DESIGN, SYNTHESIS AND CATALYTIC ACTIVITY OF Di-*N*-HETEROCYCLIC CARBENE COMPLEXES OF NICKEL AND PALLADIUM

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By

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To my loving parents

പ്രിയപ്പെട്ട പപ്പയ്ക്കും മമ്മിയ്ക്കും

ABSTRACT

N-heterocyclic carbenes (NHC) have widely been used as spectator ligands in organometallic chemistry. Chelating bidentate di-*N*-heterocyclic carbenes (diNHC) provide additional entropic stability to their complexes relative to monodentate analogues. The steric and electronic environment around the metal centre can be fine-tuned by varying the substituents on the nitrogen atoms of the diNHC ligand. Synthesis and characterization of air and moisture stable bis(diimidazolylidene)nickel(II) complexes, $[(diNHC)_2Ni]^{2+}$, and their corresponding silver(I) and palladium(II) analogues are described.

Investigations into the catalytic potential of diNHC complexes of nickel as an alternative to palladium systems in carbon-carbon coupling reactions are discussed. In the Suzuki-Miyaura coupling reaction, the $[(diNHC)_2Ni]^{2+}$ complex was active for the coupling of aryl chlorides as well as aryl fluorides. The analogously synthesized Pd(II) complexes resulted in formation of $(diNHC)PdCl_2$ species which were not active for the coupling of aryl fluorides. "Transition-metal free" coupling reactions were investigated and the results indicated that in the Mizoroki-Heck reaction, aryl iodides could be activated in the absence of nickel or palladium precatalysts when using Na_2CO_3 or NEt_3 as base, while in the Suzuki-Miyaura reaction, aryl iodides and aryl bromides could be activated without any precatalyst when K_3PO_4 was used as base.

A general route into the synthesis of non-symmetrically substituted ligand precursors has been developed. Synthesis and characterization of non-symmetrically substituted ligand precursors, and their corresponding silver(I), palladium(II) and

nickel(II) complexes are described. The activity of one of the non-symmetrically substituted (diNHC)Pd(II) complexes in the Suzuki-Miyaura coupling reaction of bulky substrates has been investigated. Non-symmetrically substituted diNHC ligand precursors with a hemi-labile pyridine arm have been synthesized and their corresponding Ni(II) and Pd(II) complexes are described.

Attempts to synthesize three-coordinate Pd(II) complexes using bulky β-diketiminato ligands are also discussed.

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LIST OF ABBREVIATIONS

Abbreviation

Ac……..……CH_3CO

acac……acetylacetonate

bipy……bipyridine

BuLi……...……..……n-butyllithium

Bz……benzyl

cod……...1,5-cyclooctadiene

Cy…….cyclohexyl

dba…….……..…dibenzylideneacetone

DMA……dimethylacetamide

DME……..ethylene glycol dimethyl ether

DMF……...*N*,*N*-dimethylformamide

DMSO……...dimethyl sulphoxide

equiv……..……....equivalent

Fc.....ferrocenyl

HRMS…….……high resolution mass spectrometry

M……..has generally been used for metals

mer……meridional

NHC……..*N*-heterocyclic carbene

NMP…….*N*-methylpyrrolidone

NMR… …….nuclear magnetic resonance

o-Tol……..……..……..*ortho*-tolyl

py…….…pyridine

R…….has generally been used for alkyls or aryls

rt…….room temperature

THF……...tetrahydrofuran

tmeda……...*N*,*N*,*N*’,*N*’-tetramethylethylenediamine

TON.....….turnover number

X…….....…has generally been used for halogens

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CHAPTER 1

INTRODUCTION

1.1 *N*-Heterocyclic Carbenes as Ligands

Carbenes are organic molecules containing an electron deficient, divalent carbon atom with two non-bonding electrons and has the general formula :CR_2. In the ground-state, the two unshared electrons may either be in the same orbital with antiparallel spins (singlet state) or in two degenerate orbitals with parallel spins (triplet state), accordingly, carbenes can have a linear or bent geometry (Figure 1-1).[1]

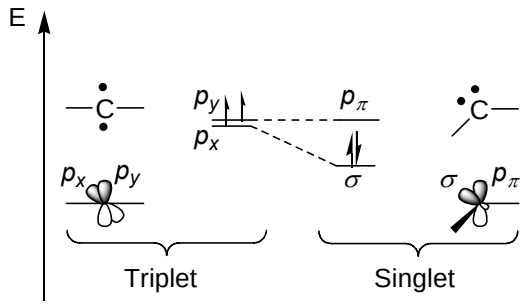


Figure 1-1. Triplet and singlet carbenes.[1]

The linear geometry suggests an *sp* hybridized carbene carbon, where the remaining two non-bonding orbitals (p_x and p_y) are degenerate and contain one electron each, giving rise to triplet carbenes. The bent geometry destroys the degeneracy of the two orbitals, with the carbene carbon adopting an sp^2 hybridization. The p_x orbital

acquires some *s* character and is stabilized in energy, and hence is occupied by the electron pair, giving rise to singlet carbenes.

Most carbenes adopt a bent geometry. In singlet carbenes, the sp^2 and p_y frontier orbitals are generally referred to as σ and p_π orbitals respectively. As a result of the difference in their electronic makeup, the singlet and triplet carbenes have very different reactivity. Singlet carbenes have both a filled and a vacant orbital and can therefore exhibit nucleophilic or electrophilic character. Triplet carbenes on the other hand are usually considered as diradicals. The steric and electronic effects of the substituents on the carbene carbon play a very important role in the ground-state spin multiplicity of the carbenes.

In 1964, Fischer *et al.* reported on the first stable transition metal complex with a carbene ligand (Figure 1-2).[2] Complexes with similar carbene ligands are generally referred to as Fischer carbene complexes. The singlet, electrophilic carbene is stabilized by a π donor substituent such as -OR, -NR_2, -SR, or phenyl, which donates electron density into the p_π carbene orbital. There is also a competing π-backdonation from the filled metal orbitals to the p_π orbital on the carbene.

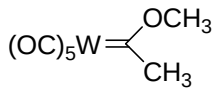


Figure 1-2. Example of a Fischer carbene.

In 1972 Schrock *et al.* synthesized a different type of transition metal complex incorporating a triplet, nucleophilic carbene ligand (Figure 1-3).[3]

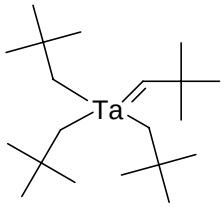
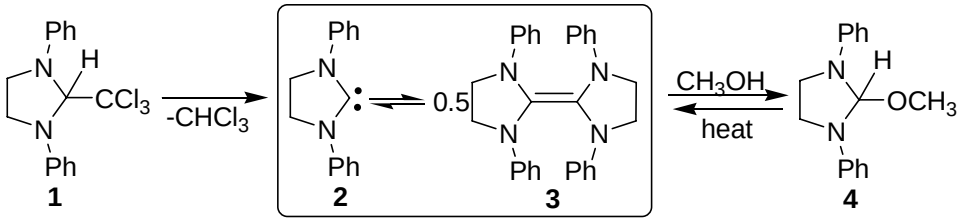


Figure 1-3. Example of a Schrock carbene.

Even before Fischer *et al.* synthesized transition metal carbene complexes, Wanzlick *et al.* had already been working on isolating free stable carbenes.[4] They found that the stability of carbenes could be dramatically improved by having strong electron donor groups as substituents on the carbenic carbon, such as amino substituents. Attempts to isolate the free carbene **2**, by thermal elimination of chloroform from **1**, led to the dimer **3**, as the exclusive product (Scheme 1-1). When methanol was added to **3**, compound **4** was obtained, which on heating gives back the dimer **3**. Based on these observations Wanzlick *et al.* proposed an equilibrium between the free carbene **2**, and the dimer **3**. The evidence in support for this equilibrium was provided by various groups.[5]

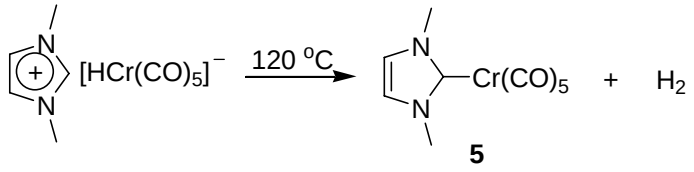
Scheme 1-1. Wanzlick equilibrium.



However, Lemal *et al.* proposed that the dimerization could be catalyzed by the presence of electrophiles and that no equilibrium existed between the carbene and the dimer.[6] The evidence in support for this proposal was later given by several groups.[7]

In 1968, Wanzlick *et al.* and Öfele *et al.* independently reported on the synthesis of the first *N*-heterocyclic carbene (NHC) transition metal complexes. Öfele *et al.* were trying to synthesize some dihydro complexes by heating heterocyclic salts of chromium. They observed an unusual side reaction while using imidazolium salts, generating the NHC chromium complex **5** (Scheme 1-2).[8]

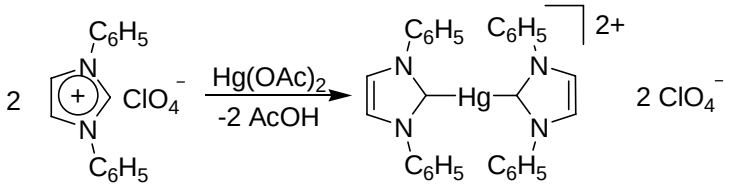
Scheme 1-2. Öfele's NHC complex.



5

Wanzlick *et al.* synthesized their complex directly by the treatment of 1,3-diphenylimidazolium perchlorate with mercury(II) acetate in DMSO (Scheme 1-3).[9] The acetate ligand on mercury causes the *in situ* deprotonation of the imidazolium salt liberating acetic acid and generating the NHC mercury complex **6**. This metal acetate route was later adopted as one of the general routes for the synthesis of several transition metal complexes as will be discussed in the following sections.

Scheme 1-3. Wanzlick's NHC complex.



6

Although chemists across the world were trying to isolate a free stable carbene, it was Bertrand *et al.* who synthesized the first isolable carbene in 1988 (Figure 1-4).[10] Unfortunately, these carbenes proved to be poor ligands due to strong P-$C_{carbene}$ multiple bond character.[11]

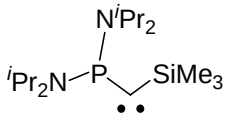
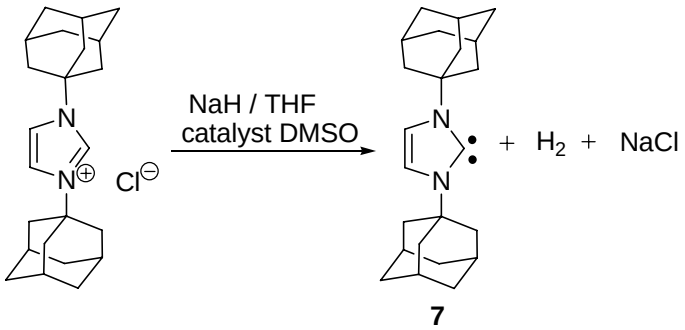


Figure 1-4. Bertrand's carbene.

The ground-breaking discovery came in 1991 when Arduengo *et al.* isolated the first singlet NHC, which are now sometimes referred to as Arduengo carbenes (Scheme 1-4).[12] These "bottle-able" carbenes were synthesized by deprotonation of the imidazolium salt with a base.

Scheme 1-4. Arduengo Carbene.



The electronic and steric environment around the carbene centre greatly contributed to the increased stability of these carbenes. NHCs have a neutral divalent

carbene carbon with six valence electrons and the nitrogen substituents bound to the carbene carbon atom stabilize the singlet state with two paired electrons in the σ-orbital of the carbene carbon by a push-pull effect. The σ-electron withdrawing nitrogens inductively stabilize the σ-non-bonding orbital of the carbene carbon, by increasing its *s*-character (Figure 1-5 (a)) while the energy of the vacant p_π orbital is increased by interaction with the symmetric combination of the nitrogen lone pairs (Figure 1-5 (b)). Combination of the two effects increases the σ-p_π energy gap (HOMO-LUMO gap) and thus favors the singlet state. The interaction of the nitrogen lone pair with the p_π orbital of the carbene carbon is reflected by a N-$C_{carbene}$ bond length of 1.36 Å in the Arduengo carbene, **7**, which is smaller than a N-C single bond length.[12] Also, the sp^2 hybridization adopted by the carbene carbon in its singlet state matches the bent geometry of the NHC five-membered ring. These electronic factors provide thermodynamic stability and the bulky substituents on the nitrogens provide kinetic stability to the NHCs.

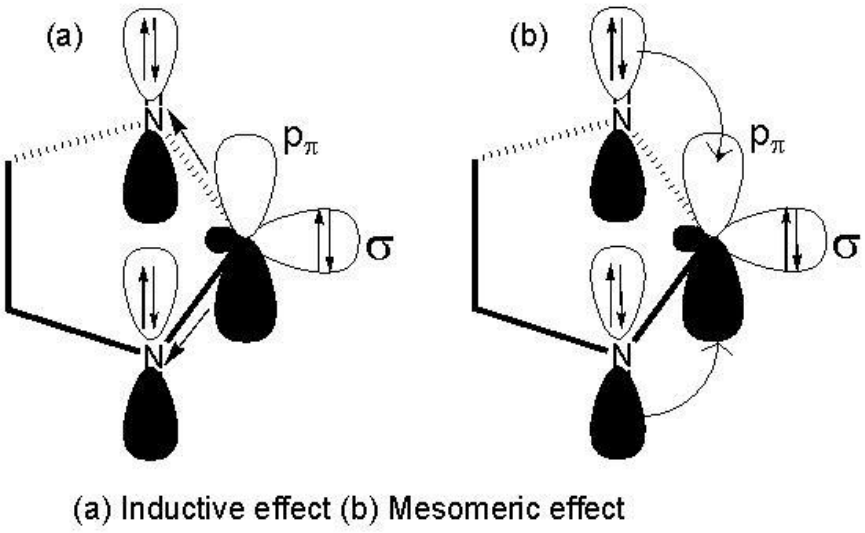


Figure 1-5. Electronic stabilization of NHC.

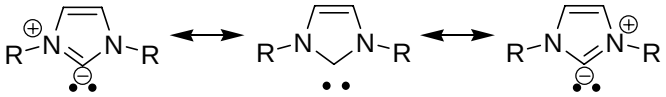
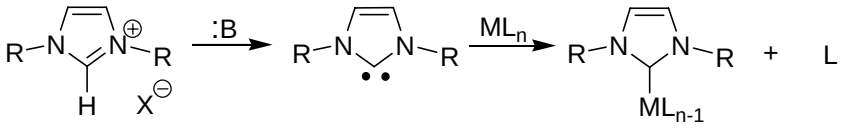


Figure 1-6. Resonance contributors of NHCs.

The zwitterionic resonance contributors of NHCs are shown in Figure 1-6. An accurate assessment of the π-backbonding was found by analyzing the dynamic ^{1}H NMR behavior of bis(diisopropylamine)carbene, [(^{i}Pr$_2$N)$_2$C:].[13] As the major part of this process involves rotation about the N-C$_{carbene}$ bond, the measured barrier to rotation of 53 KJ/mol was mostly attributed to the substantial π-component of these bonds.

Scheme 1-5. General scheme for the synthesis of NHC complexes.



:B = Base
M = Metal
L = Ligand

The general design for the synthesis of NHC complexes is shown in Scheme 1-5. NHCs have been considered to be strong σ donors and poor π acceptors. However, there have been some reports that provide evidence for substantial π^*-backdonation from the metal to the ligand.[14] The M-NHC bonding has been discussed in detail in a recent review wherein the three orbital contributions to the M-NHC bond has been shown as in Figure 1-7.[15]

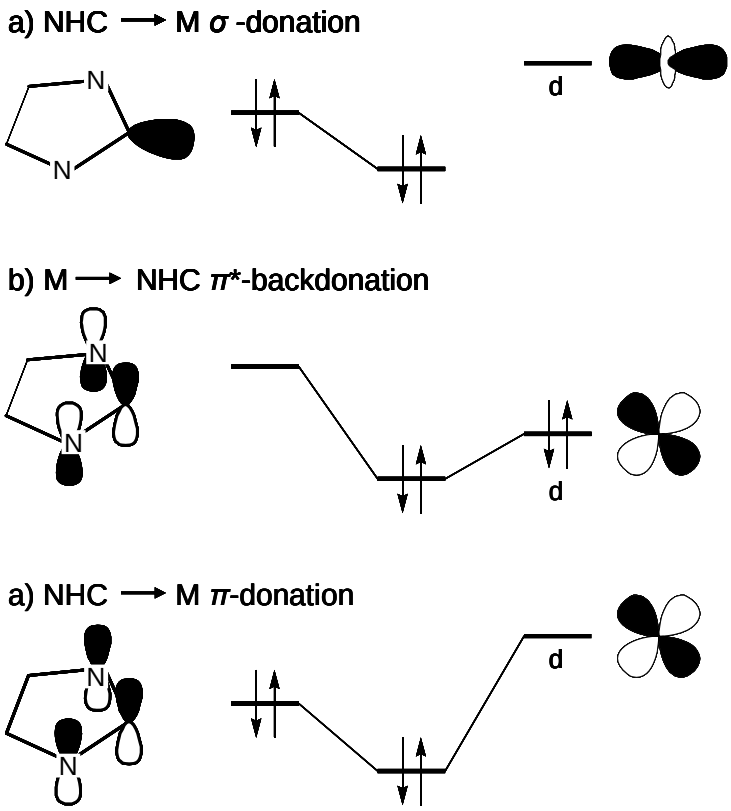


Figure 1-7. The three bonding contributions to the M-(NHC) bond.[15]

Phosphines are widely used as ligands in organometallic chemistry for designing homogeneous catalysts. NHCs are similar to phosphine ligands in that they are neutral ligands and two electron σ donors. Herrmann *et al.* were the first to realize the potential of NHCs and introduce them as spectator ligands in organometallic catalysis.[16] Grubbs *et al.* recognized the electron-donating potential of these carbenes and replaced the phosphine ligand in their first generation Grubbs catalyst with an NHC ligand. Consequently, the second generation Grubbs catalyst had exceedingly higher catalytic activity compared to their first generation catalyst in olefin metathesis and contributed to the Nobel Prize in 2005.[17] Subsequently, NHCs have largely been used as an alternative to the ubiquitous phosphine ligands in organometallic chemistry (Scheme 1-4). The

structural versatility and the stability of the NHC complexes are the two key factors that have contributed towards the growth of NHC chemistry. There have been almost 30 reviews published on NHC complexes in the past six years. In 2007, two entire issues of a journal were dedicated to NHCs.[18]

NHCs exist in a variety of ring frameworks. There are basically four-, five-, six- and seven-membered ring frameworks reported in literature (Figure 1-8), out of which the imidazolylidene framework (shown in the box) is the most commonly studied.

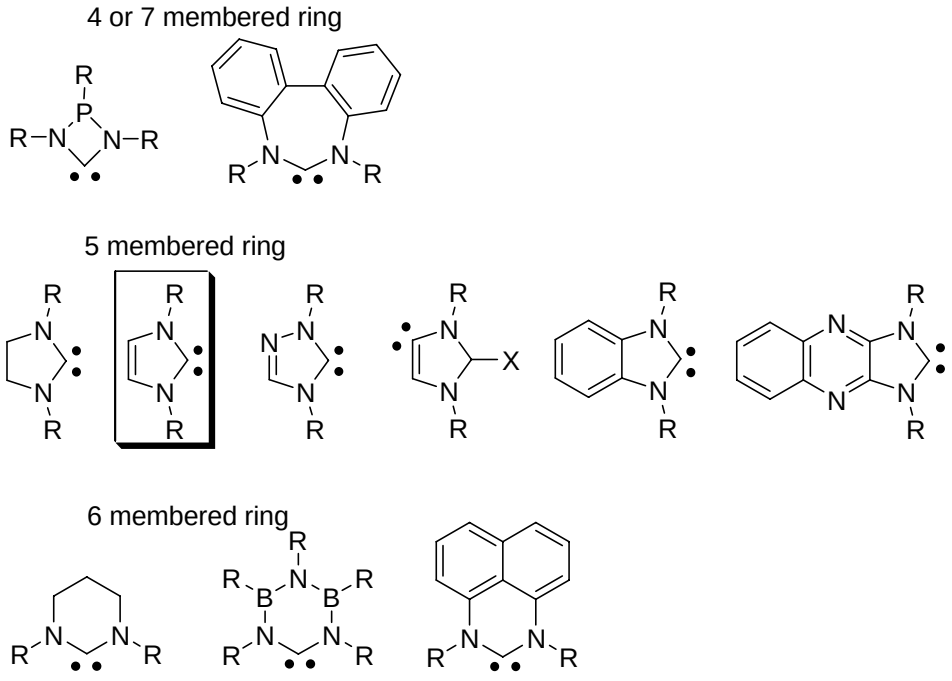
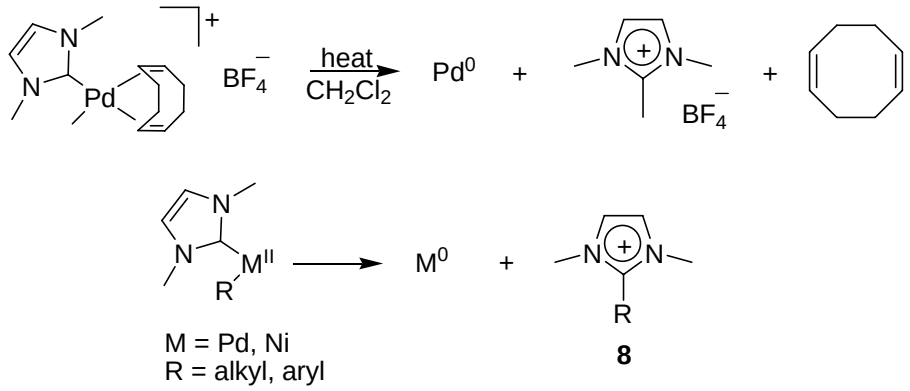


Figure 1-8. Some NHC frameworks.

Although a wide variety of monodentate NHC catalysts have been explored, a reductive elimination pathway has been observed in some NHC complexes of palladium and nickel yielding imidazolium salts such as **8** (Scheme 1-6), indicating that NHCs do not always behave as innocent ligands.[19]

Scheme 1-6. Decomposition of NHC complexes.



Chelating NHCs provide entropic stability to their complexes and chelating ligands in general have proved to be very useful in organometallic catalysis. Moreover, since palladacycles have shown high catalytic activity in coupling reactions, chelating NHCs with their strong σ-donating properties appear to be very attractive as ligands in organometallic catalysis.[20] Several examples of palladium complexes with *cis*-chelating diNHC ligands have been shown to efficiently catalyze cross coupling reactions.[21] In 2007, Peris *et al.* reviewed the structural and catalytic properties of chelating diNHC and triNHC complexes.[22] More recently they published a fresh review on the structural features and catalytic applications of polyNHC complexes.[23]

There are several examples of chelating diNHC complexes found in literature. The first example of a chelating diNHC complex was reported in 1980 by Lappert *et al.* (Figure 1-9).[24]

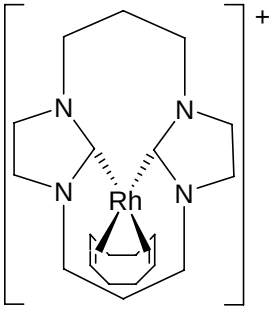


Figure 1-9. Chelating diNHC complex.

There are very few examples of triNHC ligands in literature and the ones known are tripodal-type ligand systems similar to Trofimenko's tris(pyrazolyl)borate ligands.[25] However, there are no examples of triNHC complexes of Pd(II) or Ni(II) and only one example of a tetraNHC Pd(II) complex (Figure 1-10).[26]

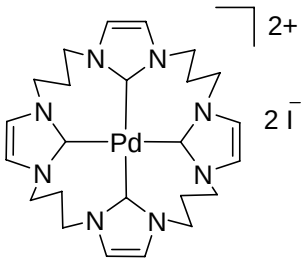


Figure 1-10. TetraNHC palladium complex.

The two main reasons for so few tri- and tetraNHC complexes are the difficulties associated with the multistep synthesis of these systems and the extremely poor solubility of their carbene precursors, *i.e.*, the tri- and tetraimidazolium salts, in most organic solvents.

Because of the enormity of NHC chemistry, the following discussions will be limited to the imidazolylidene-based chelating diNHC complexes of palladium and

nickel. Palladium is often the metal of choice among most researchers for studying the coordination chemistry and structural properties of NHCs on a metal centre. One major reason being that palladium has found catalytic applications in a variety of organic transformations especially carbon-carbon coupling reactions, which are one of the most important reactions in organic synthesis.[27] Nickel, on the other hand, has been investigated as an alternative to the much more expensive palladium in organometallic catalysis.[28]

The following sections cover a detailed review of all the imidazolylidene-based diNHC complexes of palladium and nickel found in literature.

1.2 Bidentate diNHC complexes of Palladium and Nickel

The following figure depicts a bidentate diNHC ligand on a metal, M (Figure 1-11). Based on the nature of the linker between the two imidazolylidene units, these chelating diNHC complexes have been divided in this section into three groups: (i) alkane-bridged, (ii) arene-bridged, and (iii) chiral motive-bridged.[23]

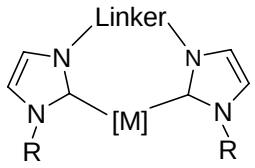


Figure 1-11. Chelating bidentate diNHC complex.

1.2.1 Alkane-bridged diNHC complexes

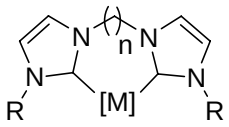
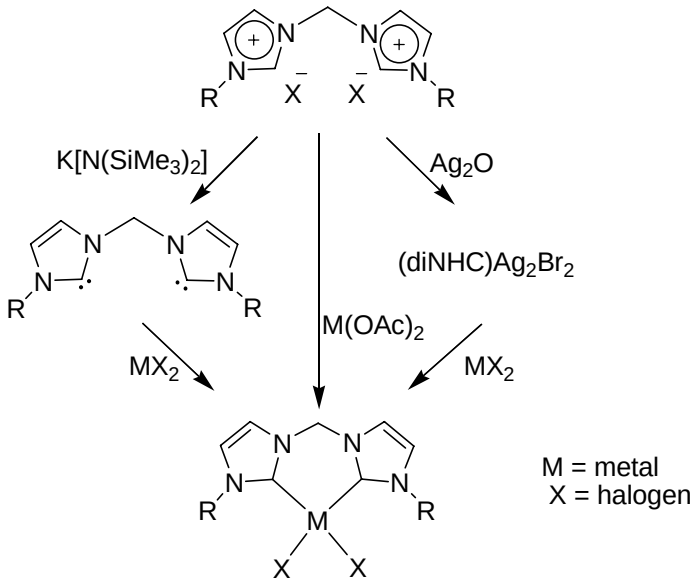


Figure 1-12. Chelating alkane-bridged diNHC complex.

Figure 1-12 illustrates a bidentate *cis*-chelating alkane-bridged diNHC ligand on a metal (M). The diNHC ligand can be easily modified by varying the *N*-substitutents and/or varying the length of the alkane chain between the two imidazolylidene units. The diNHC ligand precursor is usually a diimidazolium salt. There are basically three

synthetic routes, widely used in literature, to synthesize diNHC complexes of palladium(II) and nickel(II). These routes are: the free carbene route, the metal acetate route and the silver transmetallation route (Scheme 1-7).

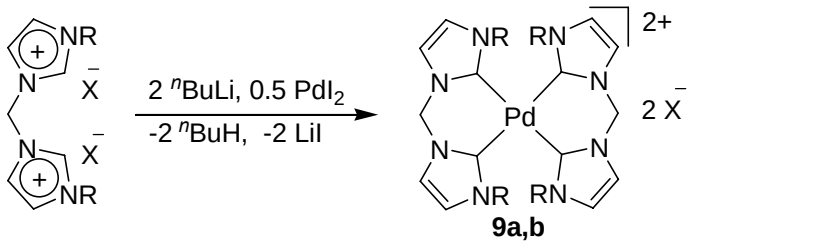
Scheme 1-7. General synthetic routes into diNHC complexes.



1.2.1.1 Alkane-bridged diNHC palladium complexes

In 1995, Fehlhammer *et al.* prepared the first examples of *cis*-chelating diNHC complex (Scheme 1-8).[29] The syntheses involved the *in situ* generation of the free dicarbenes from their corresponding diimidazolium salts using two equiv. of ^{n}BuLi in the presence of suspended palladium iodide. The air-sensitive neutral dicarbenes that were formed *in situ* were immediately trapped *via* coordination to the palladium iodide, resulting in complexes **9a**,**b** which were obtained in very low yields.

Scheme 1-8. Synthesis of the first examples of diNHC complexes of Pd.[29]



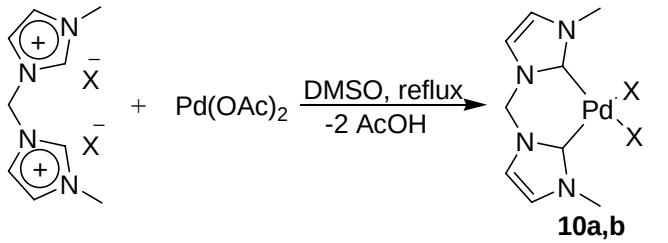
9a,b

9a: R = Me, X = I (12% yield)
9b: R = Et, X = BF_4 (14% yield)

The carbene carbons appear at 169 ppm in the ^{13}C NMR spectra of **9a**,**b**. The coordination environment of the *cis*-chelating bis(diNHC)Pd(II) complex was confirmed by single-crystal X-ray analysis which showed a distorted square-planar arrangement around the metal centre. The Pd-C distances indicated that these bonds have a single bond character. Short N-$C_{carbene}$ distances suggest significant π-donation from the nitrogen orbitals to the empty orbital of the carbene carbon, which has a very important contribution in the stabilization of the carbene. The comparatively longer C-N bonds indicate that there are two localized π systems, the NCN and the C=C. The six-membered palladacycles which include the metal, the carbene carbon atoms, the adjacent nitrogens and the methylene group bridging the two imidazolylidene units, adopt a rigid boat-shaped conformation which does not show fluxional behavior at room temperature on the NMR time scale (on a Bruker WH 270 spectrometer). This resulted in the appearance of two doublets in the ^{1}H NMR spectra of **9a**,**b** for the bridging non-equivalent methylene protons.

In 1998, Herrmann *et al.* reported the synthesis of *cis*-chelating methylene-bridged (diNHC)Pd(II) complex **10a**, *via* Wanzlick's metal acetate route resulting in a 78% yield (Scheme 1-9).[30,43]

Scheme 1-9. Synthesis of (diNHC)PdI_2 *via* the acetate route.



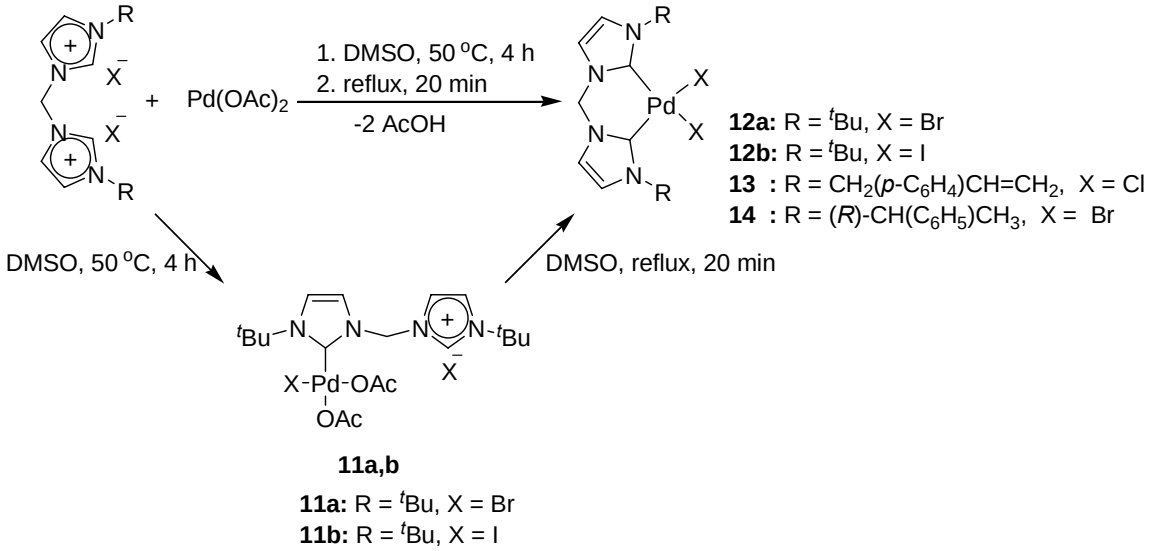
10a,b

10a: X = I
10b: X = Br

The structure of **10a** was crystallographically characterized which showed the six-membered palladacycle in a boat conformation similar to that observed by Fehlhammer *et al.* However, the bridging methylene protons exhibit a singlet in the ^{1}H NMR spectrum suggesting a fluxional behavior of the palladacycle on the NMR time scale at room temperature on a 400 MHz spectrometer. **10b** was synthesized by a similar procedure.

Herrmann *et al.* improved their above synthetic procedure and developed an efficient general synthetic protocol by optimizing the reaction conditions to involve longer reaction times, milder reaction temperatures and near quantitative yields (Scheme 1-10).[31,32] To get the best yields, the diimidazolium salt and the palladium acetate had to be heated to 50 ^{o}C in DMSO during which the intermediate palladium monocarbene complex **11** was quantitatively formed. Complex **11** was then refluxed in DMSO to obtain the desired (diNHC)PdX_2. When higher initial reaction temperatures were used for the synthesis, lower reaction yields were obtained, especially for ligands containing bulky *N*-substituents such as *tert*-butyl groups.

Scheme 1-10. Synthetic protocol for the synthesis of (diNHC)PdX_2 complexes *via* the acetate route.



Scheme 1-10 shows the synthesis of (diNHC)PdX_2 complexes with primary, secondary and tertiary alkyl substituents. (DiNHC)Pd(II) complexes are generally soluble in only highly polar solvents such as DMSO, DMF, acetonitrile, nitromethane and methanol, and are found to be insoluble in diethyl ether, dichloromethane, THF and hydrocarbons. They are also air, moisture and thermally robust, decomposing only at temperatures higher than 215 ^{o}C. The coordination environment of *cis*-chelating diNHC complexes **12b** and **14** was confirmed by X-ray crystallography which showed a distorted square-planar arrangement around the metal centre. The six-membered palladacycle adopts a fixed boat-shaped conformation as was observed in complexes **9** and **10**. The ^{1}H NMR spectrum showed two distinct doublets for the bridging methylene protons in the case of **12b**, suggesting no fast ring flipping of the palladacycle on the NMR time scale at room temperature on a 400 MHz spectrometer; whereas broad signals were obtained in the case of **12a**, **13** and **14**, suggesting a fluxional behavior of the palladacycle on the

NMR time scale at room temperature (Figure 1-13). The carbene carbons of diNHC complexes of palladium usually appear in the range of 155 - 175 ppm in the ^{13}C NMR spectra.

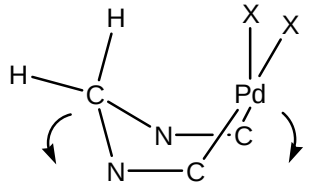


Figure 1-13. Fluxional behavior of the six-membered palladacycle.

The fluxional behavior, due to the ring inversion, in solution was studied for some complexes by determining the coalescence temperature of the two doublets.[32] It was observed that the bulkiness of the *N*-substituents and the coordinated anion had an effect on the coalescence temperature. In the case of methyl substituents and bromide anion, the ring flipping was fast at room temperature, thus producing a singlet for the bridging methylene protons in the ^{1}H NMR spectrum. Coalescence temperature for secondary alkyl substituents was found to be 128-154 ^{o}C and for tertiary alkyl substituents it was higher than 180 ^{o}C.

Sugiyama *et al.* also reported on the synthesis of several (diNHC)$PdBr_2$ corresponds with shorter reaction times compared to the previous reported synthesis of (diNHC)PdX_2 (Scheme 1-11).[33] The ^{1}H NMR spectra for **15** showed a singlet for the bridging methylene protons indicating a rapid ring flipping of the palladacycle on the NMR time scale at room temperature. However, complexes **15a-c** were not crystallographically characterized.

Scheme 1-11. Improved Synthetic protocol for the synthesis of (diNHC)PdX_2 complexes *via* the acetate route.

Strassner *et al.* prepared a variety of *cis*-chelating methylene-bridged (diNHC)Pd(II) complexes, **16a-d**, with different aryl substituents on the nitrogens (Figure 1-14) according to a similar procedure.[34] The synthesis of **17** has been patented.[35]

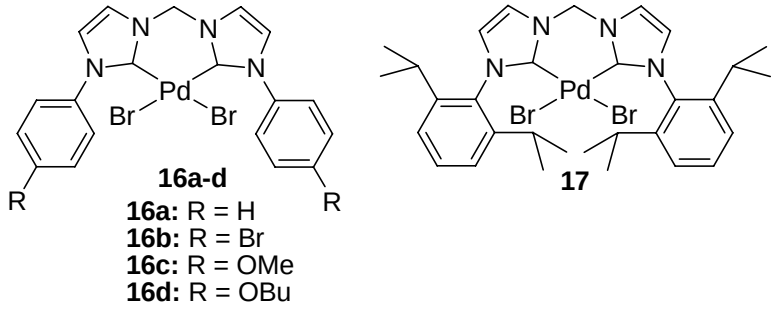
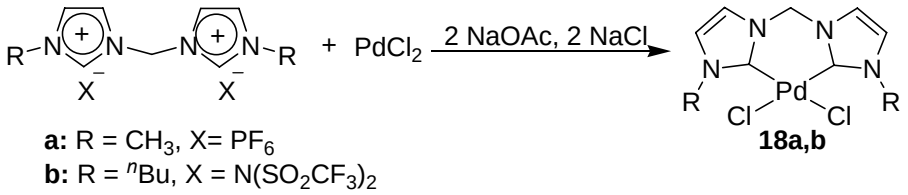


Figure 1-14. (DiNHC)$PdBr_2$ complexes with aryl substituents.

