Pd(NHC)$_2$(DMFU)] is probably the kinetic product. This implies that a thermodynamic equilibrium between bis- and mono-NHC-Pd(DMFU) complexes exists in solution, leading to the formation of **13**. In order to verify that such a process occurs in solution, the reactivity of bis-carbene complex **12** towards the electron-deficient alkene, DMFU, was investigated (Scheme 2.1).



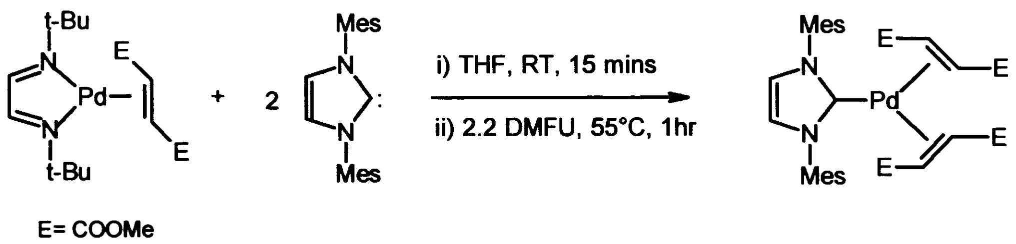
12 **13** **14**

Scheme 2.1 Equilibrium bis/mono-NHC-Pd(DMFU)

When a C$_6$D$_6$ solution of **12** was stirred at room temperature with three equivalents of DMFU, the complex was quantitatively converted into the mono-carbene complex **13** together with one equivalent of compound **14** according to ^{1}H and ^{13}C NMR spectroscopy. Compound **14** results from the reaction between an NHC ligand with one DMFU. The reaction of NHC ligands with activated olefins is well known.[17] Interestingly, the same behaviour was also observed with Ni^0-NHC complexes (see Chapter 3).

2.1.2.3. Synthesis of Pd^0(NHC-Mes)(DMFU)$_2$

Based of the above results the following procedure was developed for the synthesis of complex **13** (Scheme 2.2).

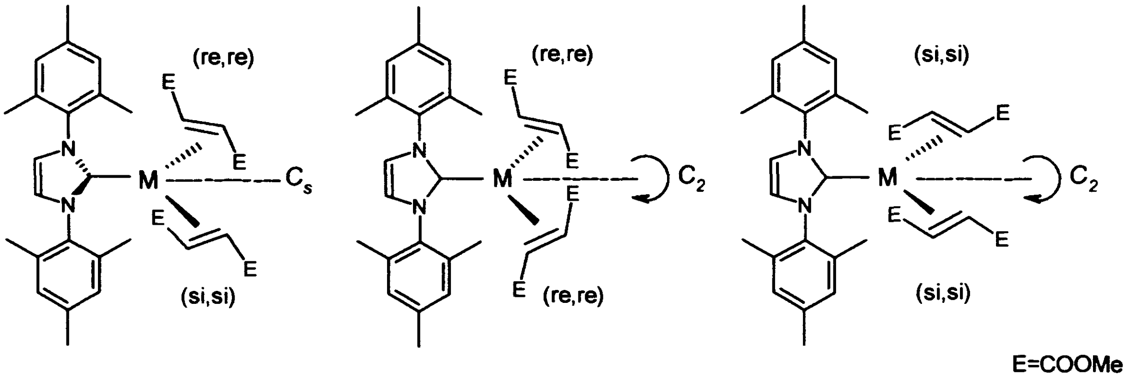


11 **13**

Scheme 2.2. Synthesis of Pd(NHC-Mes)(DMFU)$_2$ complex **13**.

Addition of two equivalents of NHC to a solution of **11**, in THF, leads to a mixture containing the complexes [Pd(NHC)$_2$(DMFU)], **12**, and **13** (Equation 2.2). Upon addition of 2.2 equivalents of the DMFU to this mixture and heating to 55°C for one hour, bis-carbene-Pd species are converted into **13**, with **14** as by-product (Equation 2.3; Scheme 2.1). Washing the mixture with diethyl ether leads to isolation of **13** as an off-white powder in 55 % yield. Complex **13** is very stable in the solid state and can be kept for an unlimited period of time under an inert atmosphere, or even in air for up to six weeks without showing any sign of degradation (according NMR). The complex is very soluble in common polar solvents (THF, toluene) and sparingly soluble in apolar solvents at room temperature (diethyl ether, *n*-hexane).

The ^1H and ^{13}C NMR spectra of **13** exhibited three different signals for the six methyl groups of the two mesityl substituents indicating that the methyl groups are in different chemical environments. The four methoxy groups of the two DMFU ligands appear as two signals, whereas the olefinic protons appear as two doublets (4.99 and 4.03 ppm, J= 10.6Hz) in the ^1H NMR, together with two different signals for the olefinic carbons (68.7 and 63.8 ppm) in the ^{13}C NMR. These olefinic signals appear at a much higher field than in the free DMFU [6.85 and 133.8 ppm (C_6D_6)] in the ^1H and ^{13}C NMR spectra, indicating donation of electron density from the palladium metal into the π^*-orbitals of the two alkenes. The NMR spectra of complex **13** exhibits half the possible proton and carbon signals (carbene carbon not included) at room temperature, which suggests that complex **13** contains either a mirror plane or a symmetry axis. Because of the prochiral nature of the alkene ligands, several stereoisomers are possible for **13** (Figure 2.2). The two DMFUs can coordinate to the metal with either a combination of different (si,si) and (re,re) enantiofaces (structure **13a** has a C_s symmetry with a mirror plane containing the metal centre and the carbene carbon), or with the same enantiofaces (si,si) and (si,si) or (re,re) and (re,re) (structures **13b** and **13c** have a C_2 symmetry axis containing the metal centre and the carbene carbon).[18]



13a **13b** **13c**

Figure 2.2. Possible stereoisomers for **13**.

This implies for **13a** that the imidazole ring must be coplanar with the coordination plane that contains the carbene carbon and the centre of the two coordinated olefinic bonds. This structure is probably unlikely for steric reasons. However, structure **13a** cannot be completely ruled out if some specific intramolecular interactions retain this conformation in solution. On the other hand, for the C_2 symmetrical isomers **13b** and **13c**, the carbene plane can twist from the coordination plane to avoid steric hindrance and both structures will show the same NMR pattern, as observed, regardless of the position of the imidazole ring. It is not possible to distinguish between the two structures **13b** and **13c** in solution as their NMR spectra will be very similar.

The solid state structure of complex **13** was confirmed by X-ray diffraction. An ORTEP diagram of **13** is shown in Figure 2.3, and selected bond distances and angles are presented in Table 2.1.

The solid state structure consists of one NHC and two DMFUs coordinated to the palladium metal centre in a slightly distorted trigonal planar geometry. The two DMFUs are coordinated to the metal in a planar fashion, via the same enantioface (stereoisomer **13b**), and with a dihedral angle between the coordination planes of the two DMFUs [Pd-C(30)-C(31) and Pd-C(24)-C(25)] of 9.88(21)°. The C=C double bonds of the coordinated DMFUs, however, [C(24)-C(25)=1.417(4) Å and C(30)-C(31)=1.412(4) Å] are elongated compared to the free olefin (1.318 Å)[19] due to reduced electron density between these bonds and metal back-donation. These values are comparable to other C=C bonds of mono-DMFU Pd^0 complexes bearing σ-donors ligands (e.g. Pd(DMFU)[(aminoferrocenyl)phosphine], 1.409 Å;[20] Pd(DMFU)(BPPFA), 1.422 Å;[21]) - (BPPFA = *N,N*-dimethyl-1-[2,1'-bis(diphenylphosphino)ferrocenyl]ethylamine).

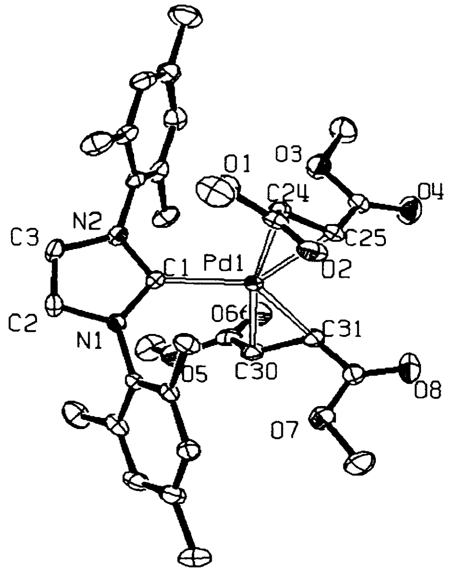


Figure 2.3. ORTEP diagram of **13**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level.

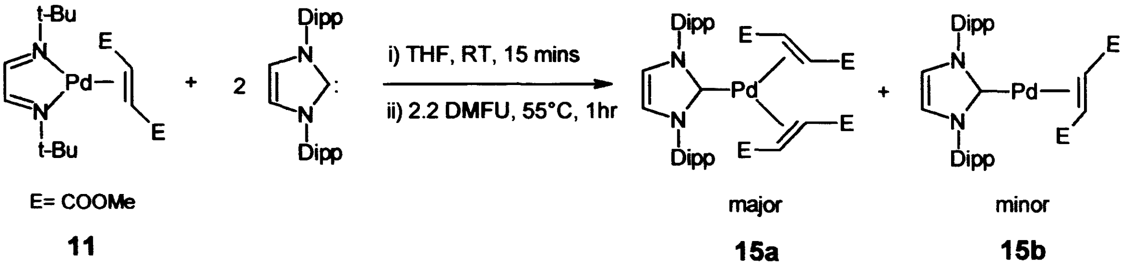
Table 2.1. Selected Bond Lengths (Å) and Angles (deg) for **13**

Pd-C(1)	2.111(3)	C(1)-Pd-C(24)	98.17(11)
Pd-C(24)	2.157(3)	C(1)-Pd-C(25)	136.48(11)
Pd-C(25)	2.141(3)	C(1)-Pd-C(30)	95.68(10)
Pd-C(30)	2.149(3)	C(1)-Pd-C(31)	133.93(11)
Pd-C(31)	2.142(3)	C(1)-Pd-C(31)	133.93(11)
C(24)-C(25)	1.417(4)	N(1)-C(1)-N(2)	104.3(2)
C(30)-C(31)	1.412(4)		

The NHC-Pd bond distance [Pd-C(1)= 2.111(3) Å] is particularly long for a Pd-NHC complex.[8] The NHC-plane is orientated at an angle of 55.58(11)° to the coordination plane of the DMFUs [C(30)-Pd-C(24)], while the mesityl substituents are able to rotate around the nitrogens of the NHC ligand with dihedral angles of 67.08(93)° and 68.00(98)° respectively relative to the NHC ring, to accommodate the two DMFUs. It is proposed that both the steric congestion around the metal centre and the repulsion between the mesityl rings and the ester groups of the DMFUs contribute to the long NHC-Pd bond.

2.1.2.4. Synthesis of Pd^0(NHC-Dipp)(DMFU)$_2$

Using the same synthetic methodology as for **13**, the analogous complex in which the nitrogens are substituted by the more bulky dipp groups (dipp = 2,6-diisopropylphenyl), was prepared (Scheme 2.3).



Scheme 2.3. Synthesis of Pd(NHC-Dipp)(DMFU)$_2$ complex **15a**.

Following this synthetic procedure and after work-up a yellow powder consisting of a mixture of bis-DMFU complex **15a** and mono-DMFU complex **15b** was isolated in a total yield of 48%. Complex **15b** was only isolated as a minor product (10 mol%) according to ^{1}H NMR spectroscopy.

The ^{1}H and ^{13}C NMR of **15a** exhibits similar features to those observed for **13**, except that **15a** shows a fluxional behaviour in solution at room temperature. The methyl groups of the two Dipp substituents appear as four different broad signals in the ^{1}H and ^{13}C NMR spectra of **15a** that indicates four sets of methyl groups in different chemical environments. The olefinic protons appear as two broad signals at room temperature (5.35 and 4.34 ppm) together with two different olefinic carbons (69.1 and 63.2 ppm). Therefore, the structure of **15a** in solution can be considered to be very similar to that envisaged for **13** , with the two alkenes coordinated via the same enantioface, providing a C_2 axis with minimisation of possible steric repulsions within the complex. The fluxional behaviour of **15a** in solution can be attributed to the important steric crowding around the metal centre in this complex.

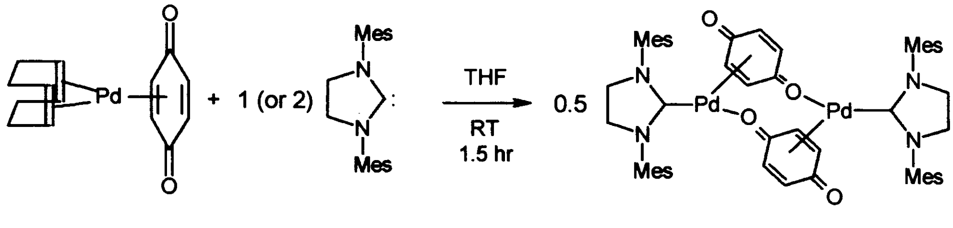
On the other hand, the minor product **15b** containing only one olefinic unit does not show fluxionality in solution. In the ^{1}H and ^{13}C NMR spectra of **15b** only two sharp doublets are observed for the methyl groups of the dipp substituents in the ^{1}H NMR together with two carbon signals in the ^{13}C NMR. The olefinic protons in **15b** appear as a unique singlet (1.11 ppm in the ^{1}H NMR) together with a unique signal for the olefinic carbons (29.7 ppm in the ^{13}C NMR). These olefinic signals appear at much higher fields than in **15a** indicating a much higher degree of metal back-bonding into the single olefinic unit of **15b**.

No evidence of equilibrium between **15a** and **15b** with liberation of a free DMFU ligand was observed by NMR spectrocopy at room temperature (C_6D_6).

2.1.2.5. Synthesis of Pd^0(saturated NHC)(BQ) dimer

Another type of activated olefins that have been shown to stabilise electron rich M^0 complexes of Group 10, are the strong π-acceptor *p*-quinone (Q) ligands.[22] We therefore investigated the behaviour of these ligands in stabilising coordinatively unsaturated NHC-Pd^0 complexes.

Addition of one equivalent of the saturated free NHC (1,3-dimesitylimidazolidin-2-ylidene) to Pd(COD)(BQ) [BQ = *p*-benzoquinone] in THF leads to exchange of the COD ligand by the carbene and formation of a dark red mixture at room temperature. Evaporation of the volatiles and washing with diethyl ether allowed isolation of complex **16** as a dark brown powder in 81% yield (Scheme 2.4). When the same reaction was carried out with two equivalents of the saturated free NHC instead of one, complex **16** was also the only isolated product. This indicates that **16** is the thermodynamically favorable product in both reactions. It is important to note that while these these studies were carried out, the group of Beller and co-workers reported the preparation of the unsaturated Pd^0(NHC)(Q) complexes **8** (BQ) and **9** (NQ) using the same synthetic route (Figure 2.1).[10]



16

Scheme 2.4. Synthesis of Pd(NHC)(BQ) dimer complex **16**.

Complex **16** is very stable in the solid state and like its unsaturated equivalent reported by Beller and co-workers, **16** is also dimeric both in solution and in the solid state. In both **8** and **16**, coordination of one of the carbonyl oxygen atoms of the coordinated benzoquinones links the two monomeric Pd(NHC)(BQ) units (Figure 2.1 and Scheme 2.4). The dimeric form of the complex makes **16** particularly insoluble in common solvents such as THF or toluene, although the complex shows good solubility and relatively good stability in dichloromethane at room temperature. The NMR spectra of **16** exhibit two kinds of olefinic signals for the coordinated BQ at room temperature. In the ^1H NMR spectrum the olefinic protons appears as two sets of doublets (5.07 and 5.04 ppm, J=8.4 and 8.6 Hz in C_6D_6; or 4.73 and 4.57 ppm, J= 8.4 and 8.3 Hz in CD_2Cl_2), and in the ^{13}C NMR spectrum the olefinic carbons appears also as two signals (108.3 and 96.4 ppm in C_6D_6, or 107.7 and 95.5 ppm in CD_2Cl_2). This could be compared with the olefinic signals of the unsaturated equivalent **8** [two doublets at 4.76 and 4.55 ppm, J= 8.3 and 8.1 Hz in the ^1H NMR and two signals at 107.9 and 95.9 ppm in the ^{13}C NMR (D_8-THF)].[10] The carbene carbon signal in **16** (215.1 ppm in the ^{13}C NMR) is comparable to carbene carbon signals found in other Pd^0 or Pd^{II} complexes bearing saturated NHC ligands.[6,23]

The solid-state structure of **16** was confirmed by X-ray diffraction methods. An ORTEP diagram of **16** is shown in Figure 2.4. Selected intramolecular bond distances and angles are presented in Table 2.2.

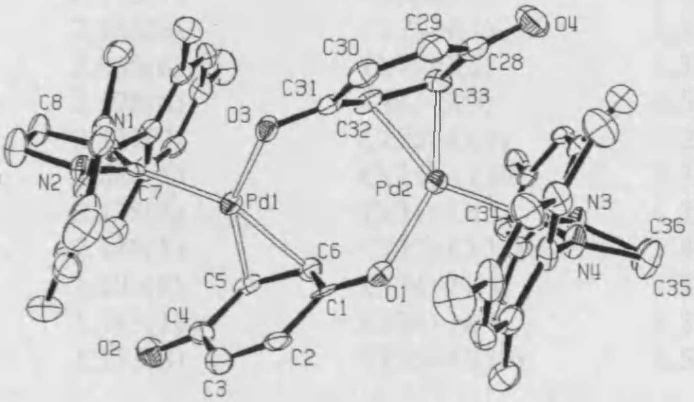


Figure 2.4. ORTEP diagram of **16**•$(CH_2Cl_2)_2$•CH_3OH. Hydrogen atoms, dichloromethane and methanol molecules are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level.

The solid state structure shows the dimeric form of **16** with a distorted trigonal-planar geometry at the two palladium centres. Although the X-ray diffraction of the 1,4-naphthoquinone bridged dimer **9** was reported for the unsaturated NHC equivalent (Figure 2.1),[10] the two complexes nevertheless show the same structural features. The carbene-Pd bonds of **16** [Pd(1)-C(7)= 2.030(6) Å and Pd(2)-C(34)= 2.034(6) Å] are within the average bond length for NHC-Pd complexes. The coordinated alkene bonds of the benzoquinone residues [C(5)-C(6)= 1.435(9) Å and C(32)-C(33)= 1.421(9) Å] are elongated compare to the uncoordinated ones [C(2)-C(3)= 1.343(10) Å and C(29)-C(30)= 1.343(9) Å]. Similarly the C=O bond of the coordinated carbonyl groups [C(1)-O(1)= 1.290(8) Å and C(31)-O(3)= 1.277(7) Å] are longer than the uncoordinated carbonyl groups [C(4)-O(2)= 1.233(8)Å and C(28)-O(4)= 1.231(8)Å]. The Pd-O bonds [Pd(1)-O(3)= 2.135(5)Å and Pd(2)-O(1)= 2.148(5) Å] are also within the expected range.[10]

Similarly to **8**, the IR spectrum of **16** shows a significant bathochromic shift of the stretching frequency ν(C=O) of the coordinated carbonyl groups as compared to the free benzoquinone ($\Delta\nu$ = 127cm^{-1} for **8** and 128cm^{-1} for **16**) as a result of the C=O bond elongation.

Table 2.2. Selected Bond Lengths (Å) and Angles (deg) for **16**

Pd(1)-C(5)	2.118(7)	C(5)-C(6)	1.435(9)
Pd(1)-C(6)	2.166(6)	C(7)-N(1)	1.342(8)
Pd(1)-C(7)	2.030(6)	C(7)-N(2)	1.339(7)
Pd(2)-C(32)	2.178(6)	C(8)-C(9)	1.522(9)
Pd(2)-C(33)	2.121(7)	C(28)-O(4)	1.231(8)
Pd(2)-C(34)	2.034(6)	C(29)-C(30)	1.343(9)
Pd(1)-O(3)	2.135(5)	C(31)-O(3)	1.277(7)
Pd(2)-O(1)	2.148(5)	C(32)-C(33)	1.421(9)
C(1)-O(1)	1.290(8)	C(34)-N(3)	1.331(8)
C(2)-C(3)	1.343(10)	C(34)-N(4)	1.341(8)
C(4)-O(2)	1.233(8)	C(35)-C(36)	1.520(9)

C(17)-Ni(1)-O(24)	99.60(9)
C(27)-Ni(2)-O(14)	95.48(9)
C(12)-C(13)-Ni(1)	117.2(2)
N(21)-C(27)-N(22)	103.4(2)
N(11)-C(17)-N(12)	103.3(2)
C(22)-C(23)-Ni(2)	119.5(2)
C(25)-C(24)-Ni(2)	97.32(18)
C(15)-C(14)-Ni(1)	98.22(17)

2.2. N-Heterocyclic Carbene Platinum(0) Complexes

2.2.1. Introduction

After Pd^0 complexes, the synthesis of coordinatively unsaturated Pt^0-NHC complexes was investigated. On starting this Pt chemistry only bis-NHC-Pt^0 complexes **17a,b** were known (Figure 2.4). Complex **17a** was made by ligand displacements in Pt(COD)$_2$ using two equivalents of the free NHC,[24] and **17b** was obtained by metal vapor synthesis.[2] During the course of this study mono-NHC type complexes **18** and **19** appeared in the literature.[16,25] Both type of complexes where made by ligand displacement reactions starting from [Pt$_2$(dae)$_3$] and using the corresponding free NHC and alkynes in the case of **19**. Both of these complexes were found to be highly selective and active catalysts for the hydrosilylation of alkenes. Subsequently, **20** was made from Pt(nbe)$_3$ and was also found to be an active catalyst for the hydrosilylation of alkenes.[26]

with the two different olefinic carbons (50.6 and 49.9 ppm in the ^{13}C NMR spectra). Like complex **13**, complex **21** is likely to present a C_2 symmetry in solution at room temperature with the two DMFUs coordinated to the metal with the same enantioface (*vide supra* discussion for complex **13**).

The solid-state structure of **21** was confirmed by X-ray diffraction methods and crystallographic details for **21** could be find elsewhere.[27]

2.3. Conclusion

Three new coordinatively unsaturated mono-NHC-Pd^0 complexes and one new mono-NHC-Pt^0 complex, all bearing bulky NHC ligands, have been synthesised and characterised. These complexes are readily synthesised and can be stored for extented periods without degradation. These complexes are thus ideal benchmark catalysts to be used in various M^0-catalysed coupling reactions.

The $Pd^0(NHC)(DMFU)_2$ type complexes are the thermodynamic products of an equilibrium existing between bis- and mono-NHC-Pd^0(DMFU) species, the equilibrium reaction being driven by the formation of an organic side product formed from an NHC-DMFU coupling process. These observations can have important implications for the exploitation of M^0-NHC chemistry (*vide infra*).

2.4. Experimental Section

2.4.1. General Comments

Materials and Methods. Unless otherwise stated all manipulations were carried out 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, diethyl ether and *n*-hexane were distilled from sodium benzophenone ketyl, and the solvents were freshly distilled under nitrogen immediately prior to use. d_6-Benzene was degassed via standard freeze/pump/thaw methods and then dried by reflux over potassium and vacuum-transferred into an ampoule equipped with a greaseless stopcock. (Dimethylfumarate) (1,4-di-*tert*-butyldiazabutadiene) palladium (0) (**11**),[15] bis(1,3-dimesitylimidazolin-2-ylidene) palladium(0) (**12**),[3,28] bis(cycloocta-1,5-diene) platinum(0),[29a] (cycloocta-1,5-diene)(1,4-benzoquinone) palladium(0),[29b] 1,3-dimesitylimidazolin-2-ylidene[30], 1,3-dimesitylimidazolidin-2-

ylidene[31a] and 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene[31b] were prepared according to published procedures. Dimethylfumarate (99%) was obtained from Acros Organics and used without further purification.

Physical and Analytical Measurements. The ^{1}H (500.13 MHz) and ^{13}C (100.63 or 125.76 MHz) NMR spectra were recorded at 293 K on Bruker DPX 400 or 500 spectrometers with chemical shifts (δ) referenced to internal solvent resonances and reported to relative TMS. Coupling constants (J) are given in Hz and NMR peaks are labelled as s = singlet, d = doublet, septet = septet, m = multiplet, br = broad. IR spectra (KBr disc) were recorded on a JASCO FT/IR-660 Plus spectrometer; abbreviations used: s = strong, m = medium, w = weak, br = broad, sh = shoulder. FAB (LSIMS) were carried out at the EPSRC National Mass Spectrometry Service Centre, Swansea (UK) and performed on a Finnigan MAT 95XP spectrometer with *m*-nitrobenzyl alcohol (NOBA) as a sample matrix. Elemental analysis were carried out by Warwick Analytical Service Ltd, Coventry (UK).

2.4.2. Preparation of compounds

Synthesis of (1,3-dimesitylimidazolin-2-ylidene) bis-(dimethylfumarate) palladium(0) (13). A THF solution (8ml) of 1,3-dimesitylimidazolin-2-ylidene (305 mg, 1.00 mmol) was added in one portion to a stirred THF solution (10ml) of (dimethylfumarate)(1,4-di-*tert*-butyldiazabutadiene) palladium(0) (200mg, 0.48 mmol) at room temperature. The dark orange solution was stirred at room temperature for 15 mins before a THF solution (20 ml) of dimethylfumarate (152 mg, 1.05 mmol) was slowly added. The dark coloured solution was then stirred at 55°C for 1 hour. The solvent was reduced to ca. 1.0 ml and diethyl ether (4 ml) added causing a precipitate to come out of the dark solution upon stirring. After 5 mins stirring at room temperature the solvent was decanted , the solid was washed with diethyl ether (2x4ml) before finally being dried in vacuo to give **(13)** as an off-white powder (yield: 184 mg, 55 %). Single crystals of **(13)** suitable for X-ray analysis were grown by slow diffusion of *n*-hexane into a THF solution of **(13)** at room temperature. ^{1}H NMR (C_6D_6, 500Mhz): δ 6.95/6.92 (2×s, 4H, arom. C*H*), 6.39 (s, 2H, imidazole C*H*), 4.99 (d, 2H, $^3J_{(HH)}$ = 10.6 Hz, olefin C*H*), 4.03 (d, 2H, $^3J_{(HH)}$ = 10.6 Hz, olefin C*H*), 3.33/3.20 (2×s, 2×6H, olefin CH_3), 2.37/2.19/1.93 (3×s, 3×6H, mesityl C*H*$_3$). ^{13}C NMR (C_6D_6, 100.63Mhz): δ 187.9 (NCN), 170.2/168.6 (COO), 138.7/137.1/135.9/135.4 (arom.C), 130.6/129.8 (arom.CH), 123.8 (imidazole CH), 68.7/63.8 (olefin CH), 51.2/50.8 (olefin CH$_3$), 21.5/19.6/18.6 (mesityl CH$_3$). IR: *v* 1717 (vs), 1712 (vs), 1707 (s, sh), 1701 (s, sh), 1696 (m, sh). MS (FAB) *m/z* (%): 714.1 (0.6) $[M-2(DMFU)+NHC]^+$, 699.1 (0.6) $[MH]^+$, 555.1 (4) $[MH-(DMFU)]^+$, 410.1 (21) $[M-2(DMFU)]^+$, 305.2 (100) $[NHC+H]^+$. Elemental Anal. Calc. for $C_{33}H_{40}N_2O_8Pd$ (699.10): C 56.69, H 5.77, N 4.01; found: C 56.73, H 5.79, N 3.92%.

Synthesis of [1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene] bis-(dimethylfumarate) palladium(0) (15).

This compound was prepared in the same manner as **(13)** using 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (389mg,1.00mmol), (dimethylfumarate)(1,4-di-*tert*-butyldiazabutadiene) palladium(0) (200mg, 0.48 mmol) and dimethylfumarate (152 mg, 1.05 mmol) to afford after reaction and work-up a yellow powder (yield: 766 mg, total yield 48%).

NMR data for [1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene] bis(dimethylfumarate) palladium(0) (15a).

^{1}H NMR (C_6D_6, 500Mhz): δ 7.24-7.39 (m; br, 6H, arom. C*H*), 6.73 (s; br , 2H, imidazole C*H*), 5.35 (br, 2H, olefin C*H*), 4.34 (br, 2H, olefin C*H*), 3.26 (s, 12H, olefin C*H*$_3$), 3.07 (m; br, 4H, *i*-Pr C*H*$_2$), 1.60/1.27/1.15/0.96 (4×br, 4×6H, *i*-Pr C*H*$_3$). ^{13}C NMR (C_6D_6, 100.63Mhz): δ 191.5 (NCN), 169.5/167.7 (br, COO), 146.1/137.6 (arom.C), 130.4 (arom.CH), 125.0 (imidazole CH), 124.9 (arom.CH), 69.1/63.2 (br, olefin CH), 51.2 (olefin CH$_3$), 29.0 (*i*-Pr CH$_2$), 27.9/25.6/24.4/22.3 (br, *i*-Pr CH$_3$).

NMR data for (1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) (dimethylfumarate) palladium(0) (15b).

^{1}H NMR (C_6D_6, 500Mhz): δ7.16-7.08 (m; br, 6H, arom. C*H*), 6.12 (s, 2H, imidazole C*H*), 3.22 (septet, 4H, $^3J_{(HH)}$ = 6.9 Hz, *i*-Pr C*H*$_2$), 3.14 (s, 6H, olefin C*H*$_3$), 1.44 (d, 12H, $^3J_{(HH)}$ = 6.9 Hz, *i*-Pr C*H*$_3$), 1.12 (d, 12H, $^3J_{(HH)}$ = 6.9 Hz, *i*-Pr C*H*$_3$), 1.11 (s, 2H, olefin C*H*). ^{13}C NMR (C_6D_6, 100.63Mhz): δ 191.7 (NCN), 173.3 (COO), 146.7/137.6 (arom.C), 129.7 (arom.CH), 125.2 (arom.CH), 119.9 (imidazole CH), 50.9 (olefin CH$_3$), 29.7 (olefin CH), 29.5 (*i*-Pr CH$_2$), 26.0/23.2 (*i*-Pr CH$_3$).

Synthesis of bis(1,4-benzoquinone) bis(1,3-dimesitylimidazolidin-2-ylidene) bis-palladium(0) (16). A THF solution (20 ml) of 1,3-dimesitylimidazolidin-2-ylidene (397 mg, 1.30 mmol) was slowly added to a solution of (cycloocta-1,5-diene)(1,4-benzoquinone) palladium(0) (398 mg, 1.24 mmol) in THF (20 ml) at room temperature. The dark red reaction mixture was stirred at room temperature for 1.5 h. The solvent was concentrated in vacuo until a volume of ca. 2 ml remained and diethyl ether (15 ml) was added. The mixture was stirred at room temperature for 5mins to give large amount of a dark precipitate. The solvent was decanted off before the solid was washed with diethyl ether (2×10ml) and dried in vacuo to afford (**16**) as a dark brown powder (yield: 520 mg, 81 %). Single crystals of **16** were obtained by slow diffusion of n-hexane into a DCM solution of **16** at 5°C. ^{1}H NMR (C_6D_6, 500.13Mhz): δ 6.75 (s, 8H, arom. C*H*), 5.07 (d, 4H, $^3J_{(HH)}$ = 8.4 Hz, bq. C*H*), 5.04 (d, 4H, $^3J_{(HH)}$ = 8.6 Hz, bq. C*H*), 3.06 (s, 8H, imidazole CH_2), 2.27 (s, 24H, *o*-CH_3), 2.11 (s, 12H, *p*-CH_3); ^{1}H NMR (CD_2Cl_2, 500.13Mhz): δ 6.86 (s, 8H, arom. C*H*), 4.73 (d, 4H, $^3J_{(HH)}$ = 8.4 Hz, bq. C*H*), 4.57 (d, 4H, $^3J_{(HH)}$ = 8.3 Hz, bq. C*H*), 3.77 (s, 8H, imidazole CH_2), 2.25 (s, 12H, *p*-CH_3), 2.08 (s, 24H, *o*-CH_3). ^{13}C NMR (C_6D_6, 125.76Mhz): δ not observed (N*C*N), not observed (*C*O), 137.9/137.4/137.4 (arom.*C*), 129.8 (arom.*C*H), 108.3/96.4 (bq. *C*H), 51.0 (imidazole *C*H_2), 21.3 (*p*-*C*H_3), 18.5 (*o*-*C*H_3); ^{13}C NMR (CD_2Cl_2, 125.76Mhz): δ 215.1 (N*C*N), 181.9/167.0 (*C*O), 137.0/136.2/136.0 (arom.*C*), 128.2 (arom.*C*H), 107.7/95.5 (bq. *C*H), 50.2 (imidazole *C*H_2), 20.1 (*p*-*C*H_3), 16.9 (*o*-*C*H_3). IR: ν 1632 (m), 1586 (s), 1518 (vs) [ν(coordinated C=O)]. MS (FAB) *m/z* (%): 826.3 (3) $[M\text{-}2(bq)]^+$, 519.2 (2) $[M/2\text{-}H]^+$, 412.0 (4) [M/2-(bq)], 307.1 (100) $[NHC+H]^+$.

Synthesis of (1,3-dimesitylimidazolin-2-ylidene) bis(dimethylfumarate) platinum (0) (21). A THF solution (8 ml) of dimethylfumarate (63 mg, 0.44 mmol) was slowly added to a stirred THF solution (7 ml) of bis(cycloocta-1,5-diene) platinum(0) (90 mg, 0.22 mmol) at room temperature. The pale yellow solution was stirred at room temperature for 20 mins after which time a THF solution (3 ml) of 1,3-dimesitylimidazolin-2-ylidene (66 mg, 0.22 mmol) was added in one portion. The yellow solution was stirred at room temperature for 1hr. The solvent was concentrated in vacuo until a volume of ca. 1 ml remained and *n*-hexane (5 ml) was added. After the mixture was stirred for 5 mins at room temperature the solvent was decanted , the solid was washed with diethyl ether/*n*-hexane (1:1 v/v) mixtures

(2x3ml) before finally being dried in vacuo to give **(21)** as an off-white powder (yield: 93 mg, 54 %). ^{1}H NMR (C_6D_6, 500Mhz): δ 6.92/6.85 (2×s, 4H, arom. C*H*), 6.33 (s, 2H, $^4J_{(PtH)}$ = 9.9 Hz, imidazole C*H*), 4.65 (d, 2H, $^3J_{(HH)}$ = 9.0 Hz, $^2J_{(PtH)}$ = 46.6 Hz, olefin C*H*), 3.47 (d, 2H, $^3J_{(HH)}$ = 9.0 Hz, $^2J_{(PtH)}$ = 62.4 Hz, olefin C*H*), 3.30/3.20 (2×s, 2×6H, olefin CH_3), 2.39/2.16/1.90 (3×s, 3×6H, mesityl CH_3). Due to the poor solubility of **(21)** in d_6-benzene the carbene carbon signal as well as the Pt-C coupling signals were not observed. ^{13}C NMR (C_6D_6, 100.63Mhz): δ not observed (NCN), 171.2/169.9 (*C*OO), 139.0/136.5/135.7/135.4 (arom.*C*), 130.5/129.8 (arom.*C*H), 124.0 (imidazole *C*H), 51.1/50.6 (olefin *C*H_3), 50.6/49.9 (olefin *C*H), 21.4/19.8/18.5 (mesityl *C*H_3). IR: ν 1717 (vs), 1712 (vs), 1707 (s, sh), 1700 (s, sh), 1696 (m, sh). For further characterisation of complex **(21)** see reference [32].

2.4.3. Ligand substitution study on (12) with dimethylfumarate

Ligand substitution reactions were carried out using complex **(12)** that was synthesised and isolated according to the literature procedure.[3,28]

To the synthesised complex **(12)** (26 mg, 0.04 mmol) was added a d_6-benzene solution (1 ml) of dimethylfumarate (16 mg, 0.11 mmol) and the yellow solution transferred into a 5 ml Youngs NMR tube under inert atmosphere. The NMR tube was sealed and placed in an oil bath at 65°C for 1hr. During that time, the solution turned to a darker colour. The solution was then immediately submitted for NMR experiments at room temperature. Analysis of the NMR spectra showed complete conversion of **(12)** into **(13)** together with the stoichiometric formation of compound **(14)**.

2.4.4. X-Ray Crystallography

Crystal structure Determination. Table 2.3 displays the main crystallographic data for the complexes **(13)** and **(16)**. All single crystal X-ray data were collected on a Bruker Nonius Kappa CCD diffractometer using graphite monochromated Mo-Kα radiation, equipped with an Oxford Cryostream cooling apparatus. The data were corrected for Lorentz and polarization effects and for absorption using SORTAV[33]. Structure solution was achieved by Direct methods (Sir-92.)[34]. Both structures were then refined by full-matrix least-squares on F^2 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 SHELXL-97,[35] with further geometrical analyses carried out with PARST,[36] implemented in the WinGX package.[37]

Table 2.3. Summary of Crystallographic Data for **13** and **16**.

	13	**16**
emperical formula	$C_{33}H_{36}N_2O_8Pd$	$C_{54}H_{60}N_4O_4Pd_2 \bullet (CH_2Cl_2)_2 \bullet CH_3OH$
fw	695.04	1243.75
cryst. Syst	monoclinic	Triclinic
space group	$P\,2_1/a$	$P\bar{1}$
a[Å]	16.6095(3)	11.1804(2)
b[Å]	10.6179(2)	13.9785(3)
c[Å]	18.3565(3)	19.4791(5)
α[deg]	90	78.6710(10)
β[deg]	92.297(2)	81.8180(10)
γ[deg]	90	68.7330(10)
V[Å^3]	3234.7(1)	2773.28(11)
Z	4	2
ρ_{calcd}[g.cm^{-3}]	1.427	1.489
F_{000}	1432	1276
μ (Mo Kα)[cm^{-1}]	6.26	8.92
T[K]	150(2)	150(2)
$2\theta_{max}$ [deg]	55.0	52.8
no. of measd rflns	32891	42300
no. of unique rflns	7380 (R_{int} = 0.1093)	11273 (R_{int} = 0.1633)
no. of params	407	652
$R1(I > 2\sigma(I))$	0.0429	0.0693
$wR2$ (all data)	0.1060	0.1797
GOF	1.043	1.022

2.5. References

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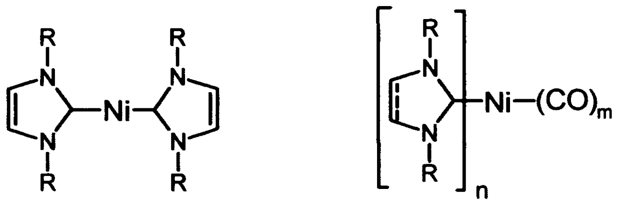
CHAPTER 3

N-Heterocyclic Carbene Complexes of Ni^0

3.1. Introduction

Relatively few NHC-Ni^0 complexes have been reported (Figure 3.1). The homoleptic bis-NHC-Ni^0 complexes **1a** and **1c** were prepared by ligand displacement reactions starting from Ni(COD)$_2$ using two equivalents of the corresponding free NHC.[1,2] Complex **1c** has shown high activity for the Kumada cross-coupling reaction of aryl fluorides.[2] Alternatively, complex **1b** was prepared by metal vapor synthesis, although in very low isolated yield (10 %).[3]

Furthermore, a number of mono- and bis-NHC-Ni^0-carbonyl type complexes **2** have been prepared (Figure 3.1), either by thermal cleavage of electron rich tetraaminoethylenes by Ni(CO)$_4$ (R = Me, Et; n = 1, 2; m = 2, 3),[4] (see Scheme 1.2c) or using the free unsaturated NHC to displace one or two carbonyl ligands from Ni(CO)$_4$.[5,6]



1a R = Mes
1b R = *t*-Bu
1c R = Dipp

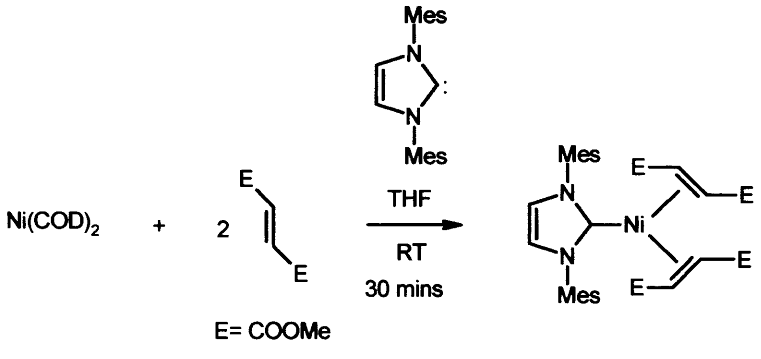
2
R = Me, Et, Cy, *t*-Bu, Mes, Dipp, Ad
n = 1, 2; m = 2, 3

Figure 3.1. Known NHC-Ni^0 complexes.[7]

3.2. Results and discussion

3.2.1. Synthesis of Ni(NHC)(DMFU)$_2$

The nickel complex of the series M^0(NHC)(DMFU)$_2$ (see Section 2.1.2.3 for Pd and Section 2.2.2.1 for Pt) was synthesised according the procedure shown in Scheme 3.1. Addition of one equivalent of the free NHC to a solution of Ni(COD)$_2$ with two equivalents of DMFU in THF, rapidly leads to the formation of a strong orange solution. Evaporation of the volatiles and washing with *n*-hexane allows the isolation of complex **3** as a orange powder in 76% yield. This complex is very stable in the solid state and may be left in air for up to six weeks without any significant degradation (NMR). Like its palladium or platinium counterparts, complex **3** is also very soluble in common polar solvents at room temperature.