Since methylene-bridged diimidazolium dichloride salts are generally hard to synthesize using the conventional procedures, a variation of the acetate route was developed to synthesize dichloro palladium diNHC complexes (Scheme 1-12).[36] $Pd(OAc)_2$ was replaced with $PdCl_2$ as the metal precursor and NaOAc was used as the base for the *in situ* deprotonation of the carbene precursors. Diimidazolium salts with weakly coordinating anions such as PF_6^- or $N(SO_2CF_3)_2^-$ were used as the carbene

precursors. Pd black was formed while heating $PdCl_2$ and NaOAc together; therefore NaCl was added to prevent the formation of palladium black.

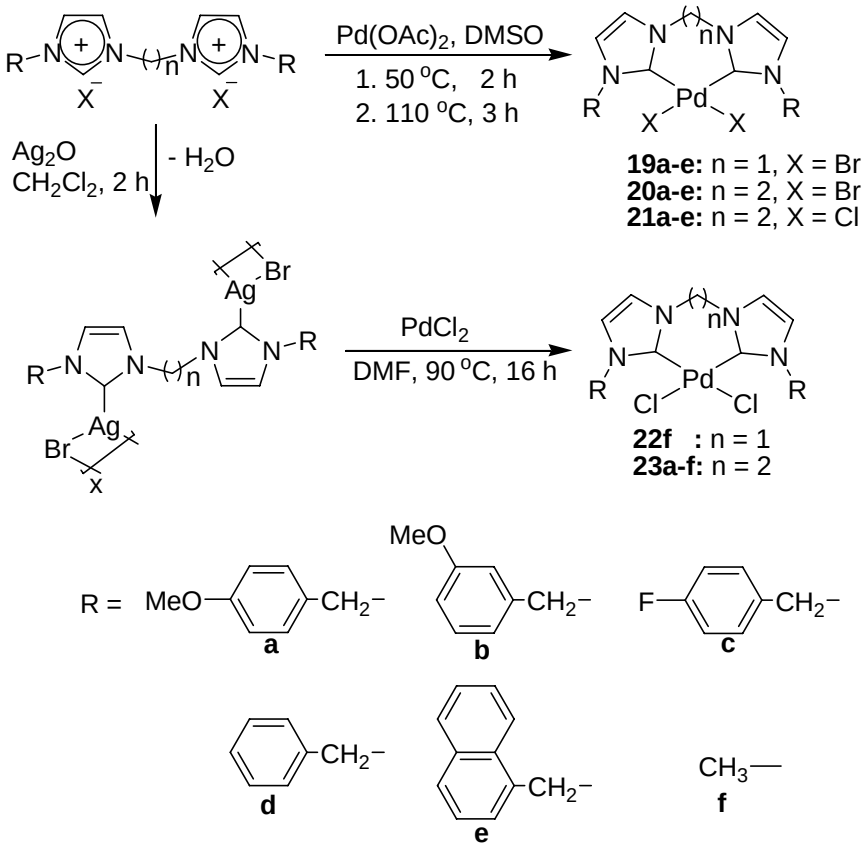
Scheme 1-12. Synthesis of (diNHC)$PdCl_2$.



a: R = CH_3, X= PF_6
b: R = ^{n}Bu, X = $N(SO_2CF_3)_2$

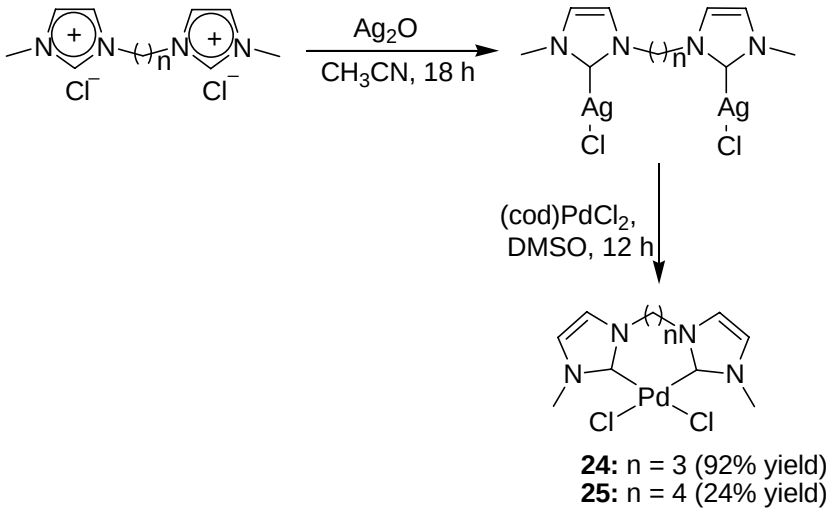
Lee *et al.* synthesized a variety of *cis*-chelating ethylene-bridged neutral (diNHC)Pd(II) complexes using Herrmann's protocol[37] as well as using the silver transmetallation route[38] (Scheme 1-13). DiNHC silver complexes can be easily prepared by using the procedure reported by Lin *et al.*[39] The diimidazolium salts are reacted with an equiv. of silver oxide at room temperature with the exclusion of light, generating the silver carbene complexes, and water is formed as a by-product. The silver carbene complexes were found to have very poor solubility and so the ^{13}C NMR spectra could not be obtained. The bridging ethylene protons in the (diNHC)Pd(II) complexes showed two separate broad signals at 4.55 ppm and 5.28 ppm. This signal broadening was attributed to the fluxional behavior of the seven-membered palladacycle in the ethylene-bridged diNHC complexes. The benzylic CH_2 protons in the Pd complexes were found to be diastereotopic exhibiting two doublets in the ^1H NMR spectra.

Scheme 1-13. Synthesis of methylene- and ethylene-bridged (diNHC)$PdCl_2$ complexes.



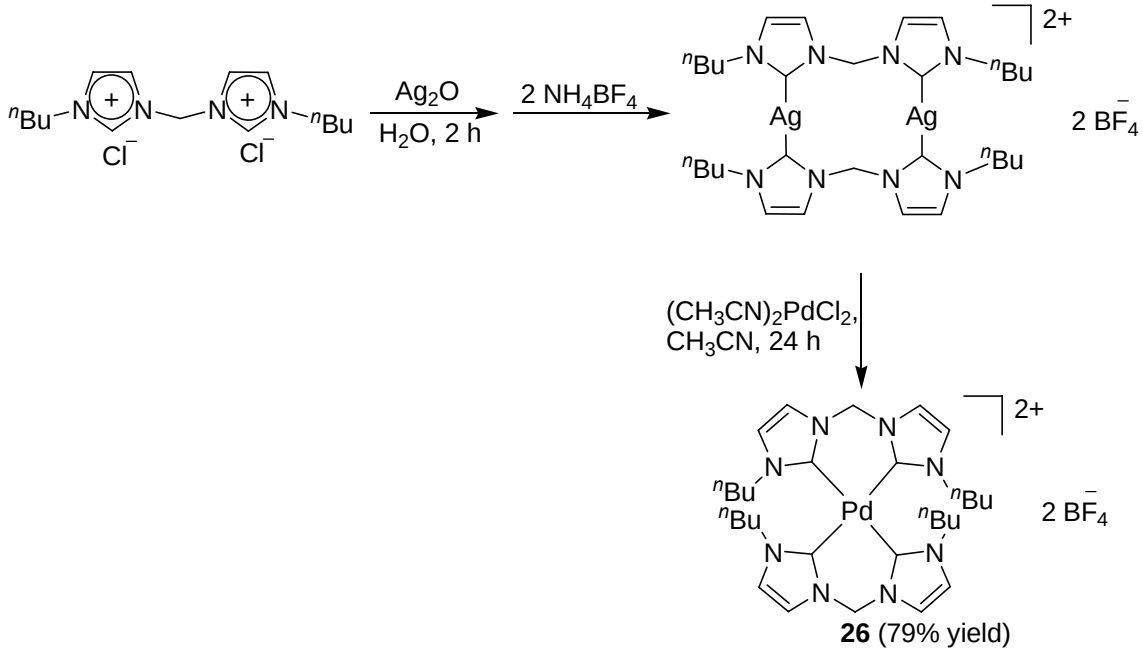
Herrmann's protocol could not be used in the synthesis of longer alkyl-bridged (diNHC)Pd(II) complexes as it led to unwanted side reactions, forming mixtures of different compounds, which were difficult to separate. Therefore, propylene- and butylene-bridged (diNHC)Pd(II) complexes have been prepared *via* the silver transmetallation route (Scheme 1-14).[40]

Scheme 1-14. Synthesis of propylene- and butylene-bridged (diNHC)$PdCl_2$ complexes.



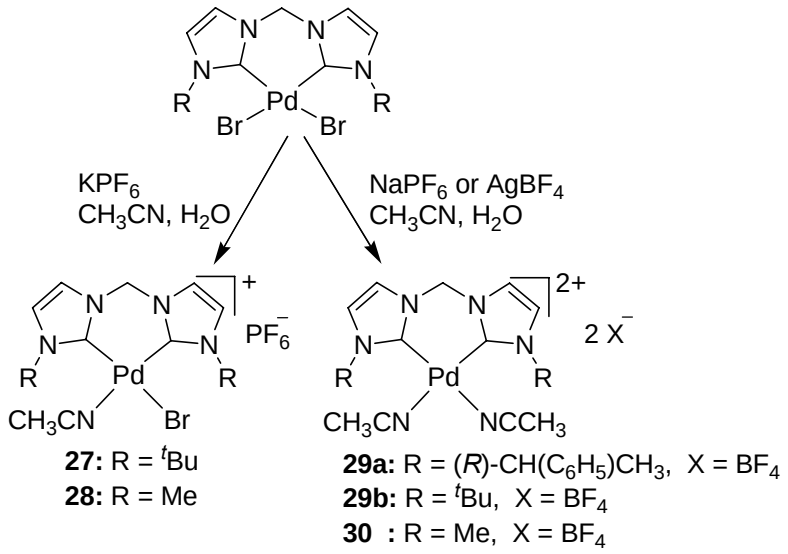
The bis(diNHC)Pd complex **26** w as synthesized *via* the silver transmetallation route (Scheme 1-15).[41] Similar bis(diNHC) palladium complexes **9a**,**b** have been synthesized before, but with very low yields (Scheme 1-8).

Scheme 1-15. Synthesis of bis(diNHC) palladium complex **26**.



Herrmann *et al.* reported on a number of mono- and dicationic *cis*-chelating methylene-bridged (diNHC)Pd(II) complexes (Scheme 1-16).[32,42]

Scheme 1-16. Synthesis of mono- and dicationic (diNHC)Pd(II) complexes.

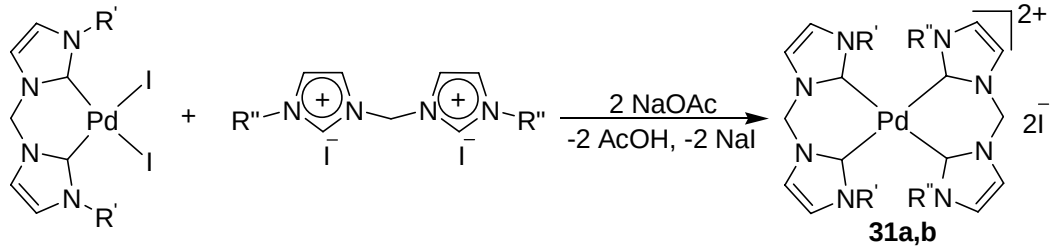


27: R = ^{t}Bu
28: R = Me

29a: R = (*R*)-CH(C_6H_5)CH_3, X = BF_4
29b: R = ^{t}Bu, X = BF_4
30 : R = Me, X = BF_4

Dicationic bis(diNHC)Pd(II) complexes have also been synthesized *via* the reaction of (diNHC)PdI_2 with diimidazolium salts with the same or different substituents on the nitrogens (Scheme 1-17).[43]

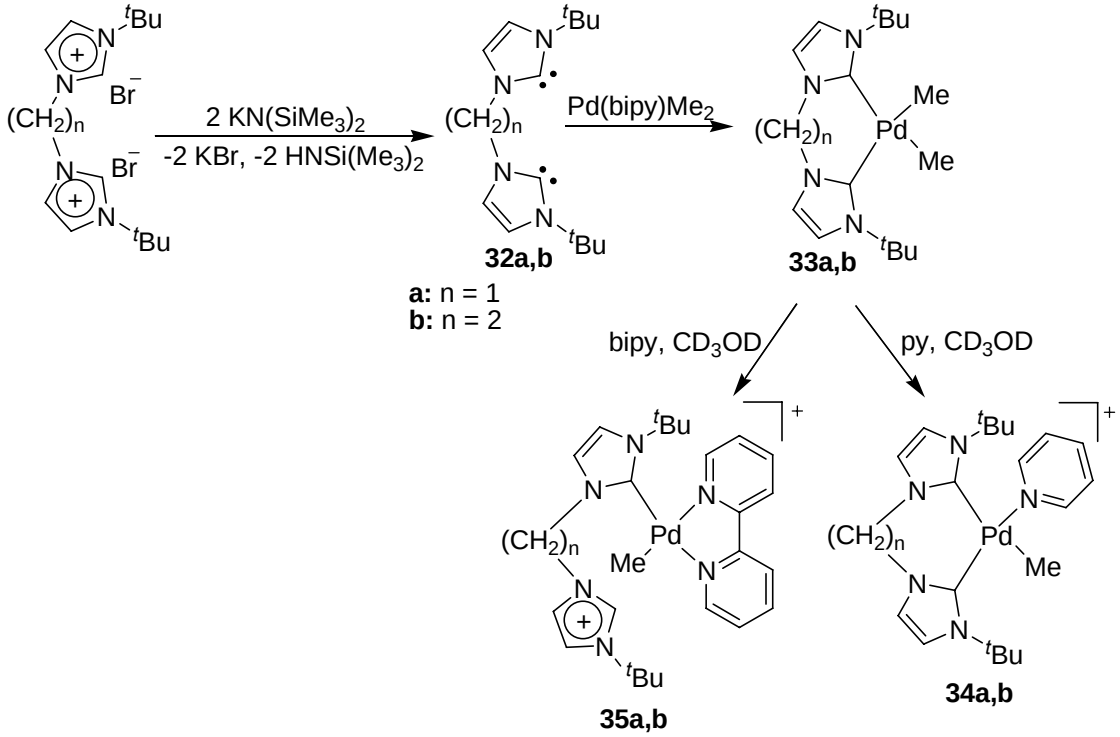
Scheme 1-17. Synthesis of mixed bis(diNHC)Pd(II) diiodide.



31a,b
31a: R' = Me, R'' = Me
31b: R' = Me, R'' = Cy

Green *et al.* synthesized neutral and monocationic, methylene- and ethylene-bridged (diNHC)Pd(II) methyl complexes (Scheme 1-18).[44] The synthesis involved the deprotonation of the diimidazolium salt using $KN(SiMe_3)_2$ as the base to generate the neutral diNHC **32a**,**b**, which was then reacted with $Pd(bipy)Me_2$ to generate complexes **33a**,**b** which are stable at room temperature for days. Addition of an equiv. of pyridine to complexes **33a**,**b** in deuterated methanol generated complexes **34a**,**b**. Addition of an equiv. of bipyridine in air to complexes **33a**,**b** in deuterated methanol generated complexes **35a**,**b**. This type of complex has been previously reported by Herrmann *et al.* **11a**,**b**.[28] **34a**,**b** and **35a**,**b** were not crystallographically characterized.

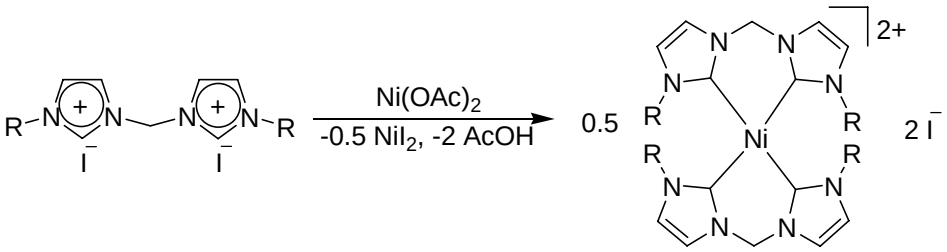
Scheme 1-18. Synthesis of (diNHC)Pd(II) methyl complexes.



1.2.1.2 Alkane-bridged diNHC nickel complexes

Compared to (diNHC)Pd(II), there are relatively few (diNHC)Ni(II) complexes reported in literature. In 1999, Herrmann *et al.* synthesized the first chelating (diNHC)Ni(II) complex *via* the acetate route (Scheme 1-19), initially described by Öfele *et al*.[43] Attempts to make methylene-bridged (diNHC)NiX_2 (X = halogen) complexes from the reaction of $Ni(OAc)_2$ with diimidazolium salts exclusively yielded a dicationic Ni(II) species with the general formula $[(diNHC)_2Ni]^{2+}$.[43]

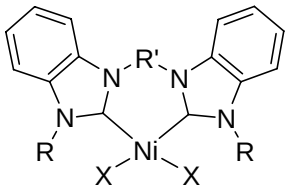
Scheme 1-19. Synthesis of bis(diNHC)NiI_2.



36a-c

36a: R = Me
36b: R = ^{i}Pr
36c: R = Cy

Formation of the neutral *cis*-dihalide complexes was never obtained even with sterically bulky *N*-substituents such as isopropyl and cyclohexyl. This is in sharp contrast to the analogous palladium reaction which readily yields the (diNHC)PdX_2 species as the preferred product.[30-33] No reaction was observed with sterically bulky *tert*-butyl substituents on the nitrogens. However, in 2009, benzimidazolylidene-based, propylene-bridged (diNHC)NiX_2 complexes were synthesized by Bouwman *et al*. (Figure 1-15).[45]



R = Me, R' = propylene, X = Br
R = Pr, R' = propylene, X = Br
R = ^{i}Pr, R' = propylene, X = Br
R = Bz, R' = propylene, X = Br

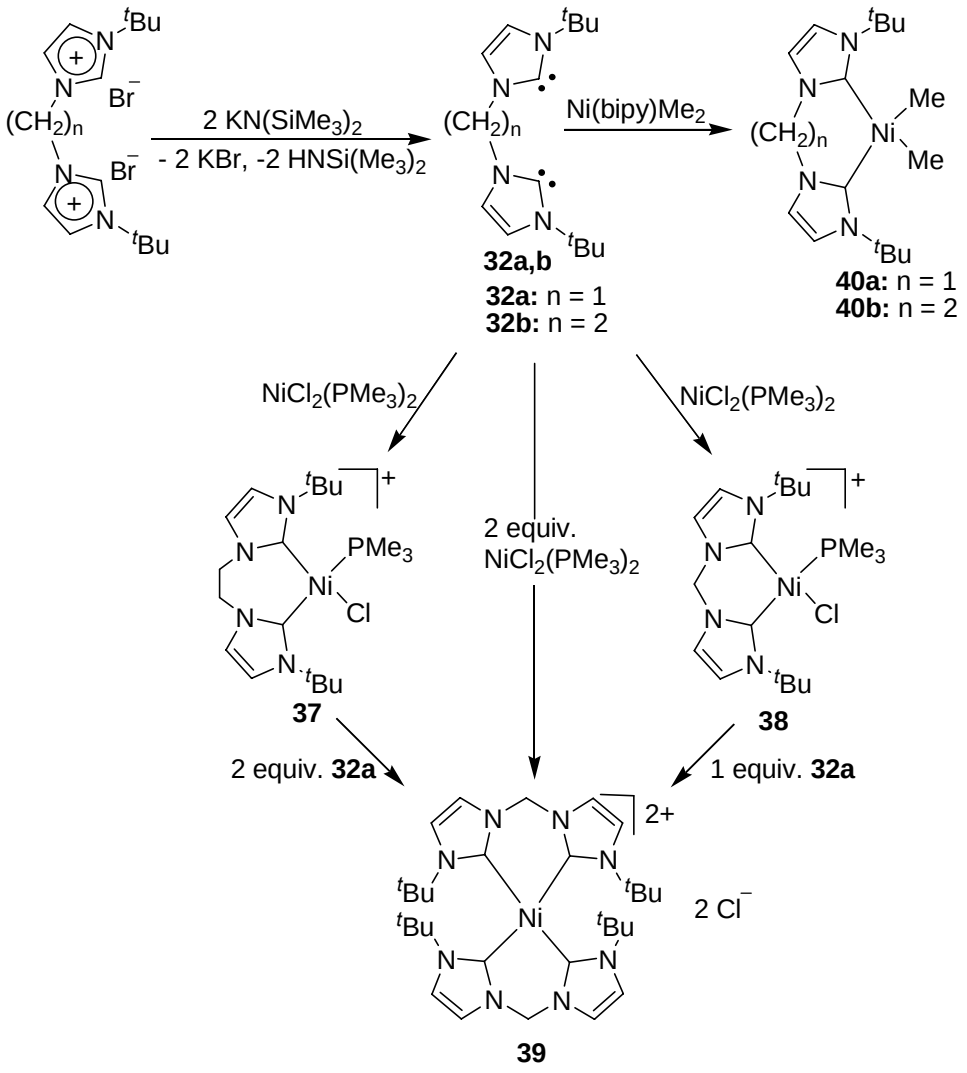
R = Ph, R' = propylene, X = Br
R = Me, R' = propylene, X = Cl
R = Me, R' = butylene, X = Br
R = Me, R' = butylene, X = Cl

Figure 1-15. Benzimidazolylidene-based, propylene-bridged (diNHC)NiX_2 complexes.

The complexes **36a-c** are soluble only in polar solvents such as DMSO and hot MeOH. The complexes also exhibit excellent air, moisture and thermal stability, decomposing only at temperatures higher than 225 ^{o}C in the solid state. The ^{1}H NMR spectrum showed two doublets for the bridging methylene protons which were unaffected even at 150 ^{o}C on a 400 MHz spectrometer. This indicates the retention of the boat-shaped six-membered nickelacycle even at high temperatures.

In 1999, Green *et al.* reported on the synthesis of dicationic methylene-bridged bis(diNHC) and monocationic ethylene- and methylene-bridged diNHC complexes of nickel (Scheme 1-20).[46] The synthesis involved the deprotonation of the diimidazolium salt using $KN(SiMe_3)_2$ to generate the neutral diNHC, **32a**,**b**, which was then reacted with $NiCl_2(PMe_3)_2$ to generate complexes **37** and **38**. Reaction of $NiCl_2(PMe_3)_2$ with two equiv. of **32a** gave the dicationic methylene-bridged bis(diNHC)Ni(II) complex **39**, which can also be prepared from **37** or **38** (Scheme 1-20). Ethylene-bridged analogues to **39** could not be synthesized. X-ray crystallography showed **39** in a *trans* double-boat conformation. Green *et al.* also reported on the neutral *cis*-diNHC methyl complexes of nickel, **40a**,**b**.[47]

Scheme 1-20. Synthesis of (diNHC)Ni(II) complexes.

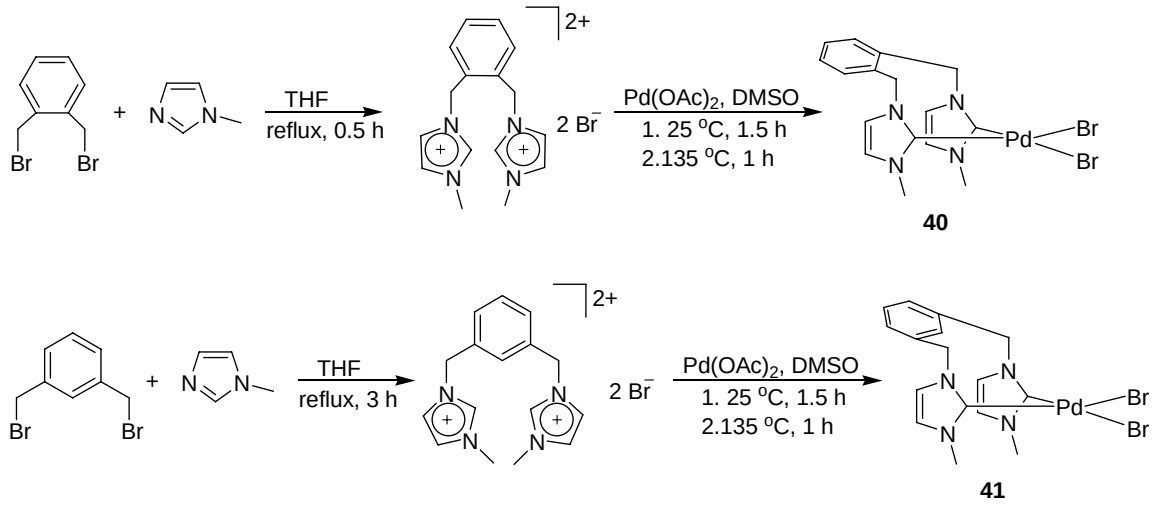


1.2.2 Arene-bridged diNHC complexes

The first examples of arene-bridged (diNHC)Pd(II) complexes were reported by Cavell *et al.*[48] The ligand precursors were synthesized by the reaction of the methyl imidazole with *meta*/*ortho* dibromoxylene (Scheme 1-21). The solubility of the complexes is very poor in most organic solvents, but it is soluble in DMSO. The carbene carbons appear at δ 160 in the ^{13}C NMR spectrum of the arene-bridged (diNHC)Pd(II)

complex, **40**. The methylene protons are diastereotopic and show two doublets in the ^{1}H NMR spectrum. **41** gave very broad signals in ^{1}H NMR spectrum, which did not resolve even at 90 ^{o}C. Due to the low solubility of the complex in NMR solvents, low temperature NMR experiments could not be carried out. The complex has not been crystallographically characterized and so the true geometry of the complex is not known.

Scheme 1-21. Synthesis of arene-bridged (diNHC)Pd(II) complexes.



Baker *et al.* have also reported on similar arene-bridged (diNHC)Pd(II) complexes (Figure 1-16).[49] Complexes **42** and **43** were synthesized using the metal acetate route in 31% and 47% yield, respectively. The palladium complex **42** exhibited good solubility in dichloromethane, chloroform, acetone and DMSO due to the presence of alkyl chains.

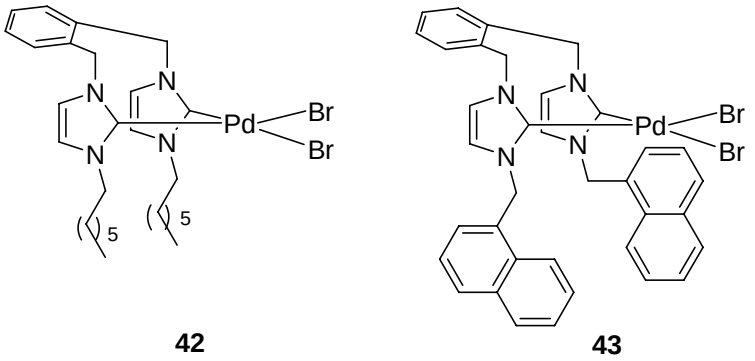
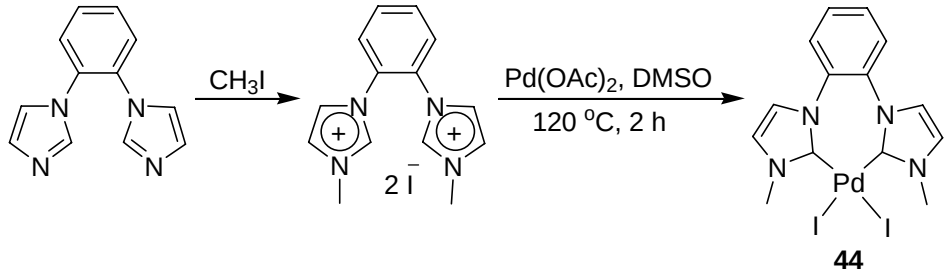


Figure 1-16. Arene-bridged (diNHC)Pd(II) complexes.

Biffis *et al.* have also reported on the synthesis of an aryl-bridged (diNHC)Pd(II) complex (Scheme 1-22).[50] The ligand precursor was synthesized by the reaction of methyl iodide with 1,1'-(1,2-phenylene)bis(imidazole) in 71% yield. Palladium complex **44** was synthesized *via* the metal acetate route in 70% yield, but it has not been crystallographically characterized.

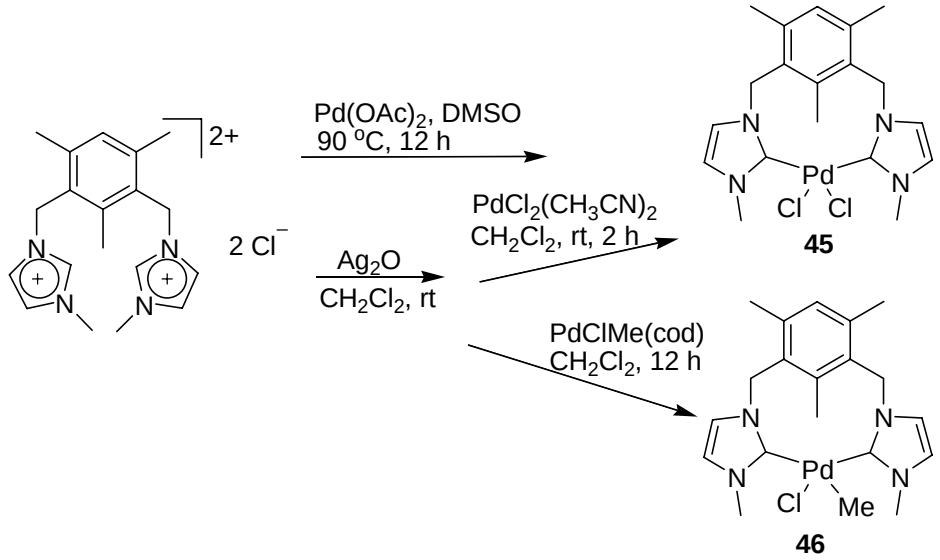
Scheme 1-22. Synthesis of phenylene-bridged (diNHC)Pd(II) complex **44**.



A number of 2,4,6-trimethylbenzene-bridged (diNHC)Pd(II) complexes have been described by Alcalde *et al.* [51] The palladium complex **45** was synthesized *via* the metal acetate route as well as the transmetallation route (Scheme 1-23). The complex exhibited broad signals in the ^{1}H NMR spectrum. There were two sets of signals in the

^{13}C spectrum, one major set of broad signals and another minor set of sharp signals. There was a sharp signal at 170.18 ppm and another broad signal at 169.60 ppm for the carbenic carbon. It was proposed that this was due to both the *trans* and *cis* diNHC palladium complexes in solution.[51] The palladium methyl complex **46** was also synthesized *via* the transmetallation route. Complexes **45** and **46** were not crystallographically characterized.

Scheme 1-23. Synthesis of 2,4,6-trimethylbenzene-bridged diNHC palladium complex.



There are no examples of arene-bridged bidentate (diNHC)Ni(II) complexes known in literature.

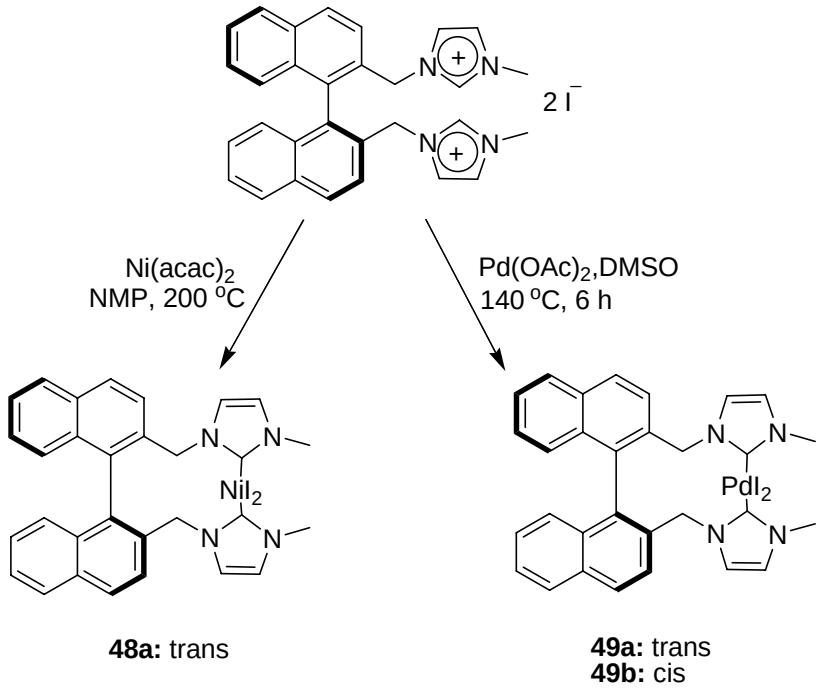
1.2.3 Chiral motive-bridged diNHC complexes

Chirality in the ligand backbone can lead to the generation of chiral catalysts that have found applications in asymmetric catalysis. However, the synthesis of the ligand

precursors that introduce chirality into the complexes often involves multiple steps. To date, there are only two examples of chiral motive-bridged diNHC complexes of palladium and nickel. The first example uses a binaphthyl bridged diNHC ligand precursor and the second example uses cyclohexyl as the bridging unit. The first example of a chiral motive-bridged diNHC complex of palladium and nickel was reported in 2000 by Rajanbabu *et al*.[52] The two imidazolylidene units were linked *via* a binaphthyl linker that introduced chirality into the system (Scheme 1-24).

The ligand precursor was reacted with $Pd(OAc)_2$ in DMSO. Both the *trans* and the *cis* diNHC palladium complexes were formed which were separated *via* chromatography and were obtained in 41% and 33% yield, respectively. The geometry of the complexes was confirmed by X-ray crystallography.

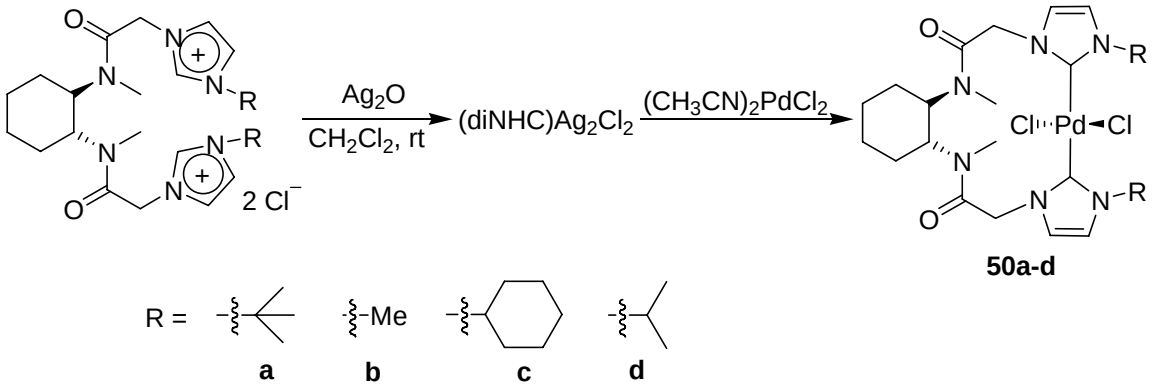
Scheme 1-24. Synthesis of chiral motive-bridged diNHC complexes.



The nickel complex was synthesized *via* the reaction of the diimidazolium salt with $Ni(acac)_2$ (Scheme 1-24).

The second example of a chiral motive-bridged diNHC complex of palladium was reported by Perry *et al*. The chiral *trans* diNHC complexes of palladium were synthesized *via* the silver transmetallation route (Scheme 1-25).[53]

Scheme 1-25. Synthesis of diNHC nickel complexes.



1.3 Tridentate diNHC complexes of Palladium and Nickel

Figure 1-17 shows a picture of a pincer diNHC carbene ligand on a metal (M). The donor (D) could be neutral (for example a pyridine ring) or anionic (for example a phenyl ring), thus giving rise to monocationic or neutral complexes in the case of palladium(II).

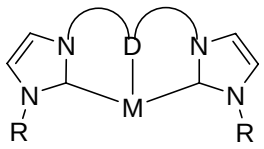
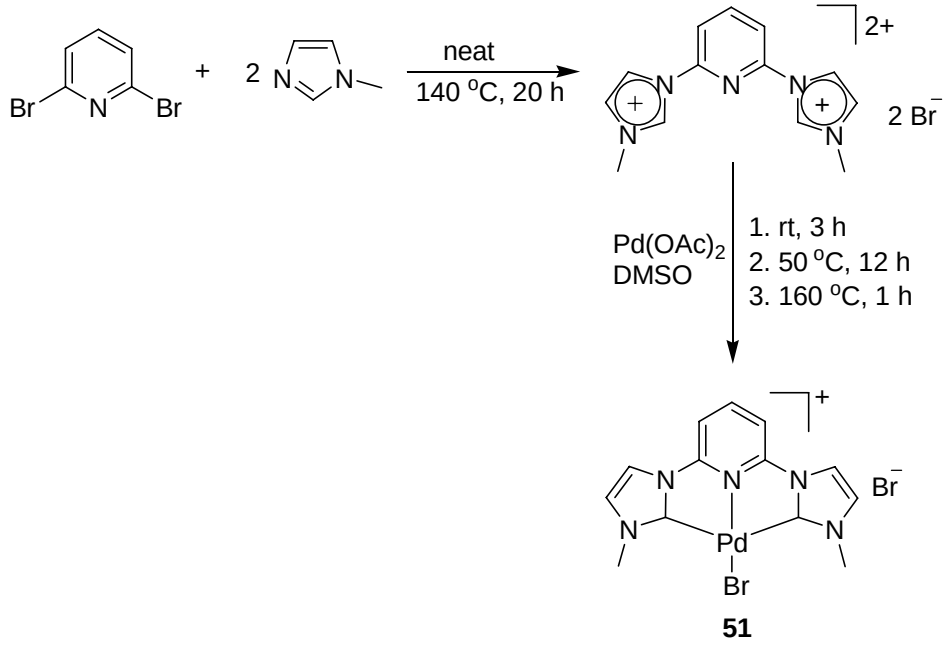


Figure 1-17. Chelating tridentate diNHC complex.

The first example of a pincer (*mer*, tridentate) diNHC palladium complex was reported in 2001 by Crabtree *et al.*[54] The carbene precursor *i.e.*, the diimidazolium salt, was synthesized by a neat reaction of *N*-methylimidazole in 2,6-dibromopyridine according to the procedure reported by Lin *et al*.[55] The diimidazolium salt was then reacted with $Pd(OAc)_2$ to give a pale yellow precipitate of the pincer (*mer*, tridentate) (diNHC)Pd(II) complex, **51**, in 70% yield (Scheme 1-26). X-ray crystallography showed that the molecule was basically flat and that the Pd-C distance is longer than in cis-chelating (diNHC)Pd(II) complexes; which was considered to be due to the *trans*-effect of the carbene ligands.

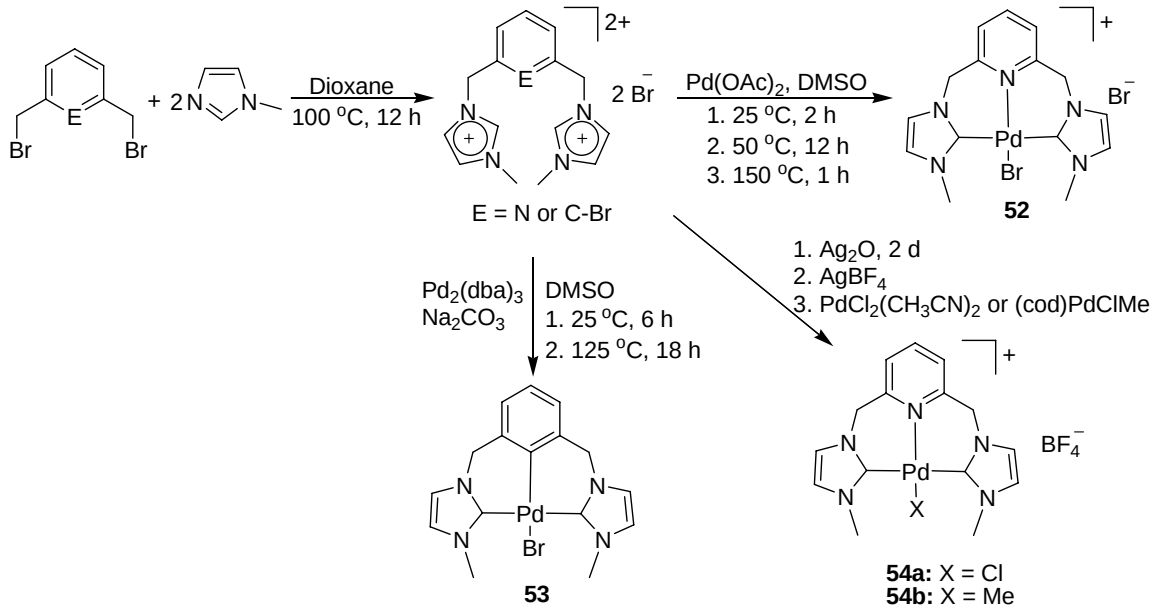
Scheme 1-26. Synthesis of tridentate (diNHC)Pd(II) complex **51**.



51

The palladium complex **51** had poor solubility and Crabtree *et al.* found that a CH_2 spacer between the rings, such as in **52**, increases the solubility and leads to complexes with twisted geometries as shown in Figure 1-18.[56] They also reported on the first examples of a neutral CCC pincer carbene Pd(II) complex, **53** (Scheme 1-27). The CCC precursor underwent an oxidative addition of the C-Br bond to Pd(0) generating the C-Pd-Br. Both complexes decompose only above 230 °C in solid state. Cavell *et al.* also reported on the synthesis of a similar CNC palladium complexes **54a**,**b** using the silver transmetallation route (Scheme 1-27).[57]

Scheme 1-27. Synthesis of tridentate (diNHC)Pd(II) complexes.



The benzylic CH_2 protons appear as two sharp doublets in the ^{1}H NMR spectrum of **53**, whereas they appear as a broad singlet in **52**, which was speculated to be due to the dynamic behavior of the rings as shown in Figure 1-18. The broad signal splits into two sharp doublets at -50 °C. Similarly the two sharp doublets in **53** achieved coalescence at 77 °C Variable-temperature ^{1}H NMR studies on complex **52** and **53** confirmed this dynamic process (Figure 1-18). There exists a rapid interconversion between the left- and right-handed twisted conformations, **A** and **B**. When the interconversion is fast, an average structure, **C**, with C_{2V} symmetry is observed in the NMR.

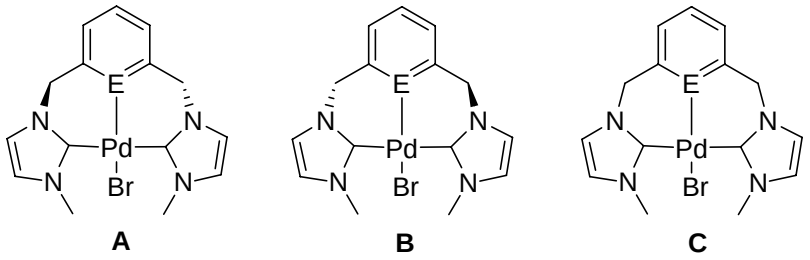


Figure 1-18. Atropisomerization of tridentate (diNHC)Pd(II) complexes in solution.

Chiral ligands play a crucial role in transition metal catalyzed asymmetric synthesis.[58] Ligands with C_2 symmetry have proven to properly control metal-catalyzed asymmetric reactions as demonstrated by diphosphines, 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), bisoxazoline (BOX), etc. In 2001, Danopoulos *et al.* reported on the synthesis of two *trans*-chelating pincer CNC Pd(II) complexes *via* the silver transmetallation route, by reaction of their corresponding silver complexes with $(cod)PdCl_2$ in CH_2Cl_2 (Figure 1-19).[59] X-ray crystallography showed that the complexes **55a,b** exhibit a helical structure with a C_2 axis along the N-Pd-Cl axis, thus generating chirality in the system as a result of the twisting around the C_2 axis, as explained above in Figure 1-18. This could be due to the puckering of the two six-membered chelate rings and the steric bulk of the nitrogen substituents. Variable temperature ^1H NMR studies indicated that the interconversion of the conformers do not take place even at 80 ^oC on a 300 MHz spectrometer. Chiral diNHC complexes are very rare in literature.

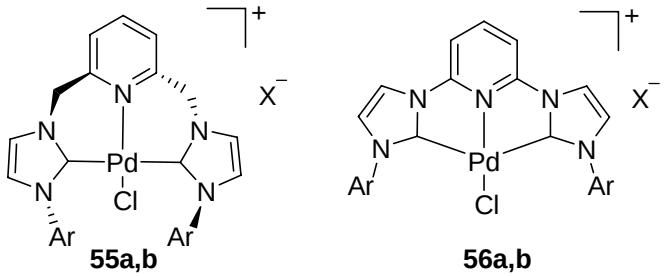


Figure 1-19. Cationic CNC Pd(II) complexes with aryl substituents.

Crabtree *et al.* have reported on the synthesis of a similar CNC Pd(II) complex, **57a**, *via* the metal acetate route[60] and Youngs *et al.* have reported on the synthesis of the CNC Pd(II) complex, **57b**, *via* the silver transmetallation route[61] (Figure 1-20). Cavell *et al.* have also reported on the synthesis of CNC Pd(II) complex **58** *via* the silver transmetallation route.[62]

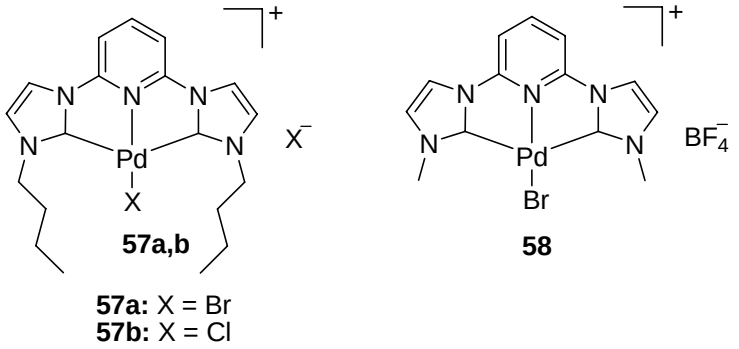


Figure 1-20. Cationic CNC Pd(II) complexes.

There is also one example of a pincer amine (diNHC)Pd(II) complex **59** synthesized by Douthwaite *et al. via* the silver transmetallation route.[63] The complex exhibits atropisomerization, interconverting between the two enantiomers at room

temperature as shown in Figure 1-21. The corresponding diNHC amido complex was synthesized by the reaction of **59** with NaH.

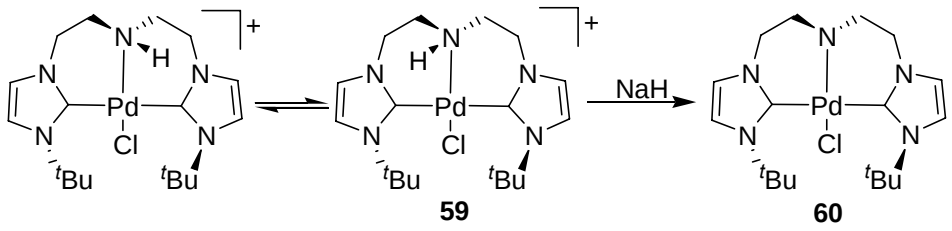
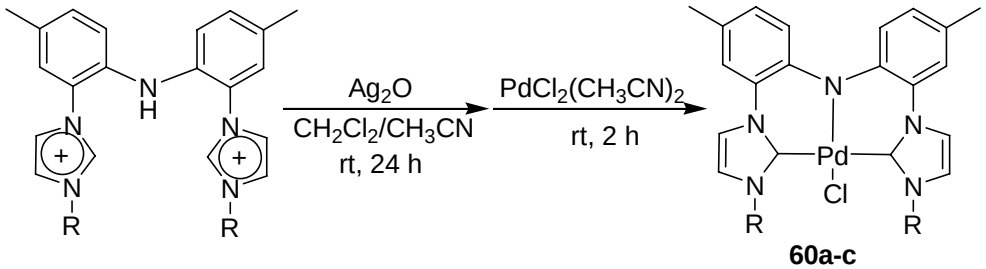


Figure 1-21. Atropizomerization of **59** and synthesis of **60**.

Luo *et al.* have also synthesized pincer amido (diNHC)Pd(II) complexes, **60a-c**, incorporating a rigid diarylamido backbone *via* the silver transmetallation route (Scheme 1-28).[64]

Scheme 1-28. Synthesis of pincer amido (diNHC)Pd(II) complexes.



60a-c

60a: R = Bz
60b: R = ^{n}Bu
60c: R = 2,4,6-trimethylbenzyl

Inamoto *et al.* were the first to synthesize a pincer (diNHC)Ni(II) complex, **61**, *via* the metal acetate route.[65] They have reported on similar pincer (diNHC)Ni(II) complexes with aromatic substituents (Figure 1-22).[66]

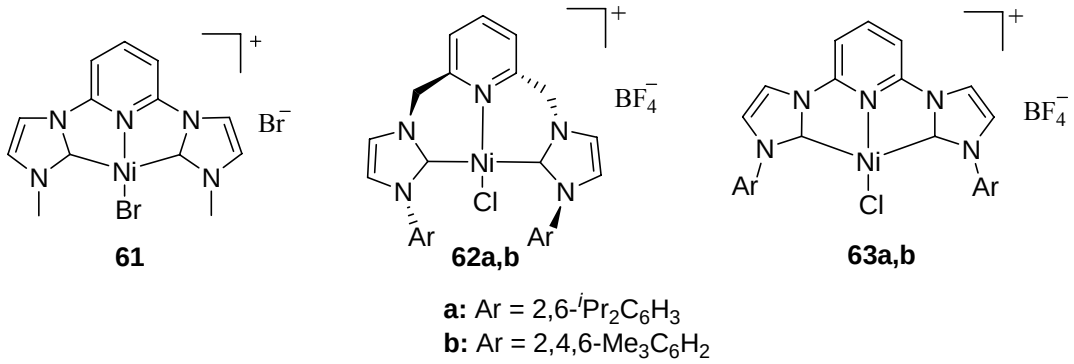


Figure 1-22. Pincer (diNHC)Ni(II) complexes.

Danopoulos *et al.* have also synthesized a similar pincer (diNHC)Ni(II) complex *via* the free carbene route, **64** (Figure 1-23).[67]

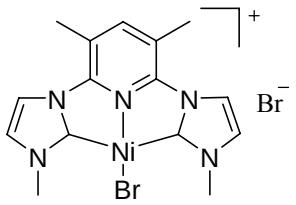
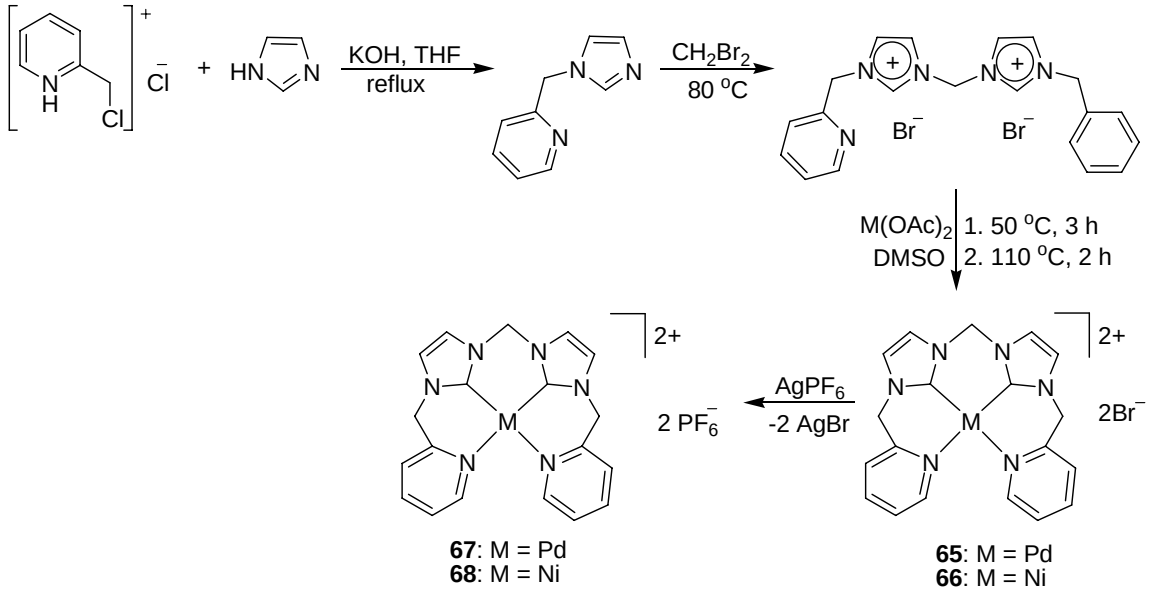


Figure 1-23. Pincer (diNHC)Ni(II) complex **64**.

1.4 Tetradentate diNHC complexes of Palladium and Nickel

While there are many examples of bi- and tridentate diNHC complexes of palladium and nickel in literature, there are fewer examples of tetradentate diNHC complexes of palladium and nickel. In 2005, Lee *et al.* synthesized the first examples of tetradenate diNHC complexes with hemi-labile pyridine arms (Scheme 1-29).[68]

Scheme 1-29. Synthesis of tetradentate diNHC complexes with hemi-labile pyridine arms.



The ligand precursor (the diimidazolium salt) was synthesized by reaction of the *N*-substituted imidazole with neat dibromomethane. The diimidazolium salt is highly hygroscopic and dissolves only in highly polar solvents such as DMSO and DMF. The metal complexes were synthesized *via* the metal acetate route. The (diNHC)Pd(II)

complex **65** was an air-sensitive, dark-yellow solid, whereas the (diNHC)Ni(II) complex **66** had better air-stability and was greenish-yellow in color. Both complexes were soluble only in DMSO and DMF. The ^{1}H NMR spectra consisted of sharp signals at room temperature. With only ^{1}H NMR spectroscopy it was challenging to discern if it was a neutral complex with no coordinated pyridine, or a dicationic complex with the pyridine arms coordinated to the metal. Both kinds of complexes exhibited similar solubilties. The general downfield shift of the pyridine protons compared to the ligand precursor was attributed to a tetradentate chelation. In the ^{1}H NMR spectrum, the methylene protons connecting the two imidazole rings, and the methylene protons connecting the pyridyl and the imidazole units are observed as two sharp singlets. The authors suggested that it could be due to the absence of a rigid tetradentate framework, indicating a fast exchange process in solution which makes the two otherwise diastereotopic protons chemically equivalent.

Two exchange mechanisms were proposed to explain this fluxional behaviour or the fast exchange process (Figure 1-24). To investigate which one of the two pathways was taking place; complexes **65** and **66** were reacted with $AgPF_6$ to give the complexes **67** and **68** by a metathesis reaction. The ^{1}H NMR spectra were found to be similar showing singlets for the methylene groups. Since PF_6^{2-} is a non-coordinating anion the possibility of a pathway B (Figure 1-24) or the chelate ring twisting looked more probable. Theoretical computation on **65** and **66** demonstrated that the sterically congested tetradentate coordination is energetically more stable when compared to bidentate coordination with dangling picolyl arms (**B** and **C** in Figure 1-24). Signal broadening was observed at low temperature in the NMR and separation of the signals

could not be obtained even when the samples were cooled to the low-temperature limit of the NMR solvents (DMF-d_7 for **65/66** and CD_2Cl_2 for **67/68**) suggesting that the twisting process is very rapid on the NMR time scale.

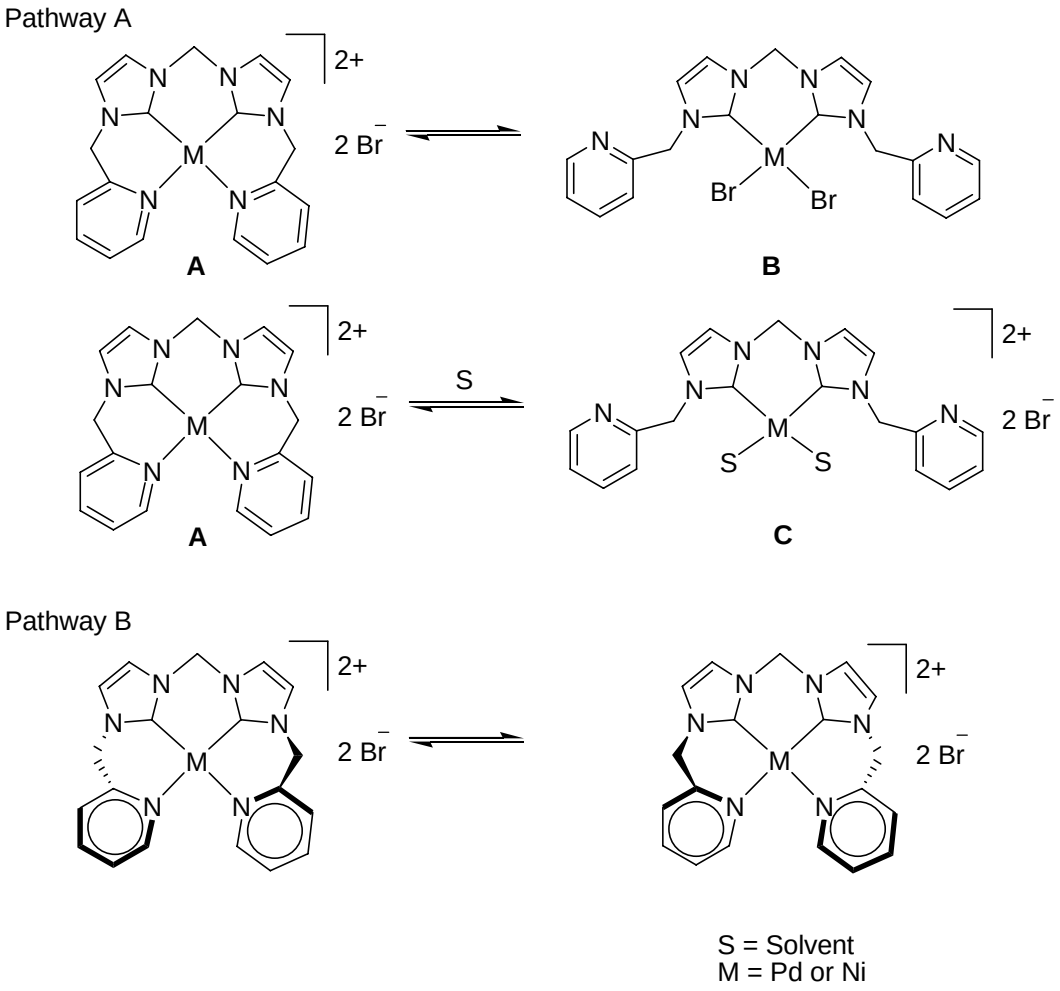
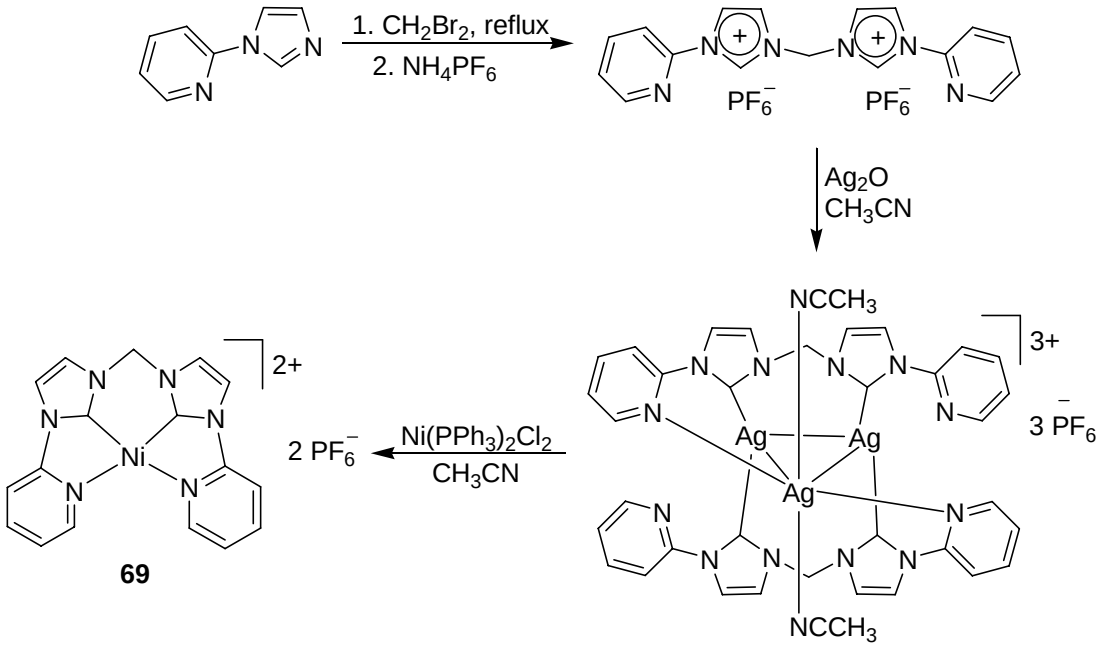


Figure 1-24. Proposed exchange mechanisms for complexes **65** and **66**.

In 2007, Chen *et al.* synthesized a very similar tetradentate diNHC nickel complex **69**, *via* the silver transmetallation route in 73% yield (Scheme 1-30).[69] The ligand precursor (the diimidazolium salt) was synthesized by refluxing 2-(imidazolyl)pyridine in dibromomethane. The resulting white precipitate was filtered and

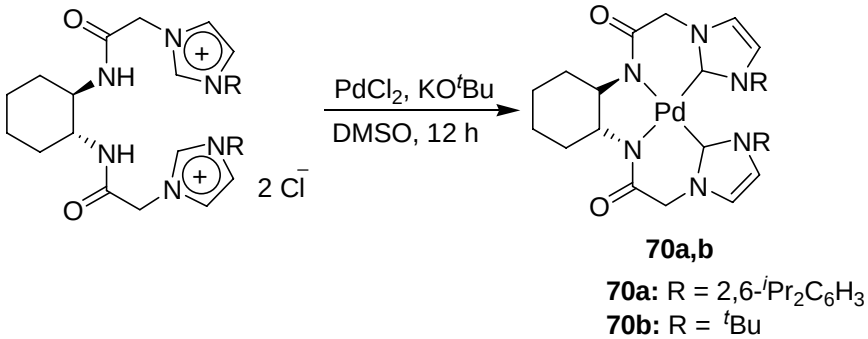
reacted with NH_4PF_6 in an aqueous solution, to yield the ligand precursor as a white precipitate in 98% yield.

Scheme 1-30. Synthesis of tetradentate diNHC nickel complex.



Finally Perry *et al.* have also synthesized the neutral tetradentate diNHC palladium(II) complexes **70a,b** (Scheme 1-31).[53]

Scheme 1-31. Synthesis of tetradentate diNHC palladium complex.



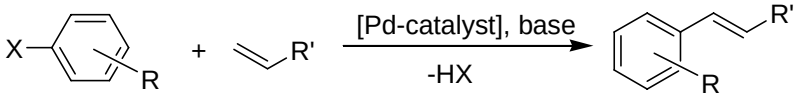
1.5 Applications of diNHC complexes of Palladium and Nickel

Herrmann *et al.* were the first to employ chelating diNHCs as spectator ligands in organometallic catalysis.[30] These *cis*-chelating diNHC ligands provide additional entropic stability to their complexes besides the strong M-$C_{carbene}$ bond. Chelating (diNHC)Pd(II) complexes have been used for a variety of catalytic applications, but mostly for carbon-carbon coupling reactions.

Carbon-carbon bond forming reactions play a very fundamental role in organic transformations. Over the past four decades, considerable research has been dedicated towards the development of highly efficient palladium-based systems that can catalyze the Mizoroki-Heck[70] and Suzuki-Miyaura[71] coupling reactions, which are amongst the most powerful tools for the formation of carbon-carbon bonds (Scheme 1-32).[72]

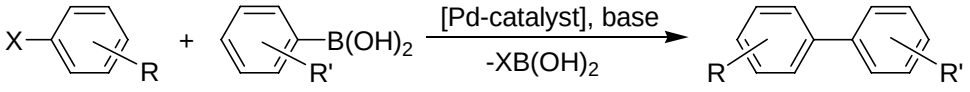
Scheme 1-32. Carbon-carbon coupling reactions.

Mizoroki-Heck reaction



X = halides or triflates

Suzuki-Miyaura reaction



X = halides or triflates

Palladacycles and monodentate NHC complexes of palladium are by-far the most active precatalysts known in literature for carbon-carbon coupling reactions. Some of them are commercially available precatalysts (Figure 1-25).[73]

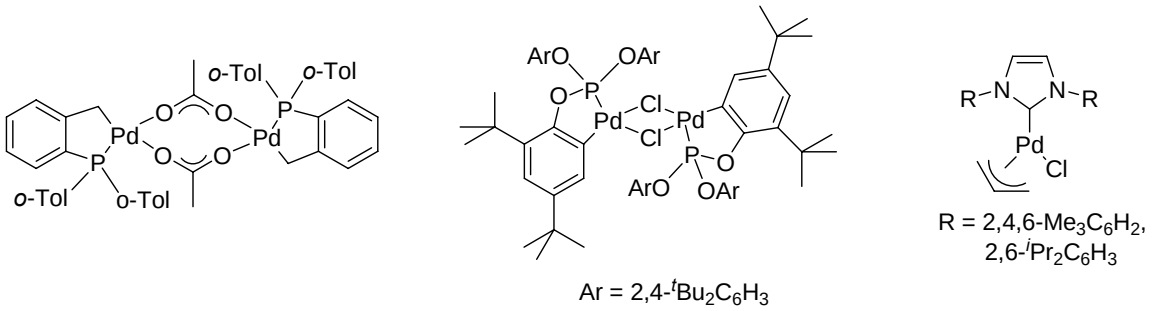


Figure 1-25. Examples of commercially available precatalysts for C-C coupling reactions.[69]

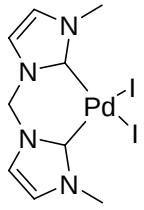
NHCs are strong sigma-donors that render the oxidative addition of aryl halides to palladium more readily.[74] Several examples of *cis*-chelating (diNHC)Pd(II) complexes have also been shown to efficiently catalyze cross-coupling reactions, such as Mizoroki-Heck and Suzuki-Miyaura coupling reactions.

Some of the challenges in C-C coupling reactions are:

1. Coupling of deactivated substrates, *i.e.,* substrates with electron donating substituents.
2. Coupling of aryl chlorides. These are abundant substrates but challenging to couple, compared to aryl bromides and aryl iodides.
3. Coupling of sterically hindered substrates.
4. Coupling of alkyl halides.
5. Formation of sp^3-sp^3 carbon-carbon bonds.

The activity of a catalyst depends on several factors, such as temperature, solvent, base, additives, concentration of the catalyst, moisture, atmosphere, etc. However, all things considered, it is the turnover number (TON) of the catalytic reaction that determines the potential of a complex as a catalyst. The TON is defined as the number of moles of product formed per mole of the catalyst.

The catalytic activity of chelating diNHC palladium complexes for carbon-carbon coupling reactions was first studied by Herrmann *et al*.[30]



10a

Figure 1-26. The first *cis*-chelating (diNHC)Pd(II) complex employed as a catalyst.

Herrmann *et al.* obtained a TON of 190 for the Heck coupling reaction of 4-bromoanisole with butyl acrylate, and 120 for 4-chloroacetophenone with butyl acrylate, using complex **10a** as catalyst (Figure 1-26). A TON of 60 was obtained in the Suzuki coupling reaction of 4-chloroacetophenone and TON of 80 for 4-bromoanisole with phenylboronic acid, respectively.

The catalytic activity of methylene-bridged (diNHC)Pd(II) complexes shown in Figure 1-27 were evaluated in the Heck coupling reaction of styrene with aryl halides by Strassner *et al.* (Table 1-1).[34]

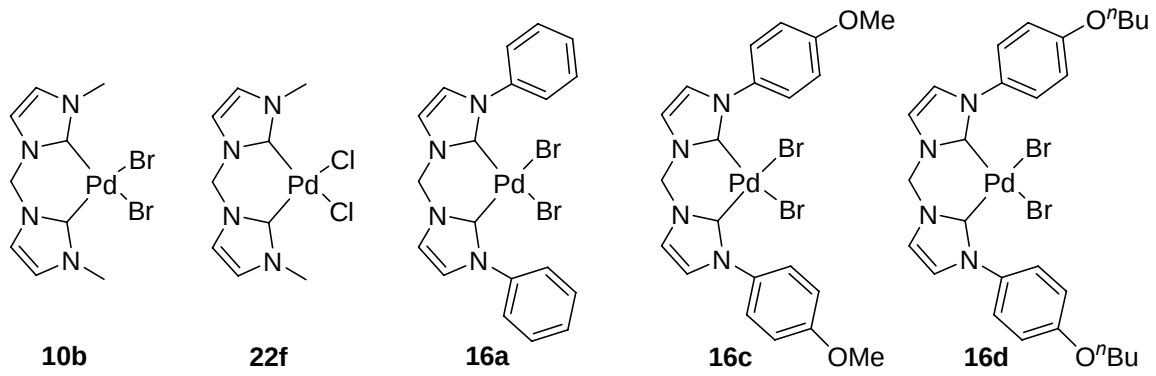
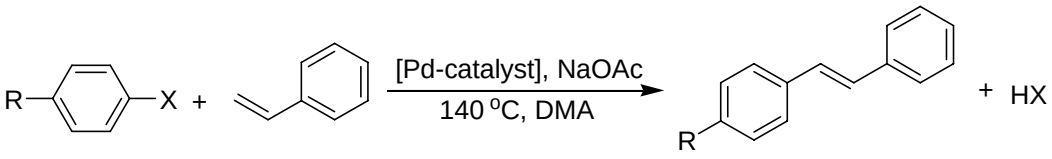


Figure 1-27. *Cis*-chelating (diNHC)Pd(II) complexes employed as catalysts.

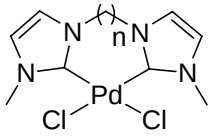
TONs of over to 700000 were obtained in the coupling reaction of styrene with bromoacetophenone (Table 1-1, entry 6). Complexes **16d** and **16c** with electron donating groups on the *para* position of the phenyl substituents were found to be the most active catalysts. **16d** gave a TON of 36000 in the coupling reaction of styrene with bromoanisole, which is a deactivating substrate (Table 1-1, entry 11) and **16c** gave a TON of 1000 in the coupling reaction of styrene with chloroacetophenone (Table 1-1, entry 12). There was no remarkable difference in the catalytic activity of (diNHC)Pd(II) bromide **10b**, and (diNHC)Pd(II) chloride **22f**, as seen from entries 1 and 2, and entries 7 and 8 of Table 1-1, indicating that the nature of the halides play little role in determining the activity of a precatalyst.

Table 1-1. Heck coupling reaction using methylene-bridged (diNHC)Pd(II) complexes.



Entry	R	X	Catalyst	mol% Catalyst	t (h)	TON
1	$C(O)CH_3$	Br	**10b**	0.5	8	80
2	$C(O)CH_3$	Br	**22f**	0.5	8	114
3	$C(O)CH_3$	Br	**22f**	0.01	8	4571
4	$C(O)CH_3$	Br	**16a**	0.5	8	49
5	$C(O)CH_3$	Br	**16c**	0.0001	28	235714
6	$C(O)CH_3$	Br	**16d**	0.0001	28	714286
7	OCH_3	Br	**10b**	0.5	8	46
8	OCH_3	Br	**22f**	0.5	8	43
9	OCH_3	Br	**16a**	0.5	8	49
10	OCH_3	Br	**16c**	0.001	30	18571
11	OCH_3	Br	**16d**	0.001	30	36428
12	$C(O)CH_3$	Cl	**16c**	0.01	30	1143
13	$C(O)CH_3$	Cl	**16d**	0.5	30	49

Strassner *et al.* have compared the catalytic activity of (diNHC)Pd(II) complexes containing alkane bridges of different lengths, n = 1-4, as shown in Figure 1-28.[40]

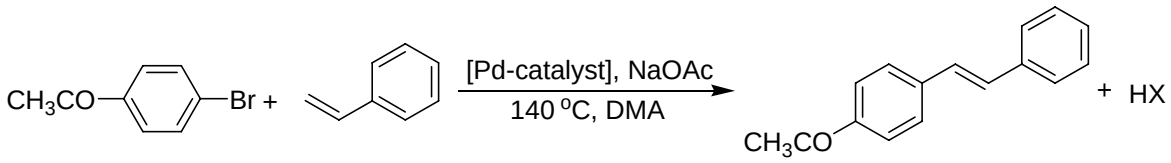


22f: n = 1
23f: n = 2
24 : n = 3
25 : n = 4

Figure 1-28. (DiNHC)Pd(II) complexes with alkane bridges of different lengths.

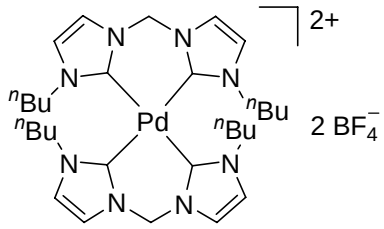
The results for the Heck coupling reaction using (diNHC)Pd(II) complexes with different length of the alkane bridge are tabulated in Table 1-2. The ethylene-bridged (diNHC)Pd(II) complex **23f** performed the best giving a TON of 70000, compared to the methylene-, propylene- and butylene-bridged (diNHC)Pd(II) complexes.

Table 1-2. Heck coupling reaction using (diNHC)Pd(II) complexes with different length of the alkane bridge.



Entry	Catalyst	t (h)	TON
1	**22f**	8	4571
2	**23f**	7.3	70714
3	**24**	7.3	60000
4	**25**	7.3	62857

The bis(diNHC)Pd(II) complex **26** has also been tested in Heck coupling reactions (Figure 1-29).[41] The complex gave a TON of 6.75 x 10^6 for the coupling of styrene and bromobenzene, although the addition of tetrabutylammonium bromide was required to obtain this high TON.