3

Scheme 3.1. Synthesis of $Ni(NHC)(DMFU)_2$ complex **3**.

The ^1H and ^{13}C NMR spectra of **3** exhibits the same features observed for its Pd or Pt counterparts. The olefinic protons appear as two doublets (4.57 and 3.90 ppm, J=10.9 Hz) together with two different olefinic carbons (64.6 and 56.7 ppm). Therefore, the structure of **3** in solution can be considered to be very similar to that envisaged for $Pd(NHC)(DMFU)_2$ (see Section 2.1.2.2) , with the two alkenes coordinated via the same enantioface, providing a C_2 axis with minimisation of possible steric repulsions within the complex.

The solid-state structure of **3** was confirmed by X-ray diffraction. An ORTEP diagram of **3** is shown in Figure 3.2. Selected intramolecular bond distances and angles are presented in Table 3.1.

The Ni complex is isostructural with its Pd counterpart, similarly the C=C bond distances of the two DMFUs are elongated compared to the free olefin, although this again is as expected. The NHC-Ni bond distance [Ni-C(1)= 1.955(3) Å] falls within the range of carbene-metal bonds of other reported mono-NHC-Ni^0 complexes,[6] while as with $Pd(NHC)(DMFU)_2$ the NHC ring is also bent out of plane to the DMFU coordination plane [C(30)-Ni-C(24)] with a dihedral angle of 54.78(30)°.

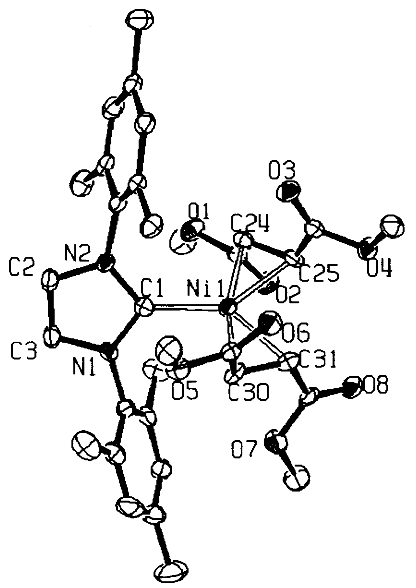


Figure 3.2. ORTEP diagram of **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50 % probability level.

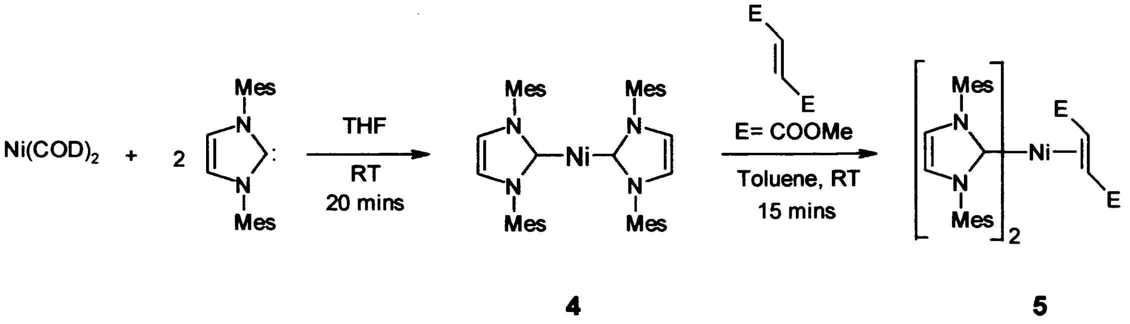
Table 3.1. Selected Bond Lengths (Å) and Angles (deg) for **3**

Ni-C(1)	1.955(3)	C(1)-Ni-C(24)	98.00(14)
Ni-C(24)	2.033(3)	C(1)-Ni-C(25)	138.20(14)
Ni-C(25)	2.012(3)	C(1)-Ni-C(30)	97.37(14)
Ni-C(30)	2.032(3)	C(1)-Ni-C(31)	136.15(15)
Ni-C(31)	2.001(3)	N(1)-C(1)-N(2)	102.4(3)
C(24)-C(25)	1.409(5)		
C(30)-C(31)	1.412(4)		

3.2.2. Synthesis of Ni^0(NHC)$_2$(DMFU)

Isolation of a compound with the molecular formula [Pd(NHC)$_2$(DMFU)] (see Section 2.1.2.1) suggest that the equivalent nickel complex might also be isolated. To isolate complex **5** the following synthetic route was adopted (Scheme 3.2).

Stirring a THF solution of Ni(COD)$_2$ with two equivalents of free NHC at room temperature affords the crude deep violet complex **4**, after evaporation of the volatiles. Addition of one equivalent of DMFU in toluene caused the solution to turn deep red, from which complex **5** could be isolated as a red solid in 61% yield.[8] Unlike its palladium equivalent, **5** is stable in solution (C_6D_6) and can be left for several days at room temperature without change (NMR). The ^{1}H and ^{13}C NMR spectra revealed a C_2 symmetry for **5** in solution at room temperature. The two mesityl groups



Scheme 3.2. Synthesis of Ni(NHC)$_2$(DMFU) complex **5**.

of each NHC ligand are chemically inequivalent due to the interaction of one side of the NHC ligands with the coordinated olefin. This feature is also reflected in the inequivalence of the two protons of the NHC backbones (two doublets at 6.22 and 5.99 ppm, J= 1.9Hz in the ^{1}H NMR). The olefinic signals (2.78 ppm in the ^{1}H and 37.0 ppm in ^{13}C NMR) appeared at significantly higher field than in **3**, probably indicating a much higher degree of back-bonding from the electron-rich (NHC)$_2$Ni-core. The solid-state structure of **5** was determined by X-ray diffraction. An ORTEP diagram of **5** is shown in Figure 3.3, and selected bond distances and angles are presented in Table 3.2.

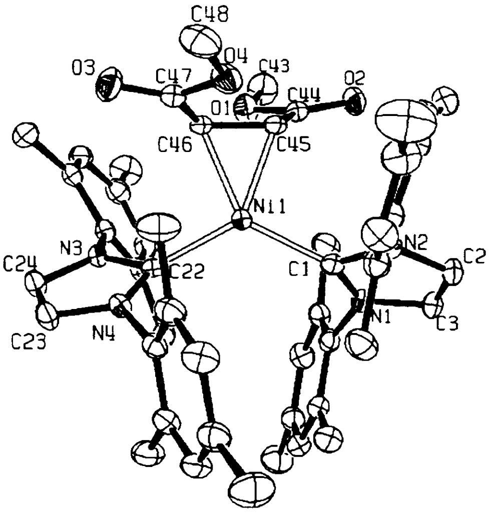


Figure 3.3. ORTEP diagram of **5**•(C$_6$D$_6$)$_3$. Hydrogen atoms and d_6-benzene molecules are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level.

The molecular structure of **5** consists of a nickel(0) metal complex with one DMFU and two NHC ligands coordinated in a trigonal planar coordination geometry. The C=C bond of the coordinated DMFU [C(45)-C(46)=1.446(3)Å] is elongated in comparison to **3**, which reflects the greater π-back-donation. The carbene-Ni bonds [Ni-C(1)=1.947(2) and Ni-C(22)=1.941(2)], are also elongated compared to that of the sole Ni^0(NHC)$_2$ complex (1.827 and 1.830 Å)[1] both in order to accommodate the DMFU ligand and due to the decrease of electron density at the metal centre (making the carbene-M bond more σ- in nature)[1].

Table 3.2. Selected Bond Lengths (Å) and Angles (deg) for **5**

Ni-C(1)	1.947(2)	C(1)-Ni-C(22)	124.31(9)
Ni-C(22)	1.941(2)	C(1)-Ni-C(45)	96.88(9)
Ni-C(45)	1.984(2)	C(22)-Ni-C(46)	96.29(9)
Ni-C(46)	1.988(2)	C(45)-Ni-(46)	42.70(9)
C(45)-C(46)	1.446(3)	N(1)-C(1)-N(2)	101.64(18)
		N(3)-C(22)-N(4)	101.61(18)

3.2.3 Synthesis of Ni^0(NHC)(DMFU) complex

After the synthesis of Ni^0(NHC)(DMFU)$_2$ complex **3**, attempts were made to isolate a NHC-Ni complex with a single NHC ligand and with only one olefinic unit to stabilise the Ni centre (Scheme 3.3).

When a stoichiometric amount of free NHC was added to a solution of Ni(COD)$_2$ containing one equivalent of DMFU in toluene or C_6D_6 at room temperature, the solution rapidly darkened. A quick-fire NMR measurement of the solution (C_6D_6) revealed the *in-situ* formation of a mixture of the mono-NHC-Ni complexes **6**, **7** and **3** (Scheme 3.3). The mono-DMFU complexes **6** and **7** are the main products formed [approximately 40 and 55 % respectively][9] after 10 mins reaction. The bis-DMFU complex **3** formed as a minor component [5 %]. However after further stirring at room temperature (24 hrs) or at 65°C (1hr.) complex **6** progressively rearranged into **7** changing the composition of the *in-situ* mixture [15 % for **6**, 80 % for **7**, and 5 % for **3**]. Stirring the solution for longer did not change this product distribution, highlighting the equilibrium between these complexes in solution (Scheme 3.3). During the work-up process, complex **6** (as well as a small proportion of **7**) is then converted into complex **3** and an unidentified compound (the latter being soluble in

3.3). The mixture does not show any decomposition even after two months in solution standing at room temperature (NMR).

The solid-state structure of **7** was confirmed by X-ray diffraction. An ORTEP diagram of **7** is shown in Figure 3.4 and selected intramolecular bond distances and angles are presented in Table 3.3. The X-ray analysis confirms the dimeric nature of **7** with the two DMFUs coordinated to the two nickel centres via the same face. The coordination geometry is distorted trigonal-planar at the two nickel centres with each nickel coordinated to one carbene ligand, the C=C bond of one DMFU and a carbonyl oxygen atom of the other DMFU ligand thereby forming a fumarate ester-bridged dimer.

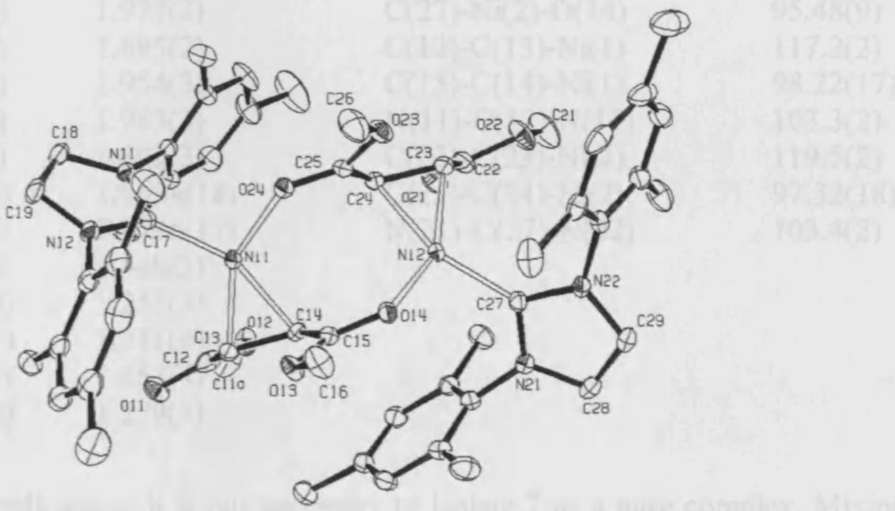


Figure 3.4. ORTEP diagram of $7 \cdot H_2O$. Hydrogen atoms, the water molecule and disordered atoms are omitted for clarity. The methoxy group on C(12) is disordered over two positions in a 66:34 ratio. Thermal ellipsoids are drawn at 30% probability level.

The carbene-Ni bonds [Ni(1)-C(17)=1.895(2) Å and Ni(2)-C(27)=1.893(3) Å] are shorter than those of **3** and **5**. Reduced steric crowding around the two Ni centres in **7** is likely to explain these shorter NHC-Ni bonds. The C=C bond of the coordinated DMFUs [C(13)-C(14)=1.448(3) Å and C(23)-C(24)=1.453(4) Å] are comparable to those in **3** and **5** reflecting some degree of π-back bonding from the nickel core, while the Ni-O bonds [Ni(1)-O(24)=1.9634(18) Å and Ni(2)-O(14)=1.9596(17) Å] are within the expected range[10]. Significant distortions can be seen at the olefinic C(14) and C(24) atoms carrying the coordinated carbonyl groups. For example the angles Ni(1)-C(14)-C(15) [98.22(17)°] or Ni(2)-C(24)-C(25) [97.32(18)°] are much smaller than the corresponding angle at olefinic C(13) [117.2(2)°] or at C(23) atoms [119.5(2)°] carrying free carbonyl groups. The two bridging carbonyls not surprisingly have slightly longer C=O bonds [C(15)-O(14)=1.255(3) Å and C(25)-O(24)=1.259(3)Å] compared to the uncoordinated carbonyls groups [C(22)-O(21)=1.211(4) Å]. This bond elongation is also revealed in the IR spectrum of **7** where the stretching frequency ν(C=O) of the coordinated carbonyl groups shows a significant bathochromic shift as compared to the free DMFU ($\Delta\nu = 133\text{cm}^{-1}$)[11].

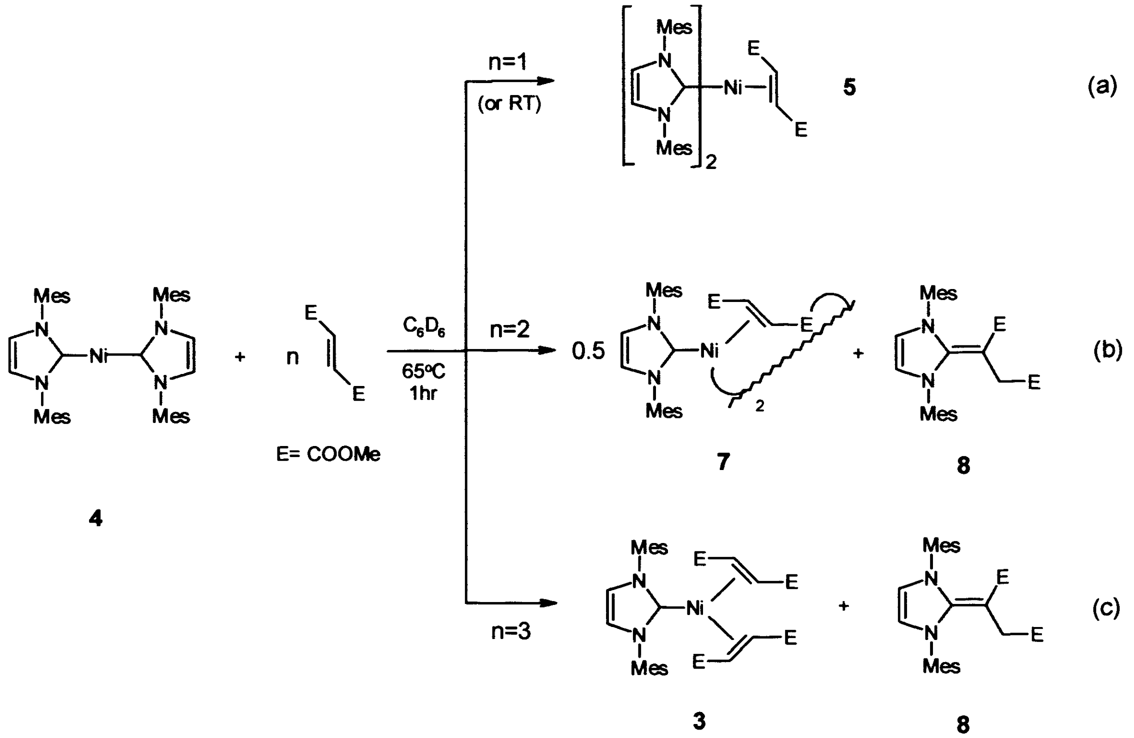
Table 4. Selected Bond Lengths (Å) and Angles (deg) for **7**

Ni(1)-C(13)	1.953(3)	C(17)-Ni(1)-O(24)	99.60(9)
Ni(1)-C(14)	1.977(2)	C(27)-Ni(2)-O(14)	95.48(9)
Ni(1)-C(17)	1.895(2)	C(12)-C(13)-Ni(1)	117.2(2)
Ni(2)-C(23)	1.954(3)	C(15)-C(14)-Ni(1)	98.22(17)
Ni(2)-C(24)	1.983(3)	N(11)-C(17)-N(12)	103.3(2)
Ni(2)-C(27)	1.893(3)	C(22)-C(23)-Ni(2)	119.5(2)
Ni(1)-O(24)	1.9634(18)	C(25)-C(24)-Ni(2)	97.32(18)
Ni(2)-O(14)	1.9596(17)	N(21)-C(27)-N(22)	103.4(2)
C(13)-C(14)	1.448(3)		
C(15)-O(14)	1.255(3)		
C(22)-O(21)	1.211(4)		
C(23)-C(24)	1.453(4)		
C(25)-O(24)	1.259(3)		

For catalytic applications it is not necessary to isolate **7** as a pure complex. Mixing stoichiometric amounts of $Ni(COD)_2$ and DMFU with one equivalent of NHC provides ready access to an *in-situ* mixture of reactive mono-coordinated NHC-Ni^0 species where essentially only one olefinic unit stabilises each electron rich nickel centre. Splitting the olefinic bridge will provide a highly coordinatively unsaturated Ni-NHC fragment. Hence this *in situ* mixture should show further interesting chemistry and provide a valuable route to catalytic intermediates for a variety of reaction types.

3.2.4. Equilibrium Considerations Bis/mono-(NHC)Ni(DMFU)

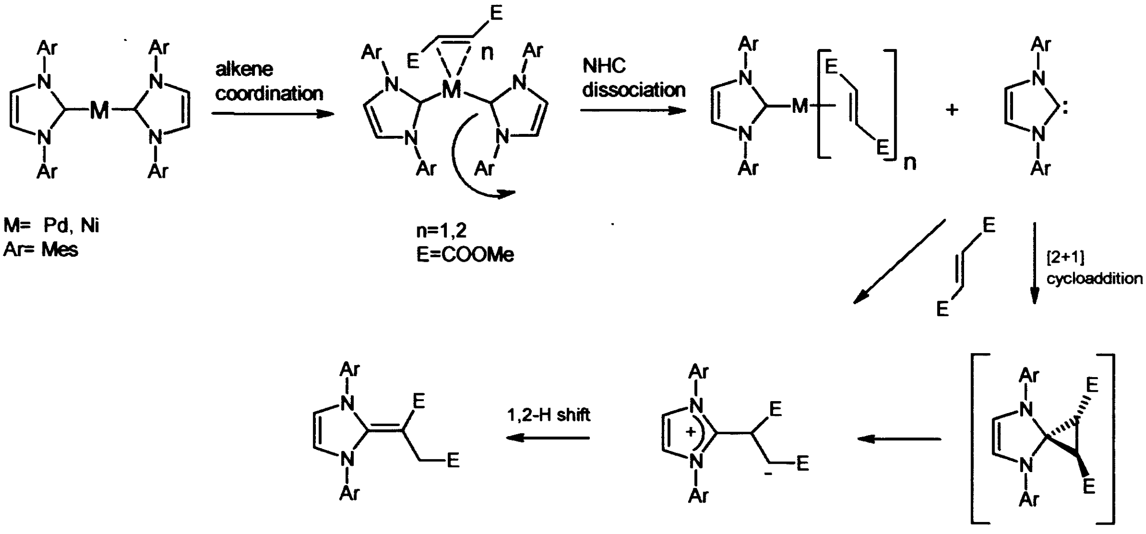
The equilibrium between bis- and mono-NHC-Pd(DMFU) species in solution leads, under mild conditions, to the thermodynamically stable Pd(NHC)(DMFU)$_2$ and an NHC-DMFU coupling product (see Scheme 2.1). The same chemistry was investigated with Ni, and the reactivity of the bis-NHC-Ni^0 complex, **4**, towards the activated alkene, DMFU, was also studied (Scheme 3.4).



Scheme 3.4. Equilibrium bis/mono-NHC-Ni(DMFU)

Heating a C_6D_6 solution of **4** with DMFU quickly leads to the quantitative formation of different Ni-DMFU complexes, depending on the amount of DMFU added. Addition of an equimolar quantity of DMFU to **4** generates the bis-NHC olefin complex **5** (Scheme 3.4a; Scheme 3.2). When two equivalents of DMFU were added to complex **4**, the bis-NHC-Ni^0 complex converts into the dimeric mono-NHC-Ni^0 olefin complex **7** [in equilibrium with approximately 20 and 5 mol % of complex **6** and **3** respectively][9], and the NHC-olefin coupling product **8** (Scheme 3.4b; Scheme 3.3). Finally adding three equivalents of the olefin converted **4** into the mono-NHC bis-olefin complex **3** as well as compound **8** (Scheme 3.4c; Scheme 3.1). These experiments demonstrate that the same equilibria, bis-/mono-NHC-M(DMFU) observed for Pd also occur with Ni under mild conditions to give the thermodynamically stable products **3**, **5**, **7**, and **8** .

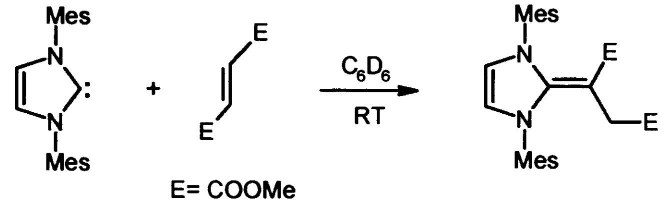
Compound **8** results from the reaction between one NHC ligand with one DMFU. Mechanistically two possible mechanisms can rationalise the formation of **8**. In an intermolecular process one NHC ligand could firstly dissociate from the bis-NHC-M^0 metal centre possibly promoted by the coordination of DMFU ligand(s) (Scheme 3.5).



8

Scheme 3.5. Proposed intermolecular mechanism leading to the formation of **8**.

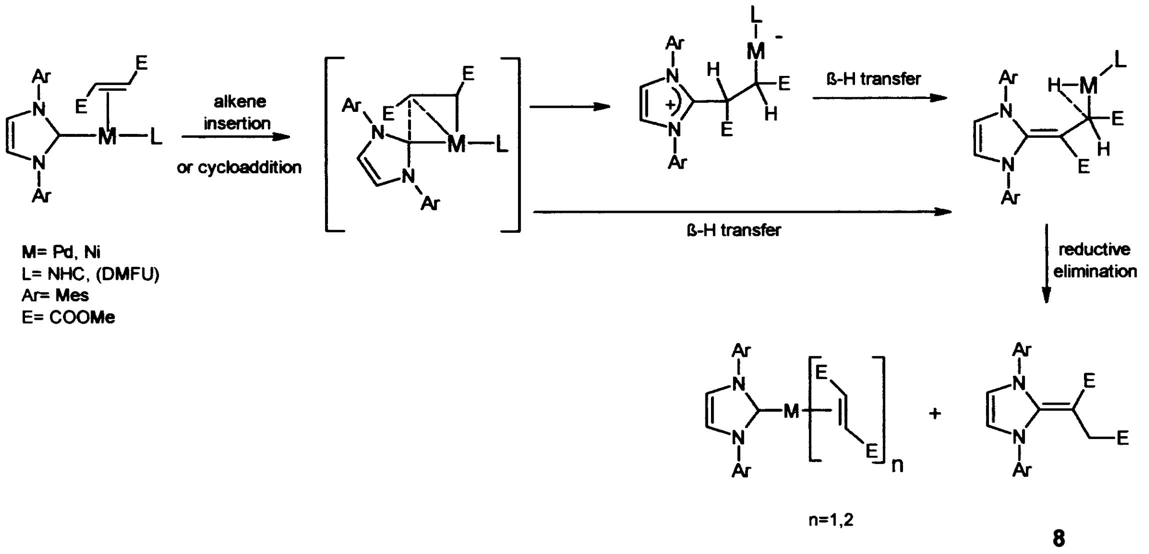
Lability of NHC ligands at a sterically encumbered two-coordinate NHC-Pd^0 centre has been demonstrated by Caddick, Cloke and co-workers where one of the NHC ligands (IDipp, ItBu) is readily displaced in solution by bulky phosphine ligands.[12] Dissociated free NHC ligand could add to the double bond of a DMFU to give compound **8**,[13] and indeed, in a separate experiment we found that free NHC reacts rapidly with the electron deficient alkene, DMFU, to give **8** (Equation 3.1).



(3.1)

8

However, an intramolecular NHC-alkene coupling reaction can also explain the formation of **8** (Scheme 3.6). Aminocarbene complexes are known to react with electron deficient alkenes to give products derived from a formal C-H insertion process.[14] An intramolecular mechanism consisting of successive cycloaddition of the alkene with the metal-carbene, β-H transfer from the formed metallocyclobutane to the metal and final C-H reductive elimination has been proposed to account for the formation of the observed products.[14a] In our case such a reaction could also give rise to compound **8** and the different mono-NHC-M^0-DMFU complexes (Scheme 3.6).



Scheme 3.6. Proposed intramolecular mechanism leading to the formation **8**.

Experimental studies such as variable temperature NMR experiments on the equilibrium shown in Scheme 3.4c performed over the temperature range 20-55 °C, did not permit discrimination between a possible inter- or intra-molecular mechanism using complex **4**, as no reaction intermediates could be identified on the NMR time scale over this range of temperature. The study of the equilibrium existing between bis-NHC-Pd^0 species and DMFU by low-temperature NMR spectroscopy has not been performed but would be of interest in order to identity possible intermediates of these reactions. The use of theoretical calculations might also help to distinguish by which mechanism these reactions are more likely to proceed.

These different equilibrium studies (Schemes 2.1 and 3.4) have important implications for the exploitation of M^0-NHC chemistry. Activated olefins such as DMFU can act as a stabilising ligand for important catalytic intermediates such as ylidene) nickel(0) (**4**),[1] bis(cycloocta-1,5-diene) nickel(0),[15] and 1,3-dimesitylimidazolin-2-ylidene[16] were prepared according to published procedures. Dimethylfumarate (99%) was obtained from Acros Organics and used without further purification.

Physical and Analytical Measurements. The ^{1}H (500.13 MHz) and ^{13}C (62.90, 100.63 or 125.76 MHz) NMR spectra were recorded at 293 K on Bruker DPX 250, 400 or 500 spectrometers with chemical shifts (δ) referenced to internal solvent resonances and reported to relative TMS. Coupling constants (J) are given in Hz and NMR peaks are labelled as s= singlet, d= doublet, t= triplet. IR spectra (KBr disc) were recorded on a JASCO FT/IR-660 Plus spectrometer; abbreviations used: s= strong, m= medium, w= weak, br= broad, sh= shoulder. APcI mass spectra were performed on a VG Fisons Platform II spectrometer. Samples were dissolved in dichloromethane, a sample cone voltage of 20 V and a corona discharge pin at 3.5kV were used. FAB (LSIMS) were carried out at the EPSRC National Mass Spectrometry Service Centre, Swansea (UK) and performed on a Finnigan MAT 95XP spectrometer with *m*-nitrobenzyl alcohol (NOBA) as a sample matrix. Elemental analysis were carried out by Warwick Analytical Service Ltd, Coventry (UK).

3.4.2. Preparation of compounds

Synthesis of (1,3-dimesitylimidazolin-2-ylidene) bis-(dimethylfumarate) nickel (0) (3). A THF solution (6ml) of dimethylfumarate (147 mg, 1.02 mmol) was slowly added to a stirred THF solution (6ml) of bis(cycloocta-1,5-diene) nickel(0) (140 mg, 0.51 mmol) at room temperature. The orange solution was stirred at room temperature for 5 mins after which time a THF solution (4 ml) of 1,3-dimesitylimidazolin-2-ylidene (155 mg, 0.51 mmol) was added in one portion. The dark orange solution was stirred at room temperature for 30 mins before the volatiles were removed in vacuo and the residue washed with *n*-hexane (3×6ml). Finally the resultant solid was dried in vacuo to afford (**3**) as an orange powder (yield: 252 mg, 76 %). Single crystals of (**3**) were obtained by slow diffusion of *n*-hexane into a THF solution of (**3**) at 5°C. ^{1}H NMR (C_6D_6, 500Mhz): δ 6.92/6.91 (2×s, 4H, arom. CH), 6.35 (s, 2H, imidazole CH), 4.57 (d, 2H, $^3J_{(HH)}$ = 10.9 Hz, olefin CH), 3.90 (d, 2H, $^3J_{(HH)}$ = 10.9 Hz, olefin CH), 3.31/3.20 (2×s, 2×6H, olefin CH_3), 2.42/2.17/1.94 (3×s, 3×6H, mesityl C*H*$_3$). ^{13}C NMR (C_6D_6, 100.63Mhz):δ 187.1 (N*C*N), 171.8/169.3 (*C*OO), 138.8/137.0/136.3/135.4 (arom.*C*), 130.6/129.9 (arom.*C*H), 125.0 (imidazole *C*H), 64.6/56.7 (olefin *C*H), 51.3/50.7 (olefin *C*H$_3$), 21.5/19.5/18.5 (mesityl *C*H$_3$). IR: ν 1715 (m, sh), 1706 (s), 1696 (m, sh), 1686 (m, sh). MS (FAB) *m/z* (%): 506.1 (46) [M-(DMFU)]$^+$, 362.0 (45) [M-2(DMFU)]$^+$, 305.1 (100) [NHC+H]$^+$. Elemental Anal. Calc. for $C_{33}H_{40}N_2O_8Ni$ (651.37): C 60.85, H 6.19, N 4.30; found: C 60.65, H 6.15, N 4.16%.

Synthesis of bis(1,3-dimesitylimidazolin-2-ylidene)(dimethyfumarate) nickel(0) (5). A THF solution (5 ml) of 1,3-dimesitylimidazolin-2-ylidene (265 mg, 0.87 mmol) was added in one portion to a stirred THF solution (10ml) of bis(cycloocta-1,5-diene) nickel(0) (120 mg, 0.44 mmol) at room temperature. The dark violet solution was stirred at room temperature for 20 mins after which time the volatiles were removed in vacuo. The crude bis-carbene nickel(0) complex (**4**) was redissolved in toluene (10 ml) to which was added with stirring a toluene solution (5 ml) of dimethylfumarate (63 mg, 0.44 mmol) in one portion. The dark red coloured solution was stirred at room temperature for 15 mins before the toluene solvent was removed in vacuo and the residue washed with *n*-hexane (2×3ml). Finally the resultant solid was dried in vacuo to give (**5**) as a pink-red powder (yield: 216 mg, 61 %). Single crystals of (**5**) were obtained by standing a saturated d_6-benzene solution of (**5**) at room temperature. ^{1}H NMR (C_6D_6, 500Mhz): δ 6.96/6.88/6.87/6.72 (4×s, 4×2H, arom. C*H*), 6.22/5.99 (2×d, 2×2H, $^3J_{(HH)}$= 1.9 Hz, imidazole C*H*), 3.22 (s, 6H, olefin C*H*$_3$), 2.78 (s, 2H, olefin C*H*), 2.66/2.27/2.23/2.22/1.84/1.51 (6×s, 6×6H, mesityl C*H*$_3$). ^{13}C NMR (C_6D_6, 125.76 Mhz): δ 199.6 (N*C*N), 175.7 (*C*OO), 139.4/139.4/138.1/137.9/137.5/137.3/136.4/136.0(arom. *C*), 130.6/130.2/129.2/128.9 (arom. *C*H), 124.3/122.8 (imidazole *C*H), 49.7 (olefin *C*H$_3$), 37.0 (olefin *C*H), 21.6/21.4/20.1/19.2/18.6 (mesityl *C*H$_3$). IR: ν 1706 (m, sh), 1679 (s), 1668 (s). MS (FAB) *m/z* (%): 666.3 (100) [M-(DMFU)]$^+$, 362.0 (12) [M-(DMFU)-NHC]$^+$, 305.0 (48) [NHC+H]$^+$, 303.0 (48) [NHC-H]$^+$. Elemental Anal. Calc. for $C_{48}H_{56}N_4O_4Ni$ (811.68): C 71.03, H 6.95, N 6.90; found: C 69.17, H 6.85, N 6.58%.

Synthesis of bis(1,3-dimesitylimidazolin-2-ylidene) bis(dimethyfumarate) bis-nickel(0) (7). A toluene solution (5ml) of dimethylfumarate (63 mg ,0.44mmol) was slowly added to a stirred solution of bis(cycloocta-1,5-diene) nickel(0) (120 mg ,0.44

mmol) in toluene (15ml) at room temperature. The orange solution was stirred at room temperature for 5 mins after which time a toluene solution (5 ml) of 1,3-dimesitylimidazolin-2-ylidene (133 mg, 0.44 mmol) was added in one portion. The dark coloured solution was then stirred at 65°C for 1hr. The volatiles were removed in vacuo and the residue washed with *n*-hexane (2×6ml) with the mixtures stirred for 10 mins each time. Finally the resultant solid was dried in vacuo to give a purple powder consisting of a mixture of the dimeric complex (**7**) (60 mol%) and the monomeric complex (**3**) (40 mol%) according NMR [yield of mixture: 143 mg, approximately 60 % (based on Ni(COD)$_2$)]. Crystals of (**7**) were grown by slow diffusion of *n*-hexane into a THF solution of a mixture of (**7**) and (**3**) at 5°C. The large deep violet crystals of (**7**) were then separated from the smaller orange crystals of (**3**). ^{1}H NMR (C_6D_6, 500Mhz): δ 7.03/6.77 (2×s, 8H, arom. C*H*), 6.26 (s, 4H, imidazole C*H*), 3.45/3.25 (2×s, 2×6H, olefin C*H*$_3$), 2.67 (d, 2H, $^3J_{(HH)}$ = 10.6 Hz, olefin C*H*), 2.50/2.16/1.96 (3×s, 3×12H, mesityl C*H*$_3$), 1.78 (d, 2H, $^3J_{(HH)}$ = 10.6 Hz, olefin C*H*). ^{13}C NMR (C_6D_6, 100.63 Mhz): δ 195.8 (N*C*N), 177.9/172.7 (*C*OO), 138.5/137.6/136.6/135.9 (arom.*C*), 129.4/129.3 (arom.*C*H), 121.9 (imidazole *C*H), 50.8/50.0 (olefin *C*H$_3$), 39.5/26.1 (olefin *C*H), 21.5/18.7/18.4 (mesityl *C*H$_3$). IR: ν 1723 (sh), 1701(s), 1685 (s), 1586 (vs, br) [ν(coordinated C=O)]. MS (FAB) *m/z* (%): 506.1 (12) [M/2]$^+$, 449.2 (100) [NHC+(DMFU)+H]$^+$, 362.0 (14) [M/2-(DMFU)]$^+$, 321.1 (51), 305.1 (78) [NHC+H]$^+$.

NMR data of the *in-situ* nickel complex (6). ^{1}H NMR (C_6D_6, 500 Mhz): δ 6.93/6.75 (2×s, 8H, arom. C*H*), 6.23 (s, 4H, imidazole C*H*), 3.34/3.29 (2×s, 2×6H, olefin C*H*$_3$), 2.38 (d, 2H, $^3J_{(HH)}$ = 9.5 Hz, olefin C*H*), 2.37/2.22/1.95 (3×s, 3×12H, mesityl C*H*$_3$), 1.96 (d, 2H, $^3J_{(HH)}$ = 10.0 Hz, olefin C*H*). ^{13}C NMR (C_6D_6, 100.63 Mhz): δ 194.9 (N*C*N), 179.8/177.8 (*C*OO), 138.3/138.0/137.1/136.7 (arom.*C*), 129.5/129.3 (arom.*C*H), 122.5 (imidazole *C*H), 51.0/50.0 (olefin *C*H$_3$), 36.0/24.5 (olefin *C*H), 21.5/18.6/18.3 (mesityl *C*H$_3$).

Synthesis of methyl 2-(1,3-dimesitylimidazolin-2-ylidene) succinate (8). A d_6-benzene solution (1 ml) of dimethylfumarate (18 mg, 0.13 mmol) was added dropwise to a stirred d_6-benzene solution (1ml) of 1,3-dimesitylimidazolin-2-ylidene (38 mg, 0.13 mmol) at room temperature over a period of 2 mins. After the addition was completed the solution was immediately transferred in an NMR tube and submitted for NMR experiment. NMR revealed quantitative formation of (**8**). The NMR solvent was removed in vacuo and the residue triturated with *n*-hexane (2×1 ml). After the solvent was decanted off the resultant solid was finally dried in vacuo to give (**8**) as an off-white powder (yield: 39 mg, 68 %). ^{1}H NMR (C_6D_6, 500Mhz): δ 6.71 (s, 4H, arom. C*H*), 5.81 (s, 2H, imidazole C*H*), 3.26 (s, 2H, C*H*$_2$COO), 3.19/3.16 (2×s, 2×3H, COOC*H*$_3$), 2.21 (s, 12H, *o*-C*H*$_3$), 2.07 (s, 6H, *p*-C*H*$_3$). ^{13}C NMR (C_6D_6, 62.90Mhz): δ 173.3/167.7 (*C*OO), 154.4 (N*C*N), 138.1/136.0/135.7 (arom. *C*), 130.1 (arom. *C*H), 118.6 (imidazole *C*H), 63.2 (*C*COO), 50.8/49.6 (COO*C*H$_3$), 34.3 (*C*H$_2$COO), 21.3 (*p*-*C*H$_3$), 18.7 (*o*-*C*H$_3$). MS (APCI) *m/z* (%): 449 (100) [MH]$^+$. Elemental Anal. Calc. $C_{27}H_{32}N_2O_4$ (448.55): C 72.30, H 7.19, N 6.25; found: C 71.61, H 7.24, N 6.16%.

3.4.3. Ligand substitution studies on (4) by dimethylfumarate

A typical experiment is described below for (**4**) and other substitution reactions with this complex were carried out in similar way in varying the stoichiometry of dimethylfumarate added.

A THF solution (3 ml) of 1,3-dimesitylimidazolin-2-ylidene (66 mg, 0.22 mmol) was added in one portion to a stirred THF solution (5ml) of bis(cycloocta-1,5-diene) nickel(0) (30 mg, 0.11 mmol) at room temperature. The dark violet solution was stirred at room temperature for 20 mins after which time the volatiles were removed in vacuo. To the crude bis-NHC-Ni^0 complex (**4**) was added a d_6-benzene solution (1 ml) of dimethylfumarate (47 mg, 0.33 mmol) and the dark solution transferred into a 5 ml Youngs NMR tube under inert atmosphere. The NMR tube was sealed and placed in an oil bath at 65°C for 1hr. During that time, the solution turned to a brownish colour. The solution was then immediately submitted for NMR experiments at room temperature. Analysis of the NMR spectra showed complete conversion of (**4**) into (**3**) together with the stoichiometric formation of compound (**8**).

3.4.4. X-Ray Crystallography

Crystal structure Determination. Table 5 displays the main crystallographic data for the complexes (**3**), (**5**) and (**7**). All single crystal X-ray data were collected on a Bruker Nonius Kappa CCD diffractometer using graphite monochromated Mo-Kα radiation, equipped with an Oxford Cryostream cooling apparatus. The data were corrected for Lorentz and polarization effects and for absorption using SORTAV[17]. Structure solution was achieved by Direct methods (Sir-92)[18] for (**3**) and by Patterson methods (Dirdif-99)[19] for (**5**) and (**7**). All structures were then refined by full-matrix least-squares on F^2 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 SHELXL-97,[20]with further geometrical analyses carried out with PARST,[21] implemented in the WinGX package.[22]

Table 5. Summary of Crystallographic Data for **3**, **5** and **7**

	3	**5**	**7**
emperical formula	$C_{33}H_{36}N_2O_8Ni$	$C_{48}H_{54}N_4O_4Ni \cdot (C_6D_6)_3$	$C_{54}H_{60}N_4Ni_2O_8 \cdot H_2O$
fw	647.35	1043.99	1028.50
cryst. syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a[Å]	14.7055(3)	10.2286(2)	10.7764(1)
b[Å]	10.9864(2)	17.0906(2)	16.4619(2)
c[Å]	19.5639(4)	18.8608(3)	29.9743(3)
α[deg]	90	116.879(1)	90
β[deg]	98.248(1)	91.591(1)	90.571(1)
γ[deg]	90	97.885(1)	90
V[Å^3]	3128.1(1)	2898.01(8)	5317.2(1)
Z	4	2	4
ρ_{calcd}[g.cm^{-3}]	1.375	1.196	1.285
F_{000}	1360	1112	2168
μ (Mo Kα)[cm^{-1}]	6.74	3.85	7.65
T[K]	150(2)	150(2)	150(2)
$2\theta_{max}$ [deg]	55.0	54.8	54.9
no. of measd rflns	37401	60692	64736
no. of unique rflns	7029 (R_{int} = 0.1358)	13032 (R_{int} = 0.0979)	11921 (R_{int} = 0.1164)
no. of params	407	690	649
$R1(I>2\sigma(I))$	0.0595	0.056	0.0531
$wR2$ (all data)	0.1548	0.1230	0.1393
GOF	1.034	1.034	1.130

3.5. References

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(8) Employing THF as the solvent commonly led to the isolation of a mixture of **5** together with complex **3** as a minor product (10-15 mol%).

(9) The relative percentages shown in square brackets are based on the amount of monomeric species present in solution and were determinated by ^1H NMR using the relative integral of the CH signal of imidazole backbone of the NHC ligand of each species.