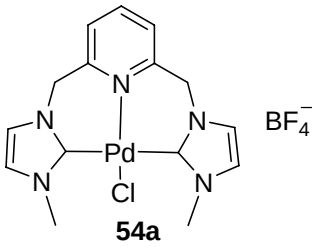


26

Figure 1-29. (DiNHC)Pd(II) complexes with alkyl bridge of different lengths.

It has been found that additives such as tetrabutylammonium salts enhance the catalytic activity in coupling reactions. The role that these additives play is not well understood, however, they have been considered to act as phase-transfer agents, activators for boronic acid by formation of a boronate complex $[ArB(OH)_3]^-[H_4N]^+$, stabilizers of the active nanoparticle metal species possibly formed by reducing the M(II) to M(0).[75]

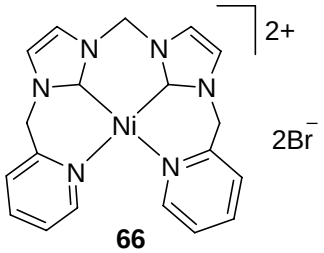
Tridentate pincer diNHC complexes of palladium have also demonstrated good catalytic activity in coupling aryl chlorides and deactivated aryl bromides with styrene. Complex **54a** gave a TON of 70000 in the Heck coupling reaction of butyl acrylate with 4-bromoacetophenone and 1000 with 4-chlorobenzaldehyde, however, addition of hydrazine hydrate was needed for the catalytic reaction (Figure 1-30).[57]



54a

Figure 1-30. Pincer (diNHC)Pd(II) complex as catalyst in C-C coupling reactions.

There are very few examples of Ni(II) complexes that have been employed as catalysts in C-C coupling reactions. When this Ph.D. project was started there was no examples of well-defined (diNHC)Ni(II) complexes used as catalysts in C-C coupling reactions in the literature. However, during the course of our research, four papers have been published that describe well-defined (diNHC)Ni(II) complexes as catalysts in C-C coupling reactions.[65,67,68,69] The tetradentate diNHC nickel(II) complex **66**, with hemi-labile pyridine arms (Figure 1-31), was the first example of a well-defined nickel complex that was used as a catalyst in C-C coupling reactions.



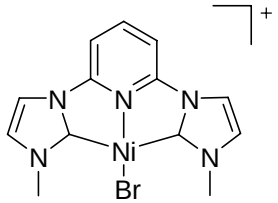
66

Figure 1-31. The first example of a well-defined (diNHC)Ni(II) complex employed as a C-C coupling catalyst.

Complex **66** demonstrated TONs of up to 100 in the coupling of phenylboronic acid with 4-bromoacetophenone, 88 with 4-chloroacetophenone, 34 with 4-bromoanisole

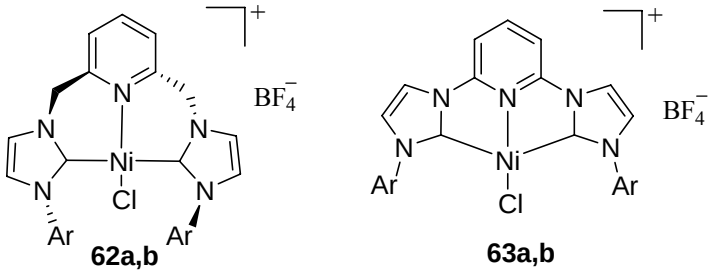
and 32 with 4-chloroanisole. However, the presence of triphenylphosphine was necessary to get these TONs, especially for aryl chlorides

The pincer-type (diNHC)Ni(II) complex **61**, reported by Inamoto *et al.*, demonstrated TONs of up to 12 in the coupling of butyl acrylate with bromobenzene and with 4-chloroacetophenone and also in the coupling of phenylboronic acid with 4-bromoacetophenone. However, tetrabutylammonium iodide was needed for the catalytic activity of complex **61** (Figure 1-32).[65]



61

Figure 1-32. Well-defined (diNHC)Ni(II) complex employed as a C-C coupling catalyst.



62a,b **63a,b**

a: Ar = 2,6-$^{i}Pr_2C_6H_3$
b: Ar = 2,4,6-$Me_3C_6H_2$

Figure 1-33. Pincer (diNHC)Ni(II) complexes employed as C-C coupling catalysts.

62a,b and **63a,b** have recently been tested in Heck coupling reactions (Figure 1-33). TONs of 83 were obtained in the coupling of styrene with 4-bromoacetophenone, 64

with 4-bromoanisole and 86 with 4-chloroacetophenone employing **62b** as the catalyst in the absence of any additives.[66]

In addition to C-C coupling reactions, (diNHC)Pd(II) complexes have also been used as catalysts in the direct CH activation of methane[36b,40] and copolymerization of ethylene and carbon monoxide.[42]

1.6 Research Objectives

The primary objective of this Ph.D. project was to investigate the catalytic potential of nickel as an alternative to palladium in C-C coupling reactions. The high cost of palladium has led researchers to explore cheaper transition metals which could replace palladium systems in cross-coupling reactions.[76] Although nickel appears to be a very promising candidate, very little effort has been dedicated to the development of nickel complexes which could be potential catalysts for these coupling reactions.[28] As an initial goal of this Ph.D. project, investigations into the synthesis of chelating diNHC complexes of nickel and evaluation of their catalytic potential in cross-coupling reactions were carried out and the results are discussed in *Chapter 2*.

The second goal was to synthesize non-symmetrically substituted diNHC ligands with a hemi-labile donor arm, D, on one of the nitrogen atoms as shown in Figure 1-34.

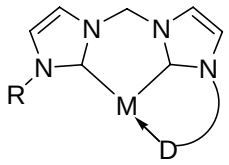


Figure 1-34. NHC complexes with hemi-labile donor arm D.

The rationale behind this ligand design would be that the strongly binding diNHC moiety would provide entropic stability to the complex and the hemi-labile, or the weakly

coordinating arm of the ligand, would allow a vacant coordination site for the substrate in catalytic reactions.

When this Ph.D. project was started, there was no example of non-symmetrically substituted diNHC ligand systems in the literature where R ≠ R' as shown in Figure 1-35.

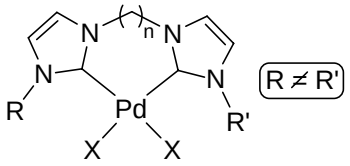


Figure 1-35. Non-symmetrically substituted (diNHC)PdX_2

Hence, to achieve the second goal, a general route into the synthesis of non-symmetrically substituted diNHC ligands had to be developed. Synthesis of the first examples of non-symmetrically substituted diimidazolium salts, their corresponding nickel and palladium diNHC complexes and their catalytic activity in Suzuki-Miyaura coupling reactions were performed and are discussed in *Chapter 3*. Synthesis of non-symmetrically substituted diNHC ligands have opened the possibilities of designing new ligand systems.

Since we developed a general route into the synthesis of non-symmetrically substituted diNHC complexes, we moved a step closer towards synthesizing non-symmetrically substituted diNHC ligands with a hemi-labile donor arm. Based on the available literature for hemi-labile donor arms on NHCs, we designed two diNHC ligand precursors with a hemi-labile donor arm on one of the nitrogen substituents; one with an imino arm and the second with a pyridine arm as shown in Figure 1-36 and discussed in *Chapter 4*.

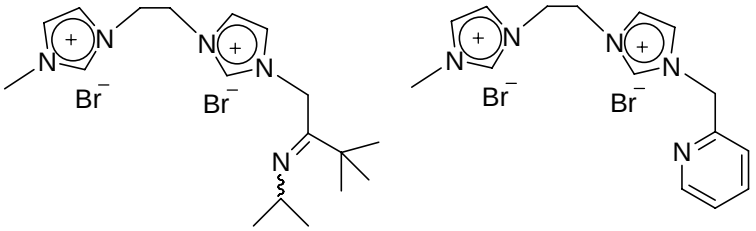


Figure 1-36. DiNHC ligand precursors with hemi-labile donor arms.

Synthesis of the tridentate diNHC ligand precursor with a pyridine arm and its corresponding nickel and palladium complexes were carried out and the results are discussed in *Chapter 4*.

Three-coordinate, 14-electron Pd(II) species are proposed intermediates in cross-coupling reactions.[77] They are not common in literature and are believed to be favored when the complexes possess sterically hindered ligands.[78] As a secondary project, synthesis of bulky β-diketiminato Pd(II) complexes for applications in the synthesis and isolation of rare three-coordinate Pd(II) species was carried out. My attempts into the synthesis of three-coordinate Pd(II) complexes is discussed in *Chapter 5*.

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CHAPTER 2

BIS-DI-*N*-HETEROCYCLIC CARBENE COMPLEXES OF NICKEL: INVESTIGATIONS INTO NICKEL CATALYZED AND "TRANSITION METAL FREE" COUPLING REACTIONS

2.1 Introduction

Carbon-carbon bond forming reactions play a very fundamental role in organic transformations. Considerable amount of research has been dedicated towards the development of highly efficient palladium-based systems that can catalyze carbon-carbon coupling reactions.[1] Palladacycles and monodentate *N*-heterocyclic carbene (NHC) palladium(II) complexes are by-far the most efficient catalysts in literature and industry.[2] However, the high cost of the palladium-based catalysts have led researchers to explore the catalytic activity of cheaper transition metals, such as, chromium,[3] iron,[4] cobalt,[5] manganese,[4b,6] ruthenium[7] and nickel,[8] which could replace the expensive palladium systems with regards to cross-coupling reactions.

Nickel has been known to catalyze nucleophilic substitution-type cross-coupling reactions between organometallic reagents and allyl, vinyl or aryl halides.[9] $NiCl_2$(dppp) (dppp = 1,3-bisdiphenylphosphinopropane) have found catalytic applications in the industrial production of styrenes *via* the Kumada coupling reaction of aryl magnesium chlorides with vinyl chloride.[10] Nickel(II) phosphine complexes, such as $NiCl_2$(dppe) (dppe = 1,2-bisdiphenylphosphinoethane), $NiCl_2$(dppf) (dppf = 1,1'-

bisdiphenylphosphinoferrocene), $NiCl_2(PPh_3)_2$ and $NiCl_2(PCy_3)_2$ in the presence of excess phosphine are general catalysts for the cross-coupling of aryl mesylates, tosylates, chlorides, bromides and iodides with arylboronic acids.[11] Although air-sensitive, Ni(0) compounds such as $Ni(cod)_2$ in the presence of 1-4 equiv. of phosphines have also been used as catalyst precursors for C-C coupling reactions.[11d] The active Ni(0) may also be generated *in situ* by reduction of Ni(II) with reductants such as Zn and BuLi. [8g,h,12] This brings about handling problems because the reductants are usually air-sensitive.

Nickel provides an attractive alternative to palladium due to its relative low cost and ability to more readily undergo oxidative addition reactions with C-Cl and C-F bonds; however, relatively little effort has been dedicated to the development of nickel complexes.[1b,13]

When this Ph.D. project was started, there were no examples of well-defined nickel complexes that were employed in C-C coupling reactions in literature. During the course of our research, several examples of nickel complexes in coupling reactions were reported (Figure 2-1) and most of them were based on NHCs.[14,15]

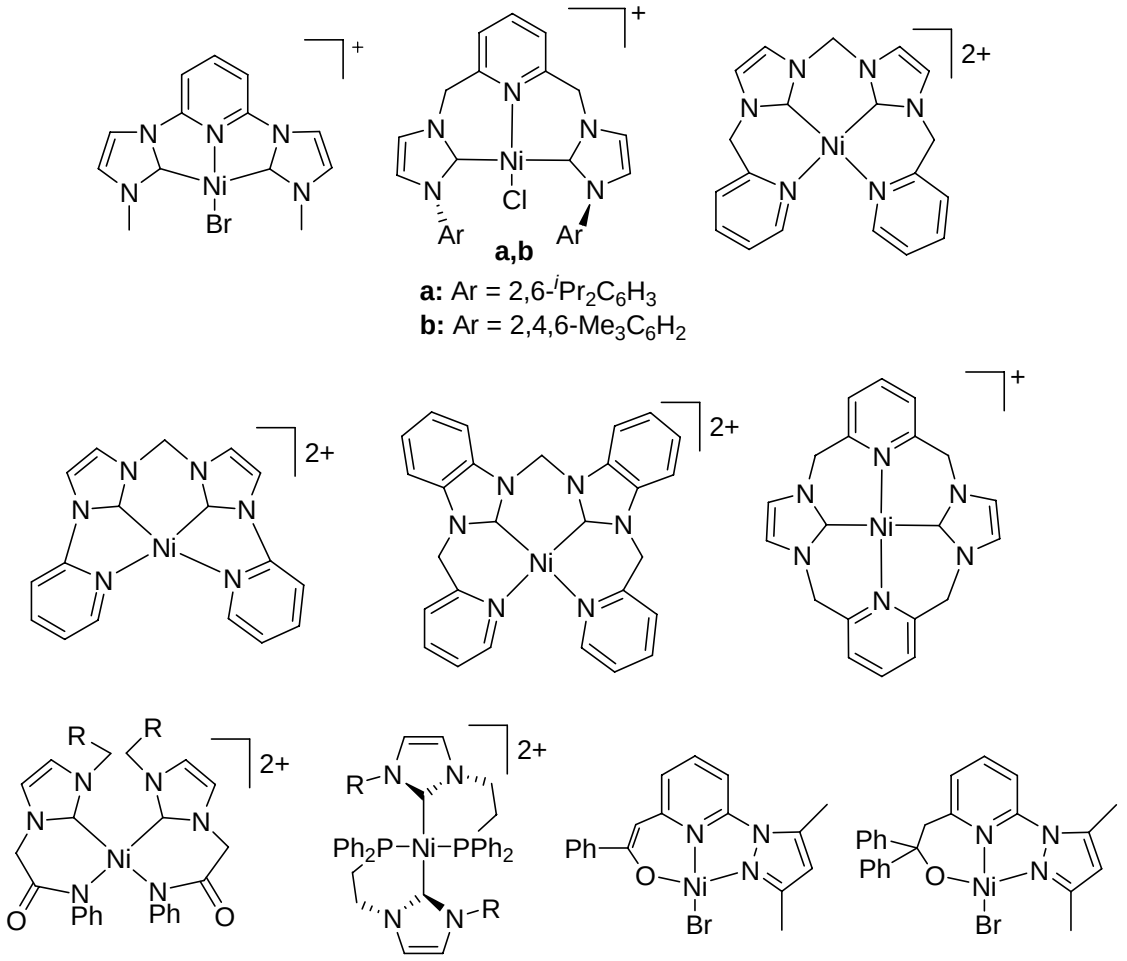

Figure 2-1. Nickel complexes employed as catalysts in carbon-carbon coupling reactions.[14,15]

We set out to synthesize *cis*-chelating bidentate NHC complexes of nickel and to evaluate their catalytic activity in cross coupling reactions. Palladium(II) complexes with *cis*-chelating bidentate NHC ligands are air and moisture stable compounds and have been shown to efficiently catalyze cross coupling reactions.[16] Recently a $[(diNHC)_2Pd]^{2+}$ complex was investigated for its catalytic activity in the Mizoroki-Heck reaction and was found to exhibit high turnover numbers in the coupling of aryl bromides and showed

potential for catalyst recyclability.[17] The analogous $[(diNHC)_2Ni]^{2+}$ complexes have, to date, not been investigated for C-C coupling reactions.

In this chapter, the synthesis of two $[(diNHC)_2Ni]^{2+}$ complexes, their Ag(I) and Pd(II) analogues, and investigations into their activity in standard Mizoroki-Heck and Suzuki-Miyaura coupling reactions will be discussed. In the course of these investigations, it was found that select bases could catalyze the coupling reactions of aryl iodides and aryl bromides *in the absence* of any Ni(II) or Pd(II) precatalyst. "Transition metal free" Suzuki-type coupling reactions employing Na_2CO_3 in the presence of Bu_4NBr have been previously described.[18] However, the authors later reported that sub-ppm levels of Pd impurities in commercially available Na_2CO_3 were likely responsible for catalyzing these reactions.[19] These results highlighted the importance of performing control experiments while investigating the catalytic C-C coupling activity of any potential nickel precatalyst.

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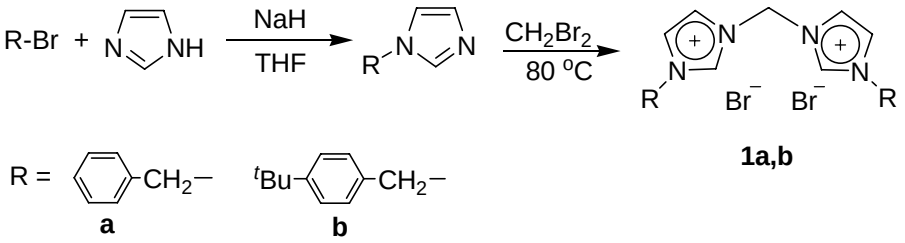
2.2 Results and Discussion

2.2.1 Synthesis of diNHC ligands

The diimidazolium salts **1a,b** were synthesized in two steps according to the literature procedure for **1a** previously reported by Lee *et al.* (Scheme 2-1).[16b] In this procedure, the *N*-benzylimidazoles were first prepared by reacting the substituted benzyl bromides with imidazole in the presence of 4 equiv. of NaH for 12 h. Heating a solution of the resulting *N*-benzylimidazole in neat dibromomethane for 2 d resulted in formation of the corresponding methylene-bridged diimidazolium salts **1a,b** in high yield. A potentially frustrating problem with diimidazolium salts and of their resulting diNHC complexes is poor solubility in common organic solvents, thus the ^{t}Bu groups in **1b** were introduced in the *para* position of the benzyl moiety to increase solubility. While diimidazolium salt **1b** and the resulting nickel and palladium complexes remained insoluble in chlorinated solvents, solubility greatly increased in polar solvents such as DMSO and DMF. The ^{1}H NMR spectra of **1a,b** in DMSO-d_6 exhibit characteristic resonances at 9.7 ppm for the protons on the C2 (NC*H*N) position of the imidazolium rings.

Scheme 2-1. Synthesis of diimidazolium salts **1a,b**.

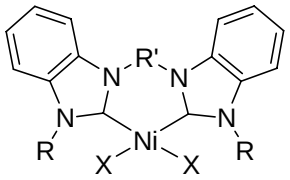


Deprotonation of **1a,b** with 2 equiv. of $K[N(SiMe_3)_2]$ in THF generated the neutral carbenes **2a,b** as evidenced by absence of the carbenic C2 proton in the ^{1}H NMR spectra (Scheme 2-2). The C4 and C5 protons on the imidazolium rings, upon deprotonation, also shift upfield from the aromatic to the olefinic region of the spectra consistent with a localized C=C bond. The ^{13}C NMR spectra of **2a,b** show a downfield shift of the bridging methylene carbon and of the methylene carbon of the benzyl groups. As well, the ^{13}C NMR spectra show the appearance of peaks at 216 and 214 ppm which are characteristic of the carbenic carbons, N*C*N, for **2a** and **2b** respectively.

2.2.2 Synthesis of diNHC complexes of Ag(I), Ni(II) and Pd(II)

Previous attempts to make methylene-bridged (diNHC)NiX_2 (X = halogen) complexes from the reaction of $Ni(OAc)_2$ with diimidazolium salts always yielded a dicationic Ni(II) species with the general formula $[(diNHC)_2Ni]^{2+}$.[20] Formation of the neutral *cis*-dihalide complexes was never observed. This is in sharp contrast to the analogous palladium reaction which readily yields the (diNHC)PdX_2 species as the preferred product.[20,21] Successful attempts have been made to synthesize monocationic [(diNHC)NiCl(PMe_3)]Cl complexes[22] while an ethylene-bridged mononuclear dialkylnickel complex, (diNHC)Ni$(CH_3)_2$,[23] has also been synthesized. However, in

2009, benzimidazolylidene-based (diNHC)NiX_2 complexes were synthesized by Bouwman *et. al*. (Figure 2-2).[24]



R = Me, R' = propylene, X = Br
R = Pr, R' = propylene, X = Br
R = ^{i}Pr, R' = propylene, X = Br
R = Bz, R' = propylene, X = Br

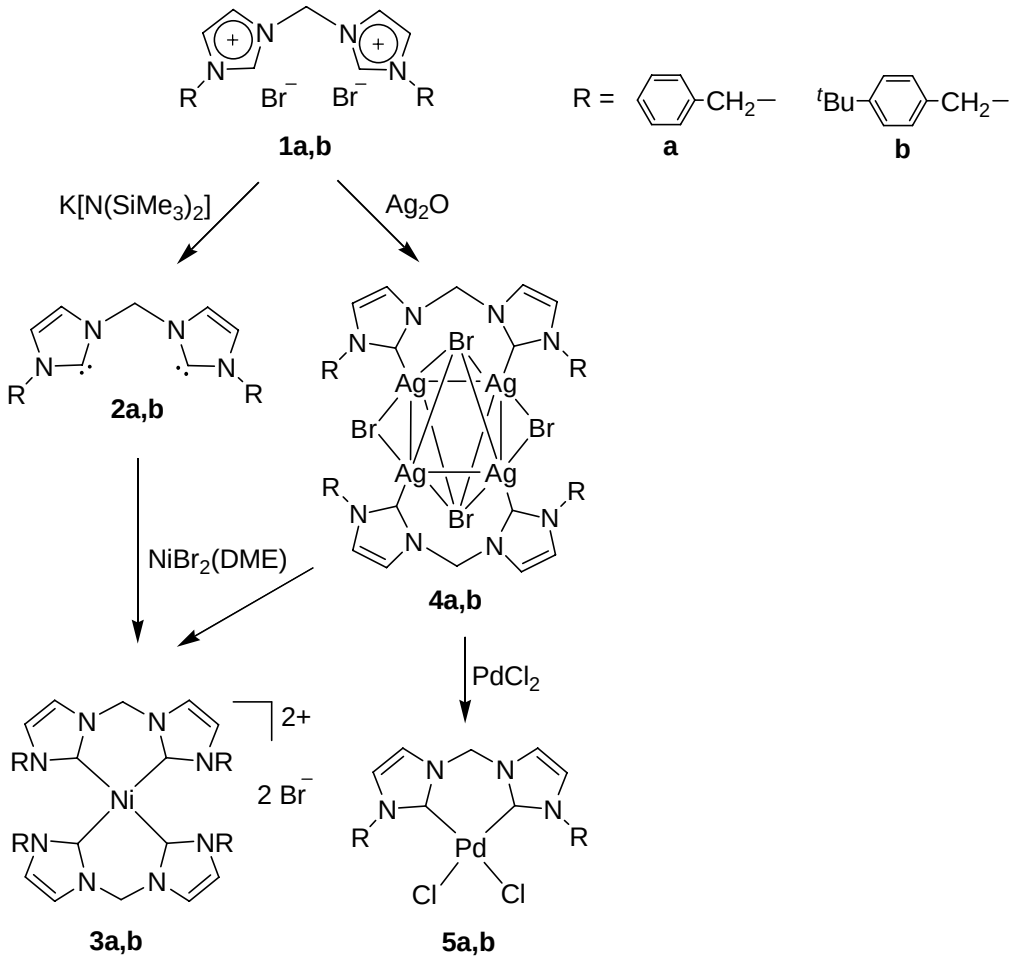
R = Ph, R' = propylene, X = Br
R = Me, R' = propylene, X = Cl
R = Me, R' = butylene, X = Br
R = Me, R' = butylene, X = Cl

Figure 2-2. Benzimidazolylidene-based (diNHC)NiX_2 complexes.

Rather than use the acetate elimination route, we investigated if direct reaction of a neutral diNHC ligand with one equiv. of a NiX_2 source could yield a *cis*-dihalide complex. However, reaction of the neutral diNHCs **2a,b** with one equiv. of $NiBr_2$(DME) afforded the homoleptic $[(diNHC)_2Ni]^{2+}$ complexes **3a,b** with two chelating diNHC ligands and two non-coordinating bromide counterions as the only isolated products (Scheme 2-2). **3a,b** were the only observed products irrespective of stoichiometry, thus the yields were optimized when two equiv. of ligand were employed. $[(DiNHC)_2Ni]^{2+}$ complexes **3a,b** are air and moisture stable and can be crystallized by slow diffusion of ether into a concentrated solution of the sample in DMF. The ^{1}H NMR spectra of **3a,b** show non-equivalent NCH_2N resonances for the two methylene bridge protons consistent with retention of configuration of the boat-shaped six-membered chelate rings at ambient temperature. The solid-state structures of complexes **3a,b** were determined by single-crystal X-ray diffraction and show a distorted square-planar geometry about the metal

centers (Figure 2-3 and 2-4, Table 2-1). The two C-Ni-C planes defined by the two chelating diNHC ligands are exactly coplanar with an average Ni-C bond length of 1.90(1)Å and a C-Ni-C bite angle of 86.1(1)˚ for **3a** and 86.3(1)˚ for **3b** for the six-membered chelate rings.

Scheme 2-2. Synthesis of diNHC complexes of Ag(I), Ni(II), and Pd(II).



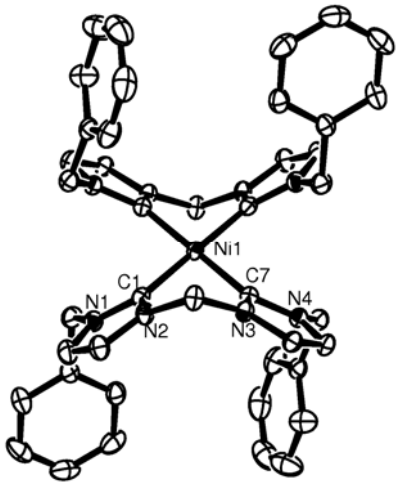


Figure 2-3. ORTEP plot of **3a** at the 50% probability level. Hydrogen atoms and the two non-coordinating bromide ions have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1-C7 = 1.896(2), Ni1-C1 = 1.906(2), C7-Ni1-C7^{i} = 180.00(11), C7-Ni1-C1^{i} = 93.90(10), C7-Ni1-C1 = 86.10(10).

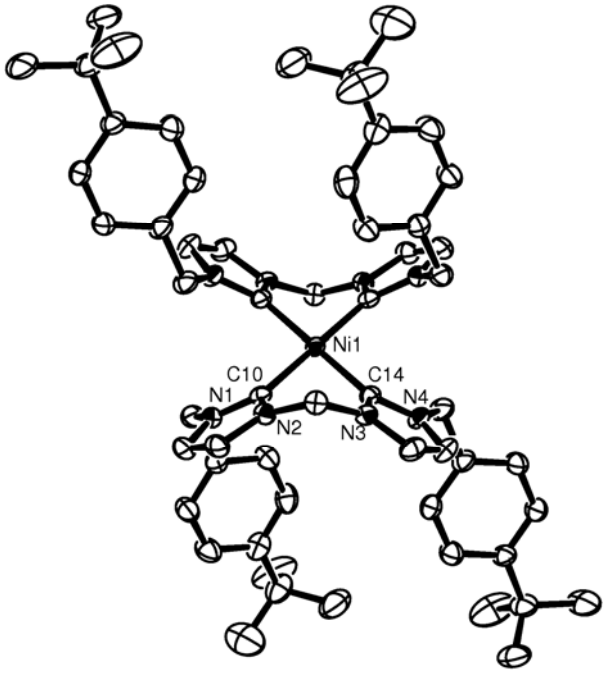


Figure 2-4. ORTEP plot of **3b** at the 50% probability level. Hydrogen atoms, non-coordinating bromide ions and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1-C10 = 1.894(3), Ni1-C14 = 1.899(3), C10-Ni1-C10^{i} = 180.00(11), C14-Ni1-C10^{i} = 93.75(11), C10-Ni1-C14 = 86.25(11).

An alternative method for the synthesis of complexes **3a,b** is *via* a transmetallation route using (diNHC)Ag(I) complexes (Scheme 2-2). The advantage of using (diNHC)Ag(I) complexes as carbene transfer agents include simple preparation directly from a diimidazolium salt and ease of handling due to air stability.[25] The new silver complexes **4a,b** were synthesized by the reaction of **1a,b** with Ag_2O in dichloromethane at room temperature based on literature procedures.[25k] These silver complexes are sparingly soluble in highly polar solvents such as DMF and DMSO and display remarkable stability towards heat, light, air and moisture. The ^1H NMR spectra of **4a,b** show the absence of any signal between 8-10 ppm indicating the successful deprotonation of the carbenic protons in **1a,b**. The remaining imidazolylidene protons, upon coordination with Ag(I) are shifted upfield while the bridging methylene protons are broadened relative to their corresponding signals in **1a,b**. The ^{13}C NMR spectra of **4a,b** show the appearance of a singlet at 181 ppm which is characteristic of a carbenic carbon for **4a,b** with no evident coupling between the carbenic carbon and the silver center. The poor solubility of the silver complexes was a hurdle in conducting low temperature NMR experiments to investigate if there was indeed any coupling observed at lower temperatures. (NHC)Ag(I) complexes containing halide ligands usually exhibit no coupling between the carbenic carbon and the silver atom indicating a weak Ag-NHC bond and fast exchange between the silver centers and the carbene moieties. Therefore, these complexes are expected to act as good carbene transfer agents for transmetallation reactions.[26] To better understand the coordination environments in **4a,b** the crystal structure of complex **4a** was determined (Figure 2-5, Table 2-1), which showed that these complexes were tetranuclear species of the general formula $Ag_4(\mu^2\text{-}Br_2)(\mu^4\text{-}Br_2)(\mu\text{-}$

diNHC)$_2$ which adopt a tetragonal bipyramidal geometry with C_i symmetry with four Ag atoms in the equatorial positions and two Br atoms in the axial positions. The Ag-Ag edges are alternatively bridged by NHC and Br ligands with weak Ag···Ag interactions (2.9-3.1Å). This structural motif is unique among structurally characterized NHC complexes of silver.[25a,d,e,j,k,26a,27]

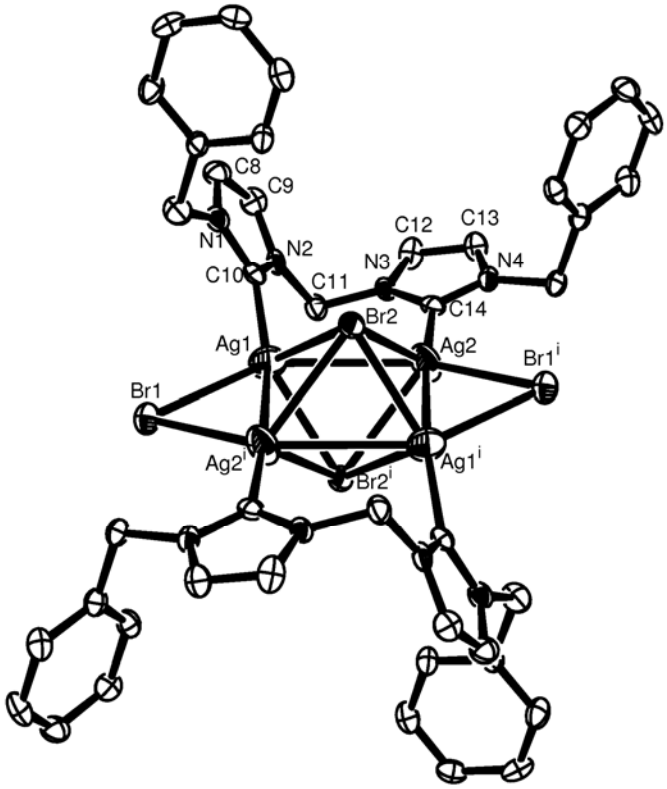


Figure 2-5. ORTEP plot of **4a** at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag(1)-C(10) = 2.081(8), Ag(2)-C(14) = 2.152(8), Ag(1)-Br(1) = 2.7237(13), Ag(1)-Br(2) = 2.8917(12), Ag(1)-Ag(2) = 3.1239(13), Ag(1)-Ag(2)^i = 2.9433(12), Ag(1)^i-Ag(2)-Ag(1) = 81.91(3).

The silver complexes **4a,b** readily undergo transmetallation with $NiBr_2$(DME) and $PdCl_2$ to give complexes **3a,b** and **5a,b** respectively. While (diNHC)$PdCl_2$ **5a** is a new complex, the bromo and iodo analogues have been previously reported.[16b,d] **5a,b** were synthesized to compare the catalytic activity of the $[(diNHC)_2Ni]^{2+}$ complexes to that of the analogously synthesized palladium complexes. The solid state structure of complex **5a** was determined by single-crystal X-ray diffraction, which showed the palladium center in the expected square-planar geometry (Figure 2-6, Table 2-1). **5a** co-crystallized with one half of a molecule of DMF.

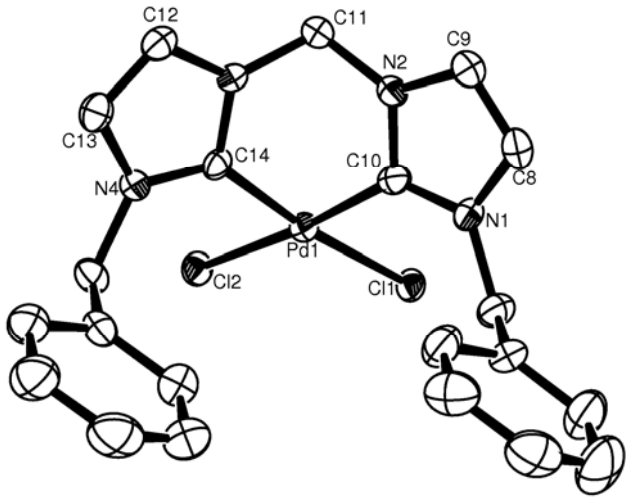


Figure 2-6. ORTEP plot of **5a**·0.5DMF at the 50% probability level. Hydrogen atoms and solvent molecule have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)-C(14) = 1.968(6), Pd(1)-C(10) = 1.972(6), Pd(1)-Cl(1) = 2.3715(15), Pd(1)-Cl(2) = 2.3720(15), C(14)-Pd(1)-C(10) = 84.2(2), Cl(1)-Pd(1)-Cl(2) = 90.24(5).

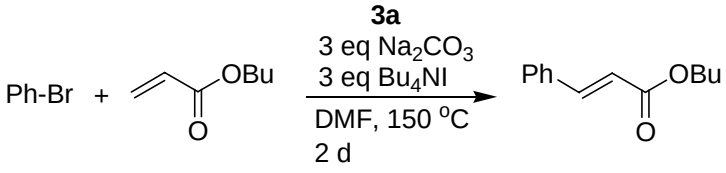
Table 2-1. Crystal data and refinement parameters for compounds **3a**, **3b**·4DMF, **4a** and **5a**·0.5DMF.

	3a	**3b**·4DMF	**4a**	**5a**·0.5DMF
formula	$C_{42}H_{40}Br_2N_8Ni$	$C_{70}H_{100}Br_2N_{12}NiO_4$	$C_{42}H_{40}Ag_4Br_4N_8$	$C_{22.5}H_{23.5}Cl_2N_{4.5}O_{0.5}Pd$
M	875.35	1392.15	1407.94	542.26
crystal system	triclinic	triclinic	triclinic	monoclinic
space group	*P*-1	*P*-1	*P*-1	*C*2/c
a, Å	9.8058(3)	11.8395(3)	9.8623(4)	30.461(2)
b, Å	10.6250(4)	13.6055(4)	9.9754(3)	7.8144(8)
c, Å	11.2120(5)	13.8460(3)	11.6153(4)	22.228(2)
α, deg	63.075(2)	80.971(2)	92.339(2)	90
β, deg	67.743(2)	69.9533(2)	96.566(2)	120.533(4)
γ, deg	71.563(2)	73.8540(2)	109.941(2)	90
Z	1	1	1	4
ρ_{calc}, mg m^{-3}	1.532	1.151	2.199	1.581
T, K	173(2)	173(2)	173(2)	173(2)
radiation, λ[Å]	0.71073	0.71073	0.71073	0.71073
F(000)	446	734	676	2192
θ range, deg	2.18 to 29.64	3.12 to 27.53	3.01 to 27.52	3.06 to 27.48
reflns collected/unique	21018/5312	29325/9199	15555/4868	32159/5215
R_{int}	0.0605	0.0599	0.0544	0.1475
final R_1(I >2σI)	R1 = 0.0423, wR2 = 0.0954	R1 = 0.0495, wR2 = 0.1241	R1 = 0.0666, wR2 = 0.1752	R1 = 0.0586, wR2 = 0.1089
R_1(all data)	R1 = 0.0674, wR2 = 0.1059	R1 = 0.0711, wR2 = 0.1347	R1 = 0.0834, wR2 = 0.1880	R1 = 0.1050, wR2 = 0.1274

2.2.3 Catalytic activity of $[(diNHC)_2Ni]^{2+}$ for coupling of aryl bromides

As a first step to evaluate the catalytic activity of $[(diNHC)_2Ni]Br_2$ complex **3a**, we carried out the Mizoroki-Heck coupling reaction of bromobenzene with butyl acrylate. The reaction conditions were optimized using this reaction and it was found that satisfactory yields were obtained with 5 mol % of **3a** in the presence of 3 equiv. of Na_2CO_3 and 3 equiv. of Bu_4NI in DMF as solvent. Long reaction times (2 days) were necessary to maximize the yield. Of the various bases explored: Na_2CO_3, NEt_3, K_2CO_3, KOAc, K_3PO_4, NaOAc, CsOAc and Cs_2CO_3, the catalyst was active only in the presence of Na_2CO_3, resulting in a yield of 50% yield. The catalyst was found to be inactive in the absence of Bu_4NI (Table 2-2, entry 3). The reaction can be carried out aerobically with only a small loss in activity (Table 2-2, entry 4).