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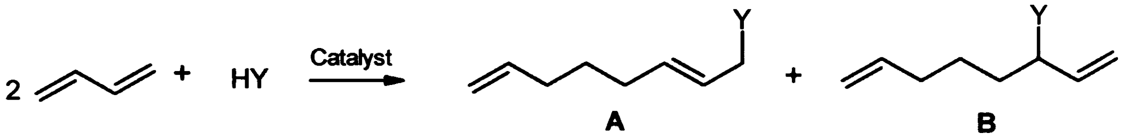
CHAPTER 4

Telomerization Reactions with NHC-Pd^0 Complexes

4.1. Introduction

In homogeneous catalysis, the telomerization reaction is defined as the oligomerization of dienes with the simultaneous addition of a nucleophile.[1] In a typical example two molecules of 1,3-diene react with one nucleophile, HY, to form the dimeric telomers A and B (Scheme 4.1). Many nucleophiles are known to take part in this process, such as H_2O, ROH, R_2NH and RCOOH.[1b] Amongst the different dienes used, butadiene and isoprene have been the most thoroughly investigated, with butadiene showing the greatest activity.

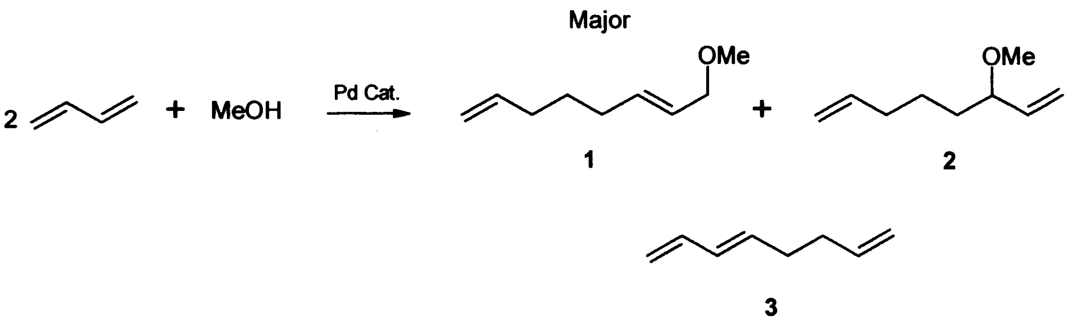


Scheme 4.1. Telomerization reaction

Several metals (Pd, Ni, Rh, Pt)[1b] are known to catalyse the telomerization reaction but metal complexes of Pd are by far the most active and selective catalysts.

The telomerization reaction is of great industrial interest since it can assemble simple and cheap starting materials, to give valuable functionalized octadienes in a 100% atom-efficient manner. The telomerization of butadiene with H_2O gives 2,7-octadien-1-ol that can be hydrogenated to give 1-octanol, an important plasticizer.[1d] This reaction was developed on an industrial scale by the Kuraray company in 1991.[2] A biphasic system has enabled the selective production of primary octadienylamines from the telomerization of butadiene with NH_3.[3] This system could also represent an attractive route for the industrial production to *n*-octylamine. The telomerization of isoprene has also been studied as a potential route to terpenoid compounds.[4]

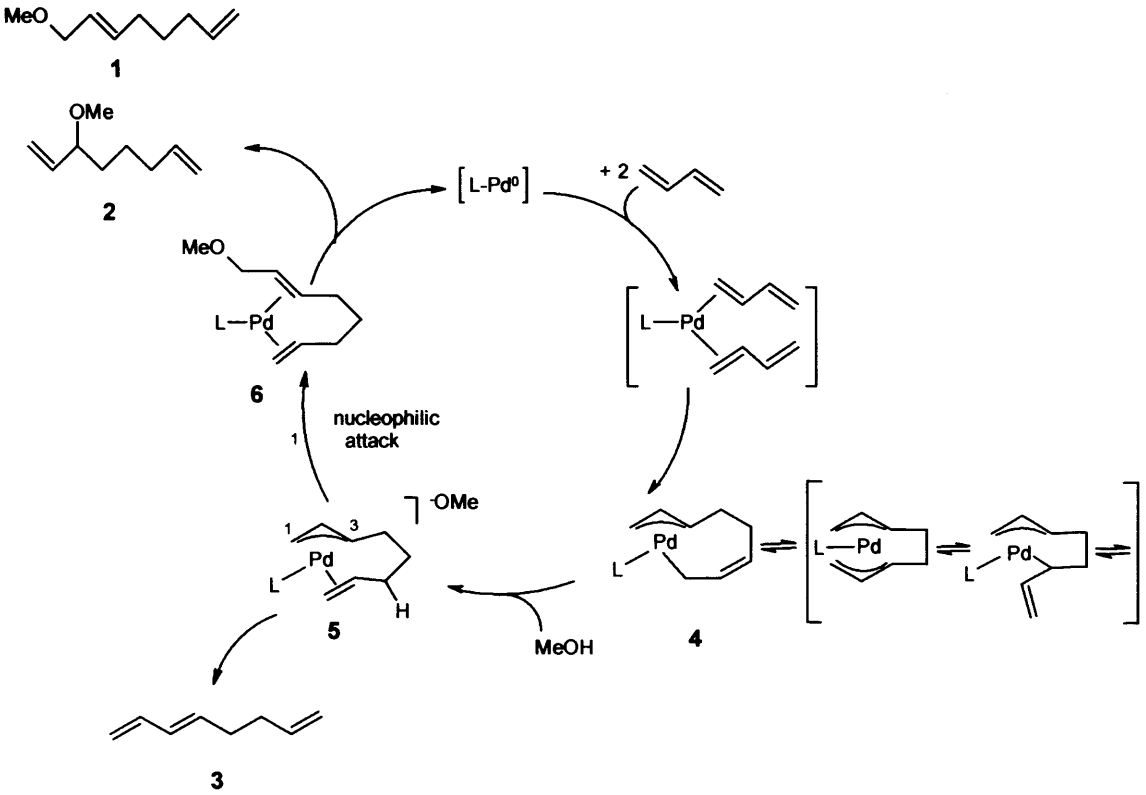
We choose to study the catalytic telomerization of butadiene with methanol (Scheme 4.2). This reaction has been extensively studied over the last past years and both mechanistic[5] and systematic optimisation studies of reaction parameters have been reported.[6,7] The best catalysts are based on mixture of $Pd(OAc)_2$ with PPh_3.[7]



Scheme 4.2. Telomerization of butadiene with methanol

Like most other telomerization reactions, the linear 1-methoxy-2,7-octadiene compound **1** is produced as the main product of the reaction while the branched 3-methoxy-2,7-octadiene compound **2** forms to a minor extent. The 1,3,7-octatriene compound **3**, resulting from the linear dimerization of butadiene, can also be obtained as a by-product of the reaction.

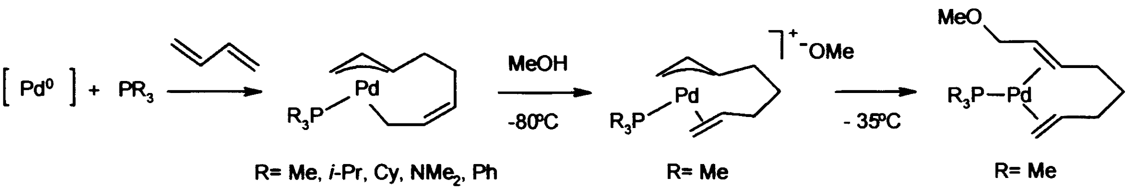
Although different mechanisms have been proposed for telomerization reactions, depending on the substrates employed,[1b] the telomerization of butadiene with methanol has been most thoroughly investigated,[5] and the generally accepted mechanism is that shown in Scheme 4.3.



Scheme 4.3. Proposed mechanism for telomerization reaction of butadiene with methanol

Oxidative coupling of two molecules of butadiene at a low-coordinated Pd^0 species, gives several C8-allylic species such as the η^1-η^3-octadienediyl-Pd^{II} complex **4**. Protonation at the C-6 position of the C-8 chain affords the η^2-η^3-octadienediyl-Pd^{II} species **5** that subsequently undergoes nucleophilic attack at the allyl group. If the nucleophile adds to the allylic C-1 position, the 1-substituted product **1** is formed (*via* **6**). On the other hand, nucleophilic addition at the C-3 position affords the 3-substituted product **2**. If nucleophilic attack does not takes place on the η^2-η^3-intermediate, the 1,3,7-octatriene compound **3** is produced by β-H abstraction at the C-4 position. Significant amounts of **3** are observed when higher alcohols are employed as nucleophiles, here β-H abstraction seems to be a more favorable process than nucleophilic attack at the allyl group.[8]

The mechanism in Scheme 4.3 has been confirmed by experimental results using phosphine ligands (Scheme 4.4).[5] Reaction of butadiene with a Pd^0 source [bis-(allyl)Pd or Pd(Cp)(allyl)] in the presence of PR_3, has allowed the isolation of complex **4**. Reaction of **4** (R=Me) with MeOH at low temperature produced complex **5**, which rearranged into the more stable η^2-η^2- complex **6** when the temperature was increased. Product displacement from **6** has been confirmed to occur in the presence of butadiene, reforming complex **4** and thus completing the catalytic cycle.

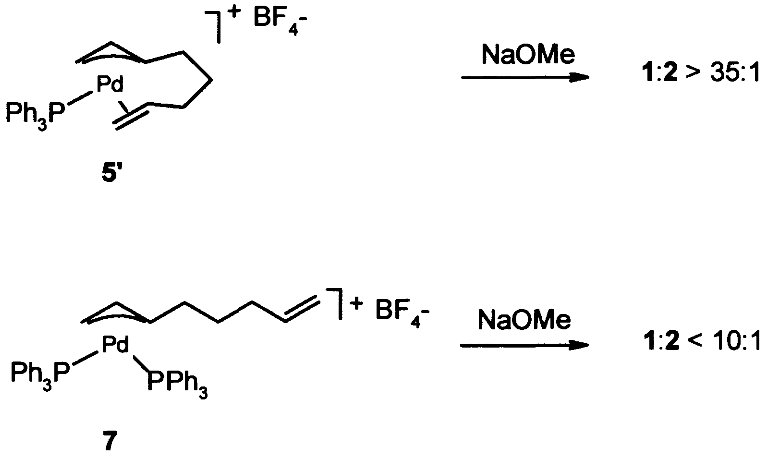


4 **5** **6**

Scheme 4.4. Isolated intermediates of the telomerization of butadiene with methanol

The product distribution of the telomerization reaction is usually very dependent on the catalytic system and conditions employed. For this reason extensive screening of the reaction parameters must be carried out in order to optimise each catalytic reaction. Apart the reaction conditions and the stoichiometry of the starting materials, the type of ligand and the amount of ligand added to the system have been found to have a major impact on the selectivity of the reaction. For the telomerization of butadiene with methanol or ammonia, a low ratio of phosphine to palladium has been found to improve the regioselectivity of the reaction (regioselectivity = ratio **1**:**2**)[3b, 6c]

This observation can be rationalised by increased competition by excess phosphine affecting the ability of the C8-allylic chain to coordinate to the palladium centre. This competition can have a detrimental effect particularly during the nucleophilic attack at **5**, the key step governing the regioselectivity of the reaction (Scheme 4.5).



Scheme 4.5. Nucleophilic attack of the methoxide anion on different allylic Pd complexes

As demonstrated experimentally,[6c] nucleophilic attack of the methoxide anion on the allyl group of the mono-phosphine complex **5'**, with the alkene functionality also coordinated, leads to a high regioselectivity of the attack (ratio **1**:**2** > 35:1). In comparison nucleophilic attack at complex **7** where the alkene has been displaced by PPh_3, gave lower regioselectivity for the nucleophilic attack (ratio **1**:**2** < 10:1). Apart from steric considerations, another reason accounting for this observation would be the *trans* effect of the coordinated alkene in **5'** decreasing the electron density at the C-1 position of the allyl group, thus making this position more prone to nucleophilic attack.[3b] These results demonstrate that a strict control of the ligand to metal ratio is necessary for control of regioselectivity in the products obtained from the telomerization reaction.

4.2. Results and Discussion

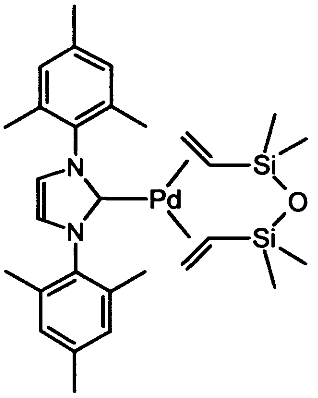
4.2.1 Telomerization of Butadiene with Methanol Using NHC Based Catalysts

The above discussion demonstrates that catalytic systems based on PPh_3 have important drawbacks for the telomerization of butadiene with methanol. Firstly, the use of an excess of ligand, often required to stabilise the metal centre especially at higher temperatures, can lead to a decrease in the regioselectivity and activity of the reaction due to competition for coordination sites during the important nucleophilic attack step of the reaction.

Additionally, this competition for coordination sites might also affect other steps of the reaction, such as the oxidative coupling of butadiene at the Pd^0 centre. Although no kinetic experiment has been reported, it can be seen from Scheme 4.4 that only one supporting ligand on the metal centre is enough to stabilise **4**. Scheme 4.4 also demonstrates that the presence of a strong σ-donor ligand on the metal, should lead to the selective production of the linear methoxyoctadiene **1**.

All of these factors lead us to believe that NHC ligands, and well defined mono-NHC-Pd^0 complexes in particular, might be especially well suited for this telomerization reaction. NHC ligands are strong σ-donor ligands that usually bind strongly to the metal even at elevated temperature. The use of a well defined mono-NHC-Pd^0 catalyst should allow the generation of a mono-ligated Pd^0 active catalyst with a strongly bound ligand. This type of active catalyst should be ideal for sustaining high activity and high selectivity in the telomerization reaction of butadiene with methanol.

It is important to note at this stage of this discussion that concurrent with our study, Beller and co-workers reported on the same reaction using the mono-NHC-Pd^0 complex **8**.[9]



8

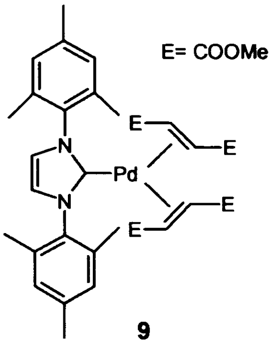
This complex, very similar to our system and stabilised with a chelating π-acce ligand, was the first reported mono-NHC-Pd^0 complex with no additional phosp ligand. This catalyst proved to be extremely active and highly selective for telomerization of butadiene with methanol, as well as with other aliphatic alcoho was also a significantly better catalyst than the standard Pd(OAc)/PPh$_3$ system. example while the phosphine based catalyst gave a mixture of **1** and **2** in 79% in a 12:1 ratio, the catalyst **8** afforded quasi-quantative yield (≥ 98%) of telomers 36:1 ratio. By lowering the catalyst amount, a TON of 267,000 over 16h resulti a TOF of 16,700h^{-1} was obtained [Note = TON and TOF are parameters use evaluate the productivity and activity of a catalyst sytem. TON: Turn Over Numb mol products/mol catalyst; TOF: Turn Over Frequency = TON/Time]. At that this was the highest catalyst productivity (TON) reported for any telomeriza reaction. Even more significant differences were seen between the two systems higher alcohols were used as nucleophiles.

In the light of Beller's report, the results presented here are preliminary results further studies have not been pursued. The conditions employed here are the sam those reported in Beller's report. The different catalysts tested for the telomeriza reaction are shown below and results are presented in Table 4.1. Pre-formed cat mono-NHC-Pd^0 complexes **9** and **10** as well as the bis-NHC-Pd^0 complex **11** very bulky dipp N-substituents[10] were tested for this reaction [dipp = 2,6- isopropyl)phenyl]. For a comparison with an *in-situ* generation of the catalyst, catalytic mixture **12** was used.[11] Also catalytic mixtures **13** and **14** were also teste study the influence of a NHC ligand bearing a hemilabile pyridyl group on catalytic system.

The NHC based Pd^0 catalysts **9-12** are active for the telomerization of butadiene methanol, selectively giving only the telomeric products **1** and **2** according to N spectroscopy, GC and GC-MS measurements. This is in accordance with most o reported NHC based catalysts, where very little or no octatriene **3** has detected.[9,11,12]

On the other hand catalytic mixtures **13** and **14** did not give any product at all, indicates that in these systems the pyridyl group completely blocks the react which is consistent with the proposed mechanism, based on a monoligated L

All pre-formed catalysts **9**, **10** and **11** are extremely active for this reaction, giving high yields of telomers in short reaction times (20 mins to 1 hr). In comparison the *in-situ* generated catalyst using **12** gave lower conversion during the same amount of time (42.6% after 1 hr). None of the systems with pre-formed catalyst reached completion, with rapid deposition of Pd black observed towards the end of the reaction. This can be attributed to a depletion of butadiene substrate at the end of the reaction leading to agglomeration of the active catalyst.



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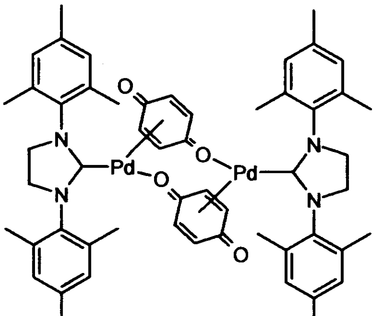

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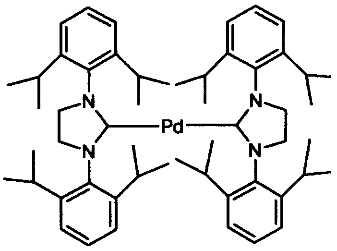

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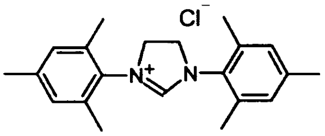
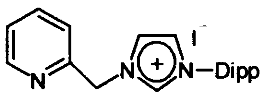


\+ $Pd(dba)_2$

12



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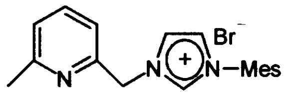
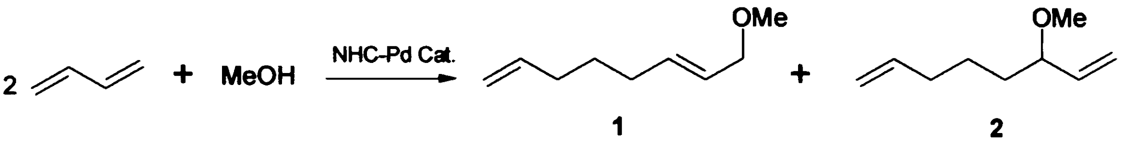


\+ $Pd(dba)_2$

14

Table 4.1. Telomerization of butadiene with MeOH[a]



Catalyst	Cat. % mol (10^{-3})	Time (h)	% yield[b] 1+2	1:2	TON	TOF (h^{-1})
9	4.9	1[c]	83.7	54:1	8574	8574
10	3.4	1[c]	89.0	33:1	13215	13215
11	4.2	0.33[c]	84.7	7:1	9994	30284
12[d]	5.0	1[e]	46.2	23:1	4566	4566
13[d]	5.0	2[e]	0	-	-	-
14[d]	4.9	2[e]	0	-	-	-

The bis-NHC-Pd^0 complex **11** is comparatively more active than **9** or **10**, with the reaction finished in only 20 minutes with a TOF of 30300 h^{-1}. This catalyst gave the best TOF obtained for this telomerization reaction at that time. It is assumed that under reaction conditions one of the NHC ligands disssociates from the sterically encumbered complex **11** to generate a mono-NHC-Pd^0 species. The lability of the NHC ligand in the homoleptic bis-NHC-Pd^0 complex **11** has been demonstrated by the ability of P(o-tolyl)$_3$, a better π-acceptor ligand than NHC, to displace an NHC ligand and form Pd^0(NHC)[P(o-tolyl)$_3$] in equilibrium with **11**.[10] Similarly, homoleptic bis-(PR$_3$)-Pd^0 complexes bearing stong σ-donor ligands (R= Cy, *i*-Pr, *o*-tolyl) are also known to undergo complete dissociation in the presence of 1,6-dienes under mild conditions to form the corresponding Pd^0(PR$_3$)(1,6-diene) complexes.[13] These equilibra can be rationalised by a relief of steric hindrance and electron density for these two-coordinate Pd^0 complexes. Assuming that carbene dissociation from **11** occurs during catalysis, the difference in TOF's between the pre-formed catalysts could be explained by their ease in generating the mono-NHC-Pd^0 active catalyst. However at this point a strict comparison between these catalytic systems could only be carried out with identical carbene ligands on the metal.

A significant difference between the pre-formed catalysts can be seen in the dramatic change in the product ratios. While complex **9** gave telomers **1** and **2** in a 54:1 ratio, the observed regioselectivity using complex **11** dropped to only 7:1; complex **10** stands between **9** and **11** with a regioselectivity of 33:1.

In term of catalyst design, it is clear that a fundamental difference exists between **9**, **10** and **11** that would account for this change in the regioselectivity of the reaction. Similar results were reported with Beller's catalyst **8**, when substituting the N-mesityl substituents of the carbene ligands by the more bulky dipp groups. While catalyst **8** gave the telomers **1** and **2** in 96% yield in a 49:1 ratio, the substituted dipp catalyst afforded the telomers in 90% with a lower regioselectivity of 12:1.[12] Therefore it is very likely here that the difference in the ligand steric bulk might also account for the observed change in the regioselectivity of the reaction.

From the observed results a general trend exists, with the more bulky ligands on the Pd^0 precatalyst giving less regioselectivity. It is thus likely that steric factors influence the regioselective attack of the nucleophile on the allyl group in reasons for the observed lower regioselectivity of the nucleophilic attack (Scheme 4.5).

4.3. Conclusion and Remarks

In conclusion, NHC-based palladium(0) pre-catalyts complexes **9-12** are very active for the telomerization of butadiene with methanol, selectively giving only the telomeric products. Our preliminary results demonstrate that the preformed complexes **9-11** are comparatively more active than the catalyst mixture **12**, where the active catalyst is generated *in-situ* from the imidazolium salt and a Pd^0 precursor. In the other hand these results show that the *in-situ* generation of a Pd catalyst using pyridyl N-substituted imidazolium salts such as in **13** and **14** completely blocks the telomerization reaction.

Amongst the different catalytic systems tested, complex **9** was the most regioselective, producing a high proportion of the linear telomer **1**. In comparison, catalyst **11**, bearing ligands with more bulky N-substituents, is a less regioselective catalyst. Further investigations aiming to study the impact of structural modifications on the N-substituents of the carbene ligands would be of interest. For example, the use of adamantyl, tert-butyl, isopropyl or neopentyl di-N-substituted NHC ligands on the pre-formed catalysts **9-11** would yield valuable information on the effect of the steric bulk of the ligand on the activity and selectivity of the reaction.

Finally, it is worthwhile to note that by optimising their catalytic system, Beller and co-workers recently reported an astonishing TON of 1,540,000 and TOF of 96,250h^{-1} using complex **8** for the telomerization of butadiene with methanol, giving the telomers with a high regioselectivity (49:1).[12] Interestingly, obtaining such high productivity and activity was only possible by progressively increasing the amount of the dimesityl-N-substituted imidazolium salt added to the catalytic mixture (ratio imidazolium salt:complex **8** = 80:1). It is clear that the use of excess ligand precursor has a positive impact on the catalytic system. Therefore with NHC ligands, and with the mesityl substituted carbene ligand in particular, a synergistic effect seems to operate during catalysis in the presence of excess ligand precursor, making the catalyst very active and selective for this reaction. Assuming that only one NHC ligand is coordinated to the metal through most of the catalytic cycle, it is possible that a second NHC ligand might act a labile ligand during the course of the catalysis.

It is also possible that the excess ligand precursor might serve as a reservoir of ligand available to stabilise the catalytic intermediates in case 2-alkylimidazolium salts are produced by NHC-hydrocarbyl reductive elimination process (See Equation 1.2).[14] Further studies on the effect of excess imidazolium salt on these systems as well as mechanistic studies on the NHC-Pd catalysed telomerization reaction are required. Furthermore, use of these NHC based catalysts for other telomerization reactions should certainly be investigated.[15]

4.4. Experimental

4.4.1. General comments

All manipulations, as well as catalytic reactions, were carried out under dry argon using standard Schlenk line techniques. Glassware was dried overnight in an oven at 120 °C or flame dried prior to use. Anhydrous methanol was obtained by refluxing the commercial product over Mg/I_2 overnight, distilled and stored over activated 4Å molecular sieves. Butadiene (Aldrich-99.9%) was condensed from the commercial cylinder into a volumetric Fischer-Porter tube containing 4Å activated molecular sieves, and the tube stored in the freezer at -20 °C. NaOH pellets (Aldrich-99.99%) were grinded under inert atmosphere until obtention of a fine powder prior to be used for catalytic reactions. The GC internal standard 2,2,4-trimethyl pentane (Aldrich-99.9%) was used as received. Complexes **(9)** and **(10)** were prepared as described in Chapter 2. Bis-[1,3-bis-(2,6-diisopropylphenyl)imidazolidin-2-ylidene] palladium(0) **(11)** was kindly provided by Prof. F.G.N. Cloke (Sussex university, UK).[10] 1,3-Dimesityl imidazolinium chloride was prepared according to the published procedure.[16]

4.4.2. Catalytic procedure

Typical procedure for the telomerization of butadiene with methanol.

A Fisher-Porter tube containing a magnetic stirrer bar and equipped with a four ways ring system with an inlet septum, a connection to the Schlenk line and a butadiene inlet, was evacuated and filled with argon three times. (1,3-Dimesitylimidazolin-2-ylidene) bis(dimethylfumarate) palladium(0) **(9)** (7.9 mg; 0.011mmol) was introduced into a Schlenk vessel, dissolved in methanol and transferred by canula to the reactor tube. In another Schlenk vessel containing sodium hydroxide in a powder form (0.29 g; 7.3 mmol), was added methanol (total MeOH 18.6 ml) and the mixture transferred by canula to the reactor tube. The tube was cooled to -20 °C and butadiene (12.53 g; 232 mmol) was condensed in (the exact amount of butadiene introduced was determinated by mass difference of the tube before and after the butadiene transfer). The reactor tube was fully immersed into a silicon oil bath at 90 °C and the reaction vigourously stirred. After stirring for 1 hr. and the appareance of Pd black, the reaction was stopped and the reactor tube cooled down. The butadiene left was bled off and 2,2,4-trimethylpentane (13.24 g; 116 mmol) was added together with diethyl ether (5ml) to help dilution of the internal standard. 500μl of the catalytic mixture was taken and dilute with diethyl ether (20 ml). The yield of the telomerization products was determinated by GC using a HP 5890 series II gas chromatgraph equipped with a SGE 50QC3/BP1 0.5 capillary column and a FID detector (GC temperature program: 1.5 min isotherm at 50 °C, 20 $°Cmin^{-1}$ to 180 °C, 5 mins isotherm at 180 °C). In order to obtain pure sample of the telomeric products for calibration, the crude reation mixture was distilled under vacuo. Products were identified by both GC-MS and NMR analysis.

4.5. References

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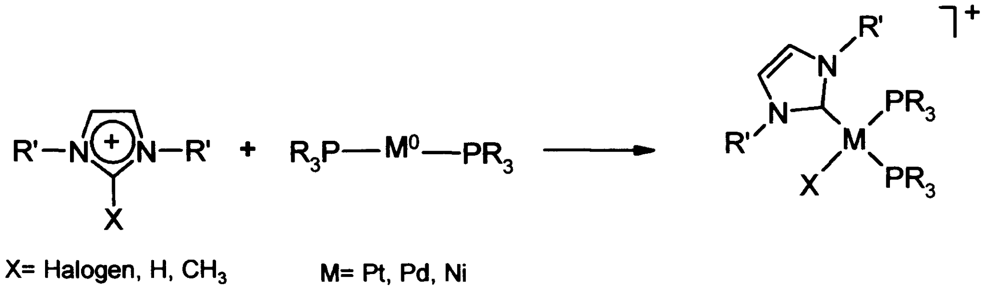
CHAPTER 5

C^2-H Oxidative Addition of Imidazolium Salts to NHC-M^0 Complexes

5.1. Introduction

Previous theoretical studies have demonstrated that the oxidative addition of the imidazolium cation to M^0 complexes of Group 10, to afford carbene M^{II} species, is a feasible process (Scheme 5.1).[1]



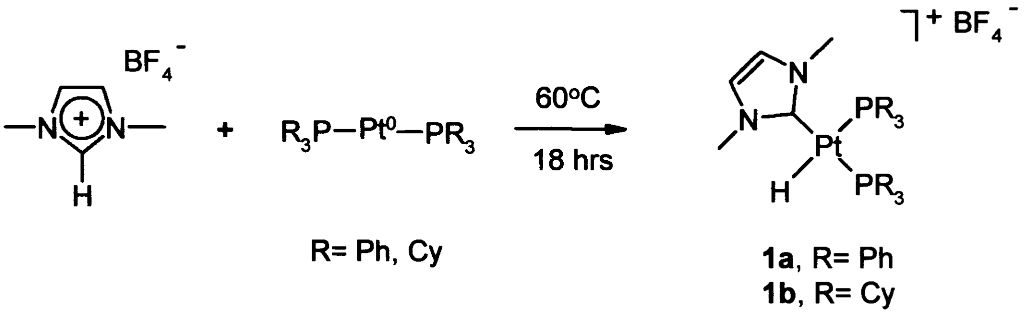
Scheme 5.1. Oxidative addition of imidazolium cations to M^0 complexes.

DFT calculations have shown that when the imidazolium cation is substituted in the 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 in an exothermic process. This suggests that under appropriate conditions the oxidative addition of these imidazolium cations to M^0 of Group 10 should be possible. The oxidative addition of imidazolium salts to M^0 complexes is an attractive method for the generation of metal-NHC complexes. Although a number of synthetic routes are known to provide access to these complexes (see Chapter 1), the oxidative addition represents an atom-efficient route starting directly from the imidazolium salt. In the case of a C^2-H substituted imidazolium cation, this route could give access to carbene-metal-hydrido species that might activate a number of catalytic processes.

Of the different parameters that could influence the oxidative addition of the imidazolium cation, calculations have shown that the oxidative addition to Pt and Ni is more exothermic than to Pd, and Ni would react with a lower activation barrier.[1] It was also found that the C^2-H oxidative addition is easier than the oxidative addition of C^2-CH_3 substituted imidazolium cations. In comparison, oxidative addition of the C^2-halo substituted imidazolium cation proceeds with an even lower activation barrier lower and with greater exothermicity. Finally, it was shown that the use of strongly basic spectator ligands on the metal favours the oxidative addition by lowering the activation barrier and increasing the exothermicity of the reaction.[1]

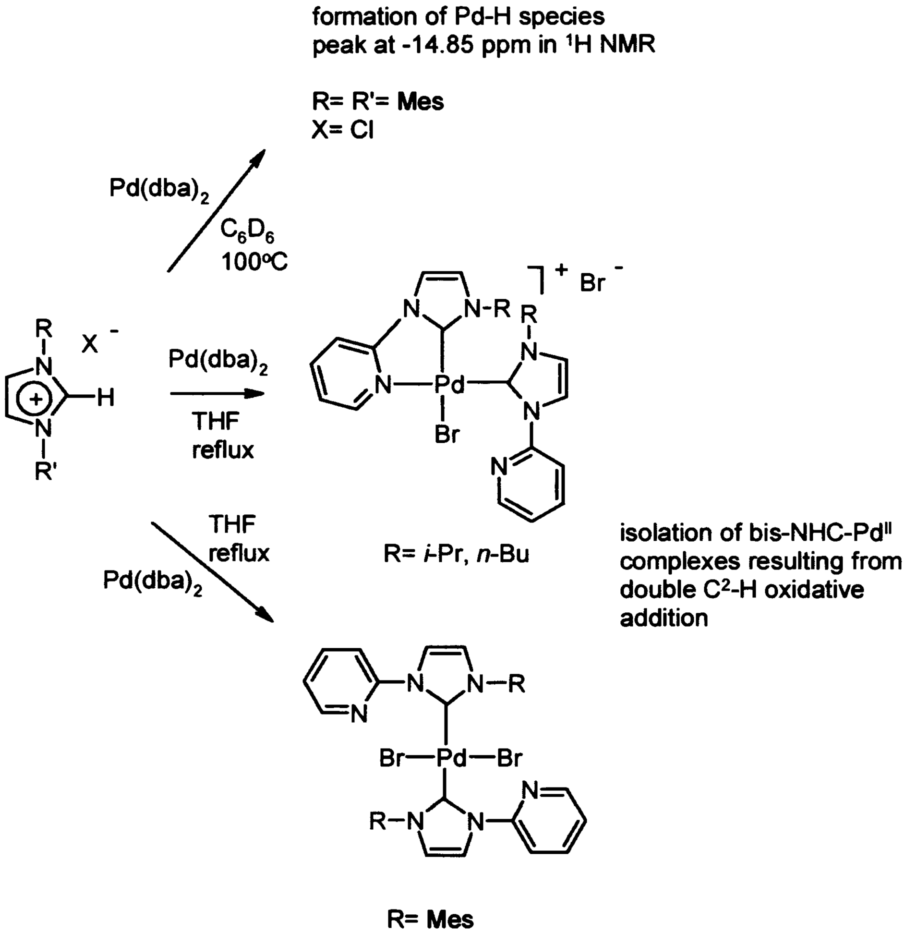
The aforementioned DFT studies suggest that factors affecting common oxidative addition reactions likewise affect the oxidative addition of the imidazolium cation to M^0.

Experimentally, oxidative addition of C^2-halo imidazolium salts has been shown to occur with M^0 complexes of Pt and Pd bearing phosphine ligands.[1-3] Similarly, oxidative addition of 2-chlorothiazolium salts has been observed with Group 10 metal (0) complexes to give the corresponding thiazol-2-ylidene M^{II} complexes.[4] In the case of C^2-H imidazolium oxidative addition, coordinatively unsaturated bis-phosphine Pt^0 complexes have been found to insert into the C-H bond of imidazolium salts to give stable carbene-Pt-hydrido complexes **1a,b** (Scheme 5.2).[1]



Scheme 5.2. Imidazolium C^2-H oxidative addition to Pt^0

Although the C^2-H oxidative addition of imidazolium salts to Pd^0 has been shown to occur in a few cases (Scheme 5.3),[16] no carbene-Pd-H complexes have been isolated. In light of these theoretical and experimental results, the behaviour of coordinatively unsaturated NHC-M^0 complexes towards the C^2-H oxidative addition of imidazolium salts was investigated. NHC ligands are strong σ-donor ligands that increase the electron density on the metal centre, making the metal complex more prone to oxidative addition reactions. The interaction of these imidazolium salts, often used as ionic liquids, with these coordinatively unsaturated NHC-M^0 complexes is also of particular interest from the point of view of using such complexes as catalysts in reactions performed in imidazolium based ionic liquid solvents.

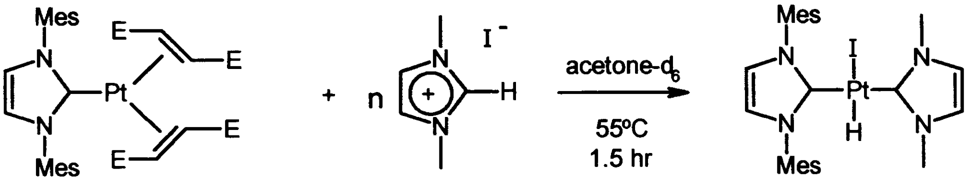


Scheme 5.3. Evidence of direct C^2-H oxidative addition of imidazolium salts to Pd^0.

5.2. Results and Discussion

5.2.1. C^2-H Oxidative Addition of Imidazolium Salts to NHC-Pt^0 Complexes

When an excess of 1,3-dimethylimidazolium iodide was added to **2** in acetone-d_6 and the solution heated to 55 °C, the mono-NHC-Pt^0 complex **2** was rapidly and completely converted, according to ^1H NMR spectroscopy, into the Pt^{II}(hydrido)$(NHC)_2$ complex **3** (Scheme 5.4). After the reaction, the two molecules of DMFU were found to be free in solution. Although the reaction was initially carried out on an NMR scale it was found that the reaction could be scaled up and **3** isolated in high yield as a thermally, air and moisture stable compound.[5]



E= COOMe n=5

2 3

Scheme 5.4. C^2-H Oxidative addition of imidazolium salt to $Pt^0(NHC)(DMFU)_2$ complex

The ^1H NMR spectra of **3**, shows coordination of the two different carbene ligands to the platinum centre with characteristic signals of the C-H on the imidazole backbone of the coordinated NHC ligands at 7.30 and 6.84 ppm with their associated Pt satellites ($^4J_{(PtH)}$ = 6.0 and 8.0 Hz, respectively). A mutual *trans*-disposition of the two carbene ligands is suggested from the ^1H and ^{13}C NMR spectra of **3** (and also by a ^1H-NOE experiment).[5] The Pt-H resonance for **3** was seen at -14.67 ppm with $^1J_{(PtH)}$ = 1727 Hz. This hydride signal is at a much lower frequency than in **1a** (*cis*-**1a** = -5.23 ppm and *trans*-**1a** = -6.03 ppm in DCM-d_2)[2] or **1b** (-7.95 ppm in DCM-d_2).[1] Previous studies have shown that in the series of *trans*-$PtHX(PR_3)_2$ complexes the Pt-H chemical shift is greatly affected by the X group *trans* to the hydride.[6] It has been proposed that a trend exists between the *trans*- influence of the X group (in terms of σ-donation ability) and the hydride chemical shift with higher *trans*-influence X groups giving higher observed chemical shifts. The presence of the iodide ligand, with its weaker *trans*-influence compared to phosphine or NHC, due to stronger σ-bonds formed by the latter ligands with the metal, would explain the high field shift of the hydride signal in **3** as compared to **1a** and **1b**.

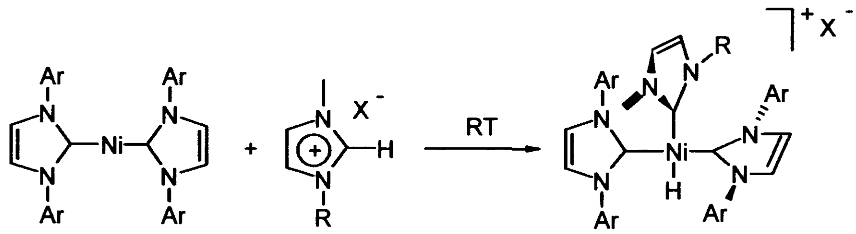
The coordination of the iodide and the proposed solid-state structure of **3** were later confirmed by X-ray diffraction.[5]

This experiment revealed that C^2-H oxidative addition of 1,3- dimethylimidazolium iodide to NHC-Pt^0 complex **2** is a facile process, generating the stable bis-NHC-Pt^{II} complex **3**. Although the exact mechanism by which the 1,3-dimethylimidazolium cation oxidatively adds to **2** is still not known, the ease by which this reaction proceeds seems to lie in the ability of this complex to lose the DMFU ligands to generate a coordinatively unsaturated and electron rich Pt^0 centre with multiple coordination sites for the imidazolium salt to oxidatively add.

5.2.2. C^2-H oxidative addition of imidazolium salts/ionic liquids to NHC-Ni^0 complexes

Following this result with the NHC-Pt^0 system, the C^2-H oxidative addition of imidazolium salts to coordinatively unsaturated NHC-Ni^0 complexes was investigated. Theoretical calculations have shown that the oxidative addition of the imidazolium cation to Ni^0 species should proceed with a lower activation barrier than to Pd^0 or Pt^0.[1]

Because of the likely instability of the Ni-hydrido complexes formed from mono-NHC-M^0 precursors as described above, it was decided to attempt the oxidative addition of imidazolium salts to bis-NHC-Ni^0 species in the hope of generating more stable products.



4
Ar= Mes

5a) R= Me, X=BF_4
b) R= Bu, X= BF_4
c) R= Bu , X= PF_6

6a-c

Scheme 5.5. C-H oxidative addition of imidazolium salts to $Ni^0(NHC)_2$ complex. Reaction conditions: a) THF, 5 min; b) Toluene, 1 hr; c) Toluene, 5 min.

When equimolar quantities of various imidazolium salts **5a-c** (typical examples of ionic liquids) were stirred at room temperature with the *in-situ* generated bis-NHC-Ni^0 complex **4**,[7] the deep purple colour of **4** quickly disappears to give a light yellow solution (Scheme 5.5). Concentration of this solution and addition of *n*-hexane led to the isolation of tris-carbene-nickel-hydrido complexes **6a-c** as pale yellow crystalline solids in 70-76 % yield.

All three complexes **6a-c** are surprisingly stable both in solution and the solid state, e.g. they can be heated at reflux in THF for 16 hr without evidence of significant degradation (NMR). They can also be stored unchanged under an inert atmosphere for an extended period of time, and they may also be manipulated in air without any sign of degradation. A mutual *trans*-disposition of the two mesityl-substituted carbene ligands is suggested by the ^{1}H and ^{13}C NMR spectra of **6a-c**; two unique signals are observed for three carbene carbons in the ^{13}C NMR of **6a-c**.

The Ni-H signals appear at -14.96, -15.02 and -15.02 ppm, respectively, in the ^{1}H NMR spectra of **6a-c** (CD_2Cl_2). These values are similar to the hydride signals in *trans*-$NiHR(PCy_3)_2$, (R= Ph, Me), where the hydride resonates at -14.8 and -15.1 ppm respectively (C_6D_6)[8] and are consistent with the presence of a ligand with a strong *trans*- influence (e.g. NHC, Ph, Me) *trans* to the hydride.[8]

The solid state structure of complex **6b** was confirmed by X-ray diffraction. An ORTEP diagram of **6b** is shown in Figure 5.1, and selected bond distances and angles are presented in Table 5.1.