Table 2-2. Catalytic activity of complex **3a** in the Mizoroki-Heck coupling reaction.[a]

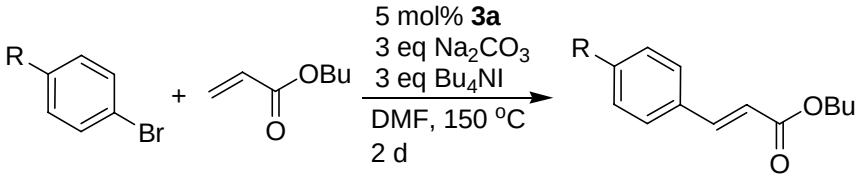


Entry	Cmpd 3a (mol %)	Bu_4NI	Conversion (%)
1	5	3 eq	50
2	1	3 eq	0
3	5	0	0
4*	5	3 eq	42

[a]Reaction conditions: aryl halide (0.5 mmol), butyl acrylate (2.5 mmol), Na_2CO_3 (1.5 mmol), Bu_4NI (1.5 mmol), DMF (3 mL). Conversions from single run. *Reaction performed under air instead of N_2.

With conditions optimized, we next carried out the nickel-catalyzed Mizoroki-Heck coupling reaction of a variety of aryl bromides. In the presence of **3a**, aryl bromides react with butyl acrylate to produce the corresponding cinnamates in reasonable yield (Table 2-3). However, the catalyst was inactive towards aryl chlorides.

Table 2-3. Mizoroki-Heck reaction of aryl bromides catalyzed by complex **3a**.[a]



Entry	R	Conversion (%)
1	H	50
2	COMe	56
3	CHO	44

[a]Reaction conditions: aryl halide (0.5 mmol), butyl acrylate (2.5 mmol), Na_2CO_3 (1.5 mmol), **3a** (0.025 mmol), Bu_4NI (1.5 mmol), DMF (3 mL). Conversion from single run.

2.2.4 "Transition metal free" coupling reactions: coupling of aryl halides and the importance of performing control reactions.

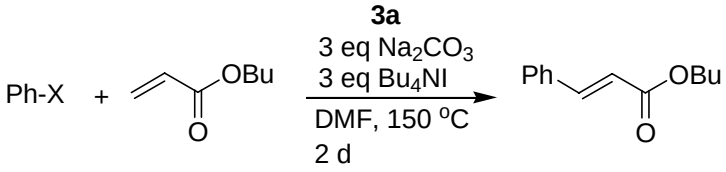
Quantitative yields were obtained in the Mizoroki-Heck coupling reaction of iodobenzene with butyl acrylate only when Na_2CO_3 or NEt_3 were used as bases (Table 2-4). To investigate if a nickel species was indeed the active catalyst, several control experiments were performed with iodobenzene and butyl acrylate. Surprisingly, it was found that quantitative yields could be obtained with Na_2CO_3 as well as NEt_3 *in the*

absence of nickel species and/or Bu_4NI (Table 2-4). However, Na_2CO_3 was not active for Mizoroki-Heck coupling reactions with aryl bromides. Thus all investigations were carried out with aryl bromides as aryl iodides can be easily coupled in the absence of a nickel precatalyst. This finding emphasizes the importance of performing control reactions when assessing the catalytic activity of a potential nickel precatalyst. Unfortunately, these tests are often neglected in the literature, especially given that many of the nickel precatalysts active for Mizoroki-Heck and Suzuki-Miyaura reactions report the coupling of aryl iodides.[14,15a,15b,28] No reaction was obtained when bromobenzene was reacted with butyl acrylate in the absence of any base, nickel species and Bu_4NI. The commercially obtained Na_2CO_3 and NEt_3 that were used in our experiments were analyzed for palladium and nickel content by ICP and the results indicated that Ni and Pd levels were <5 ppm (the detection limit of the ICP instrument used). It is likely that sub-ppm levels of Pd are responsible for the observed coupling reactions in the "transition-metal free" control reactions as palladium-catalyzed coupling reactions of aryl iodides and aryl bromides have reported activities greater than 10^6.[29] While the active species in Na_2CO_3 and NEt_3 remain unknown, a similar observation of "transition-metal free" Suzuki-type coupling reactions employing Na_2CO_3 in the presence of Bu_4NBr has been previously reported.[18] However, the authors later reported that sub-ppm levels of Pd impurities in commercially available Na_2CO_3 were likely responsible for catalyzing these reactions.[19]

The catalytic activity of the metal precursor, $NiBr_2(DME)$, was also evaluated under otherwise identical conditions to that used for the nickel complex, **3a**, and it was

found to be inactive for the Mizoroki-Heck coupling reaction of bromobenzene with butyl acrylate.

Table 2-4. Control experiments for Mizoroki-Heck coupling of aryl halides in the absence of transition metal species.[a]



Entry	X	Base	3a	Bu_4NI	Conv.(%)
1	I	Na_2CO_3	5 mol%	3 eq	100
2	I	Na_2CO_3	0	0	100
3	Br	Na_2CO_3	0	3 eq	0
4	I	NEt_3	5 mol%	3 eq	100
5	I	NEt_3	0	0	100
6	Br	NEt_3	5 mol%	3 eq	0

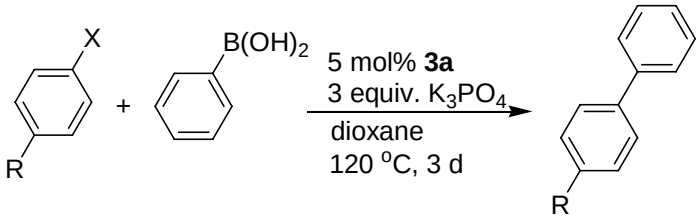
[a]Reaction conditions: aryl halide (0.5 mmol), butyl acrylate (2.5 mmol), Na_2CO_3 (1.5 mmol), Bu_4NI (1.5 mmol), DMF (3 mL). Conversion from single run.

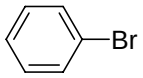
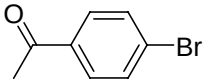
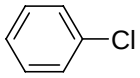
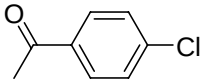
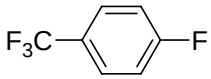
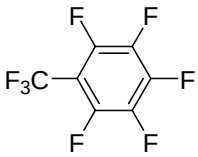
Next we investigated if there was any kind of ligand transfer from precatalyst **3a**, to the putative palladium impurities in the Na_2CO_3. This was to determine if the catalytic activity was possibly a result of NHC transfer from the nickel precatalyst to the palladium impurities. To evaluate this we investigated the Mizoroki-Heck coupling reaction of bromobenzene with butyl acrylate in the presence of (diNHC)Ag(I) complex **4a.** As mentioned above, (NHC)Ag(I) complexes have frequently been used as NHC transfer

reagents in organometallic chemistry.[23,24] If the catalytic activity was due to carbene transfer from **3a** to the putative palladium impurities in Na_2CO_3, then the coupling reaction in the presence of the corresponding (diNHC)Ag(I) complex **4a** should result in similar yields. However no activity was observed, which suggested that precatalyst **3a** was involved in the activation of aryl bromides in the Mizoroki-Heck coupling reaction.

The catalytic activity of complex **3a** in Suzuki-Miyaura coupling reactions was also investigated. Precatalyst **3a** was active for the coupling of aryl bromides, aryl chlorides and even aryl fluorides with phenylboronic acid in the presence of K_3PO_4 as base and dioxane as solvent with moderate to high yields (Table 2-5). We also observed a reverse trend in the activities of activated aryl halides compared to non-activated aryl halides. The conversions for acetyl aryl halides were lower than their corresponding aryl halides, for reasons not known to us currently. The analogously synthesized palladium precatalyst, **5a**, was also investigated in the coupling of aryl fluorides with phenylboronic acid under conditions otherwise identical for entries 5 and 6 in Table 2-5. No activity was observed for C-F activation with **5a** under these conditions.

Table 2-5. Suzuki-Miyaura cross-coupling of aryl halides with phenylboronic acid.[a]



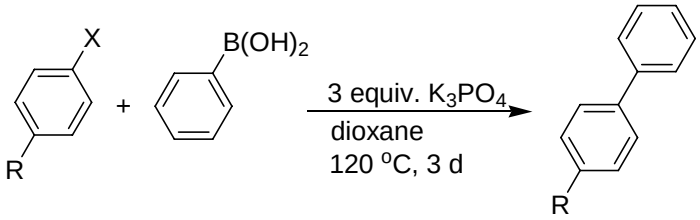
Entry	Aryl Halide	Conversion (%)
1		100
2		42
3		37
4		31
5		30[b]
6		14[b]

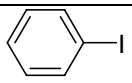
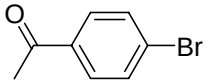
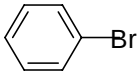
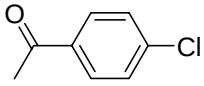
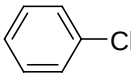
[a]Reaction conditions: aryl halide (0.5 mmol), phenylboronic acid (1.5 mmol), base (2 mmol), **3a** (0.025 mmol), solvent (3 mL), 120 °C, 3 d. [b]Determined by ^{19}F NMR based on the ratio of product to residual aryl fluoride. Conversion from single run.

To investigate if a nickel species was the active catalyst in the Suzuki-Miyaura coupling reactions, several control experiments were again performed. For the Suzuki-Miyaura reaction, it was found that aryl iodides and aryl bromides could be activated *in the absence* of nickel species when K_3PO_4 was used as base (Table 2-6). No activity for

aryl chlorides was observed. However it is inconclusive whether the nickel complex is truly catalyzing the coupling of aryl bromides for entry 2 in Table 2-5 when compared to the analogues control reaction as seen in entry 2 in Table 2-6.

Table 2-6. Control experiments for Suzuki-Miyaura coupling of aryl halides in the absence of transition metal species.[a]



Entry	Aryl Halide	Conversion (%)
1		87
2		49
3		37
4		0
5		0

[a]Reaction conditions: aryl halide (0.5 mmol), phenylboronic acid (1.5 mmol), base (2 mmol), solvent (3 mL), 120 °C, 3 d. Conversion from single run.

2.3 Conclusions

In summary, we have synthesized stable homoleptic $[(diNHC)_2Ni]^{2+}$ complexes which are active precatalysts in Mizoroki-Heck and Suzuki-Miyaura coupling reactions, however, long reaction times and relatively high catalyst loadings are required. By comparison, state of the art palladium catalyzed Suzuki-Miyaura reactions require 0.1% catalyst loading for 1 h at ambient temperature for deactivated aryl chlorides.[30] In the Suzuki-Miyaura coupling reactions, nickel precatalyst **3a** was active for the coupling of aryl chlorides as well as aryl fluorides. Analogously synthesized palladium complexes result in formation of $(diNHC)PdCl_2$ species which were not active for the coupling of aryl fluorides. More importantly, these results also emphasize the importance of performing control reactions when assessing the catalytic activity of a potential nickel precatalyst as the base employed, or more likely transition metal impurities in the base, can also act as a coupling agent in the absence of nickel precatalysts. For example, the coupling of aryl iodides in the Mizoroki-Heck reaction was observed using Na_2CO_3 as base, while the coupling of aryl iodides and aryl bromides in the Suzuki-Miyaura reaction was possible employing K_3PO_4 as base in the absence of any nickel or palladium precatalyst.

While nickel appears to be a promising alternative to palladium for catalytic carbon-carbon bond forming reactions, further research is essential to not only improve activity at the metal center, but more importantly to better understand the nature of the active species.

2.4 Experimental

General Procedure: Unless otherwise stated, all reactions were performed under N_2 using standard Schlenk techniques or in a N_2-filled drybox. THF and dichloromethane were dried using a MBraun Solvent Purification System and were stored in a glovebox. C_6D_6 was dried over Na/K and was degassed using freeze-pump-thaw technique and stored in a glovebox. Dioxane was dried over sodium and distilled prior to use. All temperatures for catalytic reactions refer to the temperature of pre-equilibrated sand baths. ^1H and ^{13}C $\{^1H\}$ NMR spectra were recorded on a Bruker 500 MHz Avance spectrometer. Chemical shifts for ^1H and ^{13}C NMR are reported in ppm in reference to the residual ^1H and ^{13}C resonances of $CDCl_3$ (^1H: δ 7.24; ^{13}C: δ 77.23), C_6D_6 (^1H: δ 7.16; ^{13}C: δ 128.39) and DMSO-d_6 (^1H: δ 2.50; ^{13}C: δ 39.51). Coupling constants are given in Hz. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. High resolution mass spectra (HRMS) were measured on an Applied Biosystem QSTAR® XL MS/MS system (ESI-QTOF). ICP analyses were done by SRC Analytical, Saskatchewan, Canada. Dibromomethane and Ag_2O were purchased from Alfa-Aesar Chemical Company and used as received. Imidazole, benzyl bromide, *tert*-butylbenzyl bromide, $NiBr_2$(DME), K[$N(SiMe_3)_2$], anhydrous DMF, and NaH were purchased from Sigma-Aldrich Chemical Company and used as received. $PdCl_2$ was obtained from PMO Pty Ltd, Australia. *N*-benzylimidazole and 1,1'-dibenzyl-3,3'-methylenediimidazolium dibromide (**1a**) was synthesized according to literature procedures.[16b]

Synthesis of 1-(4-*tert*-butylbenzyl)imidazole: A Schlenk flask was charged with imidazole (1.85g, 0.0272 mol) and NaH (2.57g, 0.107 mol) in THF (50 mL) at ambient temperature. After 5 min, 4-(*tert*-butyl)benzyl bromide (5.0 mL, 0.0272 mol) was added. The mixture was stirred for 12 h following which the solvent was removed under vacuum. Water (20 mL) and dichloromethane (30 mL) were added to the reaction products and the organic layer was separated. The organic layer was further extracted with water (2x20 mL) and the solvent was removed under vacuum to yield the product as a pale yellow solid which can be used without further purification. (4.93 g, 85%). ^{1}H NMR ($CDCl_3$): δ 7.52 (s, 1H, NC*H*N), 7.35 (d, *J* = 8.1, 2H, CH_{Ar}), 7.07 (d, *J* = 8.1, 2H, CH_{Ar}), 7.06 (s, 1H, CH_{imid}), 6.89 (s, 1H, CH_{imid}), 5.06 (s, 2H, ArCH_2N), 1.29 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$): δ 151.59 ($C_{Ar(para)}$), 137.66 (N*C*HN), 133.44 ($C_{Ar(ipso)}$), 130.00 (*C*H$_{imid}$), 127.26 (*C*H$_{Ar}$), 126.11 (*C*H$_{Ar}$), 119.50 (*C*H$_{imid}$), 50.71 (Ar*C*H$_2$N), 34.82 (*C*(CH$_3$)$_3$), 31.51 (C(*C*H$_3$)$_3$). HRMS (*m/z*): calcd for $C_{14}H_{18}N_2$ $[M]^+$: 214.147, found: 214.1475.

Synthesis of 1,1'-dibenzyl-3,3'-methylenediimidazolium dibromide (1a): A Schlenk flask was charged with *N*-benzylimidazole (1.0g, 6.32 mmol) and dibromomethane (20 mL) and stirred at 80 ^{o}C for 2 d. A white precipitate resulted which was filtered, washed with THF (3x15 mL) and dried under vacuum to yield **1a** as a white powder (1.40 g, 80%). ^{1}H NMR (DMSO-d_6): δ 9.70 (s, 2H, NC*H*N), 8.12 (s, 2H, CH_{imid}), 7.93 (s, 2H, CH_{imid}), 7.54-7.37 (m, 10H, CH_{Ar}), 6.72 (s, 2H, NCH_2N), 5.52 (s, 4H, ArCH_2N). ^{13}C NMR (DMSO-d_6): δ 137.71 (N*C*HN), 134.13 ($C_{Ar(ipso)}$), 128.98 (*C*H$_{Ar}$), 128.88

($CH_{Ar(para)}$), 128.60 (CH_{Ar}), 123.16 (CH_{imid}), 122.54 (CH_{imid}), 58.29 (NCH_2N), 52.27 ($ArCH_2N$).

Synthesis of 1,1'-di(4-*tert*-butylbenzyl)-3,3'-methylenediimidazolium dibromide (1b): A Schlenk flask was charged with *N*-*tert*-butylbenzylimidazole (1.0g, 4.67 mmol) and dibromomethane (20 mL) and stirred at 80 ^{o}C for 2 d. A white precipitate resulted which was filtered, washed with THF (3x15 mL) and dried under vacuum to yield **1b** as a white powder (1.05 g, 75%). ^{1}H NMR (DMSO-d_6): δ 9.68 (s, 2H, NC*H*N), 8.11 (s, 2H, CH_{imid}), 7.93 (s, 2H, CH_{imid}), 7.45 (d, J = 8.2, 4H, CH_{Ar}), 7.41 (d, J = 8.2, 4H, CH_{Ar}), 6.71 (s, 2H, NCH_2N), 5.46 (s, 4H, ArCH_2N), 1.27 (s, 18H, CH_3). ^{13}C NMR (DMSO-d_6): δ 151.44 ($C_{Ar(para)}$), 137.60 (N*C*HN), 131.22 ($C_{Ar(ipso)}$), 128.45 (CH_{Ar}), 125.73 (CH_{Ar}), 123.14 (CH_{imid}), 122.50 (CH_{imid}), 58.27 (NCH_2N), 51.98 ($ArCH_2N$), 34.35 ($C(CH_3)_3$), 30.98 ($C(CH_3)_3$). Anal. Calcd for $C_{29}H_{38}Br_2N_4$: C, 57.82; H, 6.36; N, 9.30. Found: C, 57.85; H, 6.21; N, 9.16. HRMS (*m/z*): calcd for $C_{29}H_{38}Br_2N_4$ [M-Br] $^{+}$: 521, found: 521.

Synthesis of 1,1'-dibenzyl-3,3'-methylenediimidazole-2,2'-diylidene (2a):

A Schlenk flask was charged with a mixture of **1a** (0.1 g, 0.204 mmol), K[$N(SiMe_3)_2$] (89.5 mg, 0.449 mmol) and THF (10 mL). The resulting mixture was stirred at room temperature for 5 min to give a pale yellow solution which was then filtered. The filtrate was dried under vacuum to yield a yellow powder of **2a** (66.1 mg, 98%). ^{1}H NMR (C_6D_6): δ 7.11-7.00 (m, 10H, CH_{Ar}), 6.99 (s, 2H, NCH_2N), 6.20 (s, 2H, CH_{imid}), 6.12 (s, 2H, CH_{imid}), 4.98 (s, 4H, ArCH_2N). ^{13}C NMR (C_6D_6): δ 216.28 (C_{imid}), 139.16 ($C_{Ar(ipso)}$),

129.08 (CH_{Ar}), 128.68 (CH_{Ar}), 128.03 (CH_{Ar}), 120.28 (CH_{imid}), 119.49 (CH_{imid}), 65.75 (NCH_2N), 55.27 ($ArCH_2N$).

Synthesis of 1,1'-methylene-3,3'-di-4-(*tert*-butyl)benzylimidazole-2,2'-diylidene (2b): A Schlenk flask was charged with a mixture of **1b** (0.1 g, 0.166 mmol), $K[N(SiMe_3)_2]$ (0.729 g, 0.365 mmol) and THF (10 mL). The resulting mixture was stirred at room temperature for 5 min to give a pale yellow solution which was then filtered. The filtrate was dried under vacuum to yield a yellow powder of **2b** (0.731 g, 98%). ^1H NMR (C_6D_6): 7.19 (d, J = 7.1, 4H, CH_{Ar}), 7.09 (d, J = 6.9, 4H, CH_{Ar}), 6.74 (s, 2H, NCH_2N), 6.26 (s, 2H, CH_{imid}), 6.03 (s, 2H, CH_{imid}), 5.06 (s, 4H, $ArCH_2N$), 1.16 (s, 18H, CH_3). ^{13}C NMR (C_6D_6): δ 214.40 (C_{imid}), 150.87 ($C_{Ar(para)}$), 135.97 ($C_{Ar(ipso)}$), 128.69 (CH_{Ar}), 126.12 (CH_{Ar}), 120.22 (CH_{imid}), 119.50 (CH_{imid}), 65.51 (NCH_2N), 55.11 ($ArCH_2N$), 34.80 ($C(CH_3)_3$), 31.74 ($C(CH_3)_3$).

Synthesis of bis(1,1'-methylene-3,3'-dibenzylimidazole-2,2'diylidene)nickel(II) dibromide (3a): A Schlenk flask was charged with a mixture of **2a** (0.500 g, 1.51 mmol), $NiBr_2$(DME) (0.234 g, 0.757 mmol) and THF (15 mL). After stirring at ambient temperature for 24 h, a pale yellow precipitate was obtained. The precipitate was filtered and washed with THF (3x10 mL) and dried under vacuum to yield a pale yellow powder. Crystals were obtained by slow diffusion of ether into a concentrated DMF solution (0.398 mg, 60%). ^1H NMR (DMSO-d_6): δ 7.75 (s, 4H, CH_{imid}), 7.39-7.29 (m, 12H, CH_{Ar}), 7.27 (s, 4H, CH_{imid}), 7.13-6.98 (m, 8H, CH_{Ar}), 6.50 (d, J = 13, 2H, NCH_aH_bN), 6.53 (d, J = 13, 2H, NCH_aH_bN), 4.85 (d, J = 15, 4H, $ArCH_aH_bN$), 4.37 (d, J = 15, 4H,

ArCH$_a$*H$_b$*N). ^{13}C NMR (DMSO-*d*$_6$): δ 171.34 (*C*$_{imid}$), 135.85(*C*$_{Ar(ipso)}$), 128.88 (*C*H$_{Ar}$), 128.24 (*C*H$_{Ar(para)}$), 127.61 (*C*H$_{Ar}$), 123.50 (*C*H$_{imid}$), 122.92 (*C*H$_{imid}$), 62.50 (N*C*H$_2$N), 52.61 (Ar*C*H$_2$N). Anal. Calcd for $C_{42}H_{40}Br_2N_8Ni$: C 57.63; H 4.61; N 12.80. Found: C 57.74; H 4.47; N 11.74. HRMS (*m/z*): calcd for $C_{42}H_{20}Br_2N_8Ni$ [M-Br] $^+$: 793.1907, found: 793.1884.

Synthesis of bis(1,1'-methylene-3,3'-di-4-(*tert*-butyl)benzylimidazole-2,2'-diylidene)nickel(II) dibromide (3b): A Schlenk flask was charged with **2b** (100 mg, 0.227 mmol), $NiBr_2$(DME) (35 mg, 0.114 mmol) and THF (10 mL). After stirring at ambient temperature for 12 h, a pale yellow precipitate was obtained. The precipitate was filtered and washed with THF (3x10 mL) and dried under vacuum to yield a white powder. Crystals were obtained by slow diffusion of ether into a concentrated DMF solution (50 mg, 40%). ^{1}H NMR (DMSO-*d*$_6$): δ 7.76 (s, 4H, C*H*$_{imid}$), 7.32 (d, *J* = 8.1, 8H, C*H*$_{Ar}$), 7.28 (s, 4H, C*H*$_{imid}$), 7.04 (d, 4H, , *J* = 8.1, 4H, *C*H$_{Ar}$), 6.46 (d, *J* = 13, 2H, NC*H$_a$*H$_b$N), 6.01 (d, *J* = 13, 2H, NCH$_a$*H$_b$*N), 4.85 (d, *J* = 15, 4H, ArC*H$_a$*H$_b$N), 4.37 (d, *J* = 15, 4H, ArCH$_a$*H$_b$*N), 1.21 (s, 36H, C*H*$_3$). ^{13}C NMR (DMSO-*d*$_6$): δ 171.23 (*C*$_{imid}$), 150.68 (*C*$_{Ar(para)}$), 133.15 (*C*$_{Ar(ipso)}$), 127.28 (*C*H$_{Ar}$), 125.28 (*C*H$_{Ar}$), 123.35 (*C*H$_{imid}$), 123.04 (*C*H$_{imid}$), 62.17 (N*C*H$_2$N), 52.21 (Ar*C*H$_2$N), 33.13 (*C*(CH$_3$)$_3$), 30.95 (C(*C*H$_3$)$_3$). HRMS (*m/z*): calcd for $C_{58}H_{72}Br_2N_8Ni$ [M-2Br]$^{2+}$: 469.2611, found: 469.2615.

Synthesis of (1,1'-dibenzyl-3,3'-methylenediimidazole-2,2'diylidene)tetrasilver(I) tetrabromide (4a): A suspension of **1a** (0.5 g, 1.02 mmol) and an equivalent amount of Ag_2O (0.236 g, 1.02 mmol) in dichloromethane (15 mL) was stirred at room temperature

for 3 d with exclusion of light under dinitrogen. The color of the suspension gradually changed from black to brown. The suspension was then filtered, washed with dichloromethane (3x10 mL) and dried under vacuum to yield **4a** as a light brown powder. Crystals were obtained by slow diffusion of ether into a concentrated DMF solution (0.646 g, 90%). ^{1}H NMR (DMSO-d_6): δ 7.87 (s, 4H, CH_{imid}), 7.59 (s, 4H, CH_{imid}), 7.24 (m, 12H, C$H_{Ar(meta\ and\ para)}$), 7.09 (m, 8H, C$H_{Ar(ortho)}$), 6.70 (br s, 4H, NCH_2N), 5.21 (s, 8H, ArCH_2N)). ^{13}C NMR (DMSO-d_6): δ 181.08 (C_{imid}), 136.58 ($C_{Ar(ipso)}$), 128.68 (CH$_{Ar}$), 128.01 (CH$_{Ar(para)}$), 127.14 (CH$_{Ar}$), 123.38 (CH$_{imid}$), 122.37 (CH$_{imid}$), 63.45 (NCH$_2$N), 54.44 (ArCH$_2$N). Anal. Calcd for $C_{42}H_{40}Br_4N_8Ag_4$: C 35.83; H 2.86; N 7.96. Found: C 36.43; H 2.72; N 8.00.

Synthesis of bis(1,1'-methylene-3,3'-di-4-(*tert*-butyl)benzylimidazole-2,2'-diylidene)tetrasilver(I) tetrabromide (4b): A suspension of **2b** (0.5 g, 0.830 mmol) and an equivalent amount of Ag_2O (0.192 g, 0.830 mmol) in dichloromethane (15 mL) was stirred at room temperature for 3 d with exclusion of light under nitrogen atmosphere. The color of the suspension gradually changed from black to white. The suspension was then filtered, washed with dichloromethane (3x10 mL) and dried under vacuum to yield **3** as a white powder (0.610 g, 90%). ^{1}H NMR (DMSO-d_6): δ 7.86 (s, 4H, CH_{imid}), 7.58 (s, 4H, CH_{imid}), 7.23 (d, J = 8.0, 8H, CH_{Ar}), 7.08 (d, J = 7.8, 8H, CH_{Ar}), 6.71 (br s, 4H, NCH_2N), 5.20 (s, 8H, ArCH_2N), 1.15 (s, 36H, C(CH_3)$_3$). ^{13}C NMR (DMSO-d_6): δ 171.23 (C_{imid}), 150.68 ($C_{Ar(para)}$), 133.15 ($C_{Ar(ipso)}$), 127.28 (CH$_{Ar}$), 125.28 (CH$_{Ar}$), 123.35 (CH$_{imid}$), 123.04 (CH$_{imid}$), 62.17 (NCH$_2$N), 52.21 (ArCH$_2$N), 33.13 (C(CH$_3$)$_3$), 30.95 (C(CH$_3$)$_3$). Anal. Calcd for $C_{58}H_{72}Br_4N_8Ag_4 \cdot 0.5(CH_2Cl_2)$: C 41.27; H 4.34; N 6.53.

Found: C 41.28; H 3.30; N 6.33. ^{1}H NMR confirmed the presence of 0.5 equiv. CH_2Cl_2 in the sample.

Alternative synthesis of Bis(1,1'-methylene-3,3'-dibenzylimidazole-2,2'diylidene)nickel(II) dibromide (3a): A suspension of **4a** (0.5 g, 0.710 mmol) and one equiv. of $NiBr_2$(DME) (110 mg, 0.355 mmol) in DMF (15 mL) was stirred at 90 ^oC for 24 h under dinitrogen. The color of the suspension gradually changed from light brown to grey. The solution was then filtered to remove the AgBr precipitate. The filtrate was concentrated under vacuum. Upon addition of diethyl ether a pale yellow precipitate was obtained which was filtered and dried under vacuum to yield **3a** as a pale yellow powder (0.140 g, 45%).

Alternative synthesis of Bis(1,1'-methylene-3,3'-di-4-(*tert*-butyl)benzylimidazole-2,2'-diylidene) nickel(II) dibromide (3b): A suspension of **4b** (0.5 g, 0.613 mmol) and one equiv. of $NiBr_2$(DME) (94.5 mg, 0.307 mmol) in DMF (10 mL) was stirred at 90 ^oC for 24 h. The color of the suspension gradually changed from light brown to grey. The solution was then filtered to remove the AgBr precipitate. The filtrate was concentrated under vacuum. Upon addition of diethyl ether a white precipitate was obtained which was filtered and dried under vacuum to yield **3b** as a white powder (0.118 g, 35%).

Synthesis of (1,1'-Methylene-3,3'-dibenzylimidazole-2,2'diylidene)palladium(II) dichloride (5a): A suspension of **4a** (0.4 g, 0.568 mmol) and two equiv. of $PdCl_2$ (101 mg, 0.568 mmol) in DMF (10 mL) was stirred at 90 ^oC for 16 h. The color of the

suspension gradually changed from light brown to grey. The solution was then filtered through a celite column to remove the AgBr precipitate. The filtrate was concentrated under vacuum. Upon addition of diethyl ether a white precipitate was obtained which was filtered and dried under vacuum to yield **5a** as a white powder (0.143 g, 48%). ^{1}H NMR (DMSO-d_6): δ 7.58 (s, 2H, CH_{imid}), 7.31 (m, 10H, CH_{Ar}), 7.27 (s, 2H, CH_{imid}), 6.49-6.25 (2 doublets (overlapping)), 2H, NCH_2N), 6.12 (d, J = 14.6, 2H, ArCH_aH$_b$N)), 5.32 (d, J = 14.6, 2H, ArCH$_a$$H_b$N). ^{13}C NMR (DMSO-$d_6$): δ 162.31 ($C_{imid}$), 156.87 ($C_{Ar(para)}$), 138.81 ($C_{Ar(ipso)}$), 128.69 ($CH_{Ar}$), 128.03 ($CH_{Ar}$), 127.97 ($CH_{imid}$), 121.94 ($CH_{imid}$), 62.46 (N$CH_2$N), 52.82 (Ar$CH_2$N). Anal. Calcd for $C_{21}H_{20}Cl_2N_4Pd$·0.5DMF: C 49.83; H 4.37; N 11.62. Found: C 48.63; H 3.90; N 11.29. HRMS (*m/z*): calcd for $C_{21}H_{20}Cl_2N_4Pd$ [M-Cl]$^+$: 471.0404, found: 471.0409.

Synthesis of (1,1'-Methylene-3,3'-di-4-(*tert*-butyl)benzylimidazole-2,2'-diylidene)palladium(II) dichloride (5b): A suspension of **4b** (0.4 g, 0.245 mmol) and two equiv. of $PdCl_2$ (87 mg, 0.49 mmol) in DMF (10 mL) was stirred at 90 ^{o}C for 16 h under nitrogen atmosphere. The color of the suspension gradually changed from light brown to grey. The solution was then filtered through a celite column to remove the AgBr precipitate. The filtrate was concentrated under vacuum. Upon addition of diethyl ether a white precipitate was obtained which was filtered and dried under vacuum to yield **5b** as a white powder (0.176 g, 58%). ^{1}H NMR (DMSO-d_6): δ 7.57 (s, 2H, CH_{imid}), 7.38 (d, 8H, J = 8.1, 4H, CH_{Ar}), 7.31 (d, J = 7.7, 4H, CH_{Ar}),), 7.20 (s, 2H, CH_{imid}), 6.33 (2 doublets (overlapping)), 2H, NCH_2N), 6.01 (d, J = 14.5, 2H, ArCH_aH$_b$N)), 5.32 (d, J = 14.5, 2H, ArCH$_a$$H_b$N), 1.25 (s, 18H, C$H_3$). ^{13}C NMR (DMSO-$d_6$): δ 156.99 ($C_{imid}$), 150.46

($C_{Ar(para)}$), 133.80 ($C_{Ar(ipso)}$), 127.87 (CH_{Ar}), 125.44 (CH_{Ar}), 122.02 (CH_{imid}), 121.73 (CH_{imid}), 62.44 (NCH_2N), 52.76 ($ArCH_2N$), 34.30 ($C(CH_3)_3$), 31.08 ($C(CH_3)_3$). Anal. Calcd for $C_{29}H_{36}Cl_2N_4Pd \cdot 0.5DMF$: C 55.97; H 6.08; N 9.63. Found: C 54.79; H 5.61; N 8.80. HRMS (*m/z*): calcd for $C_{29}H_{36}Cl_2N_4Pd$ $[M\text{-}Cl]^+$: 581.1663, found: 581.1783.

General procedure for the Mizoroki-Heck coupling reactions: In a typical experiment, an oven dried 25 mL pressure tube equipped with a stir bar was charged with 5 mol% of the catalyst (0.025 mmol), base (Na_2CO_3, 1.5 mmol), additive (Bu_4NI) and phenylboronic acid (2.5 mmol). Under nitrogen, DMF (5 mL) and aryl halides (0.5 mmol) were added via syringe. The tube was sealed with a Teflon cap and placed in pre-heated sand bath at 150 ^oC. After the specified time the tube was removed from the sand bath and water (20 mL) added followed by extraction with ether (3x10 mL). The combined organic layers were washed with saturated aqueous NaCl (10 mL), dried over anhydrous $MgSO_4$, filtered and the solvent was removed under vacuum. The residue was dissolved in $CDCl_3$ and analyzed by ^1H NMR. Yields were determined by ^1H NMR spectroscopy against the remaining aryl halide.

General procedure for the Suzuki-Miyaura coupling reactions: In a typical run, an oven dried 25 mL pressure tube equipped with a stir bar was charged with 5 mol % catalyst (0.025 mmol), base (K_3PO_4, 1.5 mmol) and phenylboronic acid (2.5 mmol). Under nitrogen, dioxane (5 mL) and aryl halide (0.5 mmol) were added via syringe. The tube was sealed with a Teflon cap and placed in pre-heated sand bath at 120 ^oC. After the specified time the tube was removed from the sand bath and water (20 mL) added

followed by extraction with dichloromethane (3x10 mL). The combined organic layers were washed with saturated aqueous NaCl (10 mL), dried over anhydrous $MgSO_4$, filtered and the internal standard (dodecahydrotriphenylene) was added. Solvent was removed under vacuum. The residue was dissolved in $CDCl_3$ and analyzed by ^1H NMR. Yields were determined by ^1H NMR spectroscopy against dodecahydrotriphenylene as the internal standard.

X-ray structure determinations: Data was collected at -100 °C on a Nonius Kappa CCD diffractometer, using the COLLECT program.[31] Cell refinement and data reductions used the programs DENZO and SCALEPACK.[32] SIR97[33] was used to solve the structures and SHELXL97[34] was used to refine the structures. ORTEP-3 for Windows[35] was used for molecular graphics and PLATON[36] was used to prepare material for publication. H atoms were placed in calculated positions with U_{iso} constrained to be 1.5 times U_{eq} of the carrier atom for methyl protons and 1.2 times U_{eq} of the carrier atom for all other hydrogen atoms.

For complex **3b**·4DMF, there is one A ALERT because of the Solvent Accessible Void of 291 A^3. This was due to a disordered solvent molecule which could not be modelled. This electron density was handled by using the SQUEEZE option in PLATON. There is a SQUEEZE addition at the end of the CIF. The two B ALERTs are due to the very different types of C atoms in the structure, ranging from phenyl and other rigid rings to disordered tert-butyl groups. The H atoms on the C atoms show the same range of U_{eq}, because they are determined by the values for the attached C atoms.

For complex **4a**, the Hirshfeld test B ALERTs assume independent bonds, not clusters such as Ag_4Br_4 in this structure. The high U_{eq} for Ag1 and Ag2 is possibly due to some disorder which could not be modelled. The low U_{eq} for Br2 is the other side of the possible disorder of the Ag atoms. The nearest atoms to Br2 are Ag1 and Ag2. The low bond precision of C-C bonds is a consequence of the heavy atom cluster.

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CHAPTER 3

NON-SYMMETRICALLY SUBSTITUTED DI-*N*-HETEROCYCLIC CARBENE PALLADIUM(II) AND NICKEL(II) COMPLEXES: SYNTHESIS, STRUCTURE AND CATALYTIC ACTIVITY

3.1 Introduction

A major portion of this chapter was published in *Journal of Organometallic Chemistry* in October 2008.[1] Written permission was obtained from all contributing authors to include material within this thesis. All the work included in this chapter is my contribution with the exception of the synthesis of **1b-5b**.

N-heterocyclic carbenes (NHCs) have received considerable attention as ligands in transition metal coordination chemistry which has resulted in the synthesis of a wide variety of stable metal-carbene complexes with numerous applications as catalysts for organic transformations.[2] Chelating di-*N*-heterocyclic carbene ligands (diNHCs) in particular are expected to provide increased entropic stability to a metal centre and consequently many reports have emerged in recent years concerning *cis*-chelating, alkane-bridged diNHCs.[3]

The second research objective as mentioned in *Chapter 1* was to synthesize non-symmetrically substituted diNHC ligands with a hemi-labile donor arm on one of the nitrogen atoms as shown in Figure 3-1.