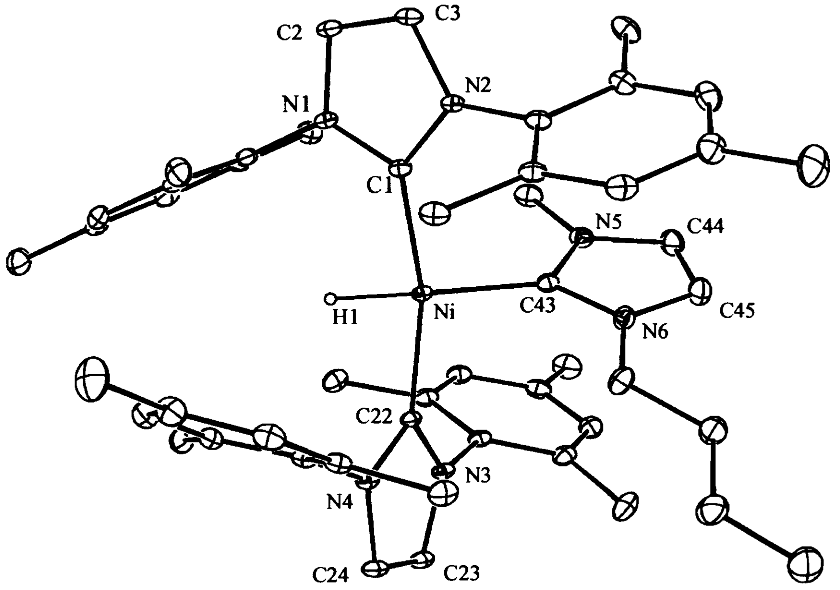


Figure 5.1. ORTEP diagram of **6b**•CH_2Cl_2. Hydrogen atoms (except H1), the BF_4^- anion and the dichloromethane molecules are omitted for clarity. Thermal ellipsoids are drawn at 25% probability level.

Table 5.1. Selected Bond Lengths (Å) and Angles (deg) for **6b**

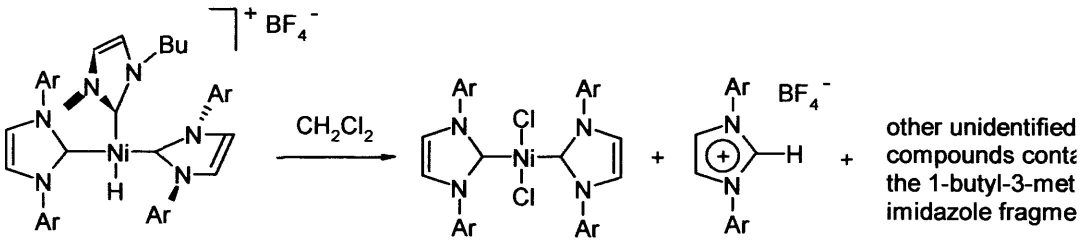
Ni-H(1)	1.38(5)	H(1)-Ni-C(43)	179(2)
Ni-C(1)	1.895(4)	C(1)-Ni-C(22)	164.22(16)
Ni-C(22)	1.891(3)	C(1)-Ni-C(43)	97.30(15)
Ni-C(43)	1.936(4)	C(22)-Ni-C(43)	98.40(15)

Complex **6b** exhibits a distorted square-planar geometry around the metal, with the two mesityl-substituted carbenes having a *trans*- disposition. Steric crowding between the two mesityl-carbenes and the 1-butyl-3-methyl-carbene causes the bulky mesityl-carbenes to be pushed towards the smaller hydride group giving an angle for C(1)-Ni-C(22) of 164.22(16)°. This deviation from the ideal theoretical angle of 180° has also been observed in other *trans*-$NiHX(PR_3)_2$, (X= imine, phenoxy group), complexes where steric hindrance within the complexes has forced the phosphine ligands to tilt toward the hydride ligand with P-Ni-P angles between 149 and 159°.[9,10]

The difference in the Ni-carbene bond lengths between the mesityl-substituted carbenes and the 1-butyl-3-methyl-carbene is significant. While the two mesityl-carbene-Ni bond distances are identical within experimental error [Ni-C(1,22) = 1.895(4), 1.891(3) Å] and fall within the average NHC-M bond length for Ni^{II} complexes (from the Cambridge Structural Database), the butyl-methyl-carbene *trans* to the hydride has a much longer carbene-metal bond [Ni-C(43) = 1.936(4) Å]. This is one of the longest carbene-Ni^{II} bonds reported.[11] This difference probably arises from the strong *trans*- influence of the hydride ligand weakening and thus lengthening the bond *trans* to it. Complex **6b** is one of the few structurally characterised Ni^{II} complexes with a terminal hydride where the hydrogen atom has been located by X-ray diffraction studies,[9,12] and is the first nickel hydride complex with NHC ligands where the hydride has been localised.[13] The Ni-H distance of 1.38(5) Å observed for **6b** falls at the bottom of the range of reported Ni-H bond distances [1.37-1.65 Å].[9,12] However, a precise determination of the H atom position would require a neutron diffraction study.[14]

Complexes **6a-b** are examples of the rare Ni-H complexes that are stable to air, light and heat.[8] The surprising stability of such complexes can be rationalised in terms of both steric and electronic effects imparted by the three carbene ligands. Steric bulk around the metal centre hinders orbital overlap between the hydride and the carbene carbons in *cis*-positions that would favour reductive elimination of an imidazolium salt.[15] As well as protecting against reductive elimination, the bulk of the mesityl-substituted carbenes forces the hydride to be *trans* to the 1-butyl-3-methyl carbene. The steric bulk around the metal and the strong NHC-M bonds give these complexes a very rigid architecture that could explain their high stability.

It is interesting to note, however, that dichloromethane solutions of complexes 6 progressively decompose with time under inert atmosphere (Scheme 5.6).
During crystal growth attempts with **6b** in dichloromethane/hexane mixtures, yell crystals of **6b** could be obtained after a few days at room temperature; howe leaving the mixture for several weeks saw the progressive formation of red cryst of **7**. Analysis of the remainder of the mixture by NMR spectroscopy also reveal the formation of 1,3-dimesitylimidazolium tetrafluoroborate together with ot unidentified compounds (Scheme 5.6). Similar red crystals form under identi conditions during crystallization of **6a** and **6c**.



6b

7

Ar= Mes

Scheme 5.6. Decomposition of tris-carbene-hydrido-nickel complex **6b** in t presence of dichloromethane.

Complex **7** was characterised by NMR spectroscopy and X-ray crystallograp (Figure 5.2; Table 5.2). Although the mechanism by which **7** forms is not known, is possible that it is the result of the oxidative addition of DCM molecules to the N complex **6b**, to form a Ni^{IV} species followed by reductive elimination, or to N complex **4** after reductive elimination of imidazolium salt **5b**. In a separa experiment DCM was added to complex **4** giving a dirty grey powder for whi NMR analysis revealed the formation of **7** together with a mixture of oth compounds.

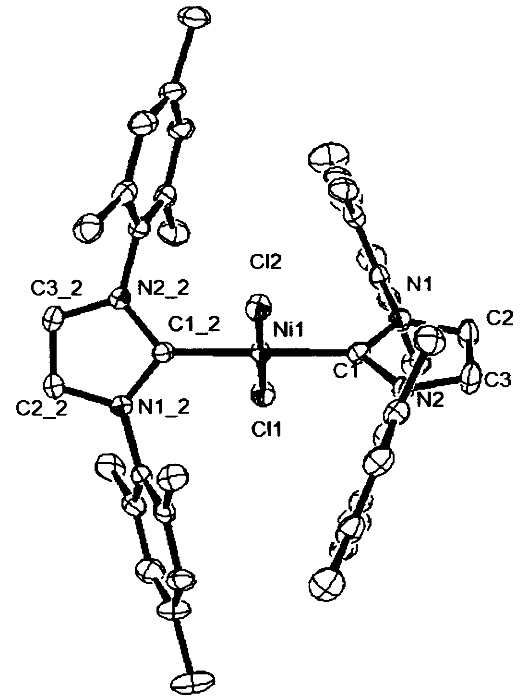


Figure 5.2. ORTEP diagram of **7**. Hydrogen atoms are omitted for clarity. Therma ellipsoids are drawn at 50% probability level.

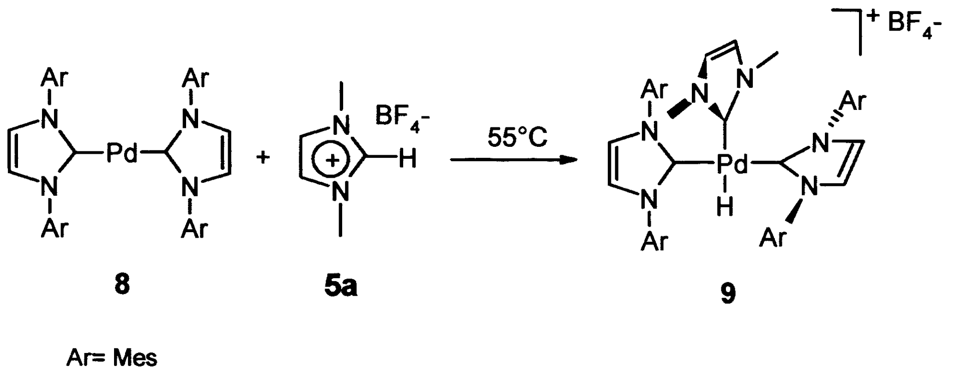
Table 5.2 Selected Bond Lengths (Å) and Angles (deg) for **7**

Ni(1)-C(1)	1.925(4)	C(1)-Ni(1)-C(1)#2	178.9(2)
Ni(1)-C(1)#2	1.925(4)	C(1)-Ni(1)-Cl(1)	89.46(11)
Ni(1)-Cl(1)	2.1899(16)	C(1)-Ni(1)-Cl(2)	90.54(11)
Ni(1)-Cl(2)	2.1966(16)	C(1)#2-Ni(1)-Cl(1)	89.46(11)
		C(1)#2-Ni(1)-Cl(2)	90.54(11)
		Cl(1)-Ni(1)-Cl(2)	180.0

In conclusion, oxidative addition of typical ionic liquid imidazolium salts to bis NHC- Ni^0 complex **4** is a facile process that occurs quickly at room temperatur yielding tris-carbene-nickel-hydrido complexes that are surprisingly stable. Thes results have important implications for transition-metal catalysed reaction performed in ionic liquids and the use of such complexes as catalysts in such system (*vide infra*).

5.2.3. C^2-H oxidative addition of imidazolium salts to NHC-Pd^0 complexes

A similar approach to that described with Ni was employed to study the oxidative addition of imidazolium salts to coordinatively unsaturated bis-NHC-Pd^0 complex **8** (Scheme 5.7).



Scheme 5.7. C^2-H oxidative addition of imidazolium salt **5a** to Pd^0 complex **8**; acetone/THF, 15 min.

When equimolar quantities of imidazolium salt **5a** and complex **8**,[17] were stirred together at 55 °C in acetone/THF mixture, the yellow colour of **8** quickly faded to give a colourless solution (Scheme 5.7). Evaporation of the solvents and trituration with *n*-hexane afforded the tris-carbene-Pd-hydrido complex **9** as an off-white powder in 62% yield.[18] Complex **9** is also stable in the solid state and can be stored under an inert atmosphere for an extended period of time. A *trans*-disposition of the two mesityl-substituted carbene ligands was inferred from the NMR spectroscopic data of **9** with two signals observed for the three carbene carbons in the ^{13}C NMR spectrum of **9**. The Pd-H signal for **9** appears at -10.06 ppm in the ^{1}H NMR spectrum (C_6D_6). For comparison the hydride signal in $PdH(NHPh)(PCy_3)_2$ appears at -13.89 ppm (C_6D_6).[10]

The solid state structure of complex **9** was confirmed by X-ray diffraction. An ORTEP diagram of **9** is shown in Figure 5.3, and selected bond distances and angles are presented in Table 5.3.

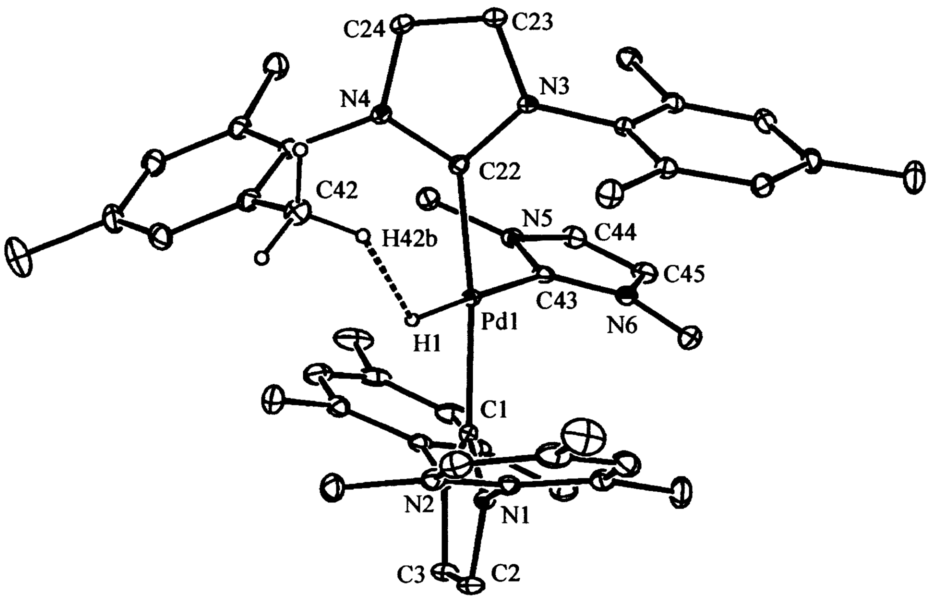


Figure 5.3. ORTEP diagram of **9**•C_3H_3. Hydrogen atoms (except H1) and the BF_4^- anion and the C_3H_3 molecule are omitted for clarity. Thermal ellipsoids are drawn at 25% probability level.

Table 5.3. Selected Bond Lengths (Å) and Angles (deg) for **9**

Pd-H(1)	1.57(3)	H(1)-Pd-(C43)	177.0(10)
Pd-C(1)	2.030(2)	C(1)-Pd-C(22)	168.02(8)
Pd-C(22)	2.031(2)	C(1)-Pd-C(43)	95.78(9)
Pd-C(43)	2.111(2)	C(22)-Pd-C(43)	96.20(8)

The molecular structure of **9** shows a distorted square-planar geometry at the palladium(II) centre. The two mesityl-carbenes are in a *trans-* disposition and are tilted towards the hydride, although slighly less so than in **6b** [C(1)-Pd-C(22) angle = 168.02(8)°]. The two mesityl-carbene-Pd bond distances are similar [Pd-C(1) = 2.030(2) and Pd-C(22) = 2.031(2) Å] and fall within the average of NHC-Pd^{II} bond lengths (from the Cambridge Structural Database); however the carbene ligand *trans* to the hydride has a much longer carbene-Pd bond, [Pd-C(43) = 2.111(2) Å]. This is also one of the longest carbene-Pd bonds reported for a Pd^{II} complex,[19] and as with **6b** is likely to arise from the strong *trans*-influence of the hydride ligand. Complex **9** is one of the few structurally characterised Pd^{II} complexes with a terminal hydride where the hydrogen atom has been located by X-ray diffraction studies,[20] and is the first NHC-Pd complex with a hydride ligand to be structurally characterised.

The Pd-H bond distances range from 1.46 to 1.65 Å for structurally characterised palladium complexes with a terminal hydride,[20] and the Pd-H distance of 1.57(3) Å observed for **9** falls within this range. However as for **6b**, a precise determination of the hydride position would require a neutron diffraction study.[14]

It is interesting to note in complex **9** a possible $H^{\delta+}\cdots H^{\delta-}$ intramolecular interaction in view of the short H42b-H1 distance of 2.07 Å (significantly less than twice the van der Waals radius for H of 2.4 Å expected in the absence of an attractive interaction) together with angles Pd–H•••H and H•••H–C of 132.0° and 129.8°.[21]

The nickel-hydride complex **6b** also shows a similar, but less significant H-H close-approch [shortest methyl-H – H(1) distance of 2.41 Å].

However care should be taken with the real existence of such an interaction in the solid state of **9**. Firstly as mentioned above the position of the hydride is not precise and secondly because crystal packing forces might also influence this close approach. In solution no interaction in the form of coupling signal between the hydride and the mesityl-H proton was observed in the ^1H NMR of **9** at room temperature. Further characterisation of this possible hydridic-to-protonic interaction is required.[21]

5.3. Conclusion

The described experimental studies demonstrate that the C^2-H oxidative addition of imidazolium salts/ionic liquids to coordinatively unsaturated Group 10 metal(0) complexes, especially those bearing strong σ-donor ligands such as NHC's, is a facile process, giving stable bis- or tris-NHC-hydrido-metal(II) complexes.

These results have important ramifications for NHC chemistry and metal-catalysed reactions performed in imidazolium-based ionic solvents (*vide infra*).

5.4. Experimental

5.4.1. General Comments

Unless otherwise stated all manipulations were carried out 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 and *n*-hexane were distilled from sodium benzophenone ketyl, toluene from sodium metal and dichloromethane from CaH_2 and the solvents were freshly distilled under nitrogen immediately prior to use. Acetone was dried over activated B_2O_3, 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 potassium and vacuum-transferred into an ampoule equipped with a greaseless stopcock. The NMR measurements were performed at room temperature on either a Varian Mercury 300 spectrometer (^1H: 300.13 Mhz), a Bruker DPX 400 spectrometer (^1H: 400.13 MHz, ^{13}C: 100.63 MHz) or a Varian Inova 500 spectometer (^{13}C: 125.70 Mhz). Chemical shifts (δ) are referenced to internal solvent resonances and reported to relative TMS. Coupling constants (J) are given in Hz and NMR peaks are labelled as s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet. IR spectra (KBr disc) were recorded on a JASCO FT/IR-660 Plus spectrometer; abbreviations used: s= strong, m= medium, w= weak, br= broad, sh= shoulder. (1,3-Dimesitylimidazolin-2-ylidene) bis(dimethylfumarate) platinum(0) (**2**) was synthetised as described in Chapter 1. 1-Butyl-3-methylimidazolium (bmiy-H) tetrafluoroborate (**5b**) and hexafluoroborate (**5c**) were obtained from Solvent Innovation GmbH (Cat. n° 99,020-1 for **5b** and 99,021-1 for **5c**, both $\geq$ 98 %), stored and manipulated in a glove box. 1,3-Dimethylimidazolium tetrafluoroborate (**5a**),[22] 1,3-dimesitylimidazolin-2-ylidene (mesityl-carbene or dmesiy),[23] bis(cycloocta-1,5-diene) nickel(0),[24] and bis(1,3-dimesitylimidazolin-2-ylidene) palladium(0) (**7**),[17] were synthesised according to literature procedures.

5.4.2. Preparation of Compounds

***In-situ* preparation of *trans*-hydrido iodo (1,3-dimesitylimidazolin-2-ylidene) (1,3-dimethylimidazolin-2-ylidene) platinum(II); (3).** To (1,3-dimesitylimidazolin-2-ylidene) bis(dimethylfumarate) platinum(0) (**2**) (50mg, 0.064 mmol) in acetone-d_6 (1ml) was added 1,3-dimethylimidazolium iodide (71mg, 0.32 mmol). The solution was transferred into a 5 ml Youngs NMR tube under inert atmosphere and the NMR tube sealed. The NMR tube was then placed in an oil bath at 55°C for 1.5 hr. The solution was then immediately submitted for NMR experiments at room temperature. Analysis of the NMR spectra showed complete conversion of (**2**) into (**3**) together with the presence of two equivalents of dimethylfumarate as free molecules. NMR data for (**3**) ^{1}H NMR (acetone-D_6, 300Mhz): δ 7.30 (s, 2H, $^4J_{(PtH)}$ = 6.0 Hz, imidazole C*H*), 6.97 (s, 4H, arom. C*H*), 6.84 (s, 2H, $^4J_{(PtH)}$ = 8.0 Hz, imidazole C*H*), 3,23 (br s, 6H, N-CH_3), 2.30 (s, 6H, *p*-CH_3), 2.26 (s, 12H, *o*-CH_3), -14.67 (s, 1H, $^1J_{(PtH)}$ = 1727 Hz, Pt-*H*). ^{13}C NMR (acetone-D_6, 125.70 Mhz):δ 179.4 (NCN), 175.7 (NCN), 137.9/137.2/133.3 (arom.*C*s), 128.7 (arom.CH), 122.0 (imidazole *C*H), 120.7 (imidazole *C*H), 36.3 (N-CH_3), 20.5 (mesityl CH_3), 19.0 (mesityl CH_3).

Synthesis of *trans*-hydrido (1,3-dimethylimidazolin-2-ylidene) bis(1,3-dimesitylimidazolin-2-ylidene) nickel(II) tetrafluoroborate; (6a). A THF solution (5ml) of 1,3-dimesitylimidazolin-2-ylidene (199mg ,0.65 mmol) was added dropwise to a THF solution (5ml) of Ni(COD)$_2$ (90 mg ,0.31 mmol) and stirred for 5 mins at room temperature. The dark violet solution was then canulated into a Schlenk containing 1,3-dimethylimidazolium tetrafluoroborate (**5a**) (53 mg, 0.29 mmol) and stirred/shaken for 5 mins at room temperature. Immediately the dark colour disappeared to give a yellow solution. THF was then concentrated in vacuo until ca. 1ml and 5ml of *n*-hexane added to precipitate the product. Washing with hexane (2x 8ml) and drying in vacuo afforded a light yellow powder.Yield 186 mg (76% based on **5a**). Single crystals were obtained by layering a DCM solution of (**6a**) with hexane at 5°C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ6.90 (s, 8H, arom. C*H*), 6.80 (s, 4H, dmesiy NC*H*), 6.39 (s, 2H, dmiy NC*H*), 2.69 (s, 6H, NCH_3), 2.33 (s, 12H, *p*-CH_3), 1.69 (s, 24H, *o*-CH_3), -14.89 (s, 1H, Ni-*H*). ^{13}C NMR (CD_2Cl_2, 100.63 Mhz): δ188.7 (NCN), 185.4 (NCN), 138.7/136.6/135.3 (arom. *C*s), 129.1 (arom. *C*H), 122.6 (dmesiy N*C*H), 121.1 (dmiy N*C*H), 36.8 (NCH_3), 20.8 (*p*-CH_3), 17.9 (*o*-CH_3). IR: ν 1955 (w, br), 1685 (m), 1609 (m).

Synthesis of *trans*-hydrido (1-butyl-3-methylimidazolin-2-ylidene) bis(1,3-dimesitylimidazolin-2-ylidene) nickel(II) tetrafluoroborate; (6b). A toluene solution (5ml) of 1,3-dimesitylimidazolin-2-ylidene (199mg ,0.65 mmol) was added dropwise to a toluene solution (5ml) of $Ni(COD)_2$ (90 mg ,0.31 mmol) and stirred for 5 mins at room temperature. The dark violet solution was then canulated into a Schlenk containing 1-butyl-3-methylimidazolium tetrafluoroborate (**5b**) (68 mg, 0.30 mmol) and stirred/shaken for 1hr at room temperature. During that time the dark colour disappeared and a precipitate came out. Toluene was then concentrated in vacuo until ca. 1ml and 10ml of *n*-hexane added to precipitate the product. Washing with hexane (2x 10ml) and drying in vacuo afforded a yellow powder. Yield 196 mg (73 % based on **5b**). Single crystals were obtained by layering a DCM solution of (**6b**) with hexane at 5°C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 6.90 (s, 8H, arom. C*H*), 6.79 (s, 4H, dmesiy NC*H*), 6.50/6.35 (2×s, 2H, bmiy NC*H*), 2.80 (s, 3H, NCH_3), 2.78 (t, 2H, $^3J_{(HH)}$ = 8.7Hz, NCH_2), 2.32 (s, 12H, *p*-CH_3), 1.72/1.69 (2×s, 24H, *o*-CH_3), 1.28 (m, 2H, CH_2), 1.16 (m, 2H, CH_2), 0.94 (t, 3H, $^3J_{(HH)}$ = 7.1Hz, CH_3), -14.95 (s, 1H, Ni-*H*). ^{13}C NMR (CD_2Cl_2, 100.63 Mhz): δ 188.9 (NCN), 185.6 (NCN), 138.5/136.9/135.4 (arom. *C*s), 129.1 (arom. *C*H), 122.7 (dmesiy N*C*H), 120.2/117.6 (bmiy N*C*H), 49.0 (NCH_2), 37.3 (NCH_3), 30.2 (CH_2), 20.7 (*p*-CH_3), 20.4 (CH_2), 18.1 (*o*-CH_3), 14.0 (CH_3). IR: ν 1950 (w, br), 1685 (m), 1609 (m).

Synthesis of *trans*-hydrido (1-butyl-3-methylimidazolin-2-ylidene) bis(1,3-dimesitylimidazolin-2-ylidene) nickel(II) hexafluorophosphate; (6c). A toluene solution (5ml) of 1,3-dimesitylimidazolin-2-ylidene (199mg ,0.65 mmol) was added dropwise to a toluene solution (5ml) of $Ni(COD)_2$ (90 mg ,0.31 mmol) and stirred for 5 mins at room temperature. The dark violet solution was then canulated into a Schlenk containing 1-butyl-3-methylimidazolium hexafluorophosphate (**5c**) (85 mg, 0.30 mmol) and stirred/shaken for 5 mins at room temperature. During that time the dark colour disappeared to give a yellow solution. Toluene was then concentrated in vacuo until ca. 1ml and 5ml of *n*-hexane added to precipitate the product as a sticky solid. Trituration of the solid followed by washing with hexane (1x 5ml) and diethyl ether (2x 5ml) afforded after drying in vacuo a yellow powder. Yield 199 mg (70 % based on **5c**). Single crystals were obtained by layering a DCM solution of (**6c**) with hexane at 5°C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ6.89 (s, 8H, arom. C*H*), 6.79 (s, 4H, dmesiy NC*H*), 6.50/6.35 (2×s, 2H, bmiy NC*H*), 2.81 (s, 3H, NCH_3), 2.78 (t, 2H,

$^3J_{(HH)}$ = 8.3Hz, NC*H*$_2$), 2.32 (s, 12H, *p*-C*H*$_3$), 1.72/1.69 (2×s, 24H, *o*-C*H*$_3$), 1.29 (m, 2H, C*H*$_2$), 1.14 (m, 2H, C*H*$_2$), 0.94 (t, 3H, $^3J_{(HH)}$ = 7.1Hz, C*H*$_3$), -14.95 (s, 1H, Ni-*H*). ^{13}C NMR (CD$_2$Cl$_2$, 100.63 Mhz): δ 188.9 (NCN), 185.6 (NCN), 138.5/136.9/135.3 (arom. *C*s), 129.1 (arom. *C*H), 122.7 (dmesiy N*C*H), 120.1/117.6 (bmiy N*C*H), 50.4 (N*C*H$_2$), 38.0 (N*C*H$_3$), 30.9 (*C*H$_2$), 21.5 (*p*-*C*H$_3$), 21.1 (*C*H$_2$), 18.8 (*o*-*C*H$_3$), 14.8 (*C*H$_3$). IR: *v* 1950 (w, br), 1685 (m), 1609 (m).

NMR data for *Trans*-dichloro bis(1,3-dimesitylimidazolin-2-ylidene) nickel(II); (7). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ 6.94 (s, 8H, arom. C*H*), 6.57 (s, 4H, imidazole C*H*), 2.46 (s, 12H, *p*-C*H*$_3$), 1.82 (s, 24H, *o*-C*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, 100.63 Mhz): δ 167.7 (NCN), 137.7/136.4 (arom. *C*s), 128.9 (arom. *C*H), 122.6 (imidazole *C*H), 21.1 (*p*-*C*H$_3$), 18.8 (*o*-*C*H$_3$).

Synthesis of *trans*-hydrido (1,3-dimethylimidazolin-2-ylidene) bis(1,3-dimesitylimidazolin-2-ylidene) palladium(II) tetrafluoroborate; (9). 1,3-Dimethylimidazolium tetrafluoroborate (**5a**) (22 mg, 0.12 mmol) and bis(1,3-dimesitylimidazolin-2-ylidene) palladium (0) (8) (90mg ,0.13 mmol) were stirred at 55°C in an acetone/THF mixture (10/2ml) for 15 mins.* During that time the yellow colour progressively disappeared to give a colourless solution. Solvents were then removed in vacuo and the sticky residue triturated and washed with 3x7 ml of *n*-hexane. Finally the solid was dried in vacuo to afford (**9**) as an off-white powder. Yield 70 mg (62% based on **5a**) . Crystals and single crystals of (**9**) were obtained on standing a saturated benzene solution of (**9**) at room temperature for a few days. ^{1}H NMR (C$_6$D$_6$, 400 Mhz): δ 6.78 (s, 2H, dmiy NC*H*), 6.75 (s, 8H, arom. C*H*), 6.02 (s, 4H, dmesiy NC*H*), 2.57 (s, 6H, NC*H*$_3$), 2.27 (s, 12H, *p*-C*H*$_3$), 1.60 (s, 24H, *o*-C*H*$_3$), -10.06 (s, 1H, Pd-*H*). ^{13}C NMR (C$_6$D$_6$, 100.63 Mhz): δ 189.2 (NCN), 182.6 (NCN), 139.2/137.3/135.7 (arom. *C*s), 129.6 (arom. *C*H), 122.5 (dmiy N*C*H), 122.4 (dmesiy N*C*H), 37.3 (N*C*H$_3$), 21.4 (*p*-*C*H$_3$), 18.2 (*o*-*C*H$_3$).

* It was found that by vigourously refluxing the mixture for 1 hr (70-80°C), the presence of the other Pd-H species seen at -15.73 ppm in the ^{1}H NMR disappeared (see note in reference 18).

5.4.3. X-Ray Crystallography

Crystal structure Determination. Table 5.4 displays the main crystallographic data for the complexes **(6b)**, **(7)** and **(9)**. All single crystal X-ray data were collected on a Bruker Nonius Kappa CCD diffractometer using graphite monochromated Mo-Kα radiation, equipped with an Oxford Cryostream cooling apparatus. The data were corrected for Lorentz and polarization effects and for absorption using SORTAV[25]. Structure solution was achieved by Direct methods (Sir-92)[26]. All structures were then refined by full-matrix least-squares on F^2 with all non hydrogen atoms assigned anisotropic displacement parameters. The H1-atom bound to the Ni or Pd metal, was located from difference maps and refined isotropically without restraints. All other 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 SHELXL-97.[27]

Table 5.4. Summary of Crystallographic Data for **6b**, **7**, **9**.

	6b	**7**	**9**
emperical formula	$C_{50}H_{63}N_6BF_4Ni \bullet (CH_2Cl_2)_2$	$C_{42}H_{48}N_4Cl_2Ni$	$C_{47}H_{57}N_6BF_4Pd \bullet C_3H_3$
fw	1063.44	738.45	938.25
cryst. syst	monoclinic	monoclinic	triclinic
space group	$P\,2_1/n$	$C2/c$	$P\bar{1}$
a[Å]	14.121(3)	20.873(4)	10.697(2)
b[Å]	15.464(3)	20.863(4)	12.118(2)
c[Å]	25.045(5)	18.756(4)	20.101(4)
α[deg]	90	90	102.78(3)
β[deg]	93.12(3)	108.71(3)	90.78(3)
γ[deg]	90	90	108.65(3)
V[Å^3]	5460.9(19)	7736(3)	2397.6(8)
Z	4	8	2
ρ_{calcd}[g.cm^{-3}]	1.293	1.268	1.300
F_{000}	2232	3120	978
μ (Mo Kα)[cm^{-1}]	6.04	6.74	4.42
T[K]	150(2)	150(2)	150(2)
$2\theta_{max}$ [deg]	50.9	50.7	52.9
no. of measd rflns	48550	13607	37840
no. of unique rflns	9970 (R_{int} = 0.0669)	7022 (R_{int} = 0.0423)	9770 (R_{int} = 0.0684)
no. of params	632	457	578
$R1(I>2\sigma(I))$	0.0679	0.0794	0.0352
$wR2$ (all data)	0.1893	0.2225	0.0873
GOF	1.042	1.05	1.031

5.5. References

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(18) Note: Together with **9**, the ^{1}H NMR of the product oftenty revealed the formation of a small amount of another Pd-hydride complex with a hydride signal at -15.73 ppm. Analysis of the different spectra suggests that the formation of this unidentified complex is related to the presence of peroxo impurities in the starting complex **8**.[17b] Formation of this Pd-H species can be suppressed by using more forcing conditions (see Experimental).

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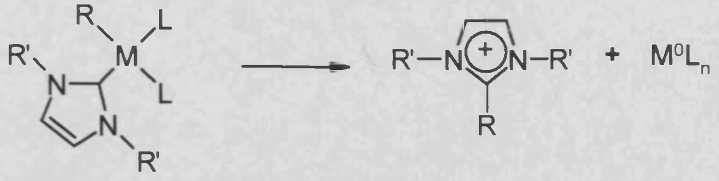
CHAPTER 6

Azolium-Alkene Catalysed Coupling Reactions

6.1. Introduction

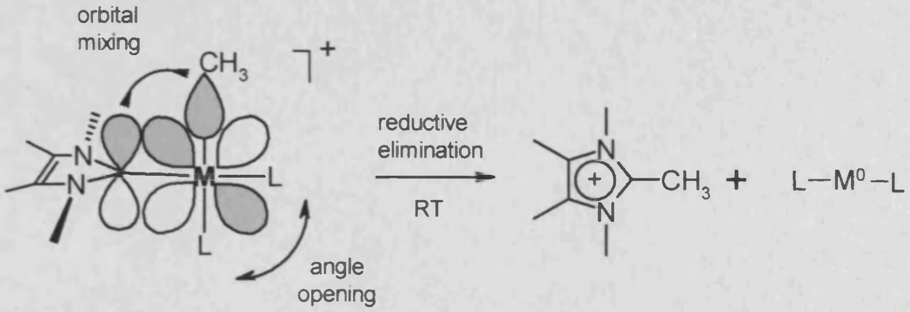
Various reports on neutral and cationic hydrocarbyl-NHC complexes of nickel and palladium have shown that such complexes can easily decompose to give 2-hydrocarbyl-imidazolium salts and M^0 species (Equation 6.1).[1-6]



(6.1)

R = alkyl, aryl; M = Ni or Pd

Kinetic and density functional studies carried out on cationic methyl-NHC-Pd complexes bearing phosphane ligands have demonstrated that these complexes decompose *via* a mechanism of concerted reductive elimination of the hydrocarbyl and the carbene ligands to give imidazolium salts.[4] The reductive elimination process effectively involves orbital overlap between the carbene carbon p_π orbital, the alkyl sp^3 orbital, and the metal d orbital, concomitent with opening of the angle between the two phosphane ligands, L (Figure 6.1).[4]

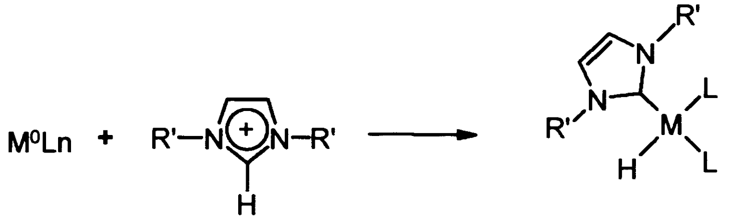


L=PMePh$_2$, P(OPh)$_3$, PPh$_3$, PCy$_3$
M=Pd

Figure 6.1. Hydrocarbyl-NHC reductive elimination process.

Although NHC ligands are held to be strongly coordinating ligands because of their high bond M-L dissociation energy,[7] the low energy reductive elimination decomposition pathway represents a serious potential deactivation process for NHC-based catalysts, particularly when intermediate complexes bearing hydrocarbyl ligands are formed during a catalytic reaction. This has been demonstrated during mechanistic studies on the oxidative addition of aryl halides to bis-(NHC)Pd^0 complexes,[2,6] or the oxidative addition of MeI to bis-(NHC)Ni^0 complexes.[2] In these studies formation of 2-aryl or 2-methyl imidazolium salts was observed in many cases. Similarly, formation of 2-hydrocarbyl imidazolium salts was also observed in studies of the stoichiometric Heck coupling with bis-(NHC)(aryl)Pd^{II} species,[2] the carbonylation of [NHC-(methyl)Pd^{II}-Cl]$_2$,[3] and during the catalytic dimerization of 1-butene with Ni^{II}-NHC complexes in toluene.[5] These observations demonstrate the generality of the NHC-hydrocarbyl reductive coupling and deactivation pathway for NHC-based catalysts.

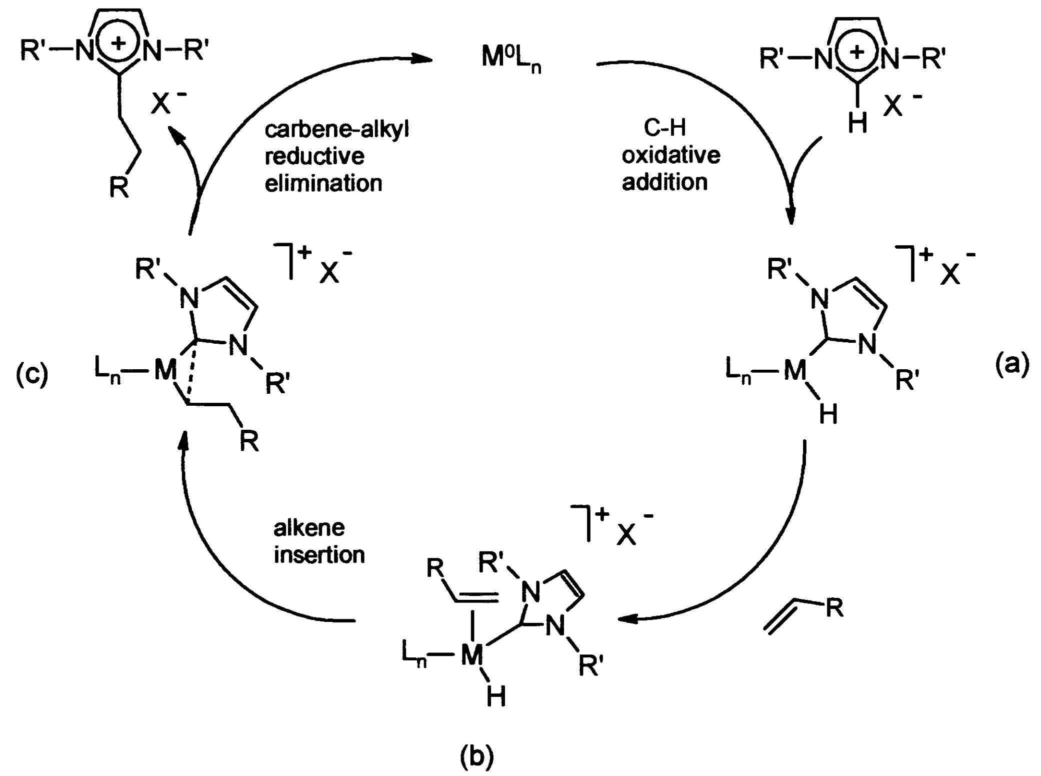
As shown hydrocarbyl-NHC-M^{II} species are capable of reductive elimination to give 2-hydrocarbyl-imidazolium salts and M^0 (Equation 6.1). Also as previously demonstrated (Chapter 5) imidazolium salts are capable of undergoing oxidative addition to M^0 species to give hydrido-NHC-M^{II} species (Equation 6.2).



(6.2)

Isolated hydride complexes: M = Pt,
L = PR$_3$'s or NHC; M = Ni, Pd, L = NHC's

In the presence of an alkene and a C^2-H imidazolium substrate, it may therefore be envisaged that a catalytic cycle, containing both of these redox processes undergone by the imidazolium salt/NHC couple (Equations 6.1 and 6.2), could be constructed (Scheme 6.1).



Scheme 6.1. Proposed catalytic cycle of the imidazolium-alkene coupling reaction.

The proposed catalytic cycle begins with the oxidative addition of an imidazolium salt to a Group 10 M^0 complex, forming a carbene-M^{II}-hydrido species (a) (Equation 6.2, Chapter 5). Alkene insertion into the resulting M^{II}-H bond of (b) produces an alkyl-M^{II} intermediate (c) that subsequently undergoes reductive elimination of the carbene and alkyl ligands to produce 2-alkyl imidazolium salt and reform M^0L_n (Equation 6.1). This novel imidazolium-alkene coupling process represents a potential catalytic methodology for producing 2-alkyl-imidazolium-type salts.

6.2. Results and Discussion

6.2.1. Optimisation of the Ni^0 catalysed imidazolium-alkene coupling

We decided to study Ni^0 complexes as catalysts for the aforementioned imidazolium-alkene coupling reaction. It has been previously demonstrated that Ni^0 has a lower activation barrier than Pd^0 or Pt^0 for the oxidative addition of imidazolium salts (Chapter 5)[8], and NHC-alkyl-Ni^{II} species readily eliminate 2-alkyl imidazolium salts.[2,5] Both of these factors suggested that Ni was the most promising Group 10 metal to trial. A test reaction was chosen (Equation 6.3) with the ionic liquid **1a** as the imidazolium salt substrate, 1-hexene as the alkene and $Ni(COD)_2$ as the Ni^0

source. The factors affecting this new catalytic process (supporting ligands, solvent, temperature and time) were investigated (Table 6.1).