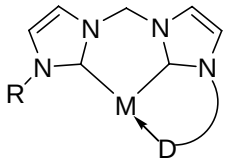


Figure 3-1. NHC complexes with hemi-labile donor arm D.

To achieve this goal, the synthesis of non-symmetrically substituted diNHC ligands had to be pursued. This chapter deals with the development of a general route into the synthesis of non-symmetrically substituted diNHC ligands and the following chapter will deal with the synthesis of non-symmetrically substituted diNHC ligands with a hemi-labile donor arm as one of the nitrogen substituents.

While the preparation of diverse symmetrically substituted diNHC ligands have been reported, there are no examples of non-symmetrically substituted diNHC ligands in the literature where R ≠ R' (Figure 3-2).[4]

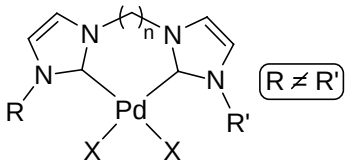
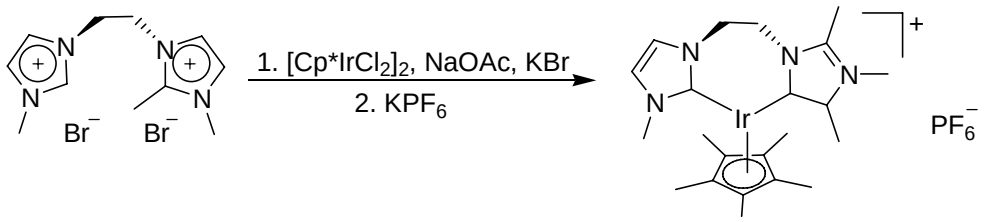


Figure 3-2. Non-symmetrically substituted (diNHC)PdX_2

There is, however, one example of a non-symmetric diNHC ligand employing variations of Crabtree's abnormal NHC ligand for applications in iridium chemistry (Scheme 3-1).[5]

Scheme 3-1. Crabtree's abnormal NHC ligands.



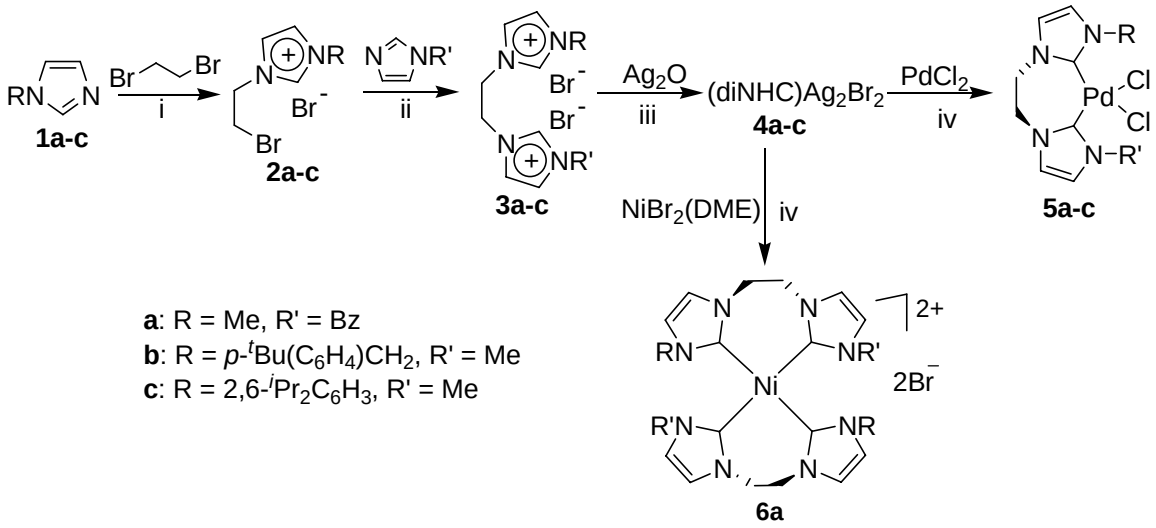
Here we report the synthesis of non-symmetrically substituted ethylene-bridged diimidazolium salts and their corresponding diNHC palladium(II) and nickel(II) complexes. Given the effectiveness of reported (diNHC)Pd(II) complexes in C-C coupling reactions[2-4], preliminary investigations into the activity of these complexes in the Suzuki-Miyaura coupling reaction of bulky substrates were performed.

3.2 Results and Discussion

3.2.1 Synthesis of ligands

The key step in the synthesis of non-symmetric imidazolium salts **3a-c** is isolation of the bromoethylimidazolium bromide precursor **2a-c** which is easily synthesized from an *N*-substituted imidazole and excess 1,2-dibromoethane (Scheme 3-2). The synthesis of **2a** has been previously reported.[6] The second step simply involves reaction of **2a-c** with one equiv of an *N*-substituted imidazole in toluene resulting in the non-symmetrically substituted diimidazolium salts **3a-c** in 90% yield. Preliminary results suggest this is a general route into non-symmetric diNHCs, provided the bromoethylimidazolium bromide precursors can be isolated. Diimidazolium salts with both aliphatic and aromatic *N*-substituents have been synthesized. The ^{1}H NMR spectra of **3a-c** in DMSO-d_6 exhibits two distinct resonances at 9.32 and 9.17 ppm for **3a**, at 9.25 and 9.12 ppm for **3b** and at 9.38 and 9.21 ppm for **3c** for the two NC*H*N protons on the two ethylene-bridged imidazolium rings. There are also four distinct resonances for the protons on the remaining four carbons of the two imidazolium rings. Single crystals of **3a**,**c** were obtained by slow diffusion of ether into a concentrated solution in DMF. The crystal structures of **3a**,**c** show an *anti* conformation of the imidazolium units about the C_2 bridge with the imidazolium units oriented in opposite directions (Figure 3-3 and 3-4, and Table 3-1).

Scheme 3-2. Synthesis of non-symmetric (diNHC)$PdCl_2$ complexes.



Conditions: (i) neat, 2 d, 80 °C; (ii) toluene, 3 d, 80-150 °C; (iii) dichloromethane, 2 h, rt; (iv) DMF, 24 h, 90 °C

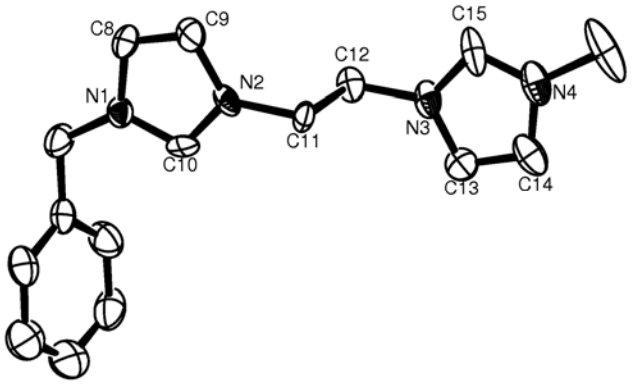


Figure 3-3. ORTEP plot of non-symmetrically substituted diimidazolium salt **3a** at the 50% probability level. The hydrogen atoms and bromide anions are omitted for clarity. Selected bond angles (°): N(2)-C(10)-N(1) = 108.4(12), N(4)-C(15)-N(3) = 108.5(16).

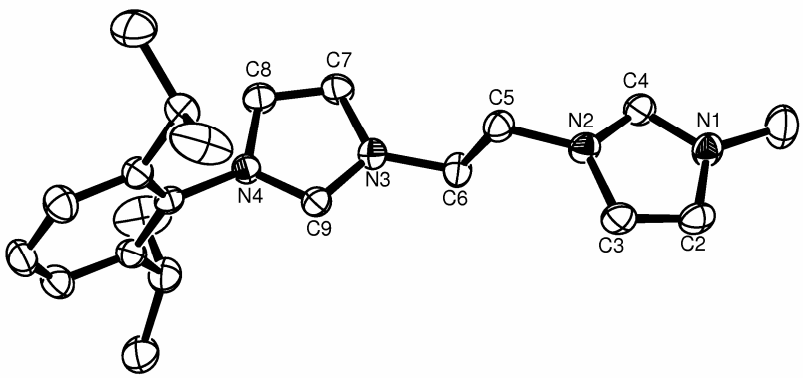


Figure 3-4. ORTEP plot of non-symmetrically substituted diimidazolium salt **3c** at the 50% probability level. The hydrogen atoms and bromide anions are omitted for clarity. Selected bond angles (°): N(2)-C(4)-N(1) = 108.5(3), N(4)-C(9)-N(3) = 108.4(2).

3.2.2 Synthesis of (diNHC)Ag(I), (diNHC)Pd(II) and bis(diNHC)Ni(II) complexes

Complexes **5a-c** were synthesized *via* a transmetallation route using (diNHC)Ag(I) complexes (Scheme 3-2). The advantage of using (diNHC)Ag(I) complexes as carbene transfer reagents include simple preparation directly from the imidazolium salt and ease of handling due to their stability in air.[7] (DiNHC)Ag(I) complexes **4a-c** were synthesized by the reaction of the diimidazolium salt precursors **3a-c** with an equivalent amount of Ag_2O according to established procedures.[4c] The ^1H NMR spectra of **4a-c** (DMSO-d_6) show the absence of any signal in the 8-10 ppm region indicating the successful deprotonation of the carbenic protons in **3a-c**. The bridging ethylene protons in **4a-c** now appear as two multiplets each integrating for two protons compared to the singlet obtained for **3a-c**. The ^{13}C NMR spectra of **4a,b** shows the appearance of two resonances at 181 and 180 ppm, and **4c** shows two overlapping signals at 179 ppm which is characteristic of the two non-symmetric carbenic (N*C*N) carbons. Elemental analysis is consistent with formation of (diNHC)Ag_2Br_2.

Subsequent reaction of the silver complexes **4a-c** with one equiv $PdCl_2$ in DMF at 90 ^{o}C for 16 h afforded the desired complexes **5a-c** in 50-60% yield, and with half an equiv of $NiBr_2$(DME) afforded the complex **6a**. The ^{13}C NMR spectra of **5** show the appearance of two resonances at 157 and 155 ppm for **5a**, at 155 and 154 ppm for **5b** and at 160 ppm for **5c** which is again characteristic of the two non-symmetric carbenic carbons. The ethylene bridge and methylene protons of the benzyl moiety exhibit broad resonances in the ^{1}H NMR spectra which is likely due to the inherent fluxionality of the seven-membered palladacycle. This phenomenon has been previously observed in reported (diNHC)Pd(II) complexes.[4b] Complexes **5a-c** are air and moisture stable. **5a,b** are soluble only in polar solvents such as DMF ad DMSO and can be crystallized by slow diffusion of ether into a concentrated solution of the sample in DMF, whereas **5c** is soluble in solvents like chloroform and dichloromethane, because of the 2,6-diisopropylphenyl substituent, and can be crystallized by slow evaporation from acetonitrile. The solid state structure of complexes **5a-c** were determined by single-crystal X-ray diffraction, which showed the palladium in a distorted square-planar geometry (Figures 3-5, 3-6 and 3-7, and Table 3-1). **5b** co-crystallized with one molecule of DMF and **5c** co-crystallized with one molecule of acetonitrile. In all the structures the palladacycles adopt boat-like conformations and in **5a,b** the benzyl moiety of the chelating diNHC ligand is oriented towards the axial face of the palladium centre. The ^{13}C NMR spectrum of **6a** shows the appearance of four resonances at 171, 170, 168 and 162 ppm which is again characteristic of the four non-symmetric carbenic carbons. There are also eight distinct resonances for the protons on the four imidazolylidene rings. The ethylene bridge and methylene protons of the benzyl moiety exhibit sharp resonances in

the ^{1}H NMR spectrum with each proton giving a distinct resonance. Complex **6a** is air and moisture stable and soluble only in polar solvents such as DMF and DMSO. Unfortunately, to date, we have not been able to grow suitable crystals of **6a** for X-ray characterization.

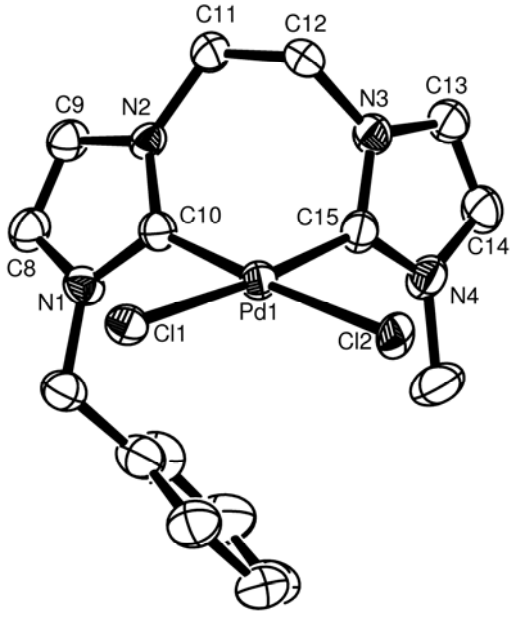


Figure 3-5. ORTEP plot of **5a** at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)-C(15) = 1.967(5), Pd(1)-C(10) = 1.982(6), C(15)-Pd(1)-C(10) = 86.3(2), N(1)-C(10)-N(2)=104.9(5), N(4)-C(15)-N(3) = 106.0(5).

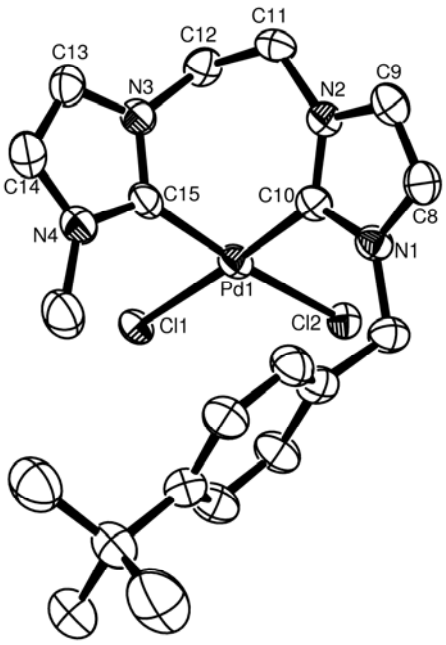


Figure 3-6. ORTEP plot of **5b**·DMF at the 50% probability level. Hydrogen atoms and the solvent molecule have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)-C(15) = 1.953(6), Pd(1)-C(10) = 1.985(6), C(15)-Pd(1)-C(10) = 85.9(2), N(2)-C(10)-N(1) = 104.5(5), N(3)-C(15)-N(4) = 104.8(5).

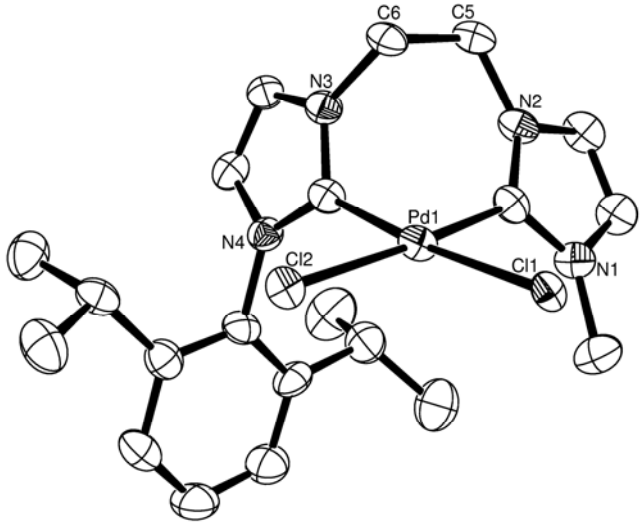


Figure 3-7. ORTEP plot of **5c**·CH_3CN at the 50% probability level. Hydrogen atoms and the solvent molecule have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)-C(4) = 1.994(8), Pd(1)-C(9) = 1.974(8), C(15)-Pd(1)-C(10) = 85.9(2), N(2)-C(4)-N(1) = 105.1(7), N(3)-C(9)-N(4) = 105.0(6).

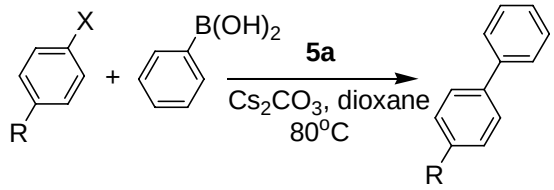
Table 3-1. Crystal data and refinement parameters for compounds **3a**, **3c**, **5a, 5b** and **5c**·CH_3CN.

	3a	**3c**	**5a**	**5b**·DMF	**5c**·CH_3CN
formula	$C_{16}H_{20}Br_2N_4$	$C_{21}H_{30}Br_2N_4$	$C_{16}H_{18}Cl_2N_4Pd$	$C_{23}H_{33}Cl_2N_5OPd$	$C_{23}H_{31}Cl_2N_5Pd$
formula wt	428.18	498.31	443.64	572.84	554.83
color	colorless	colorless	pale yellow	colorless	colorless
crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	P-1	$P2_1/c$	$P2_1/c$	$C2/c$
a, Å	27.1963(15)	8.2284(3)	8.3715(2)	13.6740(9)	35.706(2)
b, Å	5.1619(3)	9.3409(3)	17.8428(4)	14.0256(9)	8.6110(3)
c, Å	12.5926(5)	16.0074(5)	14.3790(4)	13.3806(11)	19.0188(7)
α, *deg*	90	74.969(2)	90	90	90
β, deg	91.922(3)	87.854(3)	124.492(2)	94.680(4)	118.692(2)
γ, *deg*	90	78.294(2)	90	90	90
Z	4	2	4	4	8
ρ_{calc}, mg m^{-3}	1.610	1.423	1.665	1.488	1.437
temp, K	173(2)	173(2)	173(2)	173(2)	173(2)
F(000)	856	508	888	1176	2272
θ range, deg	3.00 to 23.25	3.62 to 27.49	2.69 to 27.46	2.99 to 25.35	3.63 to 25.03
reflns collected/unique	12024/2398	16998/5327	25351/4040	19094/4659	22016/4516
R_{int}	0.1221	0.0563	0.0772	0.1088	0.1193
final R_1(I >2σI)	R1 = 0.0943, wR2 = 0.1814	R1 = 0.0396, wR2 = 0.0789	R1 = 0.0552, wR2 = 0.1412	R1 = 0.0600, wR2 = 0.1333	R1 = 0.0734, wR2 = 0.1819
R_1(all data)	R1 = 0.1219, wR2 = 0.1955	R1 = 0.0629 wR2 = 0.0886	R1 = 0.0727, wR2 = 0.1550	R1 = 0.0848, wR2 = 0.1473	R1 = 0.0961, wR2 = 0.1971

3.2.3 Catalytic activity

The catalytic activity of complex **5a** was investigated in the Suzuki-Miyaura coupling reaction of bulky and non-bulky substrates. In recent years, several powerful systems have been developed for the activation of not only *para*-substituted aryl chlorides[8] but hindered substrates such as *ortho*-substituted aryl halides as shown by Buchwald's group[9]. In our case, excellent yields were obtained in the standard coupling reaction of *para*-susbstituted aryl bromides with phenyl boronic acid when both activated and deactivated aryl bromides were employed even at very low catalyst loading (Table 3-2). However, activity significantly decreased when aryl chlorides were employed with no coupling product observed in the presence of deactivated aryl chlorides (entry 5). These results are in contrast to *trans*-$(NHC)_2PdCl_2$ complexes which show high activity for deactivated aryl chlorides under similar conditions.[10] Current state of the art for Suzuki-Miyaura reactions employing NHC complexes of palladium is 0.1% catalyst loading at ambient temperature for deactivated aryl chlorides.[11]

Table 3-2. Suzuki-Miyaura cross-coupling of aryl halides by complex **5a**[a].

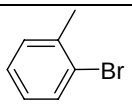
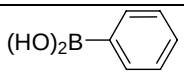
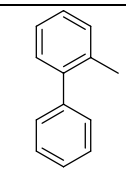
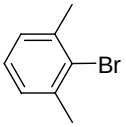
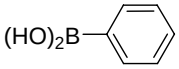
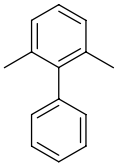
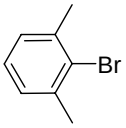
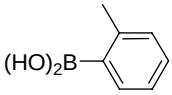
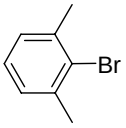
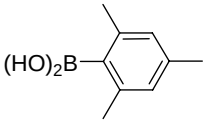
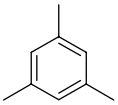
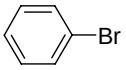
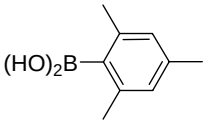
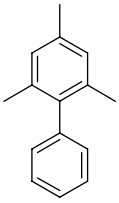
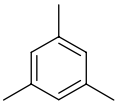


Entry	R	X	Time (h)	Catalyst (mol %)	Yield (%)[b]	TON[c]
1	COMe	Br	1	0.01	96	9600
2	OMe	Br	6	0.1	95	950
3	COMe	Cl	24	1	37	37
4	H	Cl	24	1	20	20
5	OMe	Cl	24	1	0	0

[a]Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol), precatalyst **5a**, dioxane (5 mL), 80 °C. [b]Determined by ^{1}H NMR based on internal standard dodecahydrotriphenylene from a single run. [c]TON= moles of product per mol of catalyst.

Given the recent interest in catalysts that can couple sterically hindered substrates,[8] the activity of precatalyst **5a** for the coupling of bulky substrates was investigated (Table 3). High to moderate yields were obtained for mono and di *ortho*-substituted biaryls provided the steric bulk was incorporated on only one of the coupling partners. No coupled product was obtained when both partners were sterically hindered. Attempts to couple 2,4,6-trimethylphenylboronic acid yielded mesitylene as the major product.

Table 3-3. Suzuki-Miyaura cross-coupling of bulky aryl halides and aryl boronic acids by complex **5a**.[a]

Entry	ArBr	Ar'B(OH)$_2$	Product	Conv (%)[b]
1				92
2				66
3			no rxn	0
4				80
5				13
			+	
				17

[a]Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol), precatalyst **5a**, dioxane (5 mL), 80 °C, 24 h. [b]Determined by ^{1}H NMR based on internal standard dodecahydrotriphenylene from a single run.

3.3 Conclusions

In conclusion, we have synthesized stable non-symmetrically substituted diNHC Pd(II) complexes and have investigated their catalytic activity in the Suzuki-Miyaura coupling reaction of bulky substrates. This synthetic route represents a possible general pathway into a wide variety of non-symmetrically substituted diNHC ligands. These examples of non-symmetrically substituted chelating diNHC ligand can serve in designing NHC ligands with finely tuned steric and electronic environments around the metal centre.

3.4 Experimental

General Procedures: Unless otherwise stated, all reactions were performed under N_2 using standard Schlenk techniques or in a N_2-filled drybox. Dichloromethane and THF were dried using an MBraun Solvent Purification System and were stored in a glovebox. All reaction temperatures for catalytic reactions refer to the temperature of pre-equilibrated sand baths. ^1H and ^{13}C $\{^1H\}$ NMR spectra were recorded on a Bruker 500 MHz Avance spectrometer. Chemical shifts for ^1H and ^{13}C NMR are reported in ppm in reference to the residual ^1H and ^{13}C resonances of $CDCl_3$ (^1H: δ 7.24; ^{13}C: δ 77.23) and DMSO-d_6 (^1H: δ 2.50; ^{13}C: δ 39.51). Coupling constants are given in Hz. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. High resolution mass spectra (HRMS) were measured on an Applied Biosystem QSTAR® XL MS/MS system (ESI-QTOF). 1,2-dibromoethane and Ag_2O were purchased from Alfa-Aesar Chemical Company and used as received. Imidazole, *N*-methylimidazole, benzyl bromide, *tert*-butylbenzyl bromide, anhydrous DMF, anhydrous dioxane and NaH were purchased from Sigma-Aldrich Chemical Company and used as received. $PdCl_2$ was obtained from PMO Pty Ltd, Australia. *N*-benzylimidazole[4b], 2,6-diisopropylphenyl imidazole[12] and 1-(2-Bromoethyl)-3-methylimidazolium bromide (**2a**)[6] were synthesized according to literature procedures.

Synthesis of 1-(4-*tert*-butylbenzyl)-3-(2-bromoethyl)imidazolium bromide (2b): A Schlenk flask was charged with **1b** (0.213 g, 0.994 mmol) and 1,2-dibromoethane (10

mL) under dinitrogen. After stirring for 2 d at 80 °C, the resulting white precipitate was isolated and washed with diethyl ether (3x10 mL) and dried under vacuum to yield **2b** as a white powder. (0.236 g, 59%). ^{1}H NMR (DMSO-d_6): δ 9.39 (s, 1H, NC*H*N), 7.87 (s, 1H, CH_{imid}), 7.76 (s, 1H, CH_{imid}), 7.44 (d, J = 8.3, 2H, CH_{Ar}), 7.33 (d, J = 8.3, 2H, CH_{Ar}), 5.43 (s, 2H, ArCH_2N), 4.63 (t, J = 5.8, 2H, BrCH_2CH$_2$N), 3.96 (t, J = 5.8, 2H, BrCH$_2$CH_2N), 1.26 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (DMSO-d_6): δ 151.29 ($C_{Ar(para)}$), 136.61 (N*C*HN), 131.81 ($C_{Ar(ipso)}$), 127.95 (*C*H$_{Ar}$), 125.75 (*C*H$_{Ar}$), 122.79 (*C*H$_{imid}$), 122.72 (*C*H$_{imid}$), 54.89 (Ar*C*H$_2$N), 51.68 (Br*C*H$_2$CH$_2$N), 50.20 (BrCH$_2$*C*H$_2$N), 34.34 (*C*(CH$_3$)$_3$), 30.99 (C(*C*H$_3$)$_3$). HRMS (*m/z*): calcd for $C_{16}H_{22}Br_2N_2$ [M-Br]$^+$: 321.0960, found: 321.0971.

Synthesis of 1-(2,6-diisopropylphenyl)-3-(2-bromoethyl)imidazolium bromide (2c): A Schlenk flask was charged with 2,6-diisopropylphenyl imidazole (0.5 g, 2.19 mmol) and 1,2-dibromoethane (10 mL) under dinitrogen. After stirring for 2 d at 80 °C, the resulting white precipitate was isolated and washed with diethyl ether (3x10 mL) and dried under vacuum to yield **2c** as a white powder. (0.638 g, 70%). ^{1}H NMR (DMSO-d_6): δ 9.69 (s, 1H, NC*H*N), 8.20 (s, 1H, CH_{imid}), 8.14 (s, 1H, CH_{imid}), 7.63 (t, J = 7.8, 1H, CH_{Ar}), 7.45 (d, J = 7.8, 2H, CH_{Ar}), 4.74 (t, J = 5.2, 2H, BrCH_2CH$_2$N), 4.08 (t, J = 5.3, 2H, BrCH$_2$CH_2N), 2.30 (sept, 2H, C*H*(CH$_3$)$_2$), 1.15 (d, J = 6.5, 12H, CH(CH_3)$_2$). ^{13}C NMR (DMSO-d_6): δ 145.62 ($C_{Ar(ipso)}$), 138.81 (N*C*HN), 132.03 ($C_{Ar(ipso)}$), 127.95 (*C*H$_{Ar}$), 125.75 (*C*H$_{Ar}$), 122.79 (*C*H$_{imid}$), 122.72 (*C*H$_{imid}$), 54.89 (Ar*C*H$_2$N), 51.68 (Br*C*H$_2$CH$_2$N), 51.18 (BrCH$_2$*C*H$_2$N), 32.76 (Br*C*H$_2$CH$_2$N), 28.50 (*C*H(CH$_3$)$_3$), 24.38 (CH(*C*H$_3$)$_3$), 24.17 (CH(*C*H$_3$)$_3$). HRMS (*m/z*): calcd for $C_{17}H_{24}Br_2N_2$ [M-Br]$^+$: 335.1123, found: 335.1124.

Synthesis of 1-benzyl-1'-methyl-3,3'-ethylenediimidazolium dibromide (3a): A Schlenk flask was charged with a mixture of **2a** (1.0g, 3.70 mmol), *N*-benzylimidazole (0.586 g, 3.70 mmol) and toluene (20 mL) and was stirred at 80 ^{o}C for 3 d under dinitrogen. A white precipitate was isolated, washed with THF (3x15 mL) and dried under vacuum to yield **3a** as a white powder. (1.43 g, 90%). ^{1}H NMR (DMSO-d_6): δ 9.32 (s, 1H, NC*H*N), 9.17 (s, 1H, NC*H*N), 7.86 (s, 1H, CH_{imid}), 7.77 (s, 1H, CH_{imid}), 7.72 (s, 1H, CH_{imid}), 7.64 (s, 1H, CH_{imid}), 7.48-7.36 (m, 5H, CH_{Ar}), 5.45 (s, 2H, ArCH_2N), 4.74 (s, 4H, NCH_2CH_2N), 3.84 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 137.11 (N*C*HN), 136.72 (N*C*HN), 134.57 ($C_{Ar(ipso)}$), 128.94 (*C*H$_{Ar}$), 128.73 (*C*H$_{Ar}$), 128.27 (*C*H$_{Ar}$), 123.82 (*C*H$_{imid}$), 122.88 (2C, *C*H$_{imid}$), 122.27 (*C*H$_{imid}$), 51.98 (Ar*C*H$_2$N), 48.55 (N*C*H$_2$CH$_2$N), 48.19 (NCH$_2$*C*H$_2$N), 35.98 (*C*H$_3$). HRMS (*m/z*): calcd for $C_{16}H_{20}Br_2N_4$ [M-Br]$^+$: 347.0871, found: 347.0878.

Synthesis of 1-(4-*tert*-butylbenzyl)-1'-methyl-3,3'-ethylenediimidazolium dibromide (3b): A Schlenk flask was charged with a mixture of **2b** (0.85 g, 2.11 mmol), *N*-methylimidazole (0.179 mL, 2.26 mmol) and toluene (20 mL) and was stirred at 150 ^{o}C for 3 d under nitrogen atmosphere. A white precipitate was isolated, washed with toluene (3x15 mL) and dried under vacuum to yield **3b** as a white powder. (0.96 g, 94%). ^{1}H NMR (DMSO-d_6): δ 9.25 (s, 1H, NC*H*N), 9.12 (s, 1H, NC*H*N), 7.85 (s, 1H, CH_{imid}), 7.73 (s, 2H, CH_{imid}), 7.63 (s, 1H, CH_{imid}), 7.45 (d, J = 8.2, 2H, CH_{Ar}), 7.32 (d, J = 8.2, 2H, CH_{Ar}), 5.38 (s, 2H, ArCH_2N), 4.71 (s, 4H, NCH_2CH_2N), 3.84 (s, 3H, CH_3), 1.27 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (DMSO-d_6): δ 151.32 ($C_{Ar(para)}$), 137.11 (N*C*HN), 136.63 (N*C*HN),

131.66 ($C_{Ar(ipso)}$), 128.10 (CH_{Ar}), 125.74 (CH_{Ar}), 123.89 (CH_{imid}), 122.93 (CH_{imid}), 122.87 (CH_{imid}), 122.32 (CH_{imid}), 51.73 ($ArCH_2N$), 48.60 (NCH_2CH_2N), 48.24 (NCH_2CH_2N), 35.99 (CH_3), 34.37 ($C(CH_3)_3$), 31.02 ($C(CH_3)_3$). HRMS (*m/z*): calcd for $C_{20}H_{28}Br_2N_4$ [M-Br]$^+$: 403.1491, found: 403.1500.

Synthesis of 1-(2,6-diisopropylphenyl)-1'-methyl-3,3'-ethylenediimidazolium dibromide (3c): A Schlenk flask was charged with a mixture of **2c** (0.5 g, 1.2 mmol), *N*-methylimidazole (0.095 mL, 1.2 mmol) and toluene (20 mL) and was stirred at 80 ^oC for 3 d under dinitrogen. A white precipitate was isolated, washed with THF (3x15 mL) and dried under vacuum to yield **2** as a white powder. (0.538 g, 90%). ^1H NMR (DMSO-d_6): δ 9.38 (s, 1H, NC*H*N), 9.21 (s, 1H, NC*H*N), 8.18 (s, 1H, CH_{imid}), 8.15 (s, 1H, CH_{imid}), 7.77 (s, 1H, CH_{imid}), 7.67 (s, 1H, CH_{imid}), 7.61 (t, *J* = 7.8, 1H, C$H_{Ar(para)}$), 7.44 (d, *J* = 7.8, 1H, C$H_{Ar(meta)}$), 4.85 (s, 4H, NCH_2CH_2N), 3.85 (s, 3H, CH_3), 2.11 (sept, 2H, C$H(CH_3)_2$), 1.11 (d, *J* = 7.1, 6H, CH(CH_3)$_2$), 1.09 (d, *J* = 7.1, 6H, CH(CH_3)$_2$). ^{13}C NMR (DMSO-d_6): δ 144.98 (N*C*HN), 137.90 (N*C*HN), 134.57 ($C_{Ar(ipso)}$), 128.94 (CH_{Ar}), 128.73 (CH_{Ar}), 128.27 (CH_{Ar}), 124.42 (CH_{imid}), 123.86 (CH_{imid}), 123.43 (CH_{imid}), 122.37 (CH_{imid}), 49.32 (NCH_2CH_2N), 48.12 (NCH_2CH_2N), 36.07 (CH_3), 27.89 ($CH(CH_3)_2$), 23.94 ($CH(CH_3)_2$), 23.60 ($CH(CH_3)_2$). HRMS (*m/z*): calcd for $C_{21}H_{30}Br_2N_4$ [M-2Br]$^{2+}$: 169.1229, found: 169.1226. Anal. Calcd for $C_{21}H_{30}Br_2N_4$: C 50.62; H 6.07; N 11.24. Found: C 50.48; H 6.24; N 11.33.

Synthesis of dibromo(1-benzyl-1'-methyl-3,3'-ethylenediimidazolin-2,2'-diylidene)disilver(I) (4a): A suspension of **3a** (1.0 g, 2.34 mmol) and one equiv of Ag_2O

(0.541 g, 2.34 mmol) in dichloromethane (25 mL) was stirred at room temperature for 2 h under dinitrogen in the absence of light. The color of the suspension gradually changed from black to white. The precipitate was then isolated, washed with dichloromethane (3x10 mL) and dried under vacuum to yield **4a** as a white powder (1.42 g, 95%). ^{1}H NMR (DMSO-d_6): δ 7.49 (s, 1H, CH_{imid}), 7.45 (s, 1H, CH_{imid}), 7.35 (t, J = 7.3, 2H, C$H_{Ar(meta)}$), 7.29 (t, J = 7.3, 1H, C$H_{Ar(para)}$), 7.27 (s, 1H, CH_{imid}), 7.16 (s, 1H, CH_{imid}), 7.09 (d, J = 7.3, 2H, C$H_{Ar(ortho)}$), 5.25 (s, 2H, ArCH_2N), 4.67-4.61 (m, 2H, NCH_2CH$_2$N), 4.58-4.51 (m, 2H, NCH$_2$CH_2N), 3.56 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 180.50 (N*C*N), 179.78 (N*C*N), 137.32 (*C*$_{Ar(ipso)}$), 128.67 (*C*H$_{Ar}$), 127.81 (*C*H$_{Ar(para)}$), 127.12 (*C*H$_{Ar}$), 122.88 (*C*H$_{imid}$), 122.74 (*C*H$_{imid}$), 122.57 (*C*H$_{imid}$), 121.93 (*C*H$_{imid}$), 53.93 (Ar*C*H$_2$N), 51.47 (N*C*H$_2$CH$_2$N), 50.64 (NCH$_2$*C*H$_2$N), 38.25 (*C*H$_3$). Anal. Calcd for $C_{16}H_{18}Br_2N_4Ag_2$: C, 29.94; H, 2.83; N, 8.73. Found: C, 29.78; H, 2.53; N, 8.59.

Synthesis of dibromo[1-(4-tert-butylbenzyl)-1'-methyl-3,3'-ethylenediimidazolin-2,2'-diylidene]disilver(I) (4b): A suspension of **3b** (0.403 g, 0.832 mmol) and one equiv of Ag_2O (0.193 g, 0.832 mmol) in dichloromethane (15 mL) was stirred at room temperature for 4 h under dinitrogen in the absence of light. The color of the suspension gradually changed from black to white. The precipitate was isolated, washed with dichloromethane (3x10 mL) and dried under vacuum to yield **4b** as a white powder (0.41 g, 70%). ^{1}H NMR (DMSO-d_6): δ 7.50 (s, 1H, CH_{imid}), 7.47 (s, 1H, CH_{imid}), 7.34 (d, J = 8.1, 2H, CH_{Ar}), 7.32 (s, 1H, CH_{imid}), 7.16 (s, 1H, CH_{imid}), 6.96 (d, J = 7.4, 2H, CH_{Ar}), 5.21 (s, 2H, ArCH_2N), 4.71-4.61 (m, 2H, NCH_2CH$_2$N), 4.58-4.50 (m, 2H, NCH$_2$CH_2N), 3.44 (s, 3H, CH_3), 1.23 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (DMSO-d_6): δ 180.58 (N*C*N), 179.83

(N*C*N), 150.22 ($C_{Ar(para)}$), 134.44 ($C_{Ar(ipso)}$), 126.75 (CH_{Ar}), 125.36 (CH_{Ar}), 122.98 (CH_{imid}), 122.65 (2C, CH_{imid}), 121.69 (CH_{imid}), 53.55 (ArCH_2N), 51.50 (NCH_2CH_2N), 50.50 (NCH_2CH_2N), 38.14 (CH_3), 34.22 ($C(CH_3)_3$), 31.04 ($C(CH_3)_3$). Anal. Calcd for $C_{16}H_{18}Br_2N_4Ag_2$: C, 34.41; H, 3.75; N, 8.03. Found: C, 34.51; H, 3.42; N, 7.84.