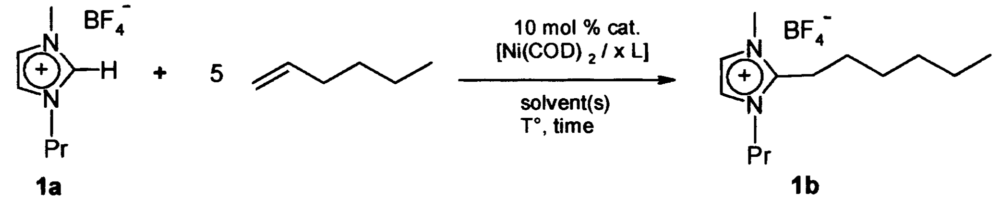
Carrying out the catalytic reactions in neat ionic liquid **1a** led to poor conversions with yields <10%. One of the reasons for such low yields probably arises from the low solubility of the alkene and the catalyst [even the pre-formed $Ni(PPh_3)_2$] in the ionic liquid solvent, thus limiting efficient interaction between the different reagents. A combination of acetone and THF was found in most cases to be the best solvent system to dissolve all the components of the catalytic mixture and obtain homogeneous systems.

In the absence of added ligand, the $Ni(COD)_2$ quickly decomposed resulting in poor reaction yields (Table 6.1, entry 1). A survey of different supporting ligands was therefore undertaken. Addition of two equivalents of bulky NHC ligand gave a low yield of the product **1b** (10 %) (Table 6.1, entry 2). In comparison, addition of one equivalent of NHC ligand afforded a better yield (30 %) in a shorter reaction time (Table 6.1, entry 3). The presence of a second equvalent of NHC ligand thus slows down the catalytic process, possibly due to the formation of stable tris-carbene-hydrido-Ni species during the catalytic reaction (see Chapter 5).

The use of two equivalents of PPh_3 produced **1b** in slightly better yield (40%) than when using NHC ligands, and at a lower temperature (Table 6.1, entry 4). However, contrary to the behaviour observed in presence of NHC ligands, the PPh_3-based system decomposes over time on heating the reaction mixture (Table 6.1, entries 4,7). The use of more basic phosphine ligands like PEt_3 (Table 6.1, entries 7-8), or more bulky and basic phosphines such as PCy_3 (Table 6.1, entries 5-6) gave comparatively lower yields of **1b** than when using PPh_3.

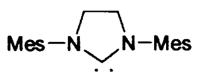
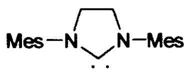
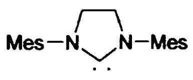
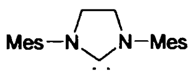
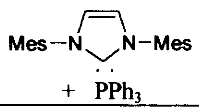
Mixed NHC/PPh_3 ligand systems quickly led to decomposition of the catalyst resulting in low yields of product (Table 6.1, entries 9-11), presumably because of the instability of an intermediate in the catalytic cycle, possibly the hydride species (Scheme 6.1a).

The use of phosphite ligands such as $P(OPh)_3$ that are weaker σ-donor but better π-acceptor ligands than PPh_3 or NHC produced only very low amounts of product even in a mixed ligand system with PPh_3 (Table 6.1, entries 12-13); catalyst decomposition was observed in all of these trials.



(6.3)

Table 6.1. Effect of reaction conditions on the imidazolium-(1-hexene) coupling.

Entry	Ligand (L)	Solvent(s)	T (°C)	Time (h)	Yield **1b** (%)[a]	Observation after reaction
1	-	Acetone-THF (3:1)	60	2	<5	Went green after 2 h.
2	2 	"	60	48	10	Yellow solution with white suspension
3		"	60	15	30	Yellow solution with white suspension
4	2 PPh_3	"	40	15	40	Green with Ni^0 black
5[b]	2 PPh_3	"	55	15	25	Green with Ni^0 black
6[b]	2 PCy_3	"	55	15	5	A white solid came out of yellow solution after 1h. Ni^0 black after reaction.
7	2 PPh_3	"	RT	48	20	Intense yellow solution
8	2 PEt_3	"	RT	48	10	Yellow solution with white suspension
9	 + 2 PPh_3	"	60	15	23	Decomposition with Ni^0 black after reaction
10	 + PPh_3	"	60	15	10	Quickly decomposed
11	 + PPh_3	"	55	15	<5	Quickly decomposed
12	2 $P(OPh)_3$	"	55	15	<5	Some decomposition after reaction
13	$P(OPh)_3$ + PPh_3	"	55	15	8	Quickly decomposed
14	dppe	"	RT	20	<5	Went green after 2h.
15	dppp	"	40	20	8	Progressively went green
16	dppb	"	40	20	14	Went green after 1h.
17	2.1 PPh_3	"	55	48	56	Progressive formation of Ni^0 black
18	2.4 PPh_3	"	55	48	30	No decomposition
19	3 PPh_3	"	60	15	33	No decomposition
20	4 PPh_3	"	60	15	28	No decomposition
21	2.1 PPh_3 + $Pd(dba)_2$	"	55	48	0	Light orange solution
22	2 PPh_3	THF	RT	15	<5	Light orange mixture
23	2 PPh_3	DCM	RT	15	<5	Went quickly green
24	2 PPh_3	Acetonitrile-THF (3:2)	RT	15	20	Went quickly green
25	2 PPh_3	Acetone-THF - Acetonitrile (3:1:0.5)	RT	66	27	No decomposition

[a] Determined by ^1H NMR spectroscopy. [b] Catalyst (4 mol %).

Chelating phosphine ligands [dppe/-p/-b=bis-(diphenylphosphine)ethane/-propane/-butane] gave lower yields of **1b** than when using two equivalents of PPh_3 (Table 6.1, entries 4 and 14-16). Amongst these the best results were obtained with dppb, the most conformationally flexible chelating phosphine ligand. Insertion of the alkene and also the reductive elimination step are probably facilitated by more flexible ligands.[4]

When using PPh_3 as the ligand, increasing the PPh_3/Ni ratio from 2 to 2.4 - 4 gave lower yields of product although the catalyst stability increased (Table 6.1, entries 4 and 17-20). We found that addition of 2.1 equivalents of PPh_3/Ni gave the best overall catalytic results (Table 6.1, entry 17). The use of solvent combinations other than acetone-THF did not improve product yields from the PPh_3-based catalytic system (Table 6.1, entries 7 and 22-25). Finally, performing the reaction under the same conditions with PPh_3 but with a Pd^0 source, $Pd(dba)_2$, did not yield any product (Table 6.1, entry 21).

In conclusion these different results demonstrate the feasibility of the imidazolium-alkene coupling reaction using Ni^0 complexes as catalyst. This reaction can be performed under mild conditions but the efficiency of the catalytic system strongly depends on the type and the amount of ligand added to the system. Best results were obtained using 2.1 equivalents of PPh_3 in an acetone-THF solvent mixture at 55 °C for 48 h.

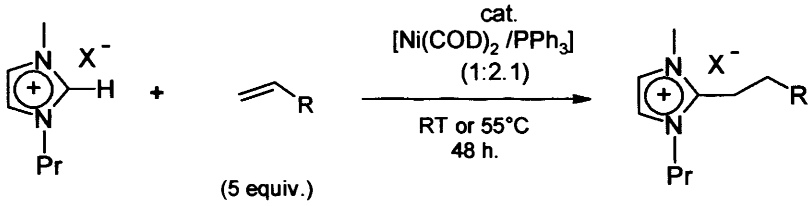
6.2.2. Scope of the Ni^0 catalysed azolium-alkene coupling

The scope of this imidazolium-alkene coupling reaction was further investigated using the above optimised reaction conditions (Equation 6.4, Table 6.2).

The various 1-alkenes (1-hexene, ethylene and styrene) undergo coupling with imidazolium salts/ionic liquids **1a** and **2a** to varying degrees, whereas *n*-butylacrylate does not react (Table 6.2).

Results followed the expected reactivity pattern for alkenes (ethylene > propylene > butene~higher alkenes), ethylene (1 bar) couples more readily with imidazolium salts than does 1-hexene (Table 6.2, entries 2-3 and 6-7).

Styrene gives lower conversions than either of the aliphatic alkenes (Table 6.2, entries 2-6 and 8); steric and/or electronic elements may be a factor in this observed behaviour. Interestingly, styrene uniquely gives rise to linear and branched isomers in a 4:1 ratio – the branched isomer has a chiral centre linking the imidazolium ring to the benzene ring. Both the tetrafluoroborate **1a** and bromide **2a** salts react with the different alkenes; with ethylene complete or nearly complete conversions were observed (Table 6.2, entries 5-6). With ionic liquid **2a** at 55 °C, almost complete conversion was observed even with a lower catalyst loading of 3% (Table 6.2, entry 6).



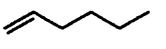
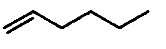
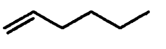
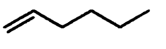
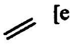
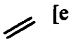
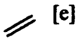
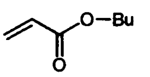
(6.4)

1a X= BF_4
2a X= Br

R= Bu, H, Ph, COOBu

1,2-b R=Bu
1,2-c R=H
2d R=Ph

Table 6.2. Scope of imidazolium C^2-H/alkene coupling reaction.[a]

Entry	Ionic Liquid	Alkene	T [°C]	Yield [%] [b]
1	**1a; 2a**		55, RT	<15 [c]
2	**1a**		55	56
3	**2a**		55	51
4	**2a**		RT	64
5	**1a**	 [e]	55	100[a]; 72[f]
6	**2a**	 [e]	55	100[a]; 95[g]
7	**2a**	 [e]	RT	35
8	**2a**		55	39 [d]
9	**1a**		55	0

[a] Conditions: Catalyst [$Ni(COD)_2/PPh_3$ (1:2.1)] (10 mol%); acetone-THF (3:1); reaction stopped after 48h. [b] Determined by ^1H NMR spectroscopy, average of two runs or more. [c] Catalytic [$Ni(COD)_2$] only. [d] Mixture of linear and branched product (4:1). [e] Pressure: 1 bar. [f] Catalyst (5 mol %). [g] Catalyst (3 mol %).

Notably, the activated alkene *n*-butylacrylate gave no coupled product at all with no reaction apparent (Table 6.2, entry 9). Here electronic factors might be involved in this behaviour. The coordination of electron deficient alkenes might reduce the electron density at the metal centre thus inhibiting the imidazolium C^2-H oxidative addition process. The stronger binding of the electron poor alkenes might also block coordination sites at the metal centre.

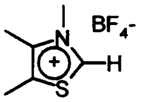
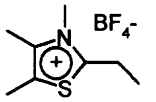
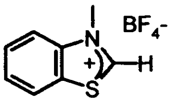
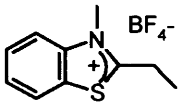
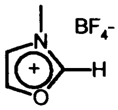
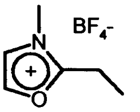
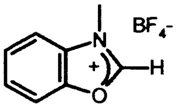
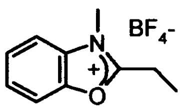
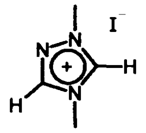
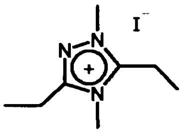
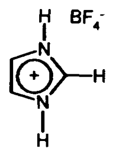
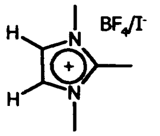
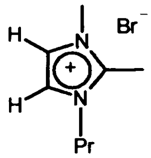
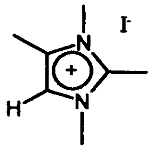
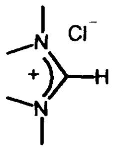
It is interesting to note that for the alkenes studied only the mono-insertion product is observed (*i.e.* for ethylene only the 2-ethyl product is formed), which suggests that under the conditions employed the rate of carbene-alkyl reductive elimination is faster than the rate of alkene insertion into the Ni-alkyl bond.

Having demonstrated that various non-activated alkenes can be used successfully in the catalytic imidazolium-alkene coupling process, several other azolium salts that are known to form NHC ligands upon abstraction of an acidic proton were also investigated in analogous catalytic reactions (Table 6.3).

Various other azolium salts (thiazolium **3a**, benzothiazolium **4a**, oxazolium **5a** and benzoxazolium salts **6a**) were found to undergo coupling with ethylene to give the corresponding 2-ethyl-substituted azolium salts **3-6c** in quantitative yield (Table 6.3, entries 1-4). Interestingly, the triazolium salt **7a** couples with ethylene at both 3 and 5 positions to give the 3,5-diethyl triazolium salt **7c** in 100% yield (Table 6.3, entry 5). This suggests that this triazolium cation is also prone to form a NHC ligand at the 3-position.[9] Mechanistic studies on the order of this coupling process occurring at the triazolium cation have not been carried out, but would be of particular interest if one can make selectively one or the other mono-substituted triazolium salt.

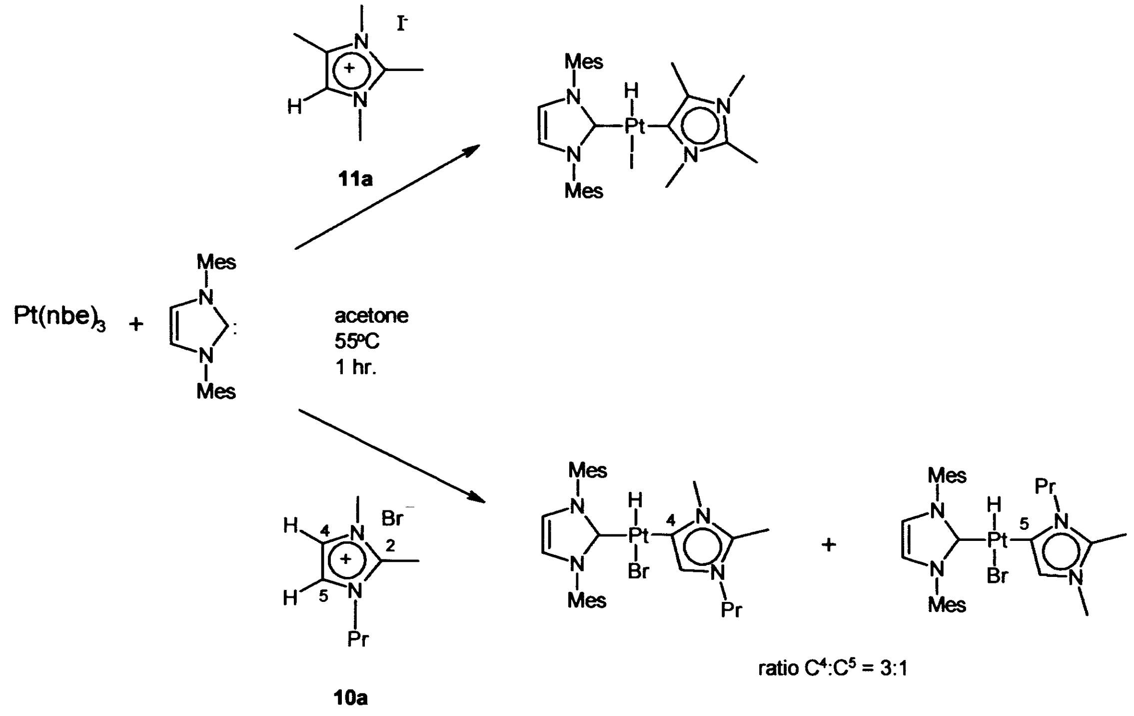
The 1,3-dihydro-imidazolium salt **8a** did not undergo coupling with ethylene under the conditions described in Table 6.3. N-H substituted azolium salts are of particular interest as substrates for catalytic azolium alkene couplings as they give potential access to 2-substituted imidazole/azole type compounds,[10] following treatment of the azolium products with a base. However, it is possible that N-H oxidative addition competes with the C^2-H oxidative addition in N-H substituted imidazolium salts, resulting in the formation of catalytically inactive Ni complexes.

Table 6.3. Scope of the azolium C-H/alkene coupling [a]

Entry	Azolium salt		Alkene[b]	Product		Yield (%) [c]
1		**3a**			**3c**	100
2		**4a**			**4c**	100
3		**5a**			**5c**	100
4		**6a**			**6c**	100
5		**7a**			**7c**	100
6		**8a**		_		no reaction
7		**9a**		–		catalyst decomposition
8		**10a**		–		slight catalyst decomposition
9		**11a**		_		catalyst decomposition
10		**12a**		_		no reaction

[a] Conditions: Catalyst [Ni(COD)$_2$/PPh$_3$ (1:2.1)] (10 mol%); acetone-THF (3:1); 55 °C; reaction stopped after 48 h. [b] Pressure: 1 bar. [c] Determined by ^{1}H NMR spectroscopy, average of two runs or more.

Furthermore, it has recently been shown that blocking the C^2 position of the imidazolium cation by a methyl group promotes $C^{4,5}$-H oxidative addition of the imidazolium cation at electron rich Pt^0 centres, forming the corresponding NHC-hydrido Pt^{II} complexes under mild conditions (Scheme 6.2).[11]



Scheme 6.2. $C^{4,5}$-H oxidative addition of imidazolium salts to a Pt^0 complex.

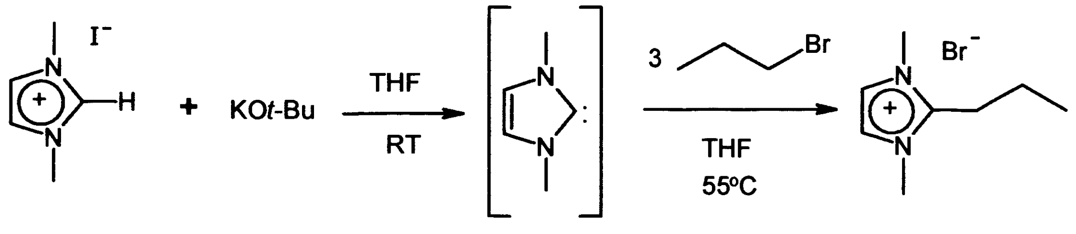
Although no alkene coupling products resulting from $C^{4,5}$-H oxidative addition and $C^{4,5}$-alkyl reductive elimination were observed in presence of the various alkenes and imidazolium salts tested here (Table 6.1 and 6.2), the behaviour of 2-methyl imidazolium salts **9-11a** in this catalytic process was investigated (Table 6.3, entries 7-9). No coupling products were formed with these substrates, and complete catalyst decomposition was observed after reactions with salts **9a** and **11a** (Table 6.3, entries 7,9). However, only comparatively slight decomposition of the catalyst was observed with imidazolium salt **10a** (Table 6.3, entry 8). This suggests that $C^{4,5}$-H oxidative addition of the imidazolium cation probably occurred with **9a** and **11a** but the catalyst decomposed during the course of the reaction, likely because of the instability of one or more of the different species formed during the catalytic cycle. In the case of **10a** the $C^{4,5}$-H oxidative addition could also occur, but perhaps to a more minor extent; alternatively, the resulting NHC-Ni species are less prone to decomposition.

Finally, the formamidinium salt **12a**, precursor to acyclic NHC's,[12] did not undergo coupling with ethylene and no reaction seemed to take place (Table 6.3, entry 10). The formamidium C^2-H oxidative addition step might be less favourable than the azolium C^2-H oxidative addition and could therefore could be one of the reasons for the apparent non-reactivity of these kinds of salts towards alkene coupling.

6.3. Conclusion and Remarks

We have developped a new Ni^0-catalysed azolium-alkene coupling reaction. A variety of alkenes and azolium salts take part in this unique example of a Ni^0-catalysed C-H activation/C-C bond formation reaction.[13] This reaction occurs under mild conditions and represents a new atom efficient catalytic reaction for the substitution of azolium salts in the 2-position. Apart from its potential synthetic value, this reaction represents the first example where azolium oxidative addition and carbene reductive elimination processes have been combined into the same catalytic cycle. These results illustrate the ease with which interconversion between azolium salts and N-heterocyclic carbene transition-metal complexes occurs even under very mild conditions, particularly under conditions where low-valent, unsaturated metal species are generated.

However, interesting to note that in our effort in trying to develop new synthetic routes for the production of 2-alkylimidazolium salts (potential new ionic liquid solvents) we also discovered that these type of salts are also accessible via a stoichiometric route as shown in Scheme 6.3.



13 **14**

Scheme 6.3. Stoichiometric synthesis of the 2-alkylimidazolium salt **14**.

Treatment of the imidazolium salt **13** with KO*t*-Bu generates the free carbene that reacts *in-situ* with bromopropane to give the corresponding 2-alkylimidazolium salt **14** in 82% yield.[14]

In terms of applicability of these two methods for the production of 2-alkylimidazolium salts, this stoichiometric route has the drawback of generating a salt as by-product (not 100% atom-efficient) and require the use of somewhat more expensive alkyl halides. However major inconvenients with the Ni^0-catalysed procedure is often the difficulty to separate the products from either the azolium starting materials or the catalyst.

6.4. Implications for NHC Chemistry and the Use of Imidazolium-Based Ionic Liquids.

These studies on the azolium-alkene coupling reaction, catalysed by the commonly used $Ni(COD)_2/PPh_3$ catalytic system, together with the demonstration that imidazolium salts can easily oxidatively add to coordinatively unsaturated Ni^0, Pd^0 and Pt^0 complexes, especially those bearing strong σ-donor ligands, to form stable NHC-hydrido-M^{II} complexes (see Chapter 5), have important implications for catalysis.

In terms of NHC chemistry, these studies demonstrate that the generation of carbene-metal-hydride species directly from the azolium salts is an easy process and readily occurs in the presence of M^0 species of group 10 metals. The direct *in situ* generation of a carbene-M-H species may provide an important atom-efficient route to active catalytic species under mild conditions. Metal-carbene complexes are being applied more and more widely in catalysis and metal-hydrides are implicated in many catalytic processes.

As demonstrated this can occur *in situ* when a coordinatively unsaturated, low valent metal species (particularly those bearing strong σ-donor ligands) are present or are formed during a reaction. Interestingly, such conditions might be ideally found when performing transition-metal catalysed reactions in imidazolium based ionic liquid solvents. Ionic liquids, in particular 1,3-dialkylimidazolium-based ionic liquids, have recently found important applications in catalysis as potentially valuable 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 these ionic liquids. Although commonly considered as inert solvents, a number of reports have suggested their possible participation during catalysis, providing a source of strong σ-donor carbene ligands under basic conditions; the generation of carbene complexes from imidazolium salts has frequently been observed in the presence of base.[16]

These studies demonstrate that in such ionic liquid solvents, the large excess of imidazolium salt present might react with low-valent Group 10 metal complexes via C^2-H oxidative addition even in the absence of base. Generation of carbene-M-hydrido species would have a major impact on the catalysis carried out in these ionic liquid media. Interestingly, in studies using NHC-Ni complexes as catalysts for alkene dimerisation, effective catalysis was only observed in the imidazolium-based ionic liquid solvent.[5] In toluene the predominant reaction was reductive elimination to give imidazolium salts and Ni^0. This suggests that the imidazolium ionic liquid stabilised the catalytic active species, possibly by pushing the equilibrium between NHC-Ni^{II} species and imidazolium salts/Ni^0 towards the formation of catalytically active NHC-Ni-H species. These studies therefore demonstrate the unique potential for employing ionic liquids concomitantly as solvent and activator to generate long lived (stabilised) active catalysts for a range of processes.

However, while the generation of carbene or carbene-metal-hydride species directly from the ionic liquid solvent may have beneficial aspects for some reactions, it can also have detrimental effect on certain catalytically active metal species. The ease by which oxidative addition of the imidazolium cation to M^0 species can occur demonstrates how such a process could easily compete with other important catalytic steps in a reaction and block coordination sites for incoming substrates at the metal centre. The quick and easy reaction of imidazolium salts/ionic liquids with coordinatively unsaturated Group 10 M^0 complexes bearing NHC ligands (see Chapter 5), all of which are used as catalyst precursors of various catalytic reactions,[17] and the remarkable stability of the resulting NHC-M^{II}-H complexes, are typical examples of how the oxidative addition of imidazolium salts can block the coordination sites of potentially active catalysts. In this sense studies of the relative rate of oxidative addition of the imidazolium cation in comparison to that of other substrates (such as for example aryl chlorides)[18] to such NHC-M^0 complexes, would be of particular interest in order to determine whether the oxidative addition of imidazolium salt/ionic liquid can effectively compete with other substrates.

Interestingly, the deactivation process resulting from the interaction of the imidazolium-based ionic liquid with the catalyst, has been demonstrated in a report on the palladium catalysed telomerization of butadiene and methanol performed in ionic liquid solvents.[19] On studying the influence of the different type of ionic liquids used on the activity of the catalyst, it was found that reactions carried out in normal 1,3-dialkyl imidazolium-based ionic liquids gave only poor conversion of butadiene to the telomerization products (<16%). However, when the same reaction was carried out in 1,2,3-trialkylimidazolium ionic liquids, with the 2-position of the imidazolium cation blocked by a methyl group, therefore making it less prone to carbene formation, complete conversion of butadiene was observed. The deactivation of the catalyst by the 1,3-dialkylimidazolium ionic liquid was also demonstrated in stoichiometric reactions. Although the formation of catalytically inactive NHC-Pd species in this system probably results from the deprotonation of the 1,3-dialkylimidazolium cation by the basic acetate ligands from the $Pd(OAc)_2$ pre-catalyst, and not from an imidazolium C^2-H oxidative addition process, such a study demonstrates how formation of NHC-M species from the ionic liquid can deactivate the catalyst in the telomerization reaction.

In conclusion, the type of imidazolium based ionic liquids to be used when performing transition-metal catalysed reactions in these ionic liquid solvents should be carefully selected.

6.5. Experimental

6.5.1. General Comments

General Methods. Unless otherwise stated all manipulations were carried out 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, diethyl ether and *n*-hexane were distilled from sodium benzophenone ketyl, toluene from sodium metal and dichloromethane from CaH_2, and the solvents were freshly distilled under nitrogen immediately prior to use. Acetone was dried over anhydrous B_2O_3 powder, stirred for 24 h. at room temperature and then distilled under argon and stored in a Schlenk bottle.[20] 3-Methyl-1-propyl-imidazolium bromide (**2a**) was made by N-quaternisation of 1-methylimidazole with bromopropane according to similar reported procedure.[21] 3-Methyl-1-propyl-imidazolium tetrafluoroborate (**1a**) was made by halide metathesis of (**2a**) with $NaBF_4$ in acetone for two days according to reported procedure.[22] Both of these ionic liquids were kept dried and degassed, stored and manipulated in a glove box. 4,5-Dimethylthiazole (Lancaster, 98%), benzothiazole (Aldrich, 96%), oxazole (Aldrich, 98%), benzoxazole (Alfa Aesar, 98%), trimethyloxonium tetrafluoroborate (Avocado, 98+%), N,N,N',N'-tetramethylformamidinium chloride (12a, Aldrich, 97 %),[23] 1-hexene (Aldrich, 99+%), *n*-butylacrylate (Acros Organics, 99+%) and ethylene (BOC Gases, 100%) were used as received without further purification. Styrene (Acros Organics, 99%) was distilled and stored at -20°C under argon. Triphenylphosphine (Aldrich, 99%) was recrystallised from anhydrous methanol. Bis-(cycloocta-1,5-diene) nickel(0) was synthesised according to literature procedure.[24]

Physical and Analytical Measurements. The ^1H (400.13 or 500.13 MHz) and ^{13}C (100.63 or 125.76 MHz) NMR spectra were recorded at 293 K on Bruker DPX 400 or 500 spectrometers with chemical shifts (δ) referenced to internal solvent resonances and reported to relative TMS. Coupling constants (J) are given in Hz and NMR peaks are labelled as s = singlet, d = doublet, t = triplet, q = quartet, sextet = sextet and m = multiplet.

Electrospray ionisation (ESI) mass spectra were performed on a VG Fisons Platform II spectrometer. Samples were dissolved in acetonitrile and an acetonitrile/water mixture was used as the eluant. An extraction cone voltage of 20V and a capilllary voltage of 3 KV were used. For 3-methyl-benzoxazolium tetrafluoroborate (**6a**) and 2-ethyl-3-methyl benzoxazolium tetrafluoroborate (**6c**), dry acetonitrile was used as both solvent and eluant for the ESI-MS. Elemental analysis were carried out by Warwick Analytical Service Ltd, Coventry (UK).

6.5.2. Catalytic procedure

General procedure for the azolium-alkene coupling reaction: a Schlenk vessel (or a 60 ml Young's Schlenk for reactions with ethylene) was charged with bis-(cycloocta-1,5-diene) nickel(0) (0.073 mmol), triphenylphosphine (0.15 mmol), and the azolium salt (0.73 mmol) in a glove box. Under argon atmosphere the alkene (3.6 mmol for 1-hexene, styrene and butylacrylate) was injected together with acetone (8 ml) (for reactions with ethylene the solvents were injected under a flow of ethylene). THF (3 ml) was then syringed into the reaction vessel and the orange/yellow solution stirred at room temperature or heated to 55°C. The Schlenk vessel was then closed (or pressurized to 1 bar with ethylene and closed) and the solution stirred for 48 h. at the corresponding temperature. During that time variable amounts of Ni^0 black formed. The solvents were then removed in vacuo and the residue taken up into CD_2Cl_2 or DMSO-D_6 and immediately submitted for ^1H NMR (may require filtration through a pad of Celite® due to Ni residues).

Separation and isolation of the azolium coupling products was carried out according the following procedures (catalytic reactions carried out with 250 to 1000 mg of azolium salt depending of the degree of conversion of the starting azolium salt and scaled up accordingly according the catalytic procedure described above):
When complete conversion of the azolium salts was observed by ^1H NMR, isolation of the products was carried out according the following procedure (method a): to the crude catalytic mixture, obtained after evaporation of the solvents, was added DCM or acetone (20 ml). The mixture was stirred at room temperature for 15 mins and then filtered through a pad of Celite®. The solvent was concentrated under vacuo to a minimium and hexane (10-15 ml) was added. The mixture was stirred at room temperature to yield a precipitate. After the solvent was decanted off the precipitate was further recrystallised from DCM/hexane or DCM/diethyl ether mixtures (1 to 3 times) and finally dried under vacuo to afford the azolium coupling products with isolated yields within 5-15 % of reported yields by ^1H NMR.
When incomplete conversion of the starting azolium salts was observed by ^1H NMR, the following separation and isolation procedure was applied (method b). To the crude catalytic mixture, obtained after evaporation of the solvents, was added KOtBu (1.5 equivalent of the unreacted azolium salt according ^1H NMR) together with THF (15 ml). The mixture was stirred for 2 hours at room temperature during which time the unreacted azolium salt is converted into a carbene and a potassium salt.[25] THF was then removed in vacuo and the residue triturated with toluene (3x 15 ml) under vigorous stirring in a warm oil bath (70°C). Each time the toluene was decanted off at room temperature. The crude product was then dissolved successively in DCM and acetone and filtered through a pad of Celite® to remove the metal salts. Finally the product was dried under vacuum to give the azolium salt products with isolated yields 10-25 % lower than the ^1H NMR determination.

6.5.3. Analytical data of the isolated azolium-alkene coupling products

2-Hexyl-3-methyl-1-propyl-imidazolium tetrafluoroborate (1b). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.39 /7.32 (2×d, 2×1H, $^3J_{(HH)}$ = 2.1 Hz, NC*H*), 4.02 (t, 2H, $^3J_{(HH)}$ = 7.5Hz, NCH_2), 3.83 (s, 3H, NCH_3), 2.94 (t, 2H, $^3J_{(HH)}$ = 8.1 Hz, 1-hexyl CH_2), 1.86 (sextet, 2H, $^3J_{(HH)}$ = 7.5 Hz, 2-propyl CH_2), 1.60 (m, 2H, 2-hexyl CH_2), 1.41 (m, 2H, 3-hexyl CH_2), 1.31 (m, 4H, 4,5-hexyl CH_2), 0.98 (t, 3H, $^3J_{(HH)}$ = 7.4 Hz, propyl CH_3), 0.88 (m, 3H, hexyl CH_3). ^{13}C NMR (CD_2Cl_2, 100.63 Mhz): δ 147.1 (NCN), 123.5/121.4 (NCH), 50.3 (NCH_2), 35.6 (NCH_3), 31.6 (4,5-hexyl CH_2), 29.2 (3-hexyl CH_2), 27.4 (2-hexyl CH_2), 23.9 (2-propyl CH_2), 23.6 (1-hexyl CH_2), 22.8 (4,5-hexyl CH_2), 14.1 (hexyl CH_3), 10.9 (propyl CH_3). MS (ESI) *m/z* (%): 209 (100) $[M-BF_4]^+$. Elemental Anal. Calc. for $C_{13}H_{25}N_2BF_4$ (296.16): C 52.72, H 8.51, N 9.46; found: C 52.88, H 8.40, N 10.64 %.

2-Hexyl-3-methyl-1-propyl-imidazolium bromide (2b). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.79/7.58 (2×d, 2×1H, $^3J_{(HH)}$ = 2.0 Hz, NC*H*), 4.07 (t, 2H, $^3J_{(HH)}$ = 7.5 Hz, NCH_2), 3.91 (s, 3H, NCH_3), 2.97 (t, 2H, $^3J_{(HH)}$ = 8.0 Hz, 1-hexyl CH_2), 1.84 (sextet, 2H, $^3J_{(HH)}$ = 7.5 Hz, 2-propyl CH_2), 1.58 (m, 2H, 2-hexyl CH_2), 1.38 (m, 2H, 3-hexyl CH_2), 1.27 (m, 4H, 4,5-hexyl CH_2), 0.94 (t, 3H, $^3J_{(HH)}$ = 7.4 Hz, propyl CH_3), 0.84 (m, 3H, hexyl CH_3). ^{13}C NMR (CD_2Cl_2, 100.63 Mhz): δ 146.8 (NCN), 123.9/121.7 (NCH), 50.3 (NCH_2), 36.1 (NCH_3), 31.6 (4,5-hexyl CH_2), 29.2 (3-hexyl CH_2), 27.5 (2-hexyl CH_2), 24.0 (2-propyl CH_2), 24.0 (1-hexyl CH_2), 22.8 (4,5-hexyl CH_2), 14.1 (hexyl CH_3), 11.1 (propyl CH_3). MS (ESI) *m/z* (%): 209 (100) $[M-Br]^+$. Elemental Anal. Calc. for $C_{13}H_{25}N_2Br$ (289.26): C 52.98, H 8.71, N 9.68; found: C 45.02, H 8.18, N 9.81 %.

2-Ethyl-3-methyl-1-propyl-imidazolium tetrafluoroborate (1c). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.27/7.23 (2×d, 2×1H, $^3J_{(HH)}$ = 2.0 Hz, NC*H*), 3.97 (t, 2H, $^3J_{(HH)}$ = 7.5 Hz, NCH_2), 3.76 (s, 3H, NCH_3), 2.94 (q, 2H, $^3J_{(HH)}$ = 7.7 Hz, ethyl CH_2), 1.78 (sextet, 2H, $^3J_{(HH)}$ = 7.5 Hz, 2-propyl CH_2), 1.21 (t, 3H, $^3J_{(HH)}$ = 7.7 Hz, ethyl CH_3), 0.90 (t, 3H, $^3J_{(HH)}$ = 7.5 Hz, propyl CH_3). ^{13}C NMR (CD_2Cl_2, 100.63 Mhz): δ 147.6 (NCN), 123.1/121.2 (NCH), 49.9 (NCH_2), 35.2 (NCH_3), 23.6 (2-propyl CH_2), 16.8 (ethyl CH_2), 11.1 (ethyl CH_3), 10.5 (propyl CH_3).

2-Ethyl-3-methyl-1-propyl-imidazolium bromide (2c). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.89/7.78 (2×s, 2×1H, NC*H*), 4.16 (t, 2H, $^3J_{(HH)}$ = 7.2 Hz, NCH_2), 3.97 (s, 3H, NCH_3), 3.11 (q, 2H, $^3J_{(HH)}$ = 7.3 Hz, ethyl CH_2), 1.80 (sextet, 2H, $^3J_{(HH)}$ = 7.2 Hz, 2-propyl CH_2), 1.21 (t, 3H, $^3J_{(HH)}$ = 7.4 Hz, ethyl CH_3), 0.90 (t, 3H, $^3J_{(HH)}$ = 7.3 Hz, propyl CH_3). ^{13}C NMR (CD_2Cl_2, 100.63 Mhz): δ 146.6 (N*C*N), 122.9/121.0 (N*C*H), 49.2 (N*C*H_2), 35.5 (N*C*H_3), 23.1 (2-propyl CH_2), 16.8 (ethyl *C*H_2), 10.9 (ethyl *C*H_3), 10.0 (propyl *C*H_3).

3-methyl-2-phenethyl-1-propyl-imidazolium bromide (2d). Mixture of linear and branched products (not separated); linear product ^{1}H NMR (acetone-D_6, 400 MHz): δ 8.13 (s, 2H, NC*H*), 7.40-7.24 (m, 5H, benzyl C*H*), 4.23 (t, 2H, $^3J_{(HH)}$ = 7.5 Hz, NCH_2), 3.97 (s, 3H, NCH_3), 3.68/3.16 (2×t, 2×2H, $^3J_{(HH)}$ = 7.4 Hz, CH_2CH_2Ph), 1.82 (sextet, 2H, $^3J_{(HH)}$ = 7.4 Hz, 2-propyl CH_2), 0.94 (t, 3H, $^3J_{(HH)}$ = 7.4 Hz, propyl CH_3). ^{13}C NMR (acetone-D_6, 100.63 Mhz): δ 147.4 (N*C*N), 140.6/130.4/130.0/128.2 (benzyl *C*H), 124.7/122.9 (N*C*H), 50.7 (N*C*H_2), 36.7 (N*C*H_3), 34.0/27.1 (*C*H_2*C*H_2Ph), 24.8 (2-propyl CH_2), 11.7 (propyl *C*H_3). Branched product ^{1}H NMR (acetone-D_6, 400 MHz): δ 8.30/8.27 (2×d, 2×1H, $^3J_{(HH)}$ = 1.7 Hz, NC*H*), 7.46-7.24 (m, 5H, benzyl C*H*), 5.47 (q, 1H, $^3J_{(HH)}$ = 7.2 Hz, C*H*Ph), 4.40 (m, 2H, NCH_2), 3.98 (s, 3H, NCH_3), 1.93 (d, 3H, $^3J_{(HH)}$ = 7.1 Hz, CH_3CHPh), 1.66 (m, 2H, 2-propyl CH_2), 0.88 (t, 3H, $^3J_{(HH)}$ = 7.4 Hz, propyl CH_3).

2-Ethyl-3,4,5-trimethyl-thiazolium tetrafluoroborate (3c). ^{1}H NMR (DMSO-D_6, 500 MHz): δ 3.87 (s, 3H, NCH_3), 3.24 (q, 2H, $^3J_{(HH)}$ = 7.1 Hz ethyl CH_2), 2.46/2.40 (2×s, 2× 3H, CCH_3), 1.34 (t, 3H, $^3J_{(HH)}$ = 7.0 Hz, ethyl CH_3). ^{13}C NMR (DMSO-D_6, 125.76 Mhz): δ 173.6 (N*C*S), 142.0/127.5 ($C^{4,5}$), 36.9 (N*C*H_3), 23.1 (ethyl *C*H_2), 11.7/11.4 (C*C*H_3), 11.6 (ethyl *C*H_3). MS (ESI) *m/z* (%): 156 (100) $[M\text{-}BF_4]^+$. Elemental Anal. Calc. for $C_8H_{14}NBF_4S$ (243.07): C 39.53, H 5.81, N 5.76; found: C 39.56, H 5.68, N 5.49 %.

2-Ethyl-3-methyl-benzothiazolium tetrafluoroborate (4c). ^{1}H NMR (DMSO-D_6, 400 MHz): δ 8.45 (d, 1H, $^3J_{(HH)}$ = 8.0 Hz, benzyl C*H*), 8.31 (d, 1H, $^3J_{(HH)}$ = 8.4 Hz, benzyl C*H*), 7.92 (t, 1H, $^3J_{(HH)}$ = 7.6 Hz, benzyl C*H*), 7.82 (t, 1H, $^3J_{(HH)}$ = 7.5 Hz, benzyl C*H*), 4.22 (s, 3H, NCH_3), 3.49 (q, 2H, $^3J_{(HH)}$ = 7.2 Hz ethyl, CH_2), 1.48 (t, 3H, $^3J_{(HH)}$ = 7.3 Hz, ethyl CH_3). ^{13}C NMR (DMSO-D_6, 100.63 Mhz): δ 182.9 (N*C*S), 141.8/128.2 (*C*^{8,9}), 129.3/127.9/124.3/116.6 (benzyl *C*H), 35.9 (N*C*H$_3$), 24.1 (ethyl *C*H$_2$), 11.5 (ethyl *C*H$_3$). MS (ESI) *m/z* (%): 178 (100) [M-BF$_4$]$^+$. Elemental Anal. Calc. for $C_{10}H_{12}NBF_4S$ (265.08): C 45.31, H 4.56, N 5.28; found: C 41.82, H 4.58, N 4.44 %.

2-Ethyl-3-methyl-oxazolium tetrafluoroborate (5c). ^{1}H NMR (DMSO-D$_6$, 500 MHz): δ 8.62/8.11 (2×s, 2×1H, C^{4,5}*H*), 3.81 (s, 3H, NC*H*$_3$), 3.15 (q, 2H, $^3J_{(HH)}$ = 7.4 Hz, ethyl C*H*$_2$), 1.31 (t, 3H, $^3J_{(HH)}$ = 7.4 Hz, ethyl C*H*$_3$). ^{13}C NMR (DMSO-D$_6$, 125.76 Mhz): δ 167.6 (N*C*O), 141.5/123.5 (*C*^{4,5}H), 34.4 (N*C*H$_3$), 19.1 (ethyl *C*H$_2$), 8.1 (ethyl *C*H$_3$). MS (ESI) *m/z* (%): 112 (100) [M-BF$_4$]$^+$.