Synthesis of dibromo[1-(2,6-diisopropylphenyl)-1'-methyl-3,3'-ethylenediimidazolin-2,2'-diylidene]disilver(I) (4c): A solution of **3c** (0.4 g, 0.803 mmol) and one equiv of Ag_2O (0.186 g, 0.803 mmol) in dichloromethane (15 mL) was stirred at room temperature for 1 d under dinitrogen in the absence of light. The color of the suspension gradually changed from black to white. The precipitate was isolated, washed with dichloromethane (3x10 mL) and dried under vacuum to yield **3** as a white powder (0.46 g, 80%). ^{1}H NMR (DMSO-d_6): δ 7.84 (s, 1H, CH_{imid}), 7.65 (s, 1H, CH_{imid}), 7.46 (t, J = 7.4, 1H, CH_{Ar}), 7.37 (s, 1H, CH_{imid}), 7.30 (d, J = 7.4, 2H, CH_{Ar}), 7.20 (s, 1H, CH_{imid}), 4.83 (m, 2H, NCH_2CH$_2$N), 4.60 (m, 2H, NCH$_2$CH_2N), 3.68 (br s, 3H, CH_3), 2.10 (br sept, 2H, CH(CH$_3$)$_2$), 1.05 (overlapping doublets, 12H, CH(CH_3)$_2$). ^{13}C NMR (DMSO-d_6): δ 179.00 (2C, N*C*N), 144.78 (C_{Ar}), 134.21 (C_{Ar}), 129.52 (CH_{Ar}), 124.75 (CH_{Ar}), 123.33 (CH_{imid}), 122.48 (CH_{imid}), 122.03 (CH_{imid}), 120.88 (CH_{imid}), 51.07 (NCH_2CH_2N), 49.94 (NCH$_2$CH_2N), 38.05 (CH_3), 27.04 ($CH(CH_3)_2$), 23.59 (CH(CH_3)$_2$), 23.40 (CH(CH_3)$_2$). Anal. Calcd for $C_{21}H_{28}Br_2N_4Ag_2$: C 35.42; H 3.96; N 7.87. Found: C 35.20; H 3.96; N 7.63.

Synthesis of dichloro(1-benzyl-1'-methyl-3,3'-ethylenediimidazolin-2,2'-diylidene)palladium(II) (5a): A suspension of **4a** (0.4 g, 0.62 mmol) and $PdCl_2$

(110 mg, 0.62 mmol) in DMF (10 mL) was stirred at 90 ^{o}C for 24 h under dinitrogen. The color of the suspension gradually changed from white to grey. The solution was then filtered to remove the AgBr precipitate. The filtrate was concentrated under vacuum. Upon addition of diethyl ether a white precipitate was obtained which was filtered and dried under vacuum to yield **5a** as a white powder. Crystals suitable for X-ray diffraction were grown by slow diffusion of ether into a concentrated solution of the sample in DMF (0.14 g, 52%). ^{1}H NMR (DMSO-d_6): δ 7.45 (br s, 2H, CH_{imid}), 7.36 (br s, 1H, CH_{imid}), 7.32 (br s, 3H, C$H_{Ar(meta\ and\ para)}$), 7.26 (br s, 1H, CH_{imid}), 7.10 (br s, 2H, C$H_{Ar(ortho)}$), 6.08 (m, 1H, ArCH_aH$_b$N)), 5.41-5.22 (m, 2H, NCH_2CH$_2$N), 5.16 (m, 1H, ArCH$_a$$H_b$N), 4.69-4.40 (m, 2H, NCH$_2$CH_2N), 3.37 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 156.68 (N*C*N), 154.87 (N*C*N), 137.52 ($C_{Ar(ipso)}$), 128.62 (*C*H$_{Ar}$), 127.67 (*C*H$_{Ar(para)}$), 127.06 (*C*H$_{Ar}$), 123.49 (*C*H$_{imid}$), 123.27 (*C*H$_{imid}$), 122.79 (*C*H$_{imid}$), 122.64 (*C*H$_{imid}$), 52.71 (Ar*C*H$_2$N), 46.94 (N*C*H$_2$CH$_2$N), 46.94 (NCH$_2$*C*H$_2$N), 37.26 (*C*H$_3$). HRMS (*m/z*): calcd for $C_{16}H_{18}Cl_2N_4Pd_2$ [M-Cl]$^{+}$: 409.0411, found: 409.0219.

Synthesis of dichloro[1-(4-tert-butylbenzyl)-1'-methyl-3,3'-ethylenediimidazolin-2,2'-diylidene]palladium(II) (5b): A suspension of **4b** (0.203 g, 0.291 mmol) and $PdCl_2$ (50 mg, 0.282 mmol) in DMF (10 mL) was stirred at 90 ^{o}C for 24 h under dinitrogen. The color of the suspension gradually changed from white to grey. The solution was then filtered to remove the AgBr formed. The filtrate was concentrated under vacuum. Upon addition of diethyl ether a white precipitate was obtained which was filtered and dried under vacuum to yield **5b** as a white powder. Crystals suitable for X-ray diffraction were grown by slow diffusion of ether into a concentrated solution of the sample in DMF (84

mg, 60%). ^{1}H NMR (DMSO-d_6): δ 7.52-7.40 (br s, 2H, CH_{Ar}), 7.39-7.30 (br s, 3H, CH_{imid}), 7.26 (br s, 1H, CH_{imid}), 7.13-6.98 (br s, 2H, CH_{imid}), 6.18-5.90 (m, 1H, ArCH_aH$_b$N), 5.32-5.11 (m, 3H, ArCH$_a$$H_b$N and NC$H_2CH_2$N), 4.68-4.35 (m, 2H, NCH$_2$CH_2N), 2.50 (s, 3H, CH_3), 1.27 (s, 9H, C(CH$_3$)$_3$). ^{13}C NMR (DMSO-d_6): δ 155.05 (N*C*N), 154.02 (N*C*N), 150.12 ($C_{Ar(para)}$), 134.59 ($C_{Ar(ipso)}$), 126.91 (*C*H$_{Ar}$), 125.34 (*C*H$_{Ar}$), 123.46 (*C*H$_{imid}$), 123.32 (*C*H$_{imid}$), 122.65 (*C*H$_{imid}$), 122.50 (*C*H$_{imid}$), 52.43 (Ar*C*H$_2$N), 47.01 (N*C*H$_2$CH$_2$N), 46.87 (NCH$_2$*C*H$_2$N), 37.15 (*C*H$_3$), 34.23 (*C*(CH$_3$)$_3$), 31.07 (C(*C*H$_3$)$_3$). HRMS (*m/z*): calcd for $C_{20}H_{26}Cl_2N_4Pd_2$ [M-Cl]$^+$: 463.0880, found: 463.0881.

Synthesis of dichloro(1-(2,6-diisopropylphenyl)-1'-methyl-3,3'-ethylenediimidazolin-2,2'-diylidene)palladium(II) (5c): A suspension of **4c** (0.181 g, 0.25 mmol) and $PdCl_2$ (45 mg, 0.25 mmol) in DMF (10 mL) was stirred at 90 ^{o}C for 24 h under dinitrogen. The color of the suspension gradually changed from white to grey. The solution was then filtered to remove the AgBr precipitate. The filtrate was concentrated under vacuum. Upon addition of diethyl ether a white precipitate was obtained which was filtered and dried under vacuum to yield **5c** as a white powder. Crystals suitable for X-ray diffraction were grown by slow diffusion of ether into a concentrated solution of the sample in DMF (57 mg, 50%). ^{1}H NMR ($CDCl_3$): δ 7.54 (s, 1H, CH_{imid}), 7.42 (t, J = 7.8, 1H, C$H_{Ar(para)}$), 7.30 (d, J = 7.6, 1H, C$H_{Ar(meta)}$), 7.15 (d, J = 7.6, 1H, C$H_{Ar(meta)}$), 7.04 (s, 1H, CH_{imid}), 6.91 (s, 1H, CH_{imid}), 6.80 (s, 1H, CH_{imid}), 6.61 (t, J = 12, 1H, NCH_2CH$_2$N), 5.08 (d, J = 14, 1H, NCH_2CH$_2$N), 4.77 (d, J = 14, 1H, NCH_2CH$_2$N), 4.54 (t, J = 12, 1H, NCH_2CH$_2$N), 4.01 (s, 3H, CH_3), 2.91 (sept, 1H, CH(CH$_3$)$_2$), 1.77 (sept, 1H, CH(CH$_3$)$_2$),

1.23 (d, J = 5.5, 3H, CH(CH_3)$_2$). 1.12 (d, J = 5.2, 3H, CH(CH_3)$_2$), 1.01 (d, J = 6.1, 3H, CH(CH_3)$_2$), 0.61 (d, J = 5.7, 3H, CH(CH_3)$_2$). ^{1}H NMR (DMSO-d_6): δ 7.75 (s, 1H, CH_{imid}), 7.48 (s, 1H, CH_{imid}), 7.54-7.41 (m, 3H, 2CH_{imid} and C$H_{Ar(para)}$), 7.38 (s, 1H, CH_{imid}), 7.32 (d, J = 7.1, 1H, C$H_{Ar(meta)}$), 7.27 (d, J = 6.9, 1H, C$H_{Ar(meta)}$), 6.22 (t, J = 12, 1H, NCH_2CH$_2$N), 4.84 (d, J = 14, 1H, NCH_2CH$_2$N), 4.65 (d, J = 14, 1H, NCH_2CH$_2$N), 3.83 (s, 3H, CH_3), 2.66 (sept, 1H, CH(CH$_3$)$_2$), 1.79 (sept, 1H, CH(CH$_3$)$_2$), 1.25 (d, J = 5.5, 3H, CH(CH_3)$_2$). 1.14 (d, J = 5.2, 3H, CH(CH_3)$_2$), 1.02 (d, J = 6.1, 3H, CH(CH_3)$_2$), 0.62 (d, J = 5.7, 3H, CH(CH_3)$_2$). ^{13}C NMR (DMSO-d_6): δ 160.04 (2C, NCN), 152.96 (C_{Ar}), 146.61 (C_{Ar}), 144.65(C_{Ar}), 134.68 (CH$_{Ar}$), 129.86 (CH$_{Ar}$), 127.39 (CH$_{Ar}$), 124.31 (CH$_{imid}$), 123.67 (CH$_{imid}$), 122.82 (CH$_{imid}$), 120.61 (CH$_{imid}$), 48.92 (NCH$_2$CH$_2$N), 46.22 (NCH$_2$$CH_2$N), 28.03, 27.76, 25.97 25.15 (CH(CH$_3$)$_2$), 22.72 (CH(CH$_3$)$_2$), 21.92 (CH(CH$_3$)$_2$). HRMS (*m/z*): calcd for $C_{21}H_{28}Cl_2N_4Pd$ [M-Cl]$^+$: 479.1037, found: 477.1031.

Synthesis of bis(1-benzyl-1'-methyl-3,3'-ethylenediimidazolin-2,2'-diylidene)nickel(II) dibromide (6a): A suspension of **4a** (0.4 g, 0.62 mmol) and $NiBr_2$(DME) (94.5 mg, 0.307 mmol) in DMF (10 mL) was stirred at 90 ^{o}C for 24 h under dinitrogen. The color of the suspension gradually changed from white to grey. The solution was then filtered to remove the AgBr precipitate. The filtrate was concentrated under vacuum. Upon addition of diethyl ether a white precipitate was obtained which was filtered and dried under vacuum to yield **6a** as a white powder. (0.14 g, 52%). ^{1}H NMR (DMSO-d_6): δ 7.53 (s, 2H, CH_{imid}), 7.47 (s, 1H, CH_{imid}), 7.37 (s, 1H, CH_{imid}), 7.36 (s, 1H, CH_{imid}), 7.31 (s, 1H, CH_{imid}), 7.30-7.25 (m, 7H, C$H_{Ar(meta\ and\ para)}$ and CH_{imid}), 7.24 (s, 1H, CH_{imid}), 7.16 (s, 1H, CH_{imid}), 6.69-6.59 (m, 4H, C$H_{Ar(ortho)}$), 5.71 (m, 1H, NCH_2CH$_2$N)),

5.38-5.23 (m, 3H, NCH_2CH$_2$N and 2H of ArCH$_a$$H_b$N), 5.22-5.14 (m, 1H, NC$H_2CH_2$N), 4.98-4.79 (m, 4H, 2H of NCH$_2$CH_2N and 2H of ArCH_aH$_b$N), 4.77-4.61 (m, 2H, NCH$_2$CH_2N), 4.51 (m, 1H, NCH$_2$CH_2N), 3.03 (s, 3H, CH_3), 2.91 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 170.99 (N*C*N), 170.05 (N*C*N), 167.99 (N*C*N), 162.28 (N*C*N), 136.84 ($C_{Ar(ipso)}$), 136.67 ($C_{Ar(ipso)}$), 128.81 (4C, *C*H$_{Ar}$), 127.52 (*C*H$_{Ar(para)}$), 127.44 (*C*H$_{Ar(para)}$), 125.12 (2C, *C*H$_{Ar}$), 124.88 (2C, *C*H$_{Ar}$), 124.60 (*C*H$_{imid}$), 124.46 (*C*H$_{imid}$), 124.40 (*C*H$_{imid}$), 124.38 (*C*H$_{imid}$), 123.69 (2C, *C*H$_{imid}$), 123.15 (*C*H$_{imid}$), 123.01 (*C*H$_{imid}$), 52.24 (Ar*C*H$_2$N), 51.88 (Ar*C*H$_2$N), 47.69 (N*C*H$_2$CH$_2$N), 47.05 (2C, N*C*H$_2$*C*H$_2$N), 46.57 (NCH$_2$*C*H$_2$N), 36.68 (*C*H$_3$), 36.30 (*C*H$_3$). HRMS (*m/z*): calcd for $C_{32}H_{36}Br_2N_8Ni$ $[M-2Br]^{2+}$: 295.1208, found: 295.1203.

General procedure for the Suzuki-Miyaura coupling reactions: In a typical run, an oven dried 25 mL sealed tube equipped with a stir bar was charged with a known mol % catalyst, base (2.0 mmol) and phenylboronic acid (1.5 mmol). Under nitrogen, dioxane (5 mL) and aryl halides (1.0 mmol) were added via syringe. The flask was placed in pre-heated sand bath at 80 ^{o}C. After the specified time the flask was removed from the sand bath and water (20 mL) was added followed by extraction with dichloromethane (3x10 mL). The combined organic layers were washed with saturated aqueous NaCl (10 mL), dried over anhydrous $MgSO_4$, filtered and the internal standard (24 mg of dodecahydrotriphenylene) was added. Solvent was removed under vacuum. The residue was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR. Yields were determined by ^{1}H NMR against the internal standard dodecahydrotriphenylene.

X-ray structure determinations: Data was collected at -100 °C on a Nonius Kappa CCD diffractometer, using the COLLECT program.[13] Cell refinement and data reductions used the programs DENZO and SCALEPACK[14] SIR97[15] was used to solve the structures and SHELXL97[16] was used to refine the structures. ORTEP-3 for Windows[17] was used for molecular graphics and PLATON[18] was used to prepare material for publication. H atoms were placed in calculated positions with U_{iso} constrained to be 1.5 times U_{eq} of the carrier atom for methyl protons and 1.2 times U_{eq} of the carrier atom for all other hydrogen atoms.

3.5 References

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CHAPTER 4

NON-SYMMETRICALLY SUBSTITUTED DI-*N*-HETEROCYCLIC CARBENE PALLADIUM(II) AND NICKEL(II) COMPLEXES WITH A HEMI-LABILE DONOR ARM

4.1 Introduction

As mentioned in *Chapter 1*, one of the research objectives was to synthesize non-symmetrically substituted diNHC ligands and their complexes. Since we developed a general route into the synthesis of non-symmetrically substituted diNHC ligands, as discussed in *Chapter 3*, our next goal was to synthesize non-symmetrically substituted diNHC ligands with a hemi-labile donor arm as one of the nitrogen substituents, as shown in Figure 4-1. This chapter deals with the synthesis of non-symmetrically substituted diNHC ligands with a hemi-labile donor arm on one of the nitrogens.

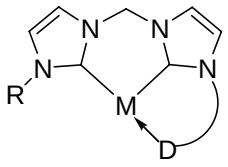
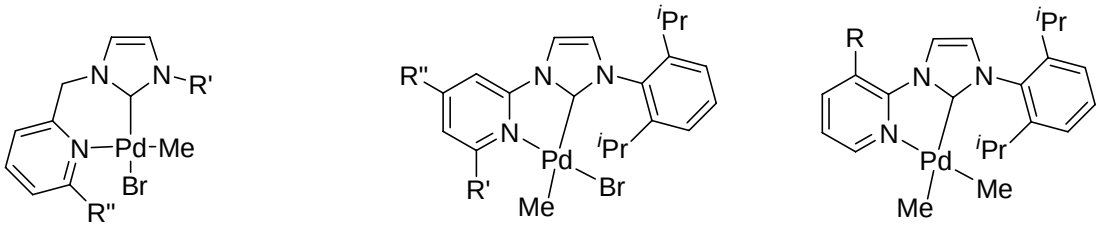


Figure 4-1. NHC complexes with hemi-labile donor arm D.

Labile ligands have been an important feature of several efficient catalysts that depend on ligand dissociation, but then again these labile ligands can also be a problem causing catalyst decomposition. Hemi-labile NHCs incorporate both a strongly binding

NHC moiety as well as a hemi-labile heteroatom donor. As mentioned in *Chapter 1*, the rationale behind the design of non-symmetrically substituted diNHC ligands with a hemi-labile functionalized neutral donor arm would be that the hemi-labile arm, or the weakly coordinating arm, would allow the formation of a vacant coordination site that are available for substrates in catalysis and also stabilize the catalytically active species after reductive elimination in the catalytic cycle. NHCs can be functionalized on either one or both nitrogen atoms, and accordingly there are examples of bi- and tridentate monoNHC palladium(II) and nickel(II) complexes with either one or two hemi-labile donor arms in literature.[1] Most of the hemi-labile functionalized arms are nitrogen-based donors, such as pyridine, imine and amine groups.

Danopoulos *et al.* have synthesized monoNHC palladium alkyl and dialkyl complexes with a hemi-labile donor on one of the nitrogens.[2] The synthesis of **1a,b** was carried out by deprotonation of the ligand precursor, *ie.*, the corresponding imidazolium bromide, with $LiN^{i}Pr_2$ and trapping the *in situ* formed free carbene with (cod)PdBrMe (Figure 4-2). All other complexes were synthesized *via* the silver transmetallation route. The dialkyl complexes **3a,b** were synthesized *via* the deprotonation of the ligand precursor, *i.e.*, the corresponding imidazolium bromide with $KN(SiMe_3)_2$ and trapping the *in situ* formed free carbene with (tmeda)$PdMe_2$.



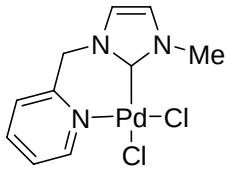
1a: R'' = H, R' = ^{t}Bu
1b: R'' = H, R' = Mes
1c: R'' = H, R' = 2,6-$^{i}Pr_2C_6H_3$
1d: R'' = CH_3, R' = 2,6-$^{i}Pr_2C_6H_3$

2a: R' = H, R'' = H
2b: R' = $SiMe_3$, R'' = H
2c: R' = H, R'' = $SiMe_3$
2d: R' = H, R'' = CF_3

3a: R = H
3b: R = CH_3

Figure 4-2. MonoNHC palladium(II) alkyl complexes with hemi-labile pyridine arm.

Jin *et al.* have synthesized a similar palladium complex **4** using the silver transmetallation route (Figure 4-3).[3]



4

Figure 4-3. MonoNHC palladium(II) dichloride complex with hemi-labile pyridine arm.

Cavell *et al.* have synthesized the monoNHC palladium alkyl complex **5** with pyridine arms on both the nitogens, *via* the silver transmetallation route.[4] However, this complex was synthesized with a very low yield of 12%. Cavell *et al.* also synthesized monoNHC palladium complex **6** with hemi-labile amino donors on both the nitrogen atoms *via* the silver transmetallation route (Figure 4-4).

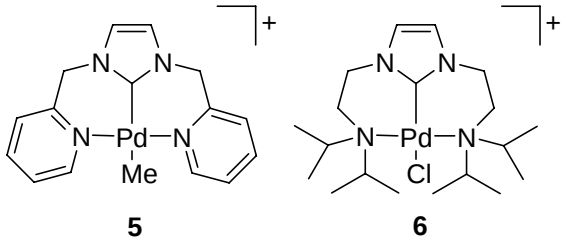
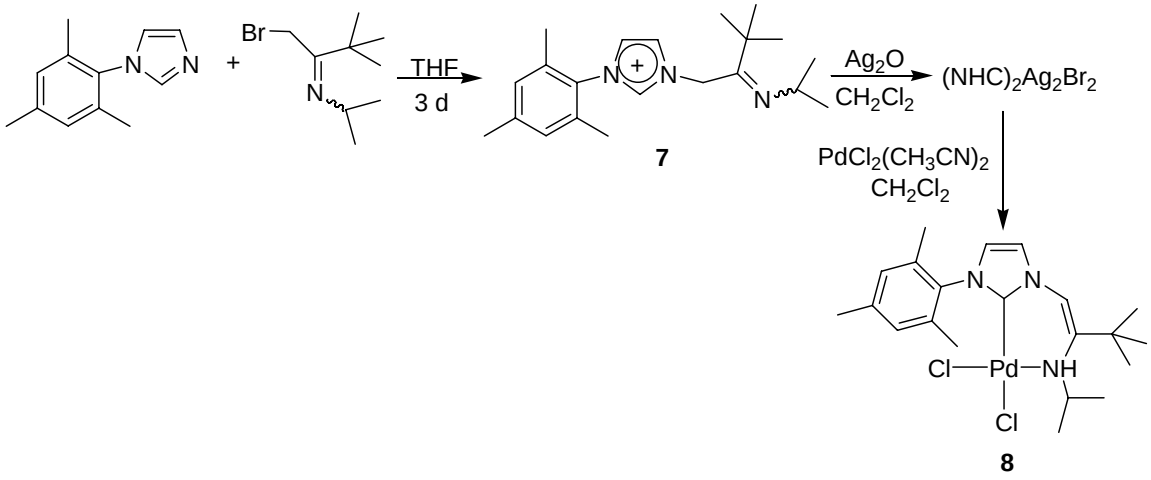


Figure 4-4. MonoNHC palladium dichloride complex with hemi-labile donor arms on both nitrogens.

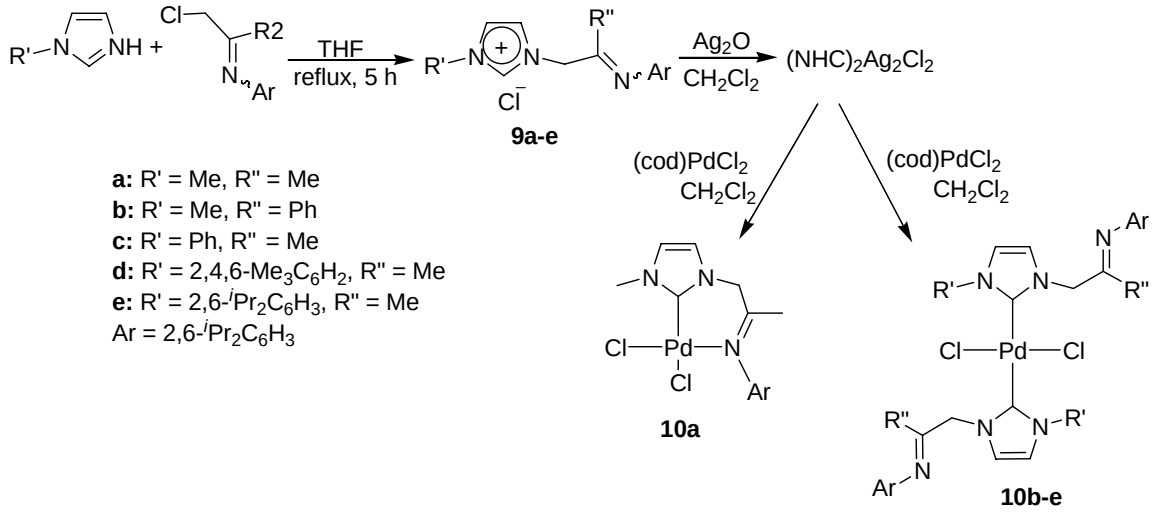
Coleman *et al.* have synthesized the imino NHC ligand precursor **7** by the reaction of the α-bromo imine, $BrCH_2C(^tBu)=N(^iPr)$, with 1-mesityl imidazole.[5] Two sets of signals were obtained in the ^1H NMR spectrum of **7**, which were assigned to the *Z* and *E* isomers, with the *Z* form being the major isomer. The corresponding silver complex was readily prepared by the reaction of **7** with Ag_2O. Transmetallation reaction of the silver(I) complex with $PdCl_2(CH_3CN)_2$ led to tautomerization of the imine moiety affording the enamine NHC palladium(II) complex **8** (Scheme 4-1).

Scheme 4-1. Synthesis of enamine NHC palladium complex.



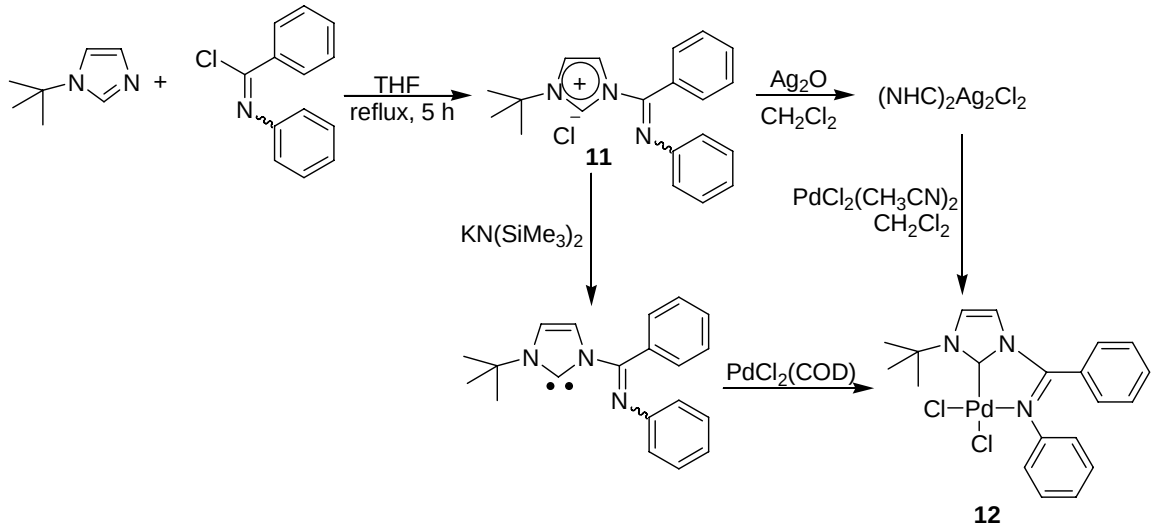
Tilset *et al.* have synthesized a number of similar imino NHC ligand precursors which did not tautomerize to the enamine form (Scheme 4-2).[6] **9a,c-e** gave exclusively the *E* isomer, while for **9b** two set of signals were obtained for the *Z* and *E* isomers. The corresponding imino NHC palladium(II) complexes **10a-e** were synthesized *via* the silver transmetallation route. **9a** gave a chelating imino NHC palladium complex **10a**, while **9b-e** gave non-chelating imino NHC palladium complex **10b-e** with two imino NHC ligands on one palladium centre.

Scheme 4-2. Synthesis of imino NHC palladium(II) complex.



Coleman *et al.* have synthesized a similar imino NHC precursor **11** and its corresponding palladium complex **12**, *via* the silver transmetallation and the free carbene route (Scheme 4-3).[7]

Scheme 4-3. Synthesis of imino NHC palladium complex **12**.



There are also examples of oxazoline-based,[8] quinoline-based[9] and phosphine-based[10] donors in literature. There are very few examples of diNHC palladium(II) and nickel(II) complexes with hemi-labile donor arms on both the nitrogens, which we have discussed in *Section 1.4: Tetradentate diNHC complexes of nickel and palladium*. However, there are no examples of diNHC ligand systems with a hemi-labile donor arm on only one of the nitrogens.

Based on the available literature and the synthetic route we developed for non-symmetrically substituted diNHC ligand precursors, we designed two diNHC ligand precursors with a hemi-labile donor arm as one of the nitrogen substituents; one with an imino arm and the second with a pyridine arm as shown in Figure 4-5.

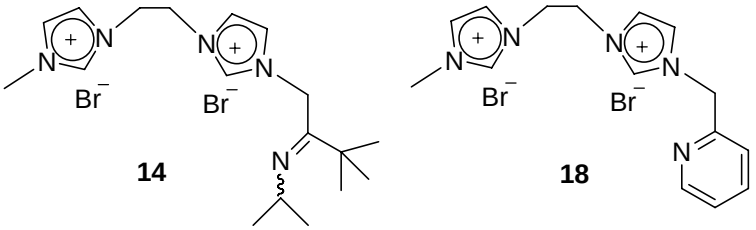


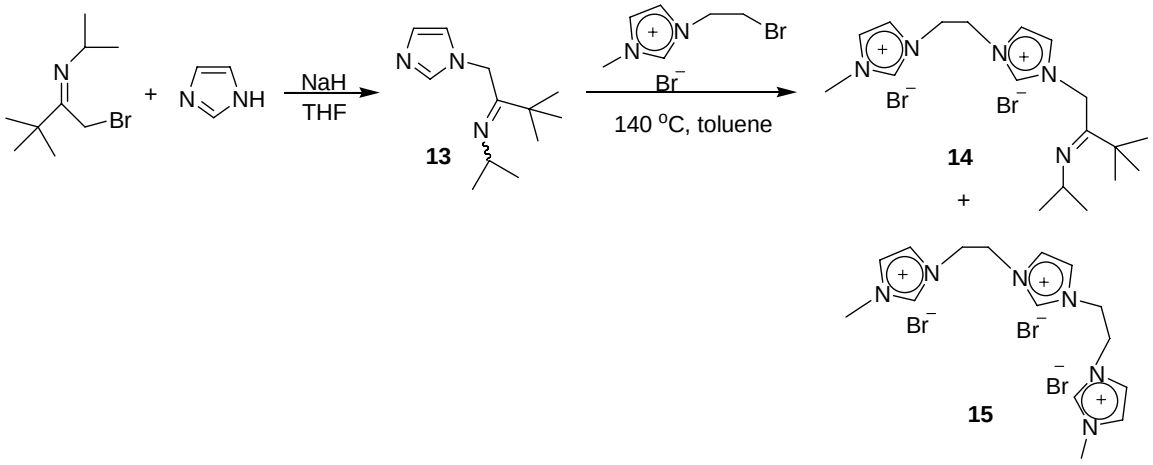
Figure 4-5. DiNHC ligand precursors with hemi-labile donor arms.

4.2 Results and Discussion

4.2.1 Synthesis of ligands

The first step in the synthesis of the diimidazolium salt **14** was the synthesis of **13**, the *N*-substituted imidazole with an imino arm. This was prepared by the reaction of α-bromo imine, $BrCH_2C(^tBu)=N(^iPr)$, with imidazole in the presence of 4 equiv. of NaH for 12 h. The second step was the reaction of **13** with one equiv. of 1-(2-Bromoethyl)-3-methylimidazolium bromide (Scheme 4-4), the synthesis of which has been previously reported.[11] The non-symmetrically substituted diimidazolium salt **14** was synthesized in 80% yield along with a side product **15**, the triimidazolium salt. We are uncertain of the mechanism through which the triimidazolium salt **15** is formed.

Scheme 4-4. Synthesis of non-symmetric dimidazolium salt **14**, with an imino arm.



The ^{1}H NMR spectra of **14** in DMSO-d_6 exhibits two distinct resonances at 9.08 and 9.00 ppm for the two NC*H*N protons on the two ethylene-bridged imidazolium rings. There are also four distinct resonances for the protons on the remaining four carbons of the two imidazolium rings.

The research with this non-symmetrically substituted diNHC ligand precursor **14** was abandoned, because of the difficulty in obtaining it pure; however we were interested in the side product **15**, which could act as a ligand precursor for triNHC complexes.

There are very few examples of triNHC ligands in literature. The first example of a triNHC complex was synthesized by Fehlhammer *et. al.* in 1996.[12] The ligand is similar to Trofimenko's tris(pyrazolyl)borate systems. Fe(III)[12] and Co(III)[13] complexes have been obtained with this triNHC ligand (Figure 4-7). TriNHC Tl(I),[14] Co(I),[15] Ni(I),[16] and Cu(I)[17] complexes are also known in literature (Figure 4-6).

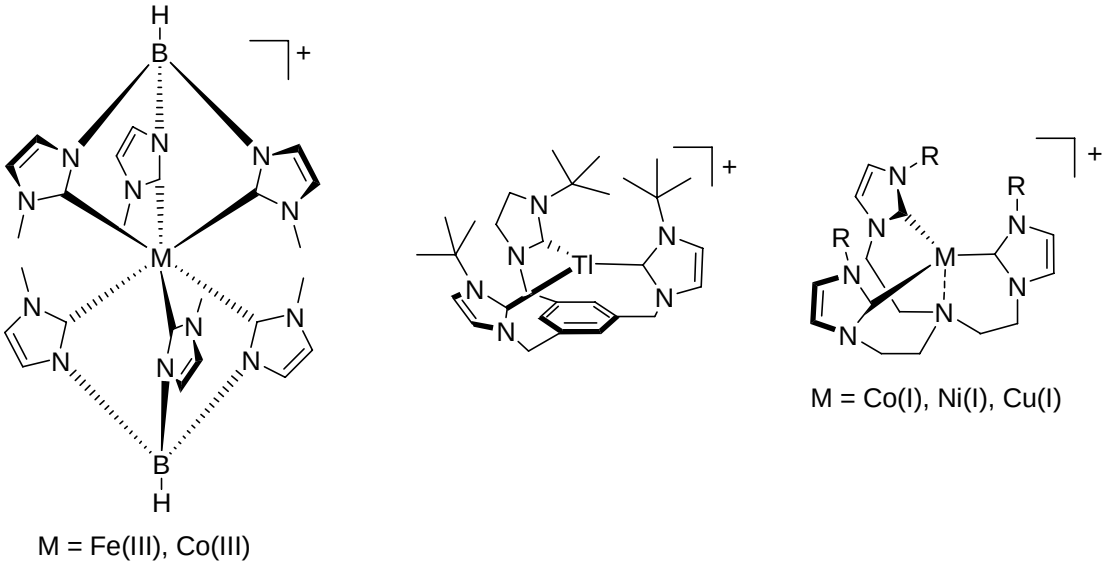
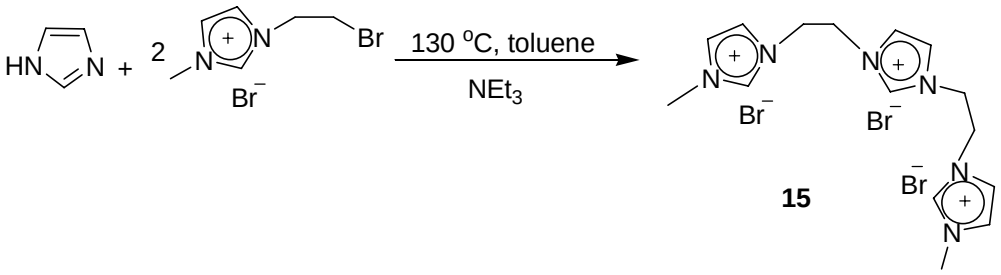


Figure 4-6. TriNHC complexes known in literature.

The triimidazolium salt **15** was hence synthesized by the reaction of two equivalents of 1-(2-Bromoethyl)-3-methylimidazolium bromide with an equivalent of imidazole in the presence of excess triethylamine (Scheme 4-5).

Scheme 4-5. Synthesis of triimidazolium salt **15**.