2-Ethyl-3-methyl-benzoxazolium tetrafluoroborate (6c).[25] ^{1}H NMR (DMSO-D$_6$, 500 MHz): δ 8.13 (m, 2H, benzyl C*H*), 7.79 (m, 2H, benzyl C*H*), 4.08 (s, 3H, NC*H*$_3$), 3.40 (q, 2H, $^3J_{(HH)}$ = 7.0 Hz, ethyl C*H*$_2$), 1.46 (t, 3H, $^3J_{(HH)}$ = 7.0 Hz, ethyl C*H*$_3$). ^{13}C NMR (DMSO-D$_6$, 125.76 Mhz): δ 171.3 (N*C*O), 147.2/130.3 (*C*^{8,9}), 128.4/127.6/114.2/112.8 (benzyl *C*H), 32.1 (N*C*H$_3$), 20.0 (ethyl *C*H$_2$), 8.1 (ethyl *C*H$_3$). MS (ESI) *m/z* (%): 162 (100) [M-BF$_4$]$^+$. Elemental Anal. Calc. for $C_{10}H_{12}NOBF_4$ (249.01): C 48.23, H 4.86, N 5.62; found: C 36.54, H 4.86, N 3.27 %.

3,5-Diethyl-1,4-dimethyl-1,2,4-triazolium iodide (7c). ^{1}H NMR (DMSO-D$_6$, 500 MHz): δ 3.98/3.73 (2×s, 2×3H, NC*H*$_3$), 3.14 (q, 2H, $^3J_{(HH)}$ = 7.7 Hz, ethyl C*H*$_2$), 2.86 (q, 2H, $^3J_{(HH)}$ = 7.4 Hz, ethyl C*H*$_2$), 1.25 (t, 3H, $^3J_{(HH)}$ = 7.4 Hz, ethyl C*H*$_3$), 1.20 (t, 3H, $^3J_{(HH)}$ = 7.7 Hz, ethyl C*H*$_3$). ^{13}C NMR (DMSO-D$_6$, 100.63 Mhz): δ 155.8/154.4 (*C*^{3,5}), 37.1/31.5 (N*C*H$_3$), 17.6/16.2 (ethyl *C*H$_2$), 10.0/9.4 (ethyl *C*H$_3$). MS (ESI) *m/z* (%): 154 (100) [M-I]$^+$. Elemental Anal. Calc. for $C_8H_{16}N_3I$ (281.14): C 34.18, H 5.74, N 14.95; found: C 32.26, H 5.56, N 14.80 %.

6.5.4. Synthesis of the starting azolium salts

3,4,5-Trimethyl-thiazolium tetrafluoroborate (3a). Trimethyloxonium tetrafluoroborate (600 mg, 4.1 mmol) was added in portions to a solution of 4,5-dimethylthiazole (482 mg, 4.3 mmol) in DCM (10 ml). The mixture was stirred at room temperature for 18 h. before the volatiles were removed in vacuo and the residue washed with diethyl ether (3× 5 ml). Finally the product was dried in vacuo to afford a white solid (yield: 752 mg, 86 %). ^{1}H NMR (DMSO-D$_6$, 400 MHz): δ

9.91 (s, 1H, C^2H), 4.07 (s, 3H, NCH_3), 2.49/2.40 (2×s, 2× 3H, CCH_3). ^{13}C NMR (DMSO-D_6, 100.63 Mhz): δ 155.5 (C^2H), 142.1/132.3 ($C^{4,5}$), 40.1 (NCH_3), 11.7/10.8 (CCH_3).

3-Methyl-benzothiazolium tetrafluoroborate (4a). This compound was prepared in the same manner as **(3a)** from trimethyloxonium tetrafluoroborate (500 mg, 3.4 mmol) and benzothiazole (480 mg, 3.6 mmol) to give an off-white solid (yield: 665 mg, 83 %). ^1H NMR (acetone-D_6, 400 MHz): δ 10.54 (s, 1H, C^2H), 8.56 (d, 1H, $^3J_{(HH)}$ = 8.2 Hz, benzyl CH), 8.45 (d, 1H, $^3J_{(HH)}$ = 8.5 Hz, benzyl CH), 8.04 (m, 1H, benzyl CH), 7.95 (m, 1H, benzyl CH), 4.66 (s, 3H, NCH_3). ^{13}C NMR (DMSO-D_6, 100.63 Mhz): δ 164.8 (C^2H), 141.0/131.1 ($C^{8,9}$), 129.4/128.3/124.9/117.0 (benzyl CH), 39.3 (NCH_3).

3-Methyl-oxazolium tetrafluoroborate (5a). Trimethyloxonium tetrafluoroborate (600 mg, 4.1 mmol) was added in portions to a solution of oxazole (294 mg, 4.3 mmol) in acetone (10 ml). The mixture was stirred at 55 °C for 17 hrs before the volatiles were removed in vacuo and the residue washed with diethyl ether (3× 5 ml). Finally the product was dried in vacuo to afford a white solid (yield: 423 mg, 61 %). ^1H NMR (DMSO-D_6, 400 MHz): δ 10.17 (s, 1H, C^2H), 8.74/8.22 (2×s, 2×1H, $C^{4,5}H$), 3.93 (s, 3H, NCH_3). ^{13}C NMR (DMSO-D_6, 100.63 Mhz): δ 155.4 (C^2H), 143.6/122.9 ($C^{4,5}H$), 35.1 (NCH_3).

3-Methyl-benzoxazolium tetrafluoroborate (6a).[26] This compound was prepared in the same manner as **(3a)** from trimethyloxonium tetrafluoroborate (600 mg, 4.1 mmol) and benzoxazole (507 mg, 4.3 mmol) to afford a white powder (yield: 672 mg, 75 %). ^1H NMR (DMSO-D_6, 400 MHz): δ 10.57 (s, 1H, C^2H), 8.20 (m, 2H, benzyl CH), 7.85 (m, 2H, benzyl CH), 4.17 (s, 3H, NCH_3). ^{13}C NMR (DMSO-D_6, 125.76 Mhz): δ 158.3 (C^2H), 148.2/129.0 ($C^{8,9}$), 129.4/128.2/115.0/113.5 (benzyl CH), 33.1 (NCH_3).

6.6. References

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APPENDIX 1

Publications

Publications from this Thesis

1. C-H Activation of Imidazolium Salts by Pt^0 at Ambient Temperature: Synthesis of Hydrido Platinium Bis(carbene) Compounds.
Duin, M. A.; Clement, N. D.; Cavell, K. J.; Elsevier, C. J. *Chem. Commun.* **2003**, 400-401.

2. Oxidative Addition of Imidazolium Salts to Ni^0 and Pd^0 – Synthesis and Structural Characterisation of Unusually Stable Metal-hydride Complexes.
Clement, N. D.; Cavell, K. J.; Jones, C.; Elsevier, C. J. *Angew. Chem. Int. Ed.* **2004**, *43*, 1277-1279.

3. Transition-Metal-Catalysed Reactions Involving Imidazolium Salt/N-Heterocyclic Carbene Couples as Substrates.
Clement, N. D.; Cavell, K. J. *Angew. Chem. Int. Ed.* **2004**, *43*, 3845-3847.

4. Palladium(N-Heterocyclic Carbene) Hydrogenation Catalysts.
Sprengers, J. W.; Wassenaar, J.; Clement, N. D.; Cavell, K. J.; Elsevier, C. J. *Angew. Chem. Int. Ed.* **2005**, *44*, 2026-2029.

5. Zero-Valent N-Heterocyclic Carbene Complexes of Pt, Pd and Ni Dimethylfumarate : Synthesis, Structure and Dynamic Behaviour.
Clement, N. D.; Cavell, K. J.; Ooi, L.-L; Submitted **2005**.

APPENDIX 2

Tables of Bond Distances and Angles

Table A2.1. Bond lengths [Å] and angles [°] for Pd(NHC)(DMFU)$_2$ complex **13** (see Chapter 2).

C(1)-N(2)	1.358(3)	C(29)-C(30)	1.476(4)	C(25)-C(24)-C(23)	117.1(3)
C(1)-N(1)	1.365(4)	C(30)-C(31)	1.412(4)	C(25)-C(24)-Pd(1)	70.15(16)
C(1)-Pd(1)	2.111(3)	C(30)-Pd(1)	2.149(3)	C(23)-C(24)-Pd(1)	114.61(19)
C(2)-C(3)	1.344(4)	C(31)-C(32)	1.484(5)	C(24)-C(25)-C(26)	120.2(3)
C(2)-N(1)	1.390(4)	C(31)-Pd(1)	2.142(3)	C(24)-C(25)-Pd(1)	71.36(16)
C(3)-N(2)	1.396(4)	C(32)-O(8)	1.209(4)	C(26)-C(25)-Pd(1)	111.26(19)
C(4)-C(9)	1.394(4)	C(32)-O(7)	1.329(4)	O(4)-C(26)-O(3)	123.0(3)
C(4)-C(5)	1.402(4)	C(33)-O(7)	1.441(4)	O(4)-C(26)-C(25)	124.3(3)
C(4)-N(2)	1.441(4)			O(3)-C(26)-C(25)	112.6(3)
C(5)-C(6)	1.386(4)	N(2)-C(1)-N(1)	104.3(2)	O(6)-C(29)-O(5)	122.9(3)
C(5)-C(10)	1.497(4)	N(2)-C(1)-Pd(1)	128.0(2)	O(6)-C(29)-C(30)	125.5(3)
C(6)-C(7)	1.394(5)	N(1)-C(1)-Pd(1)	127.7(2)	O(5)-C(29)-C(30)	111.6(3)
C(7)-C(8)	1.389(5)	C(3)-C(2)-N(1)	106.9(3)	C(31)-C(30)-C(29)	118.1(3)
C(7)-C(11)	1.506(5)	C(2)-C(3)-N(2)	106.8(3)	C(31)-C(30)-Pd(1)	70.54(16)
C(8)-C(9)	1.390(4)	C(9)-C(4)-C(5)	121.5(3)	C(29)-C(30)-Pd(1)	114.34(19)
C(9)-C(12)	1.513(4)	C(9)-C(4)-N(2)	118.5(3)	C(30)-C(31)-C(32)	120.8(3)
C(13)-C(18)	1.397(4)	C(5)-C(4)-N(2)	119.9(3)	C(30)-C(31)-Pd(1)	71.03(16)
C(13)-C(14)	1.397(4)	C(6)-C(5)-C(4)	117.9(3)	C(32)-C(31)-Pd(1)	112.9(2)
C(13)-N(1)	1.449(4)	C(6)-C(5)-C(10)	120.2(3)	O(8)-C(32)-O(7)	122.6(3)
C(14)-C(15)	1.392(4)	C(4)-C(5)-C(10)	121.9(3)	O(8)-C(32)-C(31)	124.0(3)
C(14)-C(19)	1.501(4)	C(5)-C(6)-C(7)	122.5(3)	O(7)-C(32)-C(31)	113.3(3)
C(15)-C(16)	1.380(4)	C(8)-C(7)-C(6)	117.7(3)	C(1)-N(1)-C(2)	111.0(2)
C(16)-C(17)	1.382(5)	C(8)-C(7)-C(11)	121.9(3)	C(1)-N(1)-C(13)	126.0(2)
C(16)-C(20)	1.517(5)	C(6)-C(7)-C(11)	120.4(3)	C(2)-N(1)-C(13)	122.9(2)
C(17)-C(18)	1.391(4)	C(7)-C(8)-C(9)	122.3(3)	C(1)-N(2)-C(3)	111.0(2)
C(18)-C(21)	1.515(4)	C(8)-C(9)-C(4)	118.1(3)	C(1)-N(2)-C(4)	126.6(2)
C(22)-O(1)	1.448(4)	C(8)-C(9)-C(12)	120.6(3)	C(3)-N(2)-C(4)	122.3(2)
C(23)-O(2)	1.213(4)	C(4)-C(9)-C(12)	121.2(3)	C(23)-O(1)-C(22)	116.0(3)
C(23)-O(1)	1.340(4)	C(18)-C(13)-C(14)	121.6(3)	C(26)-O(3)-C(27)	116.1(3)
C(23)-C(24)	1.482(4)	C(18)-C(13)-N(1)	119.2(2)	C(29)-O(5)-C(28)	116.3(3)
C(24)-C(25)	1.417(4)	C(14)-C(13)-N(1)	119.3(2)	C(32)-O(7)-C(33)	117.2(3)
C(24)-Pd(1)	2.157(3)	C(15)-C(14)-C(13)	117.7(3)	C(1)-Pd(1)-C(25)	136.48(11)
C(25)-C(26)	1.489(4)	C(15)-C(14)-C(19)	119.3(3)	C(1)-Pd(1)-C(31)	133.93(11)
C(25)-Pd(1)	2.141(3)	C(13)-C(14)-C(19)	122.9(3)	C(25)-Pd(1)-C(31)	89.59(12)
C(26)-O(4)	1.200(4)	C(16)-C(15)-C(14)	122.2(3)	C(1)-Pd(1)-C(30)	95.68(10)
C(26)-O(3)	1.345(4)	C(15)-C(16)-C(17)	118.4(3)	C(25)-Pd(1)-C(30)	127.60(11)
C(27)-O(3)	1.442(4)	C(15)-C(16)-C(20)	120.5(3)	C(31)-Pd(1)-C(30)	38.44(11)
C(28)-O(5)	1.445(4)	C(17)-C(16)-C(20)	121.1(3)	C(1)-Pd(1)-C(24)	98.17(11)
C(29)-O(6)	1.219(4)	C(16)-C(17)-C(18)	122.1(3)	C(25)-Pd(1)-C(24)	38.49(11)
C(29)-O(5)	1.339(4)	C(17)-C(18)-C(13)	117.9(3)	C(31)-Pd(1)-C(24)	127.83(11)
		C(17)-C(18)-C(21)	120.1(3)	C(30)-Pd(1)-C(24)	166.09(12)
		C(13)-C(18)-C(21)	121.9(3)		
		O(2)-C(23)-O(1)	122.9(3)		
		O(2)-C(23)-C(24)	126.1(3)		
		O(1)-C(23)-C(24)	111.0(3)		

Table A2.2. Bond lengths [Å] and angles [°] for $[Pd(NHC)(BQ)]_2$ complex **16** (see Chapter 2).

C(1)-O(1)	1.290(8)	C(101)-Cl(4)	1.760(8)	C(33)-C(32)-H(32)	119.6
C(1)-C(6)	1.412(9)	C(101)-Cl(3)	1.762(8)	C(31)-C(32)-H(32)	119.6
C(1)-C(2)	1.447(9)	C(101)-H(10C)	0.99	Pd(2)-C(32)-H(32)	112.4
C(1)-Pd(1)	2.596(6)	C(101)-H(10D)	0.99	C(32)-C(33)-C(28)	121.0(6)
C(2)-C(3)	1.343(10)	O(1)-Pd(2)	2.148(5)	C(32)-C(33)-Pd(2)	72.9(4)
C(2)-H(2)	0.9500	O(3)-Pd(1)	2.136(5)	C(28)-C(33)-Pd(2)	96.3(4)
C(3)-C(4)	1.497(10)	O(5)-C(55)	0.979(9)	C(32)-C(33)-H(33)	119.5
C(3)-H(3)	0.9500			C(28)-C(33)-H(33)	119.5
C(4)-O(2)	1.233(8)	O(1)-C(1)-C(6)	124.3(6)	Pd(2)-C(33)-H(33)	100.8
C(4)-C(5)	1.450(9)	O(1)-C(1)-C(2)	116.8(6)	N(3)-C(34)-N(4)	108.0(5)
C(5)-C(6)	1.435(9)	C(6)-C(1)-C(2)	118.9(7)	N(3)-C(34)-Pd(2)	125.6(5)
C(5)-Pd(1)	2.118(7)	O(1)-C(1)-Pd(1)	120.9(4)	N(4)-C(34)-Pd(2)	126.4(4)
C(5)-H(5)	0.9500	C(6)-C(1)-Pd(1)	56.6(3)	N(4)-C(35)-C(36)	102.2(5)
C(6)-Pd(1)	2.166(6)	C(2)-C(1)-Pd(1)	95.8(4)	N(4)-C(35)-H(35A)	111.3
C(6)-H(6)	0.9500	C(3)-C(2)-C(1)	122.3(7)	C(36)-C(35)-H(35A)	111.3
C(7)-N(2)	1.339(7)	C(3)-C(2)-H(2)	118.8	N(4)-C(35)-H(35B)	111.3
C(7)-N(1)	1.342(8)	C(1)-C(2)-H(2)	118.8	C(36)-C(35)-H(35B)	111.3
C(7)-Pd(1)	2.030(6)	C(2)-C(3)-C(4)	121.6(6)	H(35A)-C(35)-H(35B)	109.2
C(8)-N(1)	1.487(8)	C(2)-C(3)-H(3)	119.2	N(3)-C(36)-C(35)	102.1(5)
C(8)-C(9)	1.522(9)	C(4)-C(3)-H(3)	119.2	N(3)-C(36)-H(36A)	111.4
C(8)-H(8A)	0.9900	O(2)-C(4)-C(5)	125.0(7)	C(35)-C(36)-H(36A)	111.4
C(8)-H(8B)	0.9900	O(2)-C(4)-C(3)	119.9(6)	N(3)-C(36)-H(36B)	111.4
C(9)-N(2)	1.466(8)	C(5)-C(4)-C(3)	115.1(6)	C(35)-C(36)-H(36B)	111.4
C(9)-H(9A)	0.9900	C(6)-C(5)-C(4)	121.8(6)	H(36A)-C(36)-H(36B)	109.2
C(9)-H(9B)	0.9900	C(6)-C(5)-Pd(1)	72.2(4)	C(42)-C(37)-C(38)	122.1(6)
C(10)-C(11)	1.384(10)	C(4)-C(5)-Pd(1)	99.8(4)	C(42)-C(37)-N(3)	120.0(6)
C(10)-C(15)	1.399(9)	C(6)-C(5)-H(5)	119.1	C(38)-C(37)-N(3)	117.8(6)
C(10)-N(1)	1.436(8)	C(4)-C(5)-H(5)	119.1	C(39)-C(38)-C(37)	117.8(6)
C(11)-C(12)	1.404(9)	Pd(1)-C(5)-H(5)	98	C(39)-C(38)-C(43)	120.9(6)
C(11)-C(16)	1.521(9)	C(1)-C(6)-C(5)	119.2(6)	C(37)-C(38)-C(43)	121.3(6)
C(12)-C(13)	1.359(9)	C(1)-C(6)-Pd(1)	90.5(4)	C(38)-C(39)-C(40)	122.8(6)
C(12)-H(12)	0.9500	C(5)-C(6)-Pd(1)	68.6(4)	C(38)-C(39)-H(39)	118.6
C(13)-C(14)	1.409(10)	C(1)-C(6)-H(6)	120.4	C(40)-C(39)-H(39)	118.6
C(13)-C(17)	1.508(9)	C(5)-C(6)-H(6)	120.4	C(41)-C(40)-C(39)	116.8(6)
C(14)-C(15)	1.368(9)	Pd(1)-C(6)-H(6)	110.6	C(41)-C(40)-C(44)	123.7(6)
C(14)-H(14)	0.9500	N(2)-C(7)-N(1)	108.1(5)	C(39)-C(40)-C(44)	119.5(6)
C(15)-C(18)	1.514(10)	N(2)-C(7)-Pd(1)	125.7(5)	C(40)-C(41)-C(42)	123.9(7)
C(16)-H(16A)	0.9800	N(1)-C(7)-Pd(1)	126.0(4)	C(40)-C(41)-H(41)	118.1
C(16)-H(16B)	0.9800	N(1)-C(8)-C(9)	101.5(5)	C(42)-C(41)-H(41)	118.1
C(16)-H(16C)	0.9800	N(1)-C(8)-H(8A)	111.5	C(37)-C(42)-C(41)	116.6(6)
C(17)-H(17A)	0.9800	C(9)-C(8)-H(8A)	111.5	C(37)-C(42)-C(45)	121.0(6)
C(17)-H(17B)	0.9800	N(1)-C(8)-H(8B)	111.5	C(41)-C(42)-C(45)	122.4(7)
C(17)-H(17C)	0.9800	C(9)-C(8)-H(8B)	111.5	C(38)-C(43)-H(43A)	109.5
C(18)-H(18A)	0.9800	H(8A)-C(8)-H(8B)	109.3	C(38)-C(43)-H(43B)	109.5
C(18)-H(18B)	0.9800	N(2)-C(9)-C(8)	103.8(5)	H(43A)-C(43)-H(43B)	109.5
C(18)-H(18C)	0.9800	N(2)-C(9)-H(9A)	111	C(38)-C(43)-H(43C)	109.5
C(19)-C(20)	1.391(9)	C(8)-C(9)-H(9A)	111	H(43A)-C(43)-H(43C)	109.5
C(19)-C(24)	1.398(9)	N(2)-C(9)-H(9B)	111	H(43B)-C(43)-H(43C)	109.5
C(19)-N(2)	1.445(8)	C(8)-C(9)-H(9B)	111	C(40)-C(44)-H(44A)	109.5
C(20)-C(21)	1.398(9)	H(9A)-C(9)-H(9B)	109	C(40)-C(44)-H(44B)	109.5
C(20)-C(25)	1.506(9)	C(11)-C(10)-C(15)	121.3(6)	H(44A)-C(44)-H(44B)	109.5
C(21)-C(22)	1.381(10)	C(11)-C(10)-N(1)	118.9(6)	C(40)-C(44)-H(44C)	109.5
C(21)-H(21)	0.9500	C(15)-C(10)-N(1)	119.2(6)	H(44A)-C(44)-H(44C)	109.5
C(22)-C(23)	1.378(10)	C(10)-C(11)-C(12)	117.7(6)	H(44B)-C(44)-H(44C)	109.5

C(22)-C(26)	1.504(9)	C(10)-C(11)-C(16)	122.0(6)	C(42)-C(45)-H(45A)	109.5
C(23)-C(24)	1.419(9)	C(12)-C(11)-C(16)	120.3(6)	C(42)-C(45)-H(45B)	109.5
C(23)-H(23)	0.9500	C(13)-C(12)-C(11)	122.9(7)	H(45A)-C(45)-H(45B)	109.5
C(24)-C(27)	1.493(9)	C(13)-C(12)-H(12)	118.5	C(42)-C(45)-H(45C)	109.5
C(25)-H(25A)	0.9800	C(11)-C(12)-H(12)	118.5	H(45A)-C(45)-H(45C)	109.5
C(25)-H(25B)	0.9800	C(12)-C(13)-C(14)	117.1(6)	H(45B)-C(45)-H(45C)	109.5
C(25)-H(25C)	0.9800	C(12)-C(13)-C(17)	121.5(7)	C(51)-C(46)-C(47)	122.3(6)
C(26)-H(26A)	0.9800	C(14)-C(13)-C(17)	121.3(7)	C(51)-C(46)-N(4)	118.3(7)
C(26)-H(26B)	0.9800	C(15)-C(14)-C(13)	122.5(6)	C(47)-C(46)-N(4)	119.3(7)
C(26)-H(26C)	0.9800	C(15)-C(14)-H(14)	118.8	C(46)-C(47)-C(48)	117.7(7)
C(27)-H(27A)	0.9800	C(13)-C(14)-H(14)	118.8	C(46)-C(47)-C(52)	122.3(6)
C(27)-H(27B)	0.9800	C(14)-C(15)-C(10)	118.3(7)	C(48)-C(47)-C(52)	120.0(7)
C(27)-H(27C)	0.9800	C(14)-C(15)-C(18)	120.2(6)	C(49)-C(48)-C(47)	121.3(7)
C(28)-O(4)	1.231(8)	C(10)-C(15)-C(18)	121.5(6)	C(49)-C(48)-H(48)	119.3
C(28)-C(29)	1.469(9)	C(11)-C(16)-H(16A)	109.5	C(47)-C(48)-H(48)	119.3
C(28)-C(33)	1.478(10)	C(11)-C(16)-H(16B)	109.5	C(48)-C(49)-C(50)	119.5(6)
C(29)-C(30)	1.343(9)	H(16A)-C(16)-H(16B)	109.5	C(48)-C(49)-C(53)	121.6(7)
C(29)-H(29)	0.9500	C(11)-C(16)-H(16C)	109.5	C(50)-C(49)-C(53)	118.9(7)
C(30)-C(31)	1.480(9)	H(16A)-C(16)-H(16C)	109.5	C(49)-C(50)-C(51)	120.9(7)
C(30)-H(30)	0.9500	H(16B)-C(16)-H(16C)	109.5	C(49)-C(50)-H(50)	119.5
C(31)-O(3)	1.277(7)	C(13)-C(17)-H(17A)	109.5	C(51)-C(50)-H(50)	119.5
C(31)-C(32)	1.441(9)	C(13)-C(17)-H(17B)	109.5	C(46)-C(51)-C(50)	118.2(7)
C(31)-Pd(2)	2.598(6)	H(17A)-C(17)-H(17B)	109.5	C(46)-C(51)-C(54)	122.0(6)
C(32)-C(33)	1.421(9)	C(13)-C(17)-H(17C)	109.5	C(50)-C(51)-C(54)	119.7(7)
C(32)-Pd(2)	2.178(6)	H(17A)-C(17)-H(17C)	109.5	C(47)-C(52)-H(52A)	109.5
C(32)-H(32)	0.9500	H(17B)-C(17)-H(17C)	109.5	C(47)-C(52)-H(52B)	109.5
C(33)-Pd(2)	2.121(7)	C(15)-C(18)-H(18A)	109.5	H(52A)-C(52)-H(52B)	109.5
C(33)-H(33)	0.9500	C(15)-C(18)-H(18B)	109.5	C(47)-C(52)-H(52C)	109.5
C(34)-N(3)	1.331(8)	H(18A)-C(18)-H(18B)	109.5	H(52A)-C(52)-H(52C)	109.5
C(34)-N(4)	1.341(8)	C(15)-C(18)-H(18C)	109.5	H(52B)-C(52)-H(52C)	109.5
C(34)-Pd(2)	2.034(6)	H(18A)-C(18)-H(18C)	109.5	C(49)-C(53)-H(53A)	109.5
C(35)-N(4)	1.477(8)	H(18B)-C(18)-H(18C)	109.5	C(49)-C(53)-H(53B)	109.5
C(35)-C(36)	1.520(9)	C(20)-C(19)-C(24)	123.1(6)	H(53A)-C(53)-H(53B)	109.5
C(35)-H(35A)	0.9900	C(20)-C(19)-N(2)	118.9(6)	C(49)-C(53)-H(53C)	109.5
C(35)-H(35B)	0.9900	C(24)-C(19)-N(2)	117.8(6)	H(53A)-C(53)-H(53C)	109.5
C(36)-N(3)	1.463(8)	C(19)-C(20)-C(21)	117.3(7)	H(53B)-C(53)-H(53C)	109.5
C(36)-H(36A)	0.9900	C(19)-C(20)-C(25)	122.0(6)	C(51)-C(54)-H(54A)	109.5
C(36)-H(36B)	0.9900	C(21)-C(20)-C(25)	120.7(6)	C(51)-C(54)-H(54B)	109.5
C(37)-C(42)	1.392(9)	C(22)-C(21)-C(20)	122.6(7)	H(54A)-C(54)-H(54B)	109.5
C(37)-C(38)	1.407(9)	C(22)-C(21)-H(21)	118.7	C(51)-C(54)-H(54C)	109.5
C(37)-N(3)	1.448(8)	C(20)-C(21)-H(21)	118.7	H(54A)-C(54)-H(54C)	109.5
C(38)-C(39)	1.375(9)	C(23)-C(22)-C(21)	118.3(6)	H(54B)-C(54)-H(54C)	109.5
C(38)-C(43)	1.509(9)	C(23)-C(22)-C(26)	120.8(7)	Cl(1)-C(100)-Cl(2)	110.4(4)
C(39)-C(40)	1.401(9)	C(21)-C(22)-C(26)	120.9(7)	Cl(1)-C(100)-H(10A)	109.6
C(39)-H(39)	0.9500	C(22)-C(23)-C(24)	122.5(7)	Cl(2)-C(100)-H(10A)	109.6
C(40)-C(41)	1.376(9)	C(22)-C(23)-H(23)	118.7	Cl(1)-C(100)-H(10B)	109.6
C(40)-C(44)	1.500(9)	C(24)-C(23)-H(23)	118.7	Cl(2)-C(100)-H(10B)	109.6
C(41)-C(42)	1.398(9)	C(19)-C(24)-C(23)	116.2(6)	H(10A)-C(100)-H(10B)	108.1
C(41)-H(41)	0.9500	C(19)-C(24)-C(27)	122.8(6)	Cl(4)-C(101)-Cl(3)	110.1(5)
C(42)-C(45)	1.499(9)	C(23)-C(24)-C(27)	121.0(6)	Cl(4)-C(101)-H(10C)	109.6
C(43)-H(43A)	0.9800	C(20)-C(25)-H(25A)	109.5	Cl(3)-C(101)-H(10C)	109.6
C(43)-H(43B)	0.9800	C(20)-C(25)-H(25B)	109.5	Cl(4)-C(101)-H(10D)	109.6
C(43)-H(43C)	0.9800	H(25A)-C(25)-H(25B)	109.5	Cl(3)-C(101)-H(10D)	109.6
C(44)-H(44A)	0.9800	C(20)-C(25)-H(25C)	109.5	H(10C)-C(101)-H(10D)	108.2
C(44)-H(44B)	0.9800	H(25A)-C(25)-H(25C)	109.5	C(7)-N(1)-C(10)	125.9(5)
C(44)-H(44C)	0.9800	H(25B)-C(25)-H(25C)	109.5	C(7)-N(1)-C(8)	113.4(5)

C(45)-H(45A)	0.9800	C(22)-C(26)-H(26A)	109.5	C(10)-N(1)-C(8)	119.1(5)
C(45)-H(45B)	0.9800	C(22)-C(26)-H(26B)	109.5	C(7)-N(2)-C(19)	126.0(5)
C(45)-H(45C)	0.9800	H(26A)-C(26)-H(26B)	109.5	C(7)-N(2)-C(9)	113.0(5)
C(46)-C(51)	1.388(10)	C(22)-C(26)-H(26C)	109.5	C(19)-N(2)-C(9)	120.7(5)
C(46)-C(47)	1.391(10)	H(26A)-C(26)-H(26C)	109.5	C(34)-N(3)-C(37)	125.2(5)
C(46)-N(4)	1.436(8)	H(26B)-C(26)-H(26C)	109.5	C(34)-N(3)-C(36)	113.4(5)
C(47)-C(48)	1.415(9)	C(24)-C(27)-H(27A)	109.5	C(37)-N(3)-C(36)	120.8(5)
C(47)-C(52)	1.501(10)	C(24)-C(27)-H(27B)	109.5	C(34)-N(4)-C(46)	125.4(5)
C(48)-C(49)	1.375(10)	H(27A)-C(27)-H(27B)	109.5	C(34)-N(4)-C(35)	112.5(5)
C(48)-H(48)	0.9500	C(24)-C(27)-H(27C)	109.5	C(46)-N(4)-C(35)	122.0(5)
C(49)-C(50)	1.394(10)	H(27A)-C(27)-H(27C)	109.5	C(1)-O(1)-Pd(2)	122.2(4)
C(49)-C(53)	1.510(9)	H(27B)-C(27)-H(27C)	109.5	C(31)-O(3)-Pd(1)	121.3(4)
C(50)-C(51)	1.402(9)	O(4)-C(28)-C(29)	120.6(7)	C(7)-Pd(1)-C(5)	109.7(3)
C(50)-H(50)	0.9500	O(4)-C(28)-C(33)	123.7(6)	C(7)-Pd(1)-O(3)	99.0(2)
C(51)-C(54)	1.507(10)	C(29)-C(28)-C(33)	115.7(7)	C(5)-Pd(1)-O(3)	151.2(2)
C(52)-H(52A)	0.9800	C(30)-C(29)-C(28)	122.2(7)	C(7)-Pd(1)-C(6)	148.5(3)
C(52)-H(52B)	0.9800	C(30)-C(29)-H(29)	118.9	C(5)-Pd(1)-C(6)	39.1(2)
C(52)-H(52C)	0.9800	C(28)-C(29)-H(29)	118.9	O(3)-Pd(1)-C(6)	112.1(2)
C(53)-H(53A)	0.9800	C(29)-C(30)-C(31)	122.9(6)	C(7)-Pd(1)-C(1)	155.0(2)
C(53)-H(53B)	0.9800	C(29)-C(30)-H(30)	118.6	C(5)-Pd(1)-C(1)	61.8(2)
C(53)-H(53C)	0.9800	C(31)-C(30)-H(30)	118.6	O(3)-Pd(1)-C(1)	92.4(2)
C(54)-H(54A)	0.9800	O(3)-C(31)-C(32)	126.1(6)	C(6)-Pd(1)-C(1)	32.9(2)
C(54)-H(54B)	0.9800	O(3)-C(31)-C(30)	117.4(6)	C(34)-Pd(2)-C(33)	109.2(3)
C(54)-H(54C)	0.9800	C(32)-C(31)-C(30)	116.5(6)	C(34)-Pd(2)-O(1)	99.8(2)
C(100)-Cl(1)	1.758(8)	O(3)-C(31)-Pd(2)	122.7(4)	C(33)-Pd(2)-O(1)	150.8(2)
C(100)-Cl(2)	1.784(8)	C(32)-C(31)-Pd(2)	57.0(3)	C(34)-Pd(2)-C(32)	147.1(3)
C(100)-H(10A)	0.9900	C(30)-C(31)-Pd(2)	91.6(4)	C(33)-Pd(2)-C(32)	38.6(2)
C(100)-H(10B)	0.9900	C(33)-C(32)-C(31)	120.8(6)	O(1)-Pd(2)-C(32)	112.3(2)
		C(33)-C(32)-Pd(2)	68.5(4)	C(34)-Pd(2)-C(31)	157.7(2)
		C(31)-C(32)-Pd(2)	89.4(4)	C(33)-Pd(2)-C(31)	62.7(2)
				O(1)-Pd(2)-C(31)	91.22(19)
				C(32)-Pd(2)-C(31)	33.7(2)

Table A2.3. Bond lengths [Å] and angles [°] for Ni(NHC)(DMFU)$_2$ complex **3** (see Chapter 3).

C(1)-N(1)	1.367(4)	C(32)-O(7)	1.347(4)	C(16)-C(20)-H(20C)	109.5
C(1)-N(2)	1.388(4)	C(33)-O(7)	1.452(4)	H(20A)-C(20)-H(20C)	109.5
C(1)-Ni(1)	1.955(3)	C(33)-H(33A)	0.9800	H(20B)-C(20)-H(20C)	109.5
C(2)-C(3)	1.349(5)	C(33)-H(33B)	0.9800	C(18)-C(21)-H(21A)	109.5
C(2)-N(2)	1.387(4)	C(33)-H(33C)	0.9800	C(18)-C(21)-H(21B)	109.5
C(2)-H(2)	0.9500			H(21A)-C(21)-H(21B)	109.5
C(3)-N(1)	1.387(4)	N(1)-C(1)-N(2)	102.4(3)	C(18)-C(21)-H(21C)	109.5
C(3)-H(3)	0.9500	N(1)-C(1)-Ni(1)	128.2(2)	H(21A)-C(21)-H(21C)	109.5
C(4)-C(9)	1.387(5)	N(2)-C(1)-Ni(1)	129.4(2)	H(21B)-C(21)-H(21C)	109.5
C(4)-C(5)	1.399(5)	C(3)-C(2)-N(2)	107.1(3)	O(1)-C(22)-H(22A)	109.5
C(4)-N(2)	1.447(4)	C(3)-C(2)-H(2)	126.5	O(1)-C(22)-H(22B)	109.5
C(5)-C(6)	1.380(5)	N(2)-C(2)-H(2)	126.5	H(22A)-C(22)-H(22B)	109.5
C(5)-C(10)	1.512(5)	C(2)-C(3)-N(1)	106.4(3)	O(1)-C(22)-H(22C)	109.5
C(6)-C(7)	1.400(5)	C(2)-C(3)-H(3)	126.8	H(22A)-C(22)-H(22C)	109.5
C(6)-H(6)	0.9500	N(1)-C(3)-H(3)	126.8	H(22B)-C(22)-H(22C)	109.5
C(7)-C(8)	1.378(5)	C(9)-C(4)-C(5)	122.1(3)	O(2)-C(23)-O(1)	122.6(3)
C(7)-C(11)	1.506(5)	C(9)-C(4)-N(2)	119.9(3)	O(2)-C(23)-C(24)	126.5(3)
C(8)-C(9)	1.391(5)	C(5)-C(4)-N(2)	117.8(3)	O(1)-C(23)-C(24)	110.9(3)
C(8)-H(8)	0.9500	C(6)-C(5)-C(4)	117.8(3)	C(25)-C(24)-C(23)	117.5(3)
C(9)-C(12)	1.513(5)	C(6)-C(5)-C(10)	118.6(3)	C(25)-C(24)-Ni(1)	68.8(2)

C(10)-H(10A)	0.9800	C(4)-C(5)-C(10)	123.5(3)	C(23)-C(24)-Ni(1)	112.2(2)
C(10)-H(10B)	0.9800	C(5)-C(6)-C(7)	122.1(4)	C(24)-C(25)-C(26)	119.1(3)
C(10)-H(10C)	0.9800	C(5)-C(6)-H(6)	118.9	C(24)-C(25)-Ni(1)	70.4(2)
C(11)-H(11A)	0.9800	C(7)-C(6)-H(6)	118.9	C(26)-C(25)-Ni(1)	105.0(2)
C(11)-H(11B)	0.9800	C(8)-C(7)-C(6)	117.8(3)	O(3)-C(26)-O(4)	123.1(3)
C(11)-H(11C)	0.9800	C(8)-C(7)-C(11)	121.8(4)	O(3)-C(26)-C(25)	126.8(3)
C(12)-H(12A)	0.9800	C(6)-C(7)-C(11)	120.5(4)	O(4)-C(26)-C(25)	110.0(3)
C(12)-H(12B)	0.9800	C(7)-C(8)-C(9)	122.6(3)	O(4)-C(27)-H(27A)	109.5
C(12)-H(12C)	0.9800	C(7)-C(8)-H(8)	118.7	O(4)-C(27)-H(27B)	109.5
C(13)-C(14)	1.389(5)	C(9)-C(8)-H(8)	118.7	H(27A)-C(27)-H(27B)	109.5
C(13)-C(18)	1.394(5)	C(4)-C(9)-C(8)	117.6(3)	O(4)-C(27)-H(27C)	109.5
C(13)-N(1)	1.453(4)	C(4)-C(9)-C(12)	122.5(3)	H(27A)-C(27)-H(27C)	109.5
C(14)-C(15)	1.389(5)	C(8)-C(9)-C(12)	119.9(3)	H(27B)-C(27)-H(27C)	109.5
C(14)-C(19)	1.497(5)	C(5)-C(10)-H(10A)	109.5	O(5)-C(28)-H(28A)	109.5
C(15)-C(16)	1.390(6)	C(5)-C(10)-H(10B)	109.5	O(5)-C(28)-H(28B)	109.5
C(15)-H(15)	0.9500	H(10A)-C(10)-H(10B)	109.5	H(28A)-C(28)-H(28B)	109.5
C(16)-C(17)	1.380(5)	C(5)-C(10)-H(10C)	109.5	O(5)-C(28)-H(28C)	109.5
C(16)-C(20)	1.520(5)	H(10A)-C(10)-H(10C)	109.5	H(28A)-C(28)-H(28C)	109.5
C(17)-C(18)	1.392(5)	H(10B)-C(10)-H(10C)	109.5	H(28B)-C(28)-H(28C)	109.5
C(17)-H(17)	0.9500	C(7)-C(11)-H(11A)	109.5	O(6)-C(29)-O(5)	123.1(3)
C(18)-C(21)	1.504(5)	C(7)-C(11)-H(11B)	109.5	O(6)-C(29)-C(30)	125.3(3)
C(19)-H(19A)	0.9800	H(11A)-C(11)-H(11B)	109.5	O(5)-C(29)-C(30)	111.6(3)
C(19)-H(19B)	0.9800	C(7)-C(11)-H(11C)	109.5	C(31)-C(30)-C(29)	114.8(3)
C(19)-H(19C)	0.9800	H(11A)-C(11)-H(11C)	109.5	C(31)-C(30)-Ni(1)	68.3(2)
C(20)-H(20A)	0.9800	H(11B)-C(11)-H(11C)	109.5	C(29)-C(30)-Ni(1)	111.2(2)
C(20)-H(20B)	0.9800	C(9)-C(12)-H(12A)	109.5	C(30)-C(31)-C(32)	122.6(3)
C(20)-H(20C)	0.9800	C(9)-C(12)-H(12B)	109.5	C(30)-C(31)-Ni(1)	70.6(2)
C(21)-H(21A)	0.9800	H(12A)-C(12)-H(12B)	109.5	C(32)-C(31)-Ni(1)	109.5(2)
C(21)-H(21B)	0.9800	C(9)-C(12)-H(12C)	109.5	O(8)-C(32)-O(7)	122.5(3)
C(21)-H(21C)	0.9800	H(12A)-C(12)-H(12C)	109.5	O(8)-C(32)-C(31)	124.0(3)
C(22)-O(1)	1.451(4)	H(12B)-C(12)-H(12C)	109.5	O(7)-C(32)-C(31)	113.4(3)
C(22)-H(22A)	0.9800	C(14)-C(13)-C(18)	122.2(3)	O(7)-C(33)-H(33A)	109.5
C(22)-H(22B)	0.9800	C(14)-C(13)-N(1)	119.3(3)	O(7)-C(33)-H(33B)	109.5
C(22)-H(22C)	0.9800	C(18)-C(13)-N(1)	118.3(3)	H(33A)-C(33)-H(33B)	109.5
C(23)-O(2)	1.210(4)	C(13)-C(14)-C(15)	117.4(4)	O(7)-C(33)-H(33C)	109.5
C(23)-O(1)	1.349(4)	C(13)-C(14)-C(19)	122.3(3)	H(33A)-C(33)-H(33C)	109.5
C(23)-C(24)	1.472(5)	C(15)-C(14)-C(19)	120.3(4)	H(33B)-C(33)-H(33C)	109.5
C(24)-C(25)	1.409(5)	C(14)-C(15)-C(16)	122.0(4)	C(1)-N(1)-C(3)	112.6(3)
C(24)-Ni(1)	2.033(3)	C(14)-C(15)-H(15)	119	C(1)-N(1)-C(13)	127.5(3)
C(25)-C(26)	1.484(5)	C(16)-C(15)-H(15)	119	C(3)-N(1)-C(13)	119.8(3)
C(25)-Ni(1)	2.012(3)	C(17)-C(16)-C(15)	118.9(4)	C(2)-N(2)-C(1)	111.6(3)
C(26)-O(3)	1.208(4)	C(17)-C(16)-C(20)	121.0(4)	C(2)-N(2)-C(4)	120.2(3)
C(26)-O(4)	1.355(4)	C(15)-C(16)-C(20)	120.0(4)	C(1)-N(2)-C(4)	128.2(3)
C(27)-O(4)	1.436(4)	C(16)-C(17)-C(18)	121.2(4)	C(1)-Ni(1)-C(31)	136.15(15)
C(27)-H(27A)	0.9800	C(16)-C(17)-H(17)	119.4	C(1)-Ni(1)-C(25)	138.20(14)
C(27)-H(27B)	0.9800	C(18)-C(17)-H(17)	119.4	C(31)-Ni(1)-C(25)	85.62(15)
C(27)-H(27C)	0.9800	C(17)-C(18)-C(13)	118.2(3)	C(1)-Ni(1)-C(30)	97.37(14)
C(28)-O(5)	1.453(4)	C(17)-C(18)-C(21)	119.5(3)	C(31)-Ni(1)-C(30)	41.06(14)
C(28)-H(28A)	0.9800	C(13)-C(18)-C(21)	122.3(3)	C(25)-Ni(1)-C(30)	123.26(14)
C(28)-H(28B)	0.9800	C(14)-C(19)-H(19A)	109.5	C(1)-Ni(1)-C(24)	98.00(14)
C(28)-H(28C)	0.9800	C(14)-C(19)-H(19B)	109.5	C(31)-Ni(1)-C(24)	125.03(15)
C(29)-O(6)	1.215(4)	H(19A)-C(19)-H(19B)	109.5	C(25)-Ni(1)-C(24)	40.75(13)
C(29)-O(5)	1.339(4)	C(14)-C(19)-H(19C)	109.5	C(30)-Ni(1)-C(24)	163.81(14)
C(29)-C(30)	1.487(5)	H(19A)-C(19)-H(19C)	109.5	C(23)-O(1)-C(22)	116.3(3)
C(30)-C(31)	1.415(5)	H(19B)-C(19)-H(19C)	109.5	C(26)-O(4)-C(27)	115.5(3)
C(30)-Ni(1)	2.032(3)	C(16)-C(20)-H(20A)	109.5	C(29)-O(5)-C(28)	115.7(3)

C(31)-C(32)	1.494(5)	C(16)-C(20)-H(20B)	109.5	C(32)-O(7)-C(33)	115.4(3)
C(31)-Ni(1)	2.001(3)	H(20A)-C(20)-H(20B)	109.5		
C(32)-O(8)	1.219(4)				

Table A2.4. Bond lengths [Å] and angles [°] for Ni(NHC)$_2$(DMFU) complex **5** (see Chapter 3).

C(1)-N(1)	1.377(3)	C(58)-C(59)	1.383(5)	C(28)-C(33)-H(33B)	109.5
C(1)-N(2)	1.384(3)	C(58)-H(58)	0.9500	H(33A)-C(33)-H(33B)	109.5
C(1)-Ni(1)	1.947(2)	C(59)-C(60)	1.407(6)	C(28)-C(33)-H(33C)	109.5
C(2)-C(3)	1.334(3)	C(59)-H(59)	0.9500	H(33A)-C(33)-H(33C)	109.5
C(2)-N(2)	1.388(3)	C(60)-H(60)	0.9500	H(33B)-C(33)-H(33C)	109.5
C(2)-H(2)	0.9500	C(61)-C(66)	1.349(6)	C(39)-C(34)-C(35)	122.0(2)
C(3)-N(1)	1.392(3)	C(61)-C(62)	1.373(7)	C(39)-C(34)-N(4)	119.9(2)
C(3)-H(3)	0.9500	C(61)-H(61)	0.9500	C(35)-C(34)-N(4)	117.8(2)
C(4)-C(9)	1.391(3)	C(62)-C(63)	1.412(7)	C(36)-C(35)-C(34)	117.7(2)
C(4)-C(5)	1.397(3)	C(62)-H(62)	0.9500	C(36)-C(35)-C(42)	120.9(2)
C(4)-N(1)	1.452(3)	C(63)-C(64)	1.359(6)	C(34)-C(35)-C(42)	121.4(2)
C(5)-C(6)	1.394(3)	C(63)-H(63)	0.9500	C(35)-C(36)-C(37)	122.0(2)
C(5)-C(10)	1.508(3)	C(64)-C(65)	1.361(5)	C(35)-C(36)-H(36)	119
C(6)-C(7)	1.386(4)	C(64)-H(64)	0.9500	C(37)-C(36)-H(36)	119
C(6)-H(6)	0.9500	C(65)-C(66)	1.362(5)	C(38)-C(37)-C(36)	118.4(2)
C(7)-C(8)	1.388(4)	C(65)-H(65)	0.9500	C(38)-C(37)-C(41)	120.5(2)
C(7)-C(11)	1.517(4)	C(66)-H(66)	0.9500	C(36)-C(37)-C(41)	121.1(2)
C(8)-C(9)	1.399(3)			C(37)-C(38)-C(39)	122.2(2)
C(8)-H(8)	0.9500	N(1)-C(1)-N(2)	101.64(18)	C(37)-C(38)-H(38)	118.9
C(9)-C(12)	1.504(3)	N(1)-C(1)-Ni(1)	133.57(17)	C(39)-C(38)-H(38)	118.9
C(10)-H(10A)	0.9800	N(2)-C(1)-Ni(1)	122.51(16)	C(38)-C(39)-C(34)	117.8(2)
C(10)-H(10B)	0.9800	C(3)-C(2)-N(2)	107.0(2)	C(38)-C(39)-C(40)	120.8(2)
C(10)-H(10C)	0.9800	C(3)-C(2)-H(2)	126.5	C(34)-C(39)-C(40)	121.4(2)
C(11)-H(11A)	0.9800	N(2)-C(2)-H(2)	126.5	C(39)-C(40)-H(40A)	109.5
C(11)-H(11B)	0.9800	C(2)-C(3)-N(1)	106.7(2)	C(39)-C(40)-H(40B)	109.5
C(11)-H(11C)	0.9800	C(2)-C(3)-H(3)	126.7	H(40A)-C(40)-H(40B)	109.5
C(12)-H(12A)	0.9800	N(1)-C(3)-H(3)	126.7	C(39)-C(40)-H(40C)	109.5
C(12)-H(12B)	0.9800	C(9)-C(4)-C(5)	122.2(2)	H(40A)-C(40)-H(40C)	109.5
C(12)-H(12C)	0.9800	C(9)-C(4)-N(1)	119.9(2)	H(40B)-C(40)-H(40C)	109.5
C(13)-C(18)	1.397(3)	C(5)-C(4)-N(1)	117.4(2)	C(37)-C(41)-H(41A)	109.5
C(13)-C(14)	1.398(3)	C(6)-C(5)-C(4)	117.8(2)	C(37)-C(41)-H(41B)	109.5
C(13)-N(2)	1.438(3)	C(6)-C(5)-C(10)	120.3(2)	H(41A)-C(41)-H(41B)	109.5
C(14)-C(15)	1.387(4)	C(4)-C(5)-C(10)	121.9(2)	C(37)-C(41)-H(41C)	109.5
C(14)-C(19)	1.509(4)	C(7)-C(6)-C(5)	121.9(2)	H(41A)-C(41)-H(41C)	109.5
C(15)-C(16)	1.395(4)	C(7)-C(6)-H(6)	119	H(41B)-C(41)-H(41C)	109.5
C(15)-H(15)	0.9500	C(5)-C(6)-H(6)	119	C(35)-C(42)-H(42A)	109.5
C(16)-C(17)	1.384(4)	C(6)-C(7)-C(8)	118.4(2)	C(35)-C(42)-H(42B)	109.5
C(16)-C(20)	1.511(4)	C(6)-C(7)-C(11)	120.5(2)	H(42A)-C(42)-H(42B)	109.5
C(17)-C(18)	1.396(4)	C(8)-C(7)-C(11)	121.1(2)	C(35)-C(42)-H(42C)	109.5
C(17)-H(17)	0.9500	C(7)-C(8)-C(9)	122.0(2)	H(42A)-C(42)-H(42C)	109.5
C(18)-C(21)	1.507(3)	C(7)-C(8)-H(8)	119	H(42B)-C(42)-H(42C)	109.5
C(19)-H(19A)	0.9800	C(9)-C(8)-H(8)	119	O(1)-C(43)-H(43A)	109.5
C(19)-H(19B)	0.9800	C(4)-C(9)-C(8)	117.6(2)	O(1)-C(43)-H(43B)	109.5
C(19)-H(19C)	0.9800	C(4)-C(9)-C(12)	121.3(2)	H(43A)-C(43)-H(43B)	109.5
C(20)-H(20A)	0.9800	C(8)-C(9)-C(12)	121.1(2)	O(1)-C(43)-H(43C)	109.5
C(20)-H(20B)	0.9800	C(5)-C(10)-H(10A)	109.5	H(43A)-C(43)-H(43C)	109.5
C(20)-H(20C)	0.9800	C(5)-C(10)-H(10B)	109.5	H(43B)-C(43)-H(43C)	109.5
C(21)-H(21A)	0.9800	H(10A)-C(10)-H(10B)	109.5	O(2)-C(44)-O(1)	120.9(2)
C(21)-H(21B)	0.9800	C(5)-C(10)-H(10C)	109.5	O(2)-C(44)-C(45)	125.6(2)
C(21)-H(21C)	0.9800	H(10A)-C(10)-H(10C)	109.5	O(1)-C(44)-C(45)	113.5(2)

C(22)-N(4)	1.373(3)	H(10B)-C(10)-H(10C)	109.5	C(46)-C(45)-C(44)	120.5(2)
C(22)-N(3)	1.386(3)	C(7)-C(11)-H(11A)	109.5	C(46)-C(45)-Ni(1)	68.81(12)
C(22)-Ni(1)	1.941(2)	C(7)-C(11)-H(11B)	109.5	C(44)-C(45)-Ni(1)	117.99(17)
C(23)-C(24)	1.326(4)	H(11A)-C(11)-H(11B)	109.5	C(45)-C(46)-C(47)	120.9(2)
C(23)-N(4)	1.391(3)	C(7)-C(11)-H(11C)	109.5	C(45)-C(46)-Ni(1)	68.49(13)
C(23)-H(23)	0.9500	H(11A)-C(11)-H(11C)	109.5	C(47)-C(46)-Ni(1)	115.46(16)
C(24)-N(3)	1.384(3)	H(11B)-C(11)-H(11C)	109.5	O(3)-C(47)-O(4)	120.8(2)
C(24)-H(24)	0.9500	C(9)-C(12)-H(12A)	109.5	O(3)-C(47)-C(46)	125.3(2)
C(25)-C(30)	1.396(3)	C(9)-C(12)-H(12B)	109.5	O(4)-C(47)-C(46)	113.9(2)
C(25)-C(26)	1.402(3)	H(12A)-C(12)-H(12B)	109.5	O(4)-C(48)-H(48A)	109.5
C(25)-N(3)	1.438(3)	C(9)-C(12)-H(12C)	109.5	O(4)-C(48)-H(48B)	109.5
C(26)-C(27)	1.387(3)	H(12A)-C(12)-H(12C)	109.5	H(48A)-C(48)-H(48B)	109.5
C(26)-C(32)	1.502(3)	H(12B)-C(12)-H(12C)	109.5	O(4)-C(48)-H(48C)	109.5
C(27)-C(28)	1.390(4)	C(18)-C(13)-C(14)	121.7(2)	H(48A)-C(48)-H(48C)	109.5
C(27)-H(27)	0.9500	C(18)-C(13)-N(2)	120.5(2)	H(48B)-C(48)-H(48C)	109.5
C(28)-C(29)	1.390(4)	C(14)-C(13)-N(2)	117.4(2)	C(50)-C(49)-C(54)	120.5(4)
C(28)-C(33)	1.508(4)	C(15)-C(14)-C(13)	118.3(2)	C(50)-C(49)-H(49)	119.7
C(29)-C(30)	1.393(3)	C(15)-C(14)-C(19)	121.2(2)	C(54)-C(49)-H(49)	119.7
C(29)-H(29)	0.9500	C(13)-C(14)-C(19)	120.5(2)	C(49)-C(50)-C(51)	120.8(4)
C(30)-C(31)	1.514(3)	C(14)-C(15)-C(16)	121.9(2)	C(49)-C(50)-H(50)	119.6
C(31)-H(31A)	0.9800	C(14)-C(15)-H(15)	119	C(51)-C(50)-H(50)	119.6
C(31)-H(31B)	0.9800	C(16)-C(15)-H(15)	119	C(50)-C(51)-C(52)	119.8(4)
C(31)-H(31C)	0.9800	C(17)-C(16)-C(15)	117.7(2)	C(50)-C(51)-H(51)	120.1
C(32)-H(32A)	0.9800	C(17)-C(16)-C(20)	121.7(3)	C(52)-C(51)-H(51)	120.1
C(32)-H(32B)	0.9800	C(15)-C(16)-C(20)	120.5(3)	C(51)-C(52)-C(53)	119.6(4)
C(32)-H(32C)	0.9800	C(16)-C(17)-C(18)	122.9(2)	C(51)-C(52)-H(52)	120.2
C(33)-H(33A)	0.9800	C(16)-C(17)-H(17)	118.6	C(53)-C(52)-H(52)	120.2
C(33)-H(33B)	0.9800	C(18)-C(17)-H(17)	118.6	C(54)-C(53)-C(52)	119.7(4)
C(33)-H(33C)	0.9800	C(17)-C(18)-C(13)	117.2(2)	C(54)-C(53)-H(53)	120.1
C(34)-C(39)	1.390(3)	C(17)-C(18)-C(21)	119.7(2)	C(52)-C(53)-H(53)	120.1
C(34)-C(35)	1.403(3)	C(13)-C(18)-C(21)	123.0(2)	C(53)-C(54)-C(49)	119.5(4)
C(34)-N(4)	1.442(3)	C(14)-C(19)-H(19A)	109.5	C(53)-C(54)-H(54)	120.2
C(35)-C(36)	1.387(4)	C(14)-C(19)-H(19B)	109.5	C(49)-C(54)-H(54)	120.2
C(35)-C(42)	1.507(4)	H(19A)-C(19)-H(19B)	109.5	C(56)-C(55)-C(60)	120.5(4)
C(36)-C(37)	1.388(4)	C(14)-C(19)-H(19C)	109.5	C(56)-C(55)-H(55)	119.8
C(36)-H(36)	0.9500	H(19A)-C(19)-H(19C)	109.5	C(60)-C(55)-H(55)	119.8
C(37)-C(38)	1.384(4)	H(19B)-C(19)-H(19C)	109.5	C(55)-C(56)-C(57)	120.4(4)
C(37)-C(41)	1.511(4)	C(16)-C(20)-H(20A)	109.5	C(55)-C(56)-H(56)	119.8
C(38)-C(39)	1.390(4)	C(16)-C(20)-H(20B)	109.5	C(57)-C(56)-H(56)	119.8
C(38)-H(38)	0.9500	H(20A)-C(20)-H(20B)	109.5	C(58)-C(57)-C(56)	120.9(3)
C(39)-C(40)	1.502(4)	C(16)-C(20)-H(20C)	109.5	C(58)-C(57)-H(57)	119.6
C(40)-H(40A)	0.9800	H(20A)-C(20)-H(20C)	109.5	C(56)-C(57)-H(57)	119.6
C(40)-H(40B)	0.9800	H(20B)-C(20)-H(20C)	109.5	C(57)-C(58)-C(59)	119.6(3)
C(40)-H(40C)	0.9800	C(18)-C(21)-H(21A)	109.5	C(57)-C(58)-H(58)	120.2
C(41)-H(41A)	0.9800	C(18)-C(21)-H(21B)	109.5	C(59)-C(58)-H(58)	120.2
C(41)-H(41B)	0.9800	H(21A)-C(21)-H(21B)	109.5	C(58)-C(59)-C(60)	119.0(4)
C(41)-H(41C)	0.9800	C(18)-C(21)-H(21C)	109.5	C(58)-C(59)-H(59)	120.5
C(42)-H(42A)	0.9800	H(21A)-C(21)-H(21C)	109.5	C(60)-C(59)-H(59)	120.5
C(42)-H(42B)	0.9800	H(21B)-C(21)-H(21C)	109.5	C(55)-C(60)-C(59)	119.7(4)
C(42)-H(42C)	0.9800	N(4)-C(22)-N(3)	101.61(18)	C(55)-C(60)-H(60)	120.2
C(43)-O(1)	1.435(3)	N(4)-C(22)-Ni(1)	134.91(17)	C(59)-C(60)-H(60)	120.2
C(43)-H(43A)	0.9800	N(3)-C(22)-Ni(1)	121.72(16)	C(66)-C(61)-C(62)	120.8(5)
C(43)-H(43B)	0.9800	C(24)-C(23)-N(4)	106.8(2)	C(66)-C(61)-H(61)	119.6
C(43)-H(43C)	0.9800	C(24)-C(23)-H(23)	126.6	C(62)-C(61)-H(61)	119.6
C(44)-O(2)	1.223(3)	N(4)-C(23)-H(23)	126.6	C(61)-C(62)-C(63)	118.6(4)
C(44)-O(1)	1.360(3)	C(23)-C(24)-N(3)	107.2(2)	C(61)-C(62)-H(62)	120.7

C(44)-C(45)	1.458(3)	C(23)-C(24)-H(24)	126.4	C(63)-C(62)-H(62)	120.7
C(45)-C(46)	1.446(3)	N(3)-C(24)-H(24)	126.4	C(64)-C(63)-C(62)	119.4(5)
C(45)-Ni(1)	1.984(2)	C(30)-C(25)-C(26)	121.4(2)	C(64)-C(63)-H(63)	120.3
C(46)-C(47)	1.462(3)	C(30)-C(25)-N(3)	120.7(2)	C(62)-C(63)-H(63)	120.3
C(46)-Ni(1)	1.988(2)	C(26)-C(25)-N(3)	117.5(2)	C(63)-C(64)-C(65)	120.3(4)
C(47)-O(3)	1.214(3)	C(27)-C(26)-C(25)	118.0(2)	C(63)-C(64)-H(64)	119.8
C(47)-O(4)	1.369(3)	C(27)-C(26)-C(32)	121.5(2)	C(65)-C(64)-H(64)	119.8
C(48)-O(4)	1.436(3)	C(25)-C(26)-C(32)	120.3(2)	C(64)-C(65)-C(66)	120.6(4)
C(48)-H(48A)	0.9800	C(26)-C(27)-C(28)	122.1(2)	C(64)-C(65)-H(65)	119.7
C(48)-H(48B)	0.9800	C(26)-C(27)-H(27)	118.9	C(66)-C(65)-H(65)	119.7
C(48)-H(48C)	0.9800	C(28)-C(27)-H(27)	118.9	C(61)-C(66)-C(65)	120.3(5)
C(49)-C(50)	1.356(5)	C(27)-C(28)-C(29)	118.0(2)	C(61)-C(66)-H(66)	119.9
C(49)-C(54)	1.372(5)	C(27)-C(28)-C(33)	121.1(2)	C(65)-C(66)-H(66)	119.9
C(49)-H(49)	0.9500	C(29)-C(28)-C(33)	120.8(2)	C(1)-N(1)-C(3)	112.4(2)
C(50)-C(51)	1.360(6)	C(28)-C(29)-C(30)	122.1(2)	C(1)-N(1)-C(4)	129.51(19)
C(50)-H(50)	0.9500	C(28)-C(29)-H(29)	119	C(3)-N(1)-C(4)	117.18(19)
C(51)-C(52)	1.371(6)	C(30)-C(29)-H(29)	119	C(1)-N(2)-C(2)	112.20(19)
C(51)-H(51)	0.9500	C(29)-C(30)-C(25)	118.0(2)	C(1)-N(2)-C(13)	126.23(19)
C(52)-C(53)	1.394(7)	C(29)-C(30)-C(31)	120.1(2)	C(2)-N(2)-C(13)	120.43(19)
C(52)-H(52)	0.9500	C(25)-C(30)-C(31)	121.9(2)	C(24)-N(3)-C(22)	112.0(2)
C(53)-C(54)	1.370(6)	C(30)-C(31)-H(31A)	109.5	C(24)-N(3)-C(25)	121.99(19)
C(53)-H(53)	0.9500	C(30)-C(31)-H(31B)	109.5	C(22)-N(3)-C(25)	125.11(18)
C(54)-H(54)	0.9500	H(31A)-C(31)-H(31B)	109.5	C(22)-N(4)-C(23)	112.4(2)
C(55)-C(56)	1.358(5)	C(30)-C(31)-H(31C)	109.5	C(22)-N(4)-C(34)	127.41(19)
C(55)-C(60)	1.360(5)	H(31A)-C(31)-H(31C)	109.5	C(23)-N(4)-C(34)	119.37(19)
C(55)-H(55)	0.9500	H(31B)-C(31)-H(31C)	109.5	C(22)-Ni(1)-C(1)	124.31(9)
C(56)-C(57)	1.363(5)	C(26)-C(32)-H(32A)	109.5	C(22)-Ni(1)-C(45)	138.76(9)
C(56)-H(56)	0.9500	C(26)-C(32)-H(32B)	109.5	C(1)-Ni(1)-C(45)	96.88(9)
C(57)-C(58)	1.363(5)	H(32A)-C(32)-H(32B)	109.5	C(22)-Ni(1)-C(46)	96.29(9)
C(57)-H(57)	0.9500	C(26)-C(32)-H(32C)	109.5	C(1)-Ni(1)-C(46)	139.36(9)
		H(32A)-C(32)-H(32C)	109.5	C(45)-Ni(1)-C(46)	42.70(9)
		H(32B)-C(32)-H(32C)	109.5	C(44)-O(1)-C(43)	116.45(19)
		C(28)-C(33)-H(33A)	109.5	C(47)-O(4)-C(48)	115.2(2)

Table A2.5. Bond lengths [Å] and angles [°] for $[Ni(NHC)(DMFU)]_2$ complex **7** (see Chapter 3).

C(11A)-O(12)	1.396(6)	C(223)-H(223)	0.9300	C(12)-O(12)-C(11A)	115.4(4)
C(11A)-H(11A)	0.9600	C(224)-C(227)	1.513(4)	C(15)-O(13)-C(16)	116.8(2)
C(11A)-H(11B)	0.9600	C(225)-H(22A)	0.9600	C(15)-O(14)-Ni(2)	124.41(17)
C(11A)-H(11C)	0.9600	C(225)-H(22B)	0.9600	O(22)-C(21)-H(21A)	109.5
C(11B)-O(11)	1.429(9)	C(225)-H(22C)	0.9600	O(22)-C(21)-H(21B)	109.5
C(11B)-H(11D)	0.9600	C(226)-H(22D)	0.9600	H(21A)-C(21)-H(21B)	109.5
C(11B)-H(11E)	0.9600	C(226)-H(22E)	0.9600	O(22)-C(21)-H(21C)	109.5
C(11B)-H(11F)	0.9600	C(226)-H(22F)	0.9600	H(21A)-C(21)-H(21C)	109.5
C(12)-O(11)	1.265(4)	C(227)-H(22G)	0.9600	H(21B)-C(21)-H(21C)	109.5
C(12)-O(12)	1.310(4)	C(227)-H(22H)	0.9600	O(21)-C(22)-O(22)	121.4(3)
C(12)-C(13)	1.456(4)	C(227)-H(22I)	0.9600	O(21)-C(22)-C(23)	128.6(3)
C(13)-C(14)	1.448(3)	O(24)-Ni(1)	1.9634(18)	O(22)-C(22)-C(23)	110.0(3)
C(13)-Ni(1)	1.953(3)	O(1)-H(1O1)	0.8637	C(24)-C(23)-C(22)	118.0(3)
C(14)-C(15)	1.412(4)	O(1)-H(2O1)	0.8638	C(24)-C(23)-Ni(2)	69.42(14)
C(14)-Ni(1)	1.977(2)			C(22)-C(23)-Ni(2)	119.5(2)
C(15)-O(14)	1.255(3)	O(12)-C(11A)-H(11A)	109.5	C(25)-C(24)-C(23)	121.9(3)
C(15)-O(13)	1.356(3)	O(12)-C(11A)-H(11B)	109.5	C(25)-C(24)-Ni(2)	97.32(18)
C(16)-O(13)	1.428(4)	O(12)-C(11A)-H(11C)	109.5	C(23)-C(24)-Ni(2)	67.27(14)
C(16)-H(16A)	0.9600	O(11)-C(11B)-H(11D)	109.5	O(24)-C(25)-O(23)	118.5(2)

C(16)-H(16B)	0.9600	O(11)-C(11B)-H(11E)	109.5	O(24)-C(25)-C(24)	125.7(2)
C(16)-H(16C)	0.9600	H(11D)-C(11B)-H(11E)	109.5	O(23)-C(25)-C(24)	115.8(2)
C(17)-N(11)	1.362(3)	O(11)-C(11B)-H(11F)	109.5	O(23)-C(26)-H(26A)	109.5
C(17)-N(12)	1.368(3)	H(11D)-C(11B)-H(11F)	109.5	O(23)-C(26)-H(26B)	109.5
C(17)-Ni(1)	1.895(2)	H(11E)-C(11B)-H(11F)	109.5	H(26A)-C(26)-H(26B)	109.5
C(18)-C(19)	1.338(4)	O(11)-C(12)-O(12)	121.2(3)	O(23)-C(26)-H(26C)	109.5
C(18)-N(11)	1.389(3)	O(11)-C(12)-C(13)	120.5(3)	H(26A)-C(26)-H(26C)	109.5
C(18)-H(18)	0.9300	O(12)-C(12)-C(13)	118.3(3)	H(26B)-C(26)-H(26C)	109.5
C(19)-N(12)	1.386(4)	C(14)-C(13)-C(12)	119.2(3)	N(21)-C(27)-N(22)	103.4(2)
C(19)-H(19)	0.9300	C(14)-C(13)-Ni(1)	69.26(14)	N(21)-C(27)-Ni(2)	126.21(19)
C(110)-C(115)	1.383(5)	C(12)-C(13)-Ni(1)	117.2(2)	N(22)-C(27)-Ni(2)	130.2(2)
C(110)-C(111)	1.401(4)	C(15)-C(14)-C(13)	122.5(2)	C(29)-C(28)-N(21)	106.8(2)
C(110)-N(12)	1.437(4)	C(15)-C(14)-Ni(1)	98.22(17)	C(29)-C(28)-H(28)	126.6
C(111)-C(112)	1.389(4)	C(13)-C(14)-Ni(1)	67.51(14)	N(21)-C(28)-H(28)	126.6
C(111)-C(116)	1.496(5)	O(14)-C(15)-O(13)	118.2(2)	C(28)-C(29)-N(22)	106.6(2)
C(112)-C(113)	1.378(5)	O(14)-C(15)-C(14)	125.4(2)	C(28)-C(29)-H(29)	126.7
C(112)-H(112)	0.9300	O(13)-C(15)-C(14)	116.4(2)	N(22)-C(29)-H(29)	126.7
C(113)-C(114)	1.395(5)	O(13)-C(16)-H(16A)	109.5	C(211)-C(210)-C(215)	122.2(3)
C(113)-C(117)	1.514(5)	O(13)-C(16)-H(16B)	109.5	C(211)-C(210)-N(21)	119.5(2)
C(114)-C(115)	1.403(5)	H(16A)-C(16)-H(16B)	109.5	C(215)-C(210)-N(21)	118.3(3)
C(114)-H(114)	0.9300	O(13)-C(16)-H(16C)	109.5	C(210)-C(211)-C(212)	117.6(3)
C(115)-C(118)	1.510(5)	H(16A)-C(16)-H(16C)	109.5	C(210)-C(211)-C(216)	121.3(3)
C(116)-H(11G)	0.9600	H(16B)-C(16)-H(16C)	109.5	C(212)-C(211)-C(216)	121.1(3)
C(116)-H(11H)	0.9600	N(11)-C(17)-N(12)	103.3(2)	C(213)-C(212)-C(211)	121.9(3)
C(116)-H(11I)	0.9600	N(11)-C(17)-Ni(1)	128.59(18)	C(213)-C(212)-H(212)	119.1
C(117)-H(11J)	0.9600	N(12)-C(17)-Ni(1)	128.06(19)	C(211)-C(212)-H(212)	119.1
C(117)-H(11K)	0.9600	C(19)-C(18)-N(11)	106.6(3)	C(214)-C(213)-C(212)	118.7(3)
C(117)-H(11L)	0.9600	C(19)-C(18)-H(18)	126.7	C(214)-C(213)-C(217)	120.7(3)
C(118)-H(11M)	0.9600	N(11)-C(18)-H(18)	126.7	C(212)-C(213)-C(217)	120.5(3)
C(118)-H(11N)	0.9600	C(18)-C(19)-N(12)	107.1(2)	C(213)-C(214)-C(215)	122.0(3)
C(118)-H(11O)	0.9600	C(18)-C(19)-H(19)	126.5	C(213)-C(214)-H(214)	119
C(119)-C(120)	1.384(4)	N(12)-C(19)-H(19)	126.5	C(215)-C(214)-H(214)	119
C(119)-C(124)	1.393(4)	C(115)-C(110)-C(111)	122.6(3)	C(214)-C(215)-C(210)	117.5(3)
C(119)-N(11)	1.439(3)	C(115)-C(110)-N(12)	118.5(3)	C(214)-C(215)-C(218)	120.9(3)
C(120)-C(121)	1.391(4)	C(111)-C(110)-N(12)	118.9(3)	C(210)-C(215)-C(218)	121.5(3)
C(120)-C(125)	1.507(4)	C(112)-C(111)-C(110)	117.7(3)	C(211)-C(216)-H(21D)	109.5
C(121)-C(122)	1.387(5)	C(112)-C(111)-C(116)	121.0(3)	C(211)-C(216)-H(21E)	109.5
C(121)-H(121)	0.9300	C(110)-C(111)-C(116)	121.2(3)	H(21D)-C(216)-H(21E)	109.5
C(122)-C(123)	1.378(5)	C(113)-C(112)-C(111)	122.0(3)	C(211)-C(216)-H(21F)	109.5
C(122)-C(126)	1.527(5)	C(113)-C(112)-H(112)	119	H(21D)-C(216)-H(21F)	109.5
C(123)-C(124)	1.393(4)	C(111)-C(112)-H(112)	119	H(21E)-C(216)-H(21F)	109.5
C(123)-H(123)	0.9300	C(112)-C(113)-C(114)	118.6(3)	C(213)-C(217)-H(21G)	109.5
C(124)-C(127)	1.501(4)	C(112)-C(113)-C(117)	121.4(3)	C(213)-C(217)-H(21H)	109.5
C(125)-H(12A)	0.9600	C(114)-C(113)-C(117)	120.0(4)	H(21G)-C(217)-H(21H)	109.5
C(125)-H(12B)	0.9600	C(113)-C(114)-C(115)	121.7(3)	C(213)-C(217)-H(21I)	109.5
C(125)-H(12C)	0.9600	C(113)-C(114)-H(114)	119.1	H(21G)-C(217)-H(21I)	109.5
C(126)-H(12D)	0.9600	C(115)-C(114)-H(114)	119.1	H(21H)-C(217)-H(21I)	109.5
C(126)-H(12E)	0.9600	C(110)-C(115)-C(114)	117.3(3)	C(215)-C(218)-H(21J)	109.5
C(126)-H(12F)	0.9600	C(110)-C(115)-C(118)	121.5(3)	C(215)-C(218)-H(21K)	109.5
C(127)-H(12G)	0.9600	C(114)-C(115)-C(118)	121.2(3)	H(21J)-C(218)-H(21K)	109.5
C(127)-H(12H)	0.9600	C(111)-C(116)-H(11G)	109.5	C(215)-C(218)-H(21L)	109.5
C(127)-H(12I)	0.9600	C(111)-C(116)-H(11H)	109.5	H(21J)-C(218)-H(21L)	109.5
O(14)-Ni(2)	1.9596(17)	H(11G)-C(116)-H(11H)	109.5	H(21K)-C(218)-H(21L)	109.5
C(21)-O(22)	1.441(4)	C(111)-C(116)-H(11I)	109.5	C(224)-C(219)-C(220)	122.1(3)
C(21)-H(21A)	0.9600	H(11G)-C(116)-H(11I)	109.5	C(224)-C(219)-N(22)	119.4(2)
C(21)-H(21B)	0.9600	H(11H)-C(116)-H(11I)	109.5	C(220)-C(219)-N(22)	118.5(2)

C(21)-H(21C)	0.9600	C(113)-C(117)-H(11J)	109.5	C(221)-C(220)-C(219)	117.4(3)
C(22)-O(21)	1.211(4)	C(113)-C(117)-H(11K)	109.5	C(221)-C(220)-C(225)	121.2(3)
C(22)-O(22)	1.360(3)	H(11J)-C(117)-H(11K)	109.5	C(219)-C(220)-C(225)	121.3(3)
C(22)-C(23)	1.458(4)	C(113)-C(117)-H(11L)	109.5	C(222)-C(221)-C(220)	122.3(3)
C(23)-C(24)	1.453(4)	H(11J)-C(117)-H(11L)	109.5	C(222)-C(221)-H(221)	118.9
C(23)-Ni(2)	1.954(3)	H(11K)-C(117)-H(11L)	109.5	C(220)-C(221)-H(221)	118.9
C(24)-C(25)	1.422(4)	C(115)-C(118)-H(11M)	109.5	C(221)-C(222)-C(223)	118.5(3)
C(24)-Ni(2)	1.983(3)	C(115)-C(118)-H(11N)	109.5	C(221)-C(222)-C(226)	121.3(4)
C(25)-O(24)	1.259(3)	H(11M)-C(118)-H(11N)	109.5	C(223)-C(222)-C(226)	120.2(4)
C(25)-O(23)	1.354(3)	C(115)-C(118)-H(11O)	109.5	C(222)-C(223)-C(224)	121.8(3)
C(26)-O(23)	1.421(4)	H(11M)-C(118)-H(11O)	109.5	C(222)-C(223)-H(223)	119.1
C(26)-H(26A)	0.9600	H(11N)-C(118)-H(11O)	109.5	C(224)-C(223)-H(223)	119.1
C(26)-H(26B)	0.9600	C(120)-C(119)-C(124)	122.6(2)	C(219)-C(224)-C(223)	117.8(3)
C(26)-H(26C)	0.9600	C(120)-C(119)-N(11)	118.7(2)	C(219)-C(224)-C(227)	121.5(3)
C(27)-N(21)	1.361(3)	C(124)-C(119)-N(11)	118.7(3)	C(223)-C(224)-C(227)	120.7(3)
C(27)-N(22)	1.363(3)	C(119)-C(120)-C(121)	118.3(3)	C(220)-C(225)-H(22A)	109.5
C(27)-Ni(2)	1.893(3)	C(119)-C(120)-C(125)	121.5(3)	C(220)-C(225)-H(22B)	109.5
C(28)-C(29)	1.339(4)	C(121)-C(120)-C(125)	120.2(3)	H(22A)-C(225)-H(22B)	109.5
C(28)-N(21)	1.392(4)	C(122)-C(121)-C(120)	120.9(3)	C(220)-C(225)-H(22C)	109.5
C(28)-H(28)	0.9300	C(122)-C(121)-H(121)	119.5	H(22A)-C(225)-H(22C)	109.5
C(29)-N(22)	1.389(4)	C(120)-C(121)-H(121)	119.5	H(22B)-C(225)-H(22C)	109.5
C(29)-H(29)	0.9300	C(123)-C(122)-C(121)	118.8(3)	C(222)-C(226)-H(22D)	109.5
C(210)-C(211)	1.387(4)	C(123)-C(122)-C(126)	121.2(4)	C(222)-C(226)-H(22E)	109.5
C(210)-C(215)	1.405(4)	C(121)-C(122)-C(126)	120.0(4)	H(22D)-C(226)-H(22E)	109.5
C(210)-N(21)	1.442(3)	C(122)-C(123)-C(124)	122.5(3)	C(222)-C(226)-H(22F)	109.5
C(211)-C(212)	1.396(4)	C(122)-C(123)-H(123)	118.7	H(22D)-C(226)-H(22F)	109.5
C(211)-C(216)	1.508(4)	C(124)-C(123)-H(123)	118.7	H(22E)-C(226)-H(22F)	109.5
C(212)-C(213)	1.391(4)	C(123)-C(124)-C(119)	116.7(3)	C(224)-C(227)-H(22G)	109.5
C(212)-H(212)	0.9300	C(123)-C(124)-C(127)	121.7(3)	C(224)-C(227)-H(22H)	109.5
C(213)-C(214)	1.376(4)	C(119)-C(124)-C(127)	121.6(3)	H(22G)-C(227)-H(22H)	109.5
C(213)-C(217)	1.511(4)	C(120)-C(125)-H(12A)	109.5	C(224)-C(227)-H(22I)	109.5
C(214)-C(215)	1.393(4)	C(120)-C(125)-H(12B)	109.5	H(22G)-C(227)-H(22I)	109.5
C(214)-H(214)	0.9300	H(12A)-C(125)-H(12B)	109.5	H(22H)-C(227)-H(22I)	109.5
C(215)-C(218)	1.498(4)	C(120)-C(125)-H(12C)	109.5	C(27)-N(21)-C(28)	111.5(2)
C(216)-H(21D)	0.9600	H(12A)-C(125)-H(12C)	109.5	C(27)-N(21)-C(210)	122.9(2)
C(216)-H(21E)	0.9600	H(12B)-C(125)-H(12C)	109.5	C(28)-N(21)-C(210)	125.3(2)
C(216)-H(21F)	0.9600	C(122)-C(126)-H(12D)	109.5	C(27)-N(22)-C(29)	111.8(2)
C(217)-H(21G)	0.9600	C(122)-C(126)-H(12E)	109.5	C(27)-N(22)-C(219)	124.1(2)
C(217)-H(21H)	0.9600	H(12D)-C(126)-H(12E)	109.5	C(29)-N(22)-C(219)	124.1(2)
C(217)-H(21I)	0.9600	C(122)-C(126)-H(12F)	109.5	C(22)-O(22)-C(21)	115.4(3)
C(218)-H(21J)	0.9600	H(12D)-C(126)-H(12F)	109.5	C(25)-O(23)-C(26)	116.7(2)
C(218)-H(21K)	0.9600	H(12E)-C(126)-H(12F)	109.5	C(25)-O(24)-Ni(1)	126.77(17)
C(218)-H(21L)	0.9600	C(124)-C(127)-H(12G)	109.5	C(17)-Ni(1)-C(13)	110.83(11)
C(219)-C(224)	1.394(4)	C(124)-C(127)-H(12H)	109.5	C(17)-Ni(1)-O(24)	99.60(9)
C(219)-C(220)	1.396(4)	H(12G)-C(127)-H(12H)	109.5	C(13)-Ni(1)-O(24)	147.71(9)
C(219)-N(22)	1.436(3)	C(124)-C(127)-H(12I)	109.5	C(17)-Ni(1)-C(14)	153.90(11)
C(220)-C(221)	1.396(4)	H(12G)-C(127)-H(12I)	109.5	C(13)-Ni(1)-C(14)	43.22(10)
C(220)-C(225)	1.501(5)	H(12H)-C(127)-H(12I)	109.5	O(24)-Ni(1)-C(14)	106.38(9)
C(221)-C(222)	1.379(5)	C(17)-N(11)-C(18)	111.7(2)	C(27)-Ni(2)-C(23)	114.05(11)
C(221)-H(221)	0.9300	C(17)-N(11)-C(119)	121.6(2)	C(27)-Ni(2)-O(14)	95.48(9)
C(222)-C(223)	1.385(5)	C(18)-N(11)-C(119)	126.7(2)	C(23)-Ni(2)-O(14)	147.57(9)
C(222)-C(226)	1.518(5)	C(17)-N(12)-C(19)	111.3(2)	C(27)-Ni(2)-C(24)	156.37(11)
C(223)-C(224)	1.395(5)	C(17)-N(12)-C(110)	123.0(2)	C(23)-Ni(2)-C(24)	43.31(10)
		C(19)-N(12)-C(110)	125.6(2)	O(14)-Ni(2)-C(24)	108.14(9)
		C(12)-O(11)-C(11B)	115.8(5)	H(1O1)-O(1)-H(2O1)	105.2

Table A2.6. Bond lengths [Å] and angles [°] for Ni(H)(NHC)$_3$ complex **6b** (see Chapter 5).

Ni(1)-C(22)	1.891(3)	C(49)-C(50)	1.442(8)	C(27)-C(26)-C(25)	118.1(4)
Ni(1)-C(1)	1.895(4)	C(49)-H(49A)	0.9900	C(27)-C(26)-C(31)	120.2(4)
Ni(1)-C(43)	1.936(4)	C(49)-H(49B)	0.9900	C(25)-C(26)-C(31)	121.7(4)
Ni(1)-H(1)	1.38(5)	C(50)-H(50A)	0.9800	C(26)-C(27)-C(28)	122.4(4)
Cl(1)-C(51)	1.755(6)	C(50)-H(50B)	0.9800	C(26)-C(27)-H(27)	118.8
Cl(2)-C(51)	1.745(5)	C(50)-H(50C)	0.9800	C(28)-C(27)-H(27)	118.8
Cl(3)-C(52)	1.725(8)	C(51)-H(51A)	0.9900	C(27)-C(28)-C(29)	118.0(4)
Cl(4)-C(52)	1.700(8)	C(51)-H(51B)	0.9900	C(27)-C(28)-C(32)	120.9(4)
F(1)-B(1)	1.388(5)	C(52)-H(52A)	0.9900	C(29)-C(28)-C(32)	121.1(5)
F(2)-B(1)	1.391(5)	C(52)-H(52B)	0.9900	C(28)-C(29)-C(30)	122.2(4)
F(3)-B(1)	1.375(5)			C(28)-C(29)-H(29)	118.9
F(4)-B(1)	1.394(5)	C(22)-Ni(1)-C(1)	164.22(16)	C(30)-C(29)-H(29)	118.9
N(1)-C(1)	1.366(5)	C(22)-Ni(1)-C(43)	98.40(15)	C(29)-C(30)-C(25)	117.6(4)
N(1)-C(2)	1.392(5)	C(1)-Ni(1)-C(43)	97.30(15)	C(29)-C(30)-C(33)	119.9(4)
N(1)-C(4)	1.444(5)	C(22)-Ni(1)-H(1)	83(2)	C(25)-C(30)-C(33)	122.5(4)
N(2)-C(1)	1.367(5)	C(1)-Ni(1)-H(1)	81(2)	C(26)-C(31)-H(31A)	109.5
N(2)-C(3)	1.393(5)	C(43)-Ni(1)-H(1)	179(2)	C(26)-C(31)-H(31B)	109.5
N(2)-C(13)	1.444(5)	C(1)-N(1)-C(2)	112.1(3)	H(31A)-C(31)-H(31B)	109.5
N(3)-C(22)	1.368(4)	C(1)-N(1)-C(4)	126.0(3)	C(26)-C(31)-H(31C)	109.5
N(3)-C(23)	1.394(5)	C(2)-N(1)-C(4)	121.1(3)	H(31A)-C(31)-H(31C)	109.5
N(3)-C(25)	1.438(5)	C(1)-N(2)-C(3)	111.4(3)	H(31B)-C(31)-H(31C)	109.5
N(4)-C(22)	1.368(5)	C(1)-N(2)-C(13)	126.1(3)	C(28)-C(32)-H(32A)	109.5
N(4)-C(24)	1.395(5)	C(3)-N(2)-C(13)	121.8(3)	C(28)-C(32)-H(32B)	109.5
N(4)-C(34)	1.448(5)	C(22)-N(3)-C(23)	111.3(3)	H(32A)-C(32)-H(32B)	109.5
N(5)-C(43)	1.358(5)	C(22)-N(3)-C(25)	125.0(3)	C(28)-C(32)-H(32C)	109.5
N(5)-C(44)	1.386(6)	C(23)-N(3)-C(25)	123.0(3)	H(32A)-C(32)-H(32C)	109.5
N(5)-C(46)	1.451(6)	C(22)-N(4)-C(24)	111.3(3)	H(32B)-C(32)-H(32C)	109.5
N(6)-C(43)	1.366(5)	C(22)-N(4)-C(34)	126.0(3)	C(30)-C(33)-H(33A)	109.5
N(6)-C(45)	1.369(6)	C(24)-N(4)-C(34)	122.0(3)	C(30)-C(33)-H(33B)	109.5
N(6)-C(47)	1.472(5)	C(43)-N(5)-C(44)	111.5(4)	H(33A)-C(33)-H(33B)	109.5
C(2)-C(3)	1.335(6)	C(43)-N(5)-C(46)	123.8(4)	C(30)-C(33)-H(33C)	109.5
C(2)-H(2)	0.9500	C(44)-N(5)-C(46)	124.7(4)	H(33A)-C(33)-H(33C)	109.5
C(3)-H(3)	0.9500	C(43)-N(6)-C(45)	111.3(4)	H(33B)-C(33)-H(33C)	109.5
C(4)-C(5)	1.396(6)	C(43)-N(6)-C(47)	122.4(3)	C(39)-C(34)-C(35)	122.2(4)
C(4)-C(9)	1.402(6)	C(45)-N(6)-C(47)	126.3(4)	C(39)-C(34)-N(4)	117.9(3)
C(5)-C(6)	1.393(6)	N(1)-C(1)-N(2)	103.0(3)	C(35)-C(34)-N(4)	119.8(4)
C(5)-C(10)	1.510(6)	N(1)-C(1)-Ni(1)	127.6(3)	C(36)-C(35)-C(34)	117.3(4)
C(6)-C(7)	1.402(7)	N(2)-C(1)-Ni(1)	129.3(3)	C(36)-C(35)-C(40)	120.4(4)
C(6)-H(6)	0.9500	C(3)-C(2)-N(1)	106.2(3)	C(34)-C(35)-C(40)	122.4(4)
C(7)-C(8)	1.379(7)	C(3)-C(2)-H(2)	126.9	C(37)-C(36)-C(35)	122.4(4)
C(7)-C(11)	1.505(6)	N(1)-C(2)-H(2)	126.9	C(37)-C(36)-H(36)	118.8
C(8)-C(9)	1.388(6)	C(2)-C(3)-N(2)	107.3(3)	C(35)-C(36)-H(36)	118.8
C(8)-H(8)	0.9500	C(2)-C(3)-H(3)	126.4	C(36)-C(37)-C(38)	118.3(4)
C(9)-C(12)	1.499(6)	N(2)-C(3)-H(3)	126.4	C(36)-C(37)-C(41)	121.4(5)
C(10)-H(10A)	0.9800	C(5)-C(4)-C(9)	121.9(4)	C(38)-C(37)-C(41)	120.2(5)
C(10)-H(10B)	0.9800	C(5)-C(4)-N(1)	117.4(3)	C(37)-C(38)-C(39)	122.0(4)
C(10)-H(10C)	0.9800	C(9)-C(4)-N(1)	120.6(4)	C(37)-C(38)-H(38)	119
C(11)-H(11A)	0.9800	C(6)-C(5)-C(4)	118.0(4)	C(39)-C(38)-H(38)	119
C(11)-H(11B)	0.9800	C(6)-C(5)-C(10)	121.0(4)	C(38)-C(39)-C(34)	117.6(4)
C(11)-H(11C)	0.9800	C(4)-C(5)-C(10)	120.9(4)	C(38)-C(39)-C(42)	121.0(4)
C(12)-H(12A)	0.9800	C(5)-C(6)-C(7)	121.5(4)	C(34)-C(39)-C(42)	121.4(4)
C(12)-H(12B)	0.9800	C(5)-C(6)-H(6)	119.3	C(35)-C(40)-H(40A)	109.5
C(12)-H(12C)	0.9800	C(7)-C(6)-H(6)	119.3	C(35)-C(40)-H(40B)	109.5

C(13)-C(14)	1.395(6)	C(8)-C(7)-C(6)	118.3(4)	H(40A)-C(40)-H(40B)	109.5
C(13)-C(18)	1.399(5)	C(8)-C(7)-C(11)	122.3(4)	C(35)-C(40)-H(40C)	109.5
C(14)-C(15)	1.394(6)	C(6)-C(7)-C(11)	119.4(5)	H(40A)-C(40)-H(40C)	109.5
C(14)-C(19)	1.505(6)	C(7)-C(8)-C(9)	122.7(4)	H(40B)-C(40)-H(40C)	109.5
C(15)-C(16)	1.376(7)	C(7)-C(8)-H(8)	118.7	C(37)-C(41)-H(41A)	109.5
C(15)-H(15)	0.9500	C(9)-C(8)-H(8)	118.7	C(37)-C(41)-H(41B)	109.5
C(16)-C(17)	1.391(7)	C(8)-C(9)-C(4)	117.5(4)	H(41A)-C(41)-H(41B)	109.5
C(16)-C(20)	1.521(7)	C(8)-C(9)-C(12)	120.2(4)	C(37)-C(41)-H(41C)	109.5
C(17)-C(18)	1.395(6)	C(4)-C(9)-C(12)	122.2(4)	H(41A)-C(41)-H(41C)	109.5
C(17)-H(17)	0.9500	C(5)-C(10)-H(10A)	109.5	H(41B)-C(41)-H(41C)	109.5
C(18)-C(21)	1.506(6)	C(5)-C(10)-H(10B)	109.5	C(39)-C(42)-H(42A)	109.5
C(19)-H(19A)	0.9800	H(10A)-C(10)-H(10B)	109.5	C(39)-C(42)-H(42B)	109.5
C(19)-H(19B)	0.9800	C(5)-C(10)-H(10C)	109.5	H(42A)-C(42)-H(42B)	109.5
C(19)-H(19C)	0.9800	H(10A)-C(10)-H(10C)	109.5	C(39)-C(42)-H(42C)	109.5
C(20)-H(20A)	0.9800	H(10B)-C(10)-H(10C)	109.5	H(42A)-C(42)-H(42C)	109.5
C(20)-H(20B)	0.9800	C(7)-C(11)-H(11A)	109.5	H(42B)-C(42)-H(42C)	109.5
C(20)-H(20C)	0.9800	C(7)-C(11)-H(11B)	109.5	N(5)-C(43)-N(6)	103.0(3)
C(21)-H(21A)	0.9800	H(11A)-C(11)-H(11B)	109.5	N(5)-C(43)-Ni(1)	128.4(3)
C(21)-H(21B)	0.9800	C(7)-C(11)-H(11C)	109.5	N(6)-C(43)-Ni(1)	128.5(3)
C(21)-H(21C)	0.9800	H(11A)-C(11)-H(11C)	109.5	C(45)-C(44)-N(5)	106.5(4)
C(23)-C(24)	1.333(6)	H(11B)-C(11)-H(11C)	109.5	C(45)-C(44)-H(44)	126.8
C(23)-H(23)	0.9500	C(9)-C(12)-H(12A)	109.5	N(5)-C(44)-H(44)	126.8
C(24)-H(24)	0.9500	C(9)-C(12)-H(12B)	109.5	C(44)-C(45)-N(6)	107.8(4)
C(25)-C(30)	1.397(6)	H(12A)-C(12)-H(12B)	109.5	C(44)-C(45)-H(45)	126.1
C(25)-C(26)	1.404(5)	C(9)-C(12)-H(12C)	109.5	N(6)-C(45)-H(45)	126.1
C(26)-C(27)	1.382(6)	H(12A)-C(12)-H(12C)	109.5	N(5)-C(46)-H(46A)	109.5
C(26)-C(31)	1.498(6)	H(12B)-C(12)-H(12C)	109.5	N(5)-C(46)-H(46B)	109.5
C(27)-C(28)	1.385(6)	C(14)-C(13)-C(18)	122.0(4)	H(46A)-C(46)-H(46B)	109.5
C(27)-H(27)	0.9500	C(14)-C(13)-N(2)	119.5(3)	N(5)-C(46)-H(46C)	109.5
C(28)-C(29)	1.394(7)	C(18)-C(13)-N(2)	118.4(4)	H(46A)-C(46)-H(46C)	109.5
C(28)-C(32)	1.518(6)	C(15)-C(14)-C(13)	117.9(4)	H(46B)-C(46)-H(46C)	109.5
C(29)-C(30)	1.395(6)	C(15)-C(14)-C(19)	119.8(4)	N(6)-C(47)-C(48)	115.9(4)
C(29)-H(29)	0.9500	C(13)-C(14)-C(19)	122.3(4)	N(6)-C(47)-H(47A)	108.3
C(30)-C(33)	1.510(6)	C(16)-C(15)-C(14)	121.8(4)	C(48)-C(47)-H(47A)	108.3
C(31)-H(31A)	0.9800	C(16)-C(15)-H(15)	119.1	N(6)-C(47)-H(47B)	108.3
C(31)-H(31B)	0.9800	C(14)-C(15)-H(15)	119.1	C(48)-C(47)-H(47B)	108.3
C(31)-H(31C)	0.9800	C(15)-C(16)-C(17)	119.2(4)	H(47A)-C(47)-H(47B)	107.4
C(32)-H(32A)	0.9800	C(15)-C(16)-C(20)	120.9(5)	C(47)-C(48)-C(49)	116.6(4)
C(32)-H(32B)	0.9800	C(17)-C(16)-C(20)	119.9(5)	C(47)-C(48)-H(48A)	108.1
C(32)-H(32C)	0.9800	C(16)-C(17)-C(18)	121.3(4)	C(49)-C(48)-H(48A)	108.1
C(33)-H(33A)	0.9800	C(16)-C(17)-H(17)	119.3	C(47)-C(48)-H(48B)	108.1
C(33)-H(33B)	0.9800	C(18)-C(17)-H(17)	119.3	C(49)-C(48)-H(48B)	108.1
C(33)-H(33C)	0.9800	C(17)-C(18)-C(13)	117.8(4)	H(48A)-C(48)-H(48B)	107.3
C(34)-C(39)	1.396(6)	C(17)-C(18)-C(21)	120.6(4)	C(50)-C(49)-C(48)	114.3(5)
C(34)-C(35)	1.400(5)	C(13)-C(18)-C(21)	121.6(4)	C(50)-C(49)-H(49A)	108.7
C(35)-C(36)	1.400(6)	C(14)-C(19)-H(19A)	109.5	C(48)-C(49)-H(49A)	108.7
C(35)-C(40)	1.499(6)	C(14)-C(19)-H(19B)	109.5	C(50)-C(49)-H(49B)	108.7
C(36)-C(37)	1.377(7)	H(19A)-C(19)-H(19B)	109.5	C(48)-C(49)-H(49B)	108.7
C(36)-H(36)	0.9500	C(14)-C(19)-H(19C)	109.5	H(49A)-C(49)-H(49B)	107.6
C(37)-C(38)	1.394(7)	H(19A)-C(19)-H(19C)	109.5	C(49)-C(50)-H(50A)	109.5
C(37)-C(41)	1.509(7)	H(19B)-C(19)-H(19C)	109.5	C(49)-C(50)-H(50B)	109.5
C(38)-C(39)	1.394(6)	C(16)-C(20)-H(20A)	109.5	H(50A)-C(50)-H(50B)	109.5
C(38)-H(38)	0.9500	C(16)-C(20)-H(20B)	109.5	C(49)-C(50)-H(50C)	109.5
C(39)-C(42)	1.500(6)	H(20A)-C(20)-H(20B)	109.5	H(50A)-C(50)-H(50C)	109.5
C(40)-H(40A)	0.9800	C(16)-C(20)-H(20C)	109.5	H(50B)-C(50)-H(50C)	109.5
C(40)-H(40B)	0.9800	H(20A)-C(20)-H(20C)	109.5	Cl(2)-C(51)-Cl(1)	111.6(3)

C(40)-H(40C)	0.9800	H(20B)-C(20)-H(20C)	109.5	Cl(2)-C(51)-H(51A)	109.3
C(41)-H(41A)	0.9800	C(18)-C(21)-H(21A)	109.5	Cl(1)-C(51)-H(51A)	109.3
C(41)-H(41B)	0.9800	C(18)-C(21)-H(21B)	109.5	Cl(2)-C(51)-H(51B)	109.3
C(41)-H(41C)	0.9800	H(21A)-C(21)-H(21B)	109.5	Cl(1)-C(51)-H(51B)	109.3
C(42)-H(42A)	0.9800	C(18)-C(21)-H(21C)	109.5	H(51A)-C(51)-H(51B)	108
C(42)-H(42B)	0.9800	H(21A)-C(21)-H(21C)	109.5	Cl(4)-C(52)-Cl(3)	114.5(5)
C(42)-H(42C)	0.9800	H(21B)-C(21)-H(21C)	109.5	Cl(4)-C(52)-H(52A)	108.6
C(44)-C(45)	1.321(7)	N(3)-C(22)-N(4)	103.4(3)	Cl(3)-C(52)-H(52A)	108.6
C(44)-H(44)	0.9500	N(3)-C(22)-Ni(1)	129.4(3)	Cl(4)-C(52)-H(52B)	108.6
C(45)-H(45)	0.9500	N(4)-C(22)-Ni(1)	127.3(3)	Cl(3)-C(52)-H(52B)	108.6
C(46)-H(46A)	0.9800	C(24)-C(23)-N(3)	107.0(3)	H(52A)-C(52)-H(52B)	107.6
C(46)-H(46B)	0.9800	C(24)-C(23)-H(23)	126.5	F(3)-B(1)-F(1)	109.4(4)
C(46)-H(46C)	0.9800	N(3)-C(23)-H(23)	126.5	F(3)-B(1)-F(2)	110.0(3)
C(47)-C(48)	1.492(6)	C(23)-C(24)-N(4)	107.0(3)	F(1)-B(1)-F(2)	109.0(3)
C(47)-H(47A)	0.9900	C(23)-C(24)-H(24)	126.5	F(3)-B(1)-F(4)	109.3(3)
C(47)-H(47B)	0.9900	N(4)-C(24)-H(24)	126.5	F(1)-B(1)-F(4)	109.9(4)
C(48)-C(49)	1.557(8)	C(30)-C(25)-C(26)	121.7(4)	F(2)-B(1)-F(4)	109.3(4)
C(48)-H(48A)	0.9900	C(30)-C(25)-N(3)	119.8(3)		
C(48)-H(48B)	0.9900	C(26)-C(25)-N(3)	118.3(3)		

Table A2.7. Bond lengths [Å] and angles [°] for $Ni(Cl)_2(NHC)_2$ complex 7 (see Chapter 5).

Ni(1)-C(1)	1.925(4)	C(22)-Ni(2)-Cl(3)	89.54(13)
Ni(1)-C(1)#1	1.925(4)	Cl(3)#1-Ni(2)-Cl(3)	179.36(6)
Ni(1)-Cl(1)	2.1899(16)	C(1)-N(1)-C(2)	111.4(3)
Ni(1)-Cl(2)	2.1966(16)	C(1)-N(1)-C(4)	126.5(3)
Ni(2)-C(22)#1	1.924(4)	C(2)-N(1)-C(4)	122.1(3)
Ni(2)-C(22)	1.924(4)	C(1)-N(2)-C(3)	111.3(3)
Ni(2)-Cl(3)#1	2.1928(11)	C(1)-N(2)-C(13)	126.1(3)
Ni(2)-Cl(3)	2.1928(11)	C(3)-N(2)-C(13)	122.6(3)
N(1)-C(1)	1.357(5)	C(22)-N(3)-C(23)	110.8(3)
N(1)-C(2)	1.387(5)	C(22)-N(3)-C(25)	126.3(3)
N(1)-C(4)	1.444(5)	C(23)-N(3)-C(25)	122.8(4)
N(2)-C(1)	1.364(5)	C(22)-N(4)-C(24)	111.4(3)
N(2)-C(3)	1.383(5)	C(22)-N(4)-C(34)	126.8(3)
N(2)-C(13)	1.453(5)	C(24)-N(4)-C(34)	121.8(3)
N(3)-C(22)	1.361(5)	N(1)-C(1)-N(2)	103.7(3)
N(3)-C(23)	1.388(6)	N(1)-C(1)-Ni(1)	128.0(3)
N(3)-C(25)	1.443(5)	N(2)-C(1)-Ni(1)	128.4(3)
N(4)-C(22)	1.362(5)	C(3)-C(2)-N(1)	106.7(4)
N(4)-C(24)	1.392(5)	C(2)-C(3)-N(2)	106.9(4)
N(4)-C(34)	1.440(5)	C(5)-C(4)-C(9)	122.4(4)
C(2)-C(3)	1.339(7)	C(5)-C(4)-N(1)	119.1(4)
C(4)-C(5)	1.390(6)	C(9)-C(4)-N(1)	118.4(4)
C(4)-C(9)	1.394(6)	C(4)-C(5)-C(6)	117.8(4)
C(5)-C(6)	1.397(6)	C(4)-C(5)-C(10)	121.7(4)
C(5)-C(10)	1.510(6)	C(6)-C(5)-C(10)	120.5(4)
C(6)-C(7)	1.388(7)	C(7)-C(6)-C(5)	121.8(4)
C(7)-C(8)	1.379(7)	C(8)-C(7)-C(6)	118.4(4)
C(7)-C(11)	1.516(6)	C(8)-C(7)-C(11)	121.6(4)
C(8)-C(9)	1.398(6)	C(6)-C(7)-C(11)	120.1(4)
C(9)-C(12)	1.499(6)	C(7)-C(8)-C(9)	122.4(4)
C(13)-C(18)	1.391(6)	C(4)-C(9)-C(8)	117.3(4)
C(13)-C(14)	1.394(6)	C(4)-C(9)-C(12)	122.1(4)
C(14)-C(15)	1.403(6)	C(8)-C(9)-C(12)	120.6(4)

C(14)-C(19)	1.490(6)
C(15)-C(16)	1.377(7)
C(16)-C(17)	1.390(7)
C(16)-C(20)	1.518(6)
C(17)-C(18)	1.392(6)
C(18)-C(21)	1.510(6)
C(23)-C(24)	1.335(7)
C(25)-C(26)	1.393(6)
C(25)-C(30)	1.395(6)
C(26)-C(27)	1.392(6)
C(26)-C(31)	1.503(6)
C(27)-C(28)	1.388(6)
C(28)-C(29)	1.389(7)
C(28)-C(32)	1.523(6)
C(29)-C(30)	1.395(6)
C(30)-C(33)	1.505(6)
C(34)-C(35)	1.395(6)
C(34)-C(39)	1.397(6)
C(35)-C(36)	1.391(6)
C(35)-C(40)	1.514(6)
C(36)-C(37)	1.387(7)
C(37)-C(38)	1.398(7)
C(37)-C(41)	1.516(6)
C(38)-C(39)	1.382(6)
C(39)-C(42)	1.506(6)

C(1)-Ni(1)-C(1)#1	178.9(2)
C(1)-Ni(1)-Cl(1)	89.46(11)
C(1)#1-Ni(1)-Cl(1)	89.46(11)
C(1)-Ni(1)-Cl(2)	90.54(11)
C(1)#1-Ni(1)-Cl(2)	90.54(11)
Cl(1)-Ni(1)-Cl(2)	180
C(22)#1-Ni(2)-C(22)	179.8(2)
C(22)#1-Ni(2)-Cl(3)#1	89.54(13)
C(22)-Ni(2)-Cl(3)#1	90.46(13)
C(22)#1-Ni(2)-Cl(3)	90.46(13)

C(18)-C(13)-C(14)	123.1(4)
C(18)-C(13)-N(2)	118.5(4)
C(14)-C(13)-N(2)	118.2(4)
C(13)-C(14)-C(15)	116.6(4)
C(13)-C(14)-C(19)	122.2(4)
C(15)-C(14)-C(19)	121.2(4)
C(16)-C(15)-C(14)	122.1(4)
C(15)-C(16)-C(17)	119.1(4)
C(15)-C(16)-C(20)	120.4(4)
C(17)-C(16)-C(20)	120.5(4)
C(16)-C(17)-C(18)	121.4(4)
C(13)-C(18)-C(17)	117.6(4)
C(13)-C(18)-C(21)	121.6(4)
C(17)-C(18)-C(21)	120.8(4)
N(3)-C(22)-N(4)	103.9(3)
N(3)-C(22)-Ni(2)	128.1(3)
N(4)-C(22)-Ni(2)	127.9(3)
C(24)-C(23)-N(3)	107.6(4)
C(23)-C(24)-N(4)	106.3(4)
C(26)-C(25)-C(30)	122.8(4)
C(26)-C(25)-N(3)	118.8(4)
C(30)-C(25)-N(3)	118.3(4)
C(27)-C(26)-C(25)	117.5(4)
C(27)-C(26)-C(31)	121.1(4)
C(25)-C(26)-C(31)	121.4(4)
C(28)-C(27)-C(26)	121.6(4)
C(27)-C(28)-C(29)	119.0(4)
C(27)-C(28)-C(32)	120.4(4)
C(29)-C(28)-C(32)	120.6(4)
C(28)-C(29)-C(30)	121.6(4)
C(29)-C(30)-C(25)	117.3(4)
C(29)-C(30)-C(33)	120.9(4)
C(25)-C(30)-C(33)	121.8(4)
C(35)-C(34)-C(39)	121.8(4)
C(35)-C(34)-N(4)	118.6(4)
C(39)-C(34)-N(4)	119.5(4)
C(36)-C(35)-C(34)	118.5(4)
C(36)-C(35)-C(40)	119.8(4)
C(34)-C(35)-C(40)	121.7(4)
C(37)-C(36)-C(35)	121.1(4)
C(36)-C(37)-C(38)	118.9(4)
C(36)-C(37)-C(41)	121.2(4)
C(38)-C(37)-C(41)	119.9(4)
C(39)-C(38)-C(37)	121.7(4)
C(38)-C(39)-C(34)	118.0(4)
C(38)-C(39)-C(42)	120.6(4)
C(34)-C(39)-C(42)	121.4(4)

Table A2.8. Bond lengths [Å] and angles [°] for Pd(H)(NHC)$_3$ complex **9** (see Chapter 5).

Pd(1)-C(1)	2.030(2)	C(47)-H(47A)	0.9800	C(23)-C(24)-H(24)	126.5
Pd(1)-C(22)	2.031(2)	C(47)-H(47B)	0.9800	N(4)-C(24)-H(24)	126.5
Pd(1)-C(43)	2.111(2)	C(47)-H(47C)	0.9800	C(30)-C(25)-C(26)	122.5(2)
Pd(1)-H(1)	1.57(3)	C(48)-C(49)	1.369(8)	C(30)-C(25)-N(3)	119.3(2)
F(1)-B(1)	1.382(3)	C(48)-C(50)#1	1.388(8)	C(26)-C(25)-N(3)	118.0(2)
F(2)-B(1)	1.394(3)	C(48)-H(48)	0.9500	C(27)-C(26)-C(25)	117.5(2)
F(3)-B(1)	1.382(3)	C(49)-C(50)	1.329(8)	C(27)-C(26)-C(31)	120.8(2)
F(4)-B(1)	1.383(3)	C(49)-H(49)	0.9500	C(25)-C(26)-C(31)	121.7(2)
N(1)-C(1)	1.367(3)	C(50)-C(48)#1	1.388(8)	C(28)-C(27)-C(26)	121.5(2)
N(1)-C(2)	1.389(3)	C(50)-H(50)	0.9500	C(28)-C(27)-H(27)	119.2
N(1)-C(4)	1.440(3)			C(26)-C(27)-H(27)	119.2
N(2)-C(1)	1.359(3)	C(1)-Pd(1)-C(22)	168.02(8)	C(27)-C(28)-C(29)	119.2(2)
N(2)-C(3)	1.392(3)	C(1)-Pd(1)-C(43)	95.78(9)	C(27)-C(28)-C(32)	120.4(2)
N(2)-C(13)	1.441(3)	C(22)-Pd(1)-C(43)	96.20(8)	C(29)-C(28)-C(32)	120.4(2)
N(3)-C(22)	1.354(3)	C(1)-Pd(1)-H(1)	82.0(10)	C(28)-C(29)-C(30)	121.8(2)
N(3)-C(23)	1.388(3)	C(22)-Pd(1)-H(1)	86.0(10)	C(28)-C(29)-H(29)	119.1
N(3)-C(25)	1.443(3)	C(43)-Pd(1)-H(1)	177.0(10)	C(30)-C(29)-H(29)	119.1
N(4)-C(22)	1.371(3)	C(1)-N(1)-C(2)	111.18(19)	C(29)-C(30)-C(25)	117.5(2)
N(4)-C(24)	1.387(3)	C(1)-N(1)-C(4)	125.73(18)	C(29)-C(30)-C(33)	120.7(2)
N(4)-C(34)	1.439(3)	C(2)-N(1)-C(4)	122.94(18)	C(25)-C(30)-C(33)	121.8(2)
N(5)-C(43)	1.357(3)	C(1)-N(2)-C(3)	112.09(19)	C(26)-C(31)-H(31A)	109.5
N(5)-C(44)	1.379(3)	C(1)-N(2)-C(13)	125.35(18)	C(26)-C(31)-H(31B)	109.5
N(5)-C(46)	1.462(3)	C(3)-N(2)-C(13)	122.55(19)	H(31A)-C(31)-H(31B)	109.5
N(6)-C(43)	1.350(3)	C(22)-N(3)-C(23)	112.04(19)	C(26)-C(31)-H(31C)	109.5
N(6)-C(45)	1.388(3)	C(22)-N(3)-C(25)	124.58(18)	H(31A)-C(31)-H(31C)	109.5
N(6)-C(47)	1.449(3)	C(23)-N(3)-C(25)	123.22(19)	H(31B)-C(31)-H(31C)	109.5
C(2)-C(3)	1.339(4)	C(22)-N(4)-C(24)	111.14(19)	C(28)-C(32)-H(32A)	109.5
C(2)-H(2)	0.9500	C(22)-N(4)-C(34)	125.23(18)	C(28)-C(32)-H(32B)	109.5
C(3)-H(3)	0.9500	C(24)-N(4)-C(34)	123.61(18)	H(32A)-C(32)-H(32B)	109.5
C(4)-C(9)	1.387(4)	C(43)-N(5)-C(44)	111.9(2)	C(28)-C(32)-H(32C)	109.5
C(4)-C(5)	1.395(3)	C(43)-N(5)-C(46)	124.18(19)	H(32A)-C(32)-H(32C)	109.5
C(5)-C(6)	1.394(4)	C(44)-N(5)-C(46)	123.8(2)	H(32B)-C(32)-H(32C)	109.5
C(5)-C(10)	1.502(4)	C(43)-N(6)-C(45)	111.5(2)	C(30)-C(33)-H(33A)	109.5
C(6)-C(7)	1.391(4)	C(43)-N(6)-C(47)	124.4(2)	C(30)-C(33)-H(33B)	109.5
C(6)-H(6)	0.9500	C(45)-N(6)-C(47)	124.1(2)	H(33A)-C(33)-H(33B)	109.5
C(7)-C(8)	1.379(4)	N(2)-C(1)-N(1)	103.32(18)	C(30)-C(33)-H(33C)	109.5
C(7)-C(11)	1.517(4)	N(2)-C(1)-Pd(1)	128.85(16)	H(33A)-C(33)-H(33C)	109.5
C(8)-C(9)	1.386(4)	N(1)-C(1)-Pd(1)	127.65(16)	H(33B)-C(33)-H(33C)	109.5
C(8)-H(8)	0.9500	C(3)-C(2)-N(1)	107.4(2)	C(35)-C(34)-C(39)	121.7(2)
C(9)-C(12)	1.516(4)	C(3)-C(2)-H(2)	126.3	C(35)-C(34)-N(4)	119.2(2)
C(10)-H(10A)	0.9800	N(1)-C(2)-H(2)	126.3	C(39)-C(34)-N(4)	119.0(2)
C(10)-H(10B)	0.9800	C(2)-C(3)-N(2)	106.0(2)	C(34)-C(35)-C(36)	118.0(2)
C(10)-H(10C)	0.9800	C(2)-C(3)-H(3)	127	C(34)-C(35)-C(40)	122.1(2)
C(11)-H(11A)	0.9800	N(2)-C(3)-H(3)	127	C(36)-C(35)-C(40)	119.8(2)
C(11)-H(11B)	0.9800	C(9)-C(4)-C(5)	121.9(2)	C(37)-C(36)-C(35)	121.9(2)
C(11)-H(11C)	0.9800	C(9)-C(4)-N(1)	120.1(2)	C(37)-C(36)-H(36)	119.1
C(12)-H(12A)	0.9800	C(5)-C(4)-N(1)	117.9(2)	C(35)-C(36)-H(36)	119.1
C(12)-H(12B)	0.9800	C(6)-C(5)-C(4)	117.5(2)	C(36)-C(37)-C(38)	118.3(2)
C(12)-H(12C)	0.9800	C(6)-C(5)-C(10)	121.6(2)	C(36)-C(37)-C(41)	121.0(3)
C(13)-C(14)	1.393(4)	C(4)-C(5)-C(10)	120.9(2)	C(38)-C(37)-C(41)	120.6(3)
C(13)-C(18)	1.399(4)	C(7)-C(6)-C(5)	121.9(3)	C(37)-C(38)-C(39)	122.4(2)
C(14)-C(15)	1.396(4)	C(7)-C(6)-H(6)	119.1	C(37)-C(38)-H(38)	118.8
C(14)-C(19)	1.502(4)	C(5)-C(6)-H(6)	119.1	C(39)-C(38)-H(38)	118.8
C(15)-C(16)	1.390(5)	C(8)-C(7)-C(6)	118.4(3)	C(38)-C(39)-C(34)	117.4(2)

C(15)-H(15)	0.9500	C(8)-C(7)-C(11)	119.5(3)	C(38)-C(39)-C(42)	120.8(2)
C(16)-C(17)	1.373(5)	C(6)-C(7)-C(11)	122.0(3)	C(34)-C(39)-C(42)	121.7(2)
C(16)-C(20)	1.514(4)	C(7)-C(8)-C(9)	121.8(3)	C(35)-C(40)-H(40A)	109.5
C(17)-C(18)	1.399(4)	C(7)-C(8)-H(8)	119.1	C(35)-C(40)-H(40B)	109.5
C(17)-H(17)	0.9500	C(9)-C(8)-H(8)	119.1	H(40A)-C(40)-H(40B)	109.5
C(18)-C(21)	1.504(4)	C(8)-C(9)-C(4)	118.4(2)	C(35)-C(40)-H(40C)	109.5
C(19)-H(19A)	0.9800	C(8)-C(9)-C(12)	119.2(3)	H(40A)-C(40)-H(40C)	109.5
C(19)-H(19B)	0.9800	C(4)-C(9)-C(12)	122.4(2)	H(40B)-C(40)-H(40C)	109.5
C(19)-H(19C)	0.9800	C(5)-C(10)-H(10A)	109.5	C(37)-C(41)-H(41A)	109.5
C(20)-H(20A)	0.9800	C(5)-C(10)-H(10B)	109.5	C(37)-C(41)-H(41B)	109.5
C(20)-H(20B)	0.9800	H(10A)-C(10)-H(10B)	109.5	H(41A)-C(41)-H(41B)	109.5
C(20)-H(20C)	0.9800	C(5)-C(10)-H(10C)	109.5	C(37)-C(41)-H(41C)	109.5
C(21)-H(21A)	0.9800	H(10A)-C(10)-H(10C)	109.5	H(41A)-C(41)-H(41C)	109.5
C(21)-H(21B)	0.9800	H(10B)-C(10)-H(10C)	109.5	H(41B)-C(41)-H(41C)	109.5
C(21)-H(21C)	0.9800	C(7)-C(11)-H(11A)	109.5	C(39)-C(42)-H(42A)	109.5
C(23)-C(24)	1.342(4)	C(7)-C(11)-H(11B)	109.5	C(39)-C(42)-H(42B)	109.5
C(23)-H(23)	0.9500	H(11A)-C(11)-H(11B)	109.5	H(42A)-C(42)-H(42B)	109.5
C(24)-H(24)	0.9500	C(7)-C(11)-H(11C)	109.5	C(39)-C(42)-H(42C)	109.5
C(25)-C(30)	1.395(3)	H(11A)-C(11)-H(11C)	109.5	H(42A)-C(42)-H(42C)	109.5
C(25)-C(26)	1.402(3)	H(11B)-C(11)-H(11C)	109.5	H(42B)-C(42)-H(42C)	109.5
C(26)-C(27)	1.397(3)	C(9)-C(12)-H(12A)	109.5	N(6)-C(43)-N(5)	103.62(19)
C(26)-C(31)	1.506(3)	C(9)-C(12)-H(12B)	109.5	N(6)-C(43)-Pd(1)	129.09(17)
C(27)-C(28)	1.385(4)	H(12A)-C(12)-H(12B)	109.5	N(5)-C(43)-Pd(1)	127.25(17)
C(27)-H(27)	0.9500	C(9)-C(12)-H(12C)	109.5	C(45)-C(44)-N(5)	106.4(2)
C(28)-C(29)	1.388(4)	H(12A)-C(12)-H(12C)	109.5	C(45)-C(44)-H(44)	126.8
C(28)-C(32)	1.515(4)	H(12B)-C(12)-H(12C)	109.5	N(5)-C(44)-H(44)	126.8
C(29)-C(30)	1.392(3)	C(14)-C(13)-C(18)	122.8(2)	C(44)-C(45)-N(6)	106.6(2)
C(29)-H(29)	0.9500	C(14)-C(13)-N(2)	118.8(2)	C(44)-C(45)-H(45)	126.7
C(30)-C(33)	1.509(3)	C(18)-C(13)-N(2)	118.3(2)	N(6)-C(45)-H(45)	126.7
C(31)-H(31A)	0.9800	C(13)-C(14)-C(15)	117.0(3)	N(5)-C(46)-H(46A)	109.5
C(31)-H(31B)	0.9800	C(13)-C(14)-C(19)	122.3(2)	N(5)-C(46)-H(46B)	109.5
C(31)-H(31C)	0.9800	C(15)-C(14)-C(19)	120.7(3)	H(46A)-C(46)-H(46B)	109.5
C(32)-H(32A)	0.9800	C(16)-C(15)-C(14)	122.2(3)	N(5)-C(46)-H(46C)	109.5
C(32)-H(32B)	0.9800	C(16)-C(15)-H(15)	118.9	H(46A)-C(46)-H(46C)	109.5
C(32)-H(32C)	0.9800	C(14)-C(15)-H(15)	118.9	H(46B)-C(46)-H(46C)	109.5
C(33)-H(33A)	0.9800	C(17)-C(16)-C(15)	118.7(3)	N(6)-C(47)-H(47A)	109.5
C(33)-H(33B)	0.9800	C(17)-C(16)-C(20)	121.4(3)	N(6)-C(47)-H(47B)	109.5
C(33)-H(33C)	0.9800	C(15)-C(16)-C(20)	119.9(3)	H(47A)-C(47)-H(47B)	109.5
C(34)-C(35)	1.395(3)	C(16)-C(17)-C(18)	122.2(3)	N(6)-C(47)-H(47C)	109.5
C(34)-C(39)	1.403(3)	C(16)-C(17)-H(17)	118.9	H(47A)-C(47)-H(47C)	109.5
C(35)-C(36)	1.395(4)	C(18)-C(17)-H(17)	118.9	H(47B)-C(47)-H(47C)	109.5
C(35)-C(40)	1.508(4)	C(17)-C(18)-C(13)	117.1(3)	C(49)-C(48)-C(50)#1	119.7(6)
C(36)-C(37)	1.384(4)	C(17)-C(18)-C(21)	121.1(3)	C(49)-C(48)-H(48)	120.1
C(36)-H(36)	0.9500	C(13)-C(18)-C(21)	121.7(3)	C(50)#1-C(48)-H(48)	120.1
C(37)-C(38)	1.386(4)	C(14)-C(19)-H(19A)	109.5	C(50)-C(49)-C(48)	122.8(6)
C(37)-C(41)	1.515(4)	C(14)-C(19)-H(19B)	109.5	C(50)-C(49)-H(49)	118.6
C(38)-C(39)	1.389(4)	H(19A)-C(19)-H(19B)	109.5	C(48)-C(49)-H(49)	118.6
C(38)-H(38)	0.9500	C(14)-C(19)-H(19C)	109.5	C(49)-C(50)-C(48)#1	117.5(6)
C(39)-C(42)	1.507(3)	H(19A)-C(19)-H(19C)	109.5	C(49)-C(50)-H(50)	121.2
C(40)-H(40A)	0.9800	H(19B)-C(19)-H(19C)	109.5	C(48)#1-C(50)-H(50)	121.2
C(40)-H(40B)	0.9800	C(16)-C(20)-H(20A)	109.5	F(1)-B(1)-F(3)	110.1(3)
C(40)-H(40C)	0.9800	C(16)-C(20)-H(20B)	109.5	F(1)-B(1)-F(4)	109.5(2)
C(41)-H(41A)	0.9800	H(20A)-C(20)-H(20B)	109.5	F(3)-B(1)-F(4)	110.0(2)
C(41)-H(41B)	0.9800	C(16)-C(20)-H(20C)	109.5	F(1)-B(1)-F(2)	109.7(2)
C(41)-H(41C)	0.9800	H(20A)-C(20)-H(20C)	109.5	F(3)-B(1)-F(2)	108.5(2)
C(42)-H(42A)	0.9800	H(20B)-C(20)-H(20C)	109.5	F(4)-B(1)-F(2)	108.9(2)

C(42)-H(42B)	0.9800	C(18)-C(21)-H(21A)	109.5
C(42)-H(42C)	0.9800	C(18)-C(21)-H(21B)	109.5
C(44)-C(45)	1.341(4)	H(21A)-C(21)-H(21B)	109.5
C(44)-H(44)	0.9500	C(18)-C(21)-H(21C)	109.5
C(45)-H(45)	0.9500	H(21A)-C(21)-H(21C)	109.5
C(46)-H(46A)	0.9800	H(21B)-C(21)-H(21C)	109.5
C(46)-H(46B)	0.9800	N(3)-C(22)-N(4)	103.41(18)
C(46)-H(46C)	0.9800	N(3)-C(22)-Pd(1)	127.36(15)
		N(4)-C(22)-Pd(1)	129.15(16)
		C(24)-C(23)-N(3)	106.4(2)
		C(24)-C(23)-H(23)	126.8
		N(3)-C(23)-H(23)	126.8
		C(23)-C(24)-N(4)	107.0(2)