The ^{1}H NMR spectra of **15** in DMSO-d_6 exhibits two distinct resonances at 9.27 and 9.19 ppm with an integral ratio of 1:2 for the three NC*H*N protons on the three ethylene-bridged imidazolium rings. There are also three distinct resonances for the protons on the remaining six carbons of the three imidazolium rings. Single crystals of **15** were obtained by slow diffusion of ether into a concentrated solution in DMF (Figure 4-7).[18]

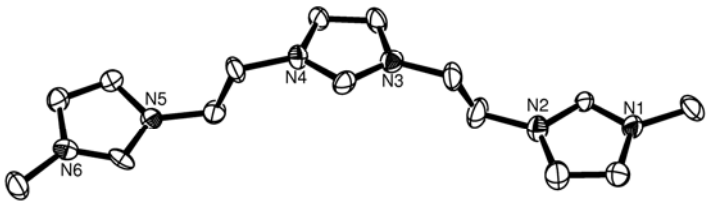
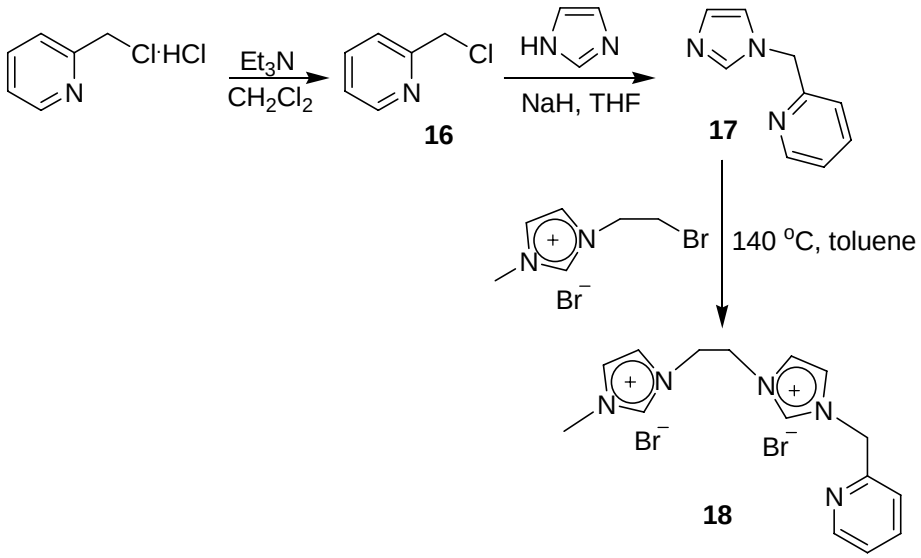


Figure 4-7. ORTEP plot of non-symmetrically substituted triimidazolium salt **15**, at the 50% probability level. The hydrogen atoms and bromide anions are omitted for clarity. Selected bond angles (°): N(2)-C(4)-N(1) = 110.9(9), N(4)-C(9)-N(3) = 109.5(9), N(6)-C(14)-N(5) = 110.5(9).

The diimidazolium salt, **18**, was synthesized by the reaction of 2-(1*H*-Imidazol-1-ylmethyl)pyridine, **17**, with one equiv. of 1-(2-Bromoethyl)-3-methylimidazolium bromide (Scheme 4-6). The non-symmetrically substituted diimidazolium salt, **18**, was synthesized in 82% yield. The ^{1}H NMR spectra of **18** in DMSO-d_6 exhibits two distinct resonances at 9.32 and 9.17 ppm for the two NC*H*N protons on the two ethylene-bridged imidazolium rings. There are also four distinct resonances for the protons on the remaining four carbons of the two imidazolium rings.

Scheme 4-6. Synthesis of non-symmetric dimidazolium salt **6** with a pyridine arm.

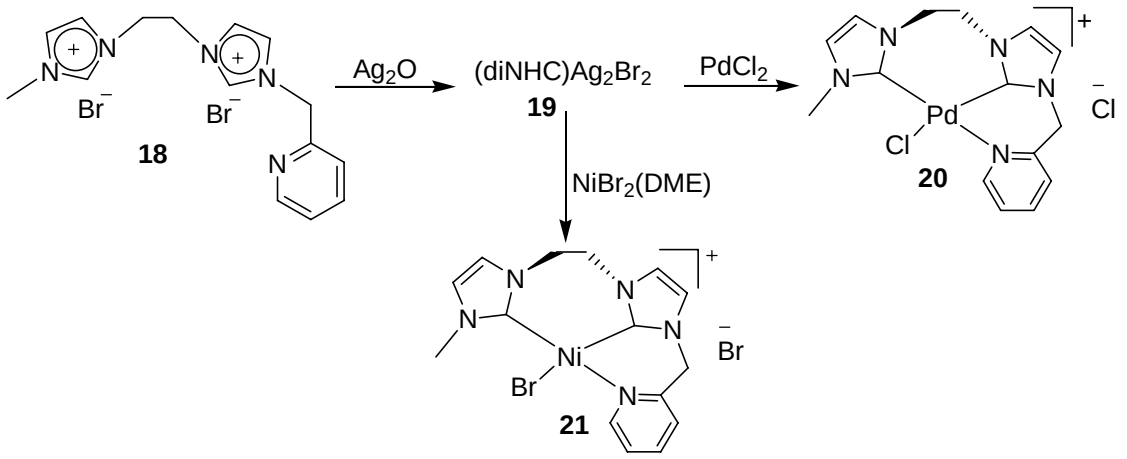


4.2.2 Synthesis of (diNHC)Ag(I), (diNHC)Pd(II) and (diNHC)Ni(II) complexes with a hemi-labile pyridine arm

Palladium(II) and nickel(II) complexes **20** and **21**, were synthesized *via* a transmetallation route using (diNHC)Ag(I) complexes (Scheme 4-7). The advantage of using (diNHC)Ag(I) complexes as carbene transfer reagents include simple preparation

directly from the imidazolium salt and ease of handling due to their stability in air.[19] (DiNHC)Ag(I) complex **19** was synthesized by the reaction of the diimidazolium salt precursor **18** with an equivalent amount of Ag_2O according to established procedures.[20] The ^{1}H NMR spectra of **19** (DMSO-d_6) show two multiplets each integrating for two protons for the bridging ethylene protons in **19** as compared to the singlet obtained for **18**. The ^{13}C NMR spectrum of **19** shows two overlapping signals at 179 ppm for the two non-symmetric carbenic (N*C*N) carbons.

Scheme 4-7. Synthesis of Ag(I), Ni(II) and Pd(II) complexes with a hemi-labile pyridine arm.



Subsequent reaction of the silver complex **19** with one equiv. $PdCl_2$ in DMF at 90 ^{o}C for 24 h afforded the desired complex **20** and when reacted with an equivalent of $NiBr_2$(DME) afforded the complex **21** in 50-60% yield. The ^{1}H NMR and ^{13}C NMR spectra for **20** and **21** (DMSO-d_6) show distinct sharp resonances for each proton and carbon nuclei. The ^{13}C NMR spectra show two resonances at 152.5 and 152.4 ppm for **20** and 154.3 and 154.2 for **21** which corresponds to the two non-symmetric carbenic

carbons. Complexes **20** and **21** are hygroscopic and are soluble only in polar solvents such as DMF, DMSO and acetonitrile.

The proposed structures of **20** and **21** as shown in Scheme 4-7 have not yet been verified by X-ray crystallography and could exist in solution as the neutral analogues as shown in Figure 4-8. Unfortunately, to date we have not been able to grow suitable crystals.

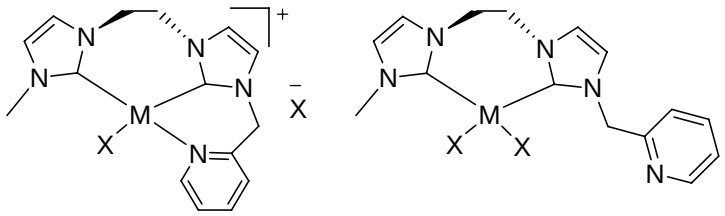


Figure 4-8. Proposed structures for the nickel(II) and palladium(II) complexes **20** and **21**.

Due to time constraints it was not possible to study the potential of these complexes in C-C coupling reactions for this thesis work. As future work it would be interesting to explore the activity of both the nickel and palladium complexes with hemi-labile pyridine arm in C-C coupling reactions. This work will be continued by my colleagues in the Foley group.

4.3 Conclusions

In conclusion, we have synthesized a non-symmetrically substituted diNHC ligand precursor with hemi-labile pyridine arms on one of the nitrogen atoms and also their corresponding silver(I), palladium(II) and nickel(II) complexes. Although the complexes have been characterized *via* spectroscopic techniques, the coordination environment around the metal centre is, as of yet, uncertain and needs to be investigated using X-ray crystallography.

4.4 Experimental

General Procedures: Unless otherwise stated, all reactions were performed under N_2 using standard Schlenk techniques or in a N_2-filled drybox. Dichloromethane, toluene, and THF were dried using a MBraun Solvent Purification System and were stored in a glovebox. Acetonitrile was dried over CaH_2, distilled and stored under nitrogen over type 4A molecular sieves. NEt_3 was dried with KOH and then distilled and stored under nitrogen. All reaction temperatures for catalytic reactions refer to the temperature of pre-equilibrated sand baths. ^1H and ^{13}C $\{^1H\}$ NMR spectra were recorded on a Bruker 500 MHz Avance spectrometer. Chemical shifts for ^1H and ^{13}CNMR are reported in ppm in reference to the residual ^1H and ^{13}C resonances of $CDCl_3$ (^1H: δ 7.24; ^{13}C: δ 77.23) and DMSO-d_6 (^1H: δ 2.50; ^{13}C: δ 39.51). Coupling constants are given in Hz. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. High resolution mass spectra (HRMS) were measured on an Applied Biosystem QSTAR® XL MS/MS system (ESI-QTOF). Ag_2O were purchased from Alfa-Aesar Chemical Company and used as received. 2-Picolyl chloride hydrochloride, $NiBr_2$(DME), imidazole, *N*-methylimidazole and NaH were purchased from Sigma-Aldrich Chemical Company and used as received. $PdCl_2$ was obtained from PMO Pty Ltd, Australia. α-bromo imine, $BrCH_2C(^tBu)=N(^iPr)$,[21] and 1-(2-Bromoethyl)-3-methylimidazolium bromide[11] were synthesized according to literature procedures.

Synthesis of 1-[$CH_2C(^tBu)=N(^iPr)$]imidazole (13): A Schlenk flask was charged with imidazole (2.32 g, 0.0341 mol) and NaH (3.27 g, 0.136 mol) in THF (50 mL) under dinitrogen at ambient temperature. After 5 min, the α-bromo imine, $BrCH_2C(^tBu)=N(^iPr)$ (7.5 g, 0.0341 mol), was added. The mixture was stirred for 12 h following which the solvent was removed under vacuum. Water (20 mL) and dichloromethane (30 mL) were added to the reaction products and the organic layer was separated. The organic layer was further extracted with water (2x20 mL) and the solvent was removed under vacuum to yield **13** as reddish oil. (6.96 g, 98%). ^{1}H NMR ($CDCl_3$): δ 7.18 (s, 1H, NC*H*N), 6.79 (s, 1H, CH_{imid}), 6.57 (s, 1H, CH_{imid}), 4.42 (s, 2H, CH_2N), 3.40 (sept, *J* = 6.2, 1H, C$H(CH_3)_2$), 0.83 (s, 9H, C(CH_3)$_3$), 0.79 (d, *J* = 6.2, 6H, CH(CH_3)$_2$. ^{13}C NMR ($CDCl_3$): δ 165.19 (*C*=N), 136.72 (N*C*HN), 129.08 (*C*H$_{imid}$), 118.68 (*C*H$_{imid}$), 50.90 (*C*H$_2$N), 40.06 (*C*(CH$_3$)$_3$), 39.97 (*C*H(CH$_3$)$_2$) 27.65 (C(*C*H$_3$)$_3$), 23.34 (CH(*C*H$_3$)$_2$). HRMS (*m/z*): calcd for $C_{12}H_{21}N_3$ $[M+H]^+$: 208.1808, found: 208.1806.

Synthesis of 1-{$CH_2C(^tBu)=N(^iPr)$}-1'-methyl-3,3'-ethylenediimidazolium dibromide (14): A Schlenk flask was charged with a mixture of **13** (1.0g, 4.82 mmol), 1-(2-Bromoethyl)-3-methylimidazolium bromide (1.3 g, 4.82 mmol) and toluene (20 mL) and was stirred at 80 ^{o}C for 3 d under dinitrogen. A white precipitate was isolated, washed with THF (3x15 mL) and dried under vacuum to yield **14** as a white powder. The trisimidazolium salt **15** was also formed as a side product in 10% yield. (1.83 g, 80%). ^{1}H NMR (DMSO-d_6): δ 9.08 (s, 1H, NC*H*N), 9.00 (s, 1H, NC*H*N), 7.80 (s, 1H, CH_{imid}), 7.76 (s, 1H, CH_{imid}), 7.69 (s, 1H, CH_{imid}), 7.68 (s, 1H, CH_{imid}), 5.65 (s, 2H, NCH_2), 4.74 (m, 2H, NCH_2CH_2N), 4.74 (m, 2H, NCH_2CH_2N). 3.85 (s, 3H, CH_3), 3.29 (sept, *J* = 6.5, 1H,

C*H*(CH_3)$_2$), 1.19 (s, 9H, C(C*H*$_3$)$_3$), 1.17 (d, *J* = 6.5, 6H, CH(C*H*$_3$)$_2$. ^{13}C NMR (DMSO-*d*$_6$): δ 137.71 (N*C*HN), 137.04 (N*C*HN), 124.25 (*C*H$_{imid}$), 124.08 (*C*H$_{imid}$), 122.21 (*C*H$_{imid}$), 122.03 (*C*H$_{imid}$), 54.21 (*C*H$_2$N), 48.50 (N*C*H$_2$CH$_2$N), 48.32 (NCH$_2$*C*H$_2$N), 40.06 (*C*(CH_3)$_3$), 43.01 (*C*H(CH_3)$_2$), 36.02 (*C*H$_3$), 27.65 (C(*C*H$_3$)$_3$), 25.72 (CH(*C*H$_3$)$_2$).

Synthesis of the triimidazolium tribromide (15): A Schlenk flask was charged with a mixture of imidazole (0.1 g, 1.47 mmol), 1-(2-Bromoethyl)-3-methylimidazolium bromide (0.79 g, 2.94 mmol), NEt_3 (0.5 mL) and toluene (20 mL) and was stirred at 110 ^{o}C for 3 d under dinitrogen. A white precipitate was isolated, washed with THF (3x15 mL) and dried under vacuum to yield **15** as a white powder. (0.62 g, 80%). ^{1}H NMR (DMSO-*d*$_6$): δ 9.27 (s, 1H, NC*H*N), 9.19 (s, 2H, NC*H*N), 7.74 (s, 2H, C*H*$_{imid}$), 7.71 (s, 2H, C*H*$_{imid}$), 7.69 (s, 2H, C*H*$_{imid}$), 4.74 (m, 8H, NC*H*$_2$C*H*$_2$N), 3.87 (s, 6H, C*H*$_3$). ^{13}C NMR (DMSO-*d*$_6$): δ 137.16 (3C, N*C*HN), 123.86 (2C, *C*H$_{imid}$), 122.83 (2C, *C*H$_{imid}$), 122.37 (2C, *C*H$_{imid}$), 48.63 (2C, N*C*H$_2$CH$_2$N), 48.12 (2C, NCH$_2$*C*H$_2$N), 36.07 (2C, *C*H$_3$). HRMS (*m/z*): calcd for $C_{15}H_{23}Br_3N_6$ $[M\text{-}Br]^+$: 447.0330, found: 447.0461.

Neutralization of 2-picolyl chloride hydrochloride to form 2-picolyl chloride (16): 2-picolyl chloride hydrochloride (1.0 g, 6.10 mmol) dissolved in dichloromethane (10 mL) was reacted with NEt_3 (0.85 mL, 6.10 mmol). The dichloromethane mixture was washed with water (2 x 10 mL) and the organic layer was dried over anhydrous magnesium sulfate. The solvent was removed under vacuum to yield hygroscopic yellow oil. (0.78 g, 100 %) ^{1}H NMR ($CDCl_3$): δ 8.55 (d, *J* = 4.6 Hz, 1H, py-*H6*), 7.70 (virtual t, 1H, py-*H4*), 7.45 (d, *J* = 7.8 Hz, 1H, py-*H3*), 7.21 (m, 1H, py-*H5*), 4.65 (s, 2H, C*H*$_2$).

Synthesis of 2-(1H-Imidazol-1-ylmethyl)pyridine (17): Imidazole (0.42 g, 6.10 mmol) was dissolved in THF (10 mL) and slowly reacted with sodium hydride (0.88 g, 36.6 mmol). After 15 minutes of stirring 2-picolyl chloride (0.77 g, 6.10 mmol) was added to the above mixture and stirred overnight. The solution was filtered and the solvent was pumped down to give air sensitive yellow solid. (0.70 g, 72 %). ^{1}H NMR ($CDCl_3$): δ 8.55 (d, *J* = 4.7 Hz, 1H, py-*H6*), 7.62 (virtual t, 1H, py-*H4*), 7.58 (s, 1H, NC*H*N), 7.20 (m, 1H, py-*H5*), 7.17 (s, 1H, CH_{imid}), 7.05 (s, 1H, CH_{imid}), 6.91 (d, *J* = 7.8 Hz, 1H, py-*H3*), 5.21 (s, 2H, NCH_2). ^{13}C NMR ($CDCl_3$): δ 155.6 (*C*H_{py}), 149.2 (*C*H_{py}), 137.2 (N*C*HN), 136.9 (*C*H_{py}), 129.4 (*C*H_{py}), 122.6 (*C*H_{py}), 120.7 (*C*H_{imid}), 119.1 (*C*H_{imid}), 51.8 (*C*H_2N).

Synthesis of 1-(2-picolyl)-1'-methyl-3,3'-methylenediimidazolium dibromide (18): Compound **17** (0.50 g, 3.14 mmol) and 1-(2-Bromoethyl)-3-methylimidazolium bromide (0.85 g, 3.14 mmol) in toluene (5 mL) were heated at 100 ^{o}C for 2 d. The solvent was removed under vacuum and the residue was washed with 1:1 DCM/diethyl ether mixture several times to give hygroscopic white solid. (1.1 g, 82 %). ^{1}H NMR (DMSO-d_6): δ 9.16 (s, 1H, NC*H*N), 9.14 (s, 1H, NC*H*N), 8.82 (d, *J* = 5.9 Hz, 1H, py-*H6*), 8.52 (virtual t, 1H, py-*H4*), 7.97 (d, J = 8.1 Hz, 1H, py-*H3*), 7.91 (virtual t, 1H, py-*H5*), 7.72 (s, 1H, CH_{imid}), 7.71 (s, 1H, CH_{imid}), 7.68 (s, 2H, CH_{imid}), 3.89 (s, 2H, NCH_2), 3.88 (s, 4H, NCH_2CH_2N), 2.74 (s, 3H, NCH_3). ^{13}C NMR (DMSO-d_6): δ 153.37 (*C*$_{py}$), 149.54 (*C*H_{py}), 137.50 (*C*H_{py}), 137.38 (N*C*HN), 137.14 (N*C*HN), 129.09 (*C*H_{py}), 128.40 (*C*H_{py}), 123.80 (*C*H_{imid}), 123.65 (*C*H_{imid}), 123.55 (*C*H_{imid}), 122.56 (2C, *C*H_{py}), 122.31 (*C*H_{imid}), 54.95

(CH_2N), 48.49 (NCH_2CH_2N), 48.26 (NCH_2CH_2N), 36.00 (NCH_3). HRMS (*m/z*): calcd for $C_{15}H_{19}Br_2N_5$ $[M\text{-}2Br\text{-}H]^+$: 268.1562, found: 268.1580.

Synthesis of dibromo[1-(2-picolyl)-1'-methyl-3,3'-ethylenediimidazolin-2,2'-diylidene]disilver (19): A suspension of **18** (0.2 g, 0.466 mmol) and one equiv. of Ag_2O (0.108 g, 0.466 mmol) in dichloromethane (15 mL) was stirred at room temperature for 1 d under dinitrogen in the absence of light. The color of the suspension gradually changed from black to light brown. The precipitate was isolated, washed with dichloromethane (3x10 mL) and dried under vacuum to yield **19** as a light brown powder (0.254 g, 85%). ^{1}H NMR (DMSO-d_6): δ 8.51 (br, 1H, py-*H6*), 7.80 (t, *J* = 7.0 Hz, 1H, py-*H4*), 7.52 (s, 1H, CH_{imid}), 7.43 (s, 1H, CH_{imid}), 7.32 (br m, 1H, py-*H3*), 7.26 (s, 1H, CH_{imid}), 7.19 (s, 1H, CH_{imid}), 7.11-7.01 (br m, 1H, py-*H5*), 5.36 (s, 2H, NCH_2) 4.65 (br s, 2H, NCH_2CH_2N), 4.58 (br s, 2H, NCH_2CH_2N), 3.60 (br s, 3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 179.00 (2C, N*C*N), 144.78 (C_{Ar}), 134.21 (C_{Ar}), 129.52 (CH_{Ar}), 124.75 (CH_{Ar}), 123.33 (CH_{imid}), 122.48 (CH_{imid}), 122.03 (CH_{imid}), 120.88 (CH_{imid}), 51.07 (NCH_2CH_2N), 49.94 (NCH_2CH_2N), 38.05 (CH_3), 27.04 ($CH(CH_3)_2$), 23.59 ($CH(CH_3)_2$), 23.40 ($CH(CH_3)_2$).

Synthesis of chloro[1-(2-picolyl)-1'-methyl-3,3'-ethylenediimidazolin-2,2'-diylidene]palladium(II) chloride (20): A suspension of **19** (0.2 g, 0.312 mmol) and $PdCl_2$ (55 mg, 0.312 mmol) in acetonitrile (10 mL) was stirred at 90 ^{o}C for 24 h under dinitrogen. The color of the suspension gradually changed from white to grey. The solution was then filtered to remove the AgBr precipitate. The filtrate was concentrated under vacuum. Upon addition of diethyl ether a pale yellow precipitate was obtained

which was filtered and dried under vacuum to yield **20** as a yellow powder. (92 mg, 55%). ^{1}H NMR (DMSO-d_6): δ 9.03 (d, J = 5.1 Hz, 1H, py-*H6*), 8.16 (virtual t, 1H, py-*H4*), 7.80 (d, 1H, J = 7.7 Hz, py-*H3*), 7.81 (virtual t, 1H, py-*H5*), 7.79 (s, 1H, CH_{imid}), 7.60 (s, 1H, CH_{imid}), 7.48 (s, 1H, CH_{imid}), 7.40 (s, 1H, CH_{imid}), 5.72 (d, J = 15 Hz, 1H, NCH_2), 5.60 (d, J = 15 Hz, 2H, NCH_2), 5.51 (virtual t, 1H, NCH_2), 4.70 (d, J = 15 Hz, 1H, NCH_2CH_2N), 4.46 (d, J = 15 Hz, 1H, NCH_2CH_2N), 4.27 (virtual t, 1H, NCH_2CH_2N), 3.89 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 154.38 ($C_{py(ipso)}$), 152.50 (N*C*N), 152.40 (N*C*N), 150.66 (*C*H_{py}), 140.70 (*C*H_{py}), 125.70 (*C*H_{py}), 124.85 (*C*H_{py}), 124.82 (*C*H_{imid}), 123.77 (*C*H_{imid}), 122.79 (*C*H_{imid}), 121.76 (*C*H_{imid}), 54.47 (*C*H_2N), 50.11 (NCH_2CH_2N), 45.90 (NCH_2CH_2N), 37.57 (*C*H_3). HRMS (*m/z*): calcd for $C_{15}H_{17}Cl_2N_5Pd$ $[M\text{-}Cl]^+$: 408.0201, found: 408.0207.

Synthesis of bromo[1-(2-picolyl)-1'-methyl-3,3'-ethylenediimidazolin-2,2'-diylidene]nickel(II) bromide (21): A suspension of **19** (0.2 g, 0.312 mmol) and $NiBr_2$(DME) (96 mg, 0.312 mmol) in acetonitrile (10 mL) was stirred at 90 ^{o}C for 24 h under dinitrogen. The color of the suspension immediately changed to green. The solution was then filtered to remove the AgBr precipitate. The filtrate was concentrated under vacuum. Upon addition of diethyl ether a greenish yellow precipitate was obtained which was filtered and dried under vacuum to yield **21** as a hygroscopic greenish yellow powder. (91 mg, 60%). ^{1}H NMR (DMSO-d_6): δ 9.11 (d, J = 5.1 Hz, 1H, py-*H6*), 8.04 (virtual t, 1H, py-*H4*), 7.72 (d, 1H, J = 7.6 Hz, py-*H3*), 7.64 (s, 1H, CH_{imid}), 7.72 (virtual t, 1H, py-*H5*), 7.48 (s, 1H, CH_{imid}), 7.34 (s, 1H, CH_{imid}), 7.31 (s, 1H, CH_{imid}), 6.33 (virtual t, 1H, NCH_2CH_2N), 6.30 (d, J = 15 Hz, 1H, NCH_2), 5.66 (d, J = 15 Hz, 1H, NCH_2), 4.83

(d, J = 15 Hz, 1H, $NCH_2C\mathit{H}_2N$), 4.39 (d, J = 15 Hz, 1H, $NCH_2C\mathit{H}_2N$), 4.12 (virtual t, 1H, $NC\mathit{H}_2CH_2N$), 3.97 (s, 3H, $C\mathit{H}_3$). ^{13}C NMR (DMSO-d_6): δ 156.28 ($C_{py(ipso)}$), 154.30 (N*C*N), 154.20 (N*C*N), 152.84 ($C\mathrm{H}_{py}$), 139.90 ($C\mathrm{H}_{py}$), 125.50 ($C\mathrm{H}_{py}$), 124.37 ($C\mathrm{H}_{py}$), 124.09 ($C\mathrm{H}_{imid}$), 124.07 ($C\mathrm{H}_{imid}$), 123.10 ($C\mathrm{H}_{imid}$), 121.75 ($C\mathrm{H}_{imid}$), 53.59 ($C\mathrm{H}_2N$), 49.03 ($NC\mathrm{H}_2CH_2N$), 45.39 ($NCH_2C\mathrm{H}_2N$), 37.70 ($C\mathrm{H}_3$). HRMS (*m/z*): calcd for $C_{15}H_{17}Br_2N_5Ni$ $[M\text{-}2Br+CH_3COO]^+$ (CH_3COOH was used as ionizing agent): 384.0964, found: 384.0956.

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(18) Crystal data for **15·H$_2$O**: $C_{15}H_{25}Br_3N_6O$, FW = 545.14, colorless, triclinic, space group *P*-1, a = 7.2455(4) Å, b = 9.0825(5) Å, c = 16.1017(9) Å, α = 87.026(3)°, β = 83.576(4)°, γ = 86.089(5)°, Z = 2, ρ_{calc}: 1.725 mg/m^3, 12303 collected

reflections, 3699 unique (R_{int} = 0.1003), Final R indices [I> 2σ(I)] were R1 = 0.0731, wR2 = 0.2019. Data was collected at -100 °C on a Nonius Kappa CCD diffractometer, using the COLLECT program. Cell refinement and data reductions used the programs DENZO and SCALEPACK. SHELXS-97 was used to solve the structures and SHELXL-97 was used to refine the structures. ORTEP-3 for Windows was used for molecular graphics and PLATON was used to prepare material for publication. H atoms were placed in calculated positions with U_{iso} constrained to be 1.5 times U_{eq} of the carrier atom for methyl protons and 1.2 times U_{eq} of the carrier atom for all other hydrogen atoms.

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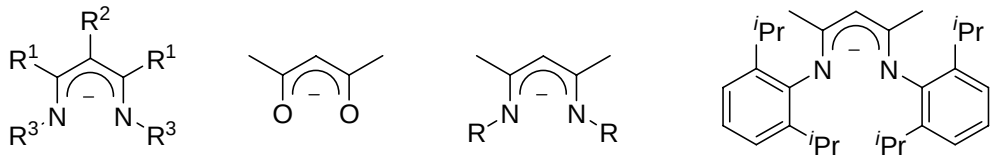
CHAPTER 5

ATTEMPTS TO SYNTHESIZE THREE-COORDINATE PALLADIUM(II) COMPLEXES

5.1 Introduction

β-diketiminato ligands are a class of versatile, bidentate, monoanionic, four electron, nitrogen-donor ligands (**I**). The first examples of complexes using these ligands were synthesized by Canadian researchers in 1968.[1] These ligands have recently gained popularity in coordination chemistry mainly due to the fact that the steric and electronic environments around the metal centre can be easily tuned by varying the substituents on the nitrogen donors of the ligand. These ligand systems have been complexed with elements across the periodic table, which include, s-, p-, d- and f-block elements.[2] Among these ligand systems, the ones derived from the isoelectronic parent ligand acetylacetonate, acac, (**II**), and nicknamed nacnac, (**III**) have become very popular in coordination chemistry (Figure 5-1). These ligands are often synthesized by a simple condensation reaction of a primary amine with 2,4-pentanedione.



I **II** **III** **IV**

Figure 5-1. Acac and nacnac ligands.

The nacnac ligand with bulky 2,6-diisopropylphenyl substituents on the nitrogen donors (**IV**)[3] has been used to stabilize unusual oxidation states and geometries, for example, main group elements such as Mg(I),[4] Al(I),[5] Ga(I),[6] Ge(II)[3b] and In(I)[7] (Figure 5-2); while transition metals in unusual oxidation states include V(I)[8] Cr(I)[9], Cr(II),[10] Ni(I),[11] Zn(I)[12] (Figure 5-3).

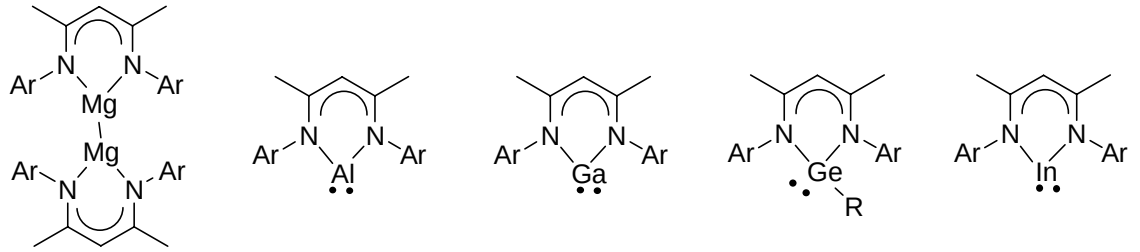


Figure 5-2. Unusual oxidation states of main group elements stabilized using the nacnac ligand (**IV**).

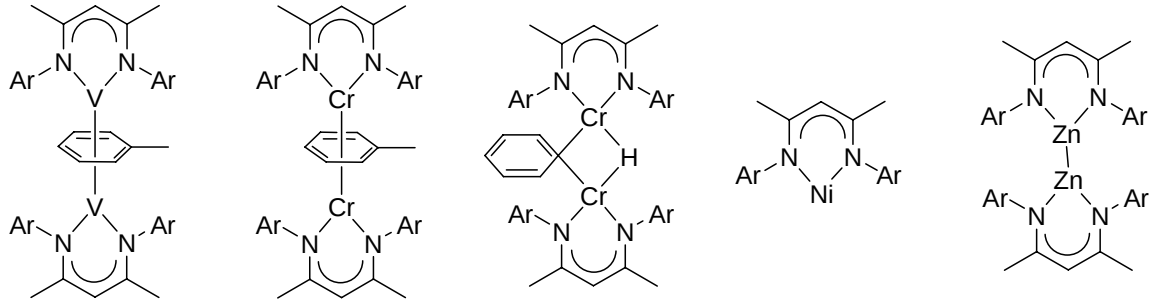


Figure 5-3. Unusual oxidation states of transition elements stabilized using the nacnac ligand (**IV**).

The same ligand has also been used to isolate and characterize rare three-coordinate Fe(II),[13] Cu(II)[14] and Zn(II)[15] and five-coordinate Pt(IV)[16] complexes (Figure 5-4)

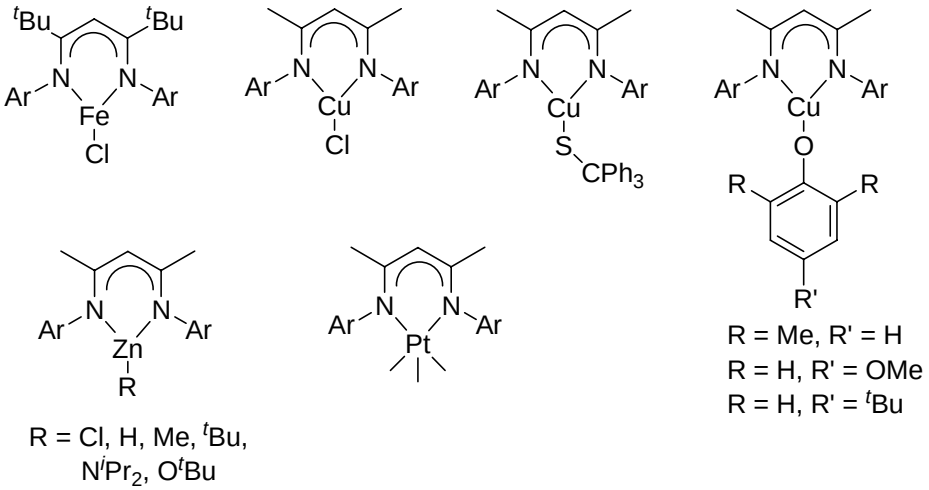
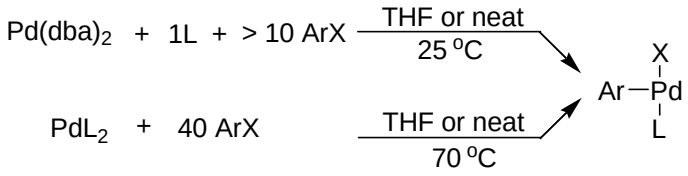


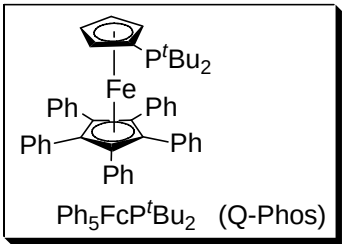
Figure 5-4. Rare coordination geometries of transition metals stabilized using the nacnac ligand (**IV**).

Coordinatively and electronically unsaturated transition-metal complexes are short-lived intermediates in a large number of catalytic reactions.[17] These species containing a vacant coordination site on the metal are extremely difficult to characterize because of their poor stability and high reactivity. Three-coordinate, 14-electron Pd(II) species are proposed intermediates in cross-coupling reactions.[18] They are not common in literature and are believed to be favored when the complexes possess sterically hindered ligands.[19] Hartwig *et al.* have synthesized several three-coordinate 14-electron palladium(II) complexes (Scheme 5-1 and Scheme 5-2).[20] However, all these complexes appear to be stabilized by a weak agostic interaction of the metal with one of the ligand C-H bond positioned at the fourth coordination site of the T-shaped palladium complex.

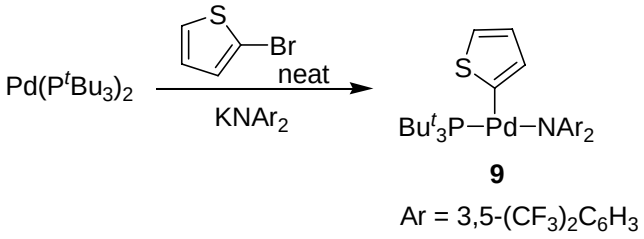
Scheme 5-1. Three-coordinate 14-electron arylpalladium(II) halide complexes.



1: L = 1-AdP^{t}Bu$_2$, X = Br, Ar = Ph
2: L = 2-AdP^{t}Bu$_2$, X = Br, Ar = Ph
3: L = 1-AdP^{t}Bu$_2$, X = I, Ar = Ph
4: L = P^{t}Bu$_3$, X = I, Ar = 2,4-xylyl
5: L = P^{t}Bu$_3$, X = I, Ar = Ph
6: L = P^{t}Bu$_3$, X = Br, Ar = Ph
7: L = Q-Phos, X = Br, Ar = Ph
8: L = Q-Phos, X = I, Ar = Ph



Scheme 5-2. Three-coordinate 14-electron palladium(II) amide complexes.

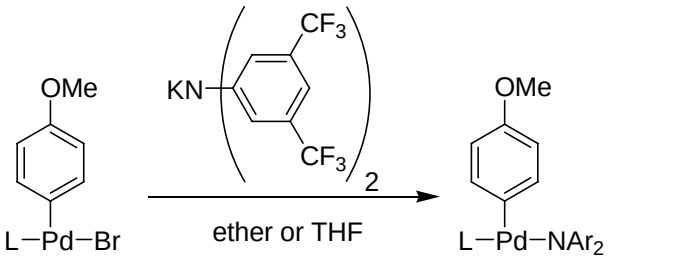


9

Ar = 3,5-$(CF_3)_2C_6H_3$

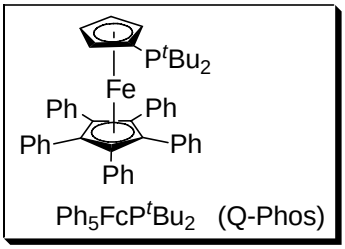
There are only three examples of crystallographically characterized truly three-coordinate Pd(II) complexes without any agostic interactions, **10a-c** (Scheme 5-3).[21]

Scheme 5-3. Three-coordinate 14-electron arylpalladium(II) amide complexes.



10a-c

10a: L = P^{t}Bu$_3$
10b: L = Ph$_5$FcP^{t}Bu$_2$
10c: L = FcP^{t}Bu$_2$
Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$



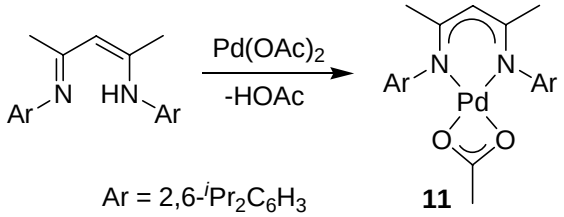
We wanted to synthesize three-coordinate palladium(II) complexes stabilized using the steric bulk of the nanac ligand **IV**. Our rationale was that the steric bulk around the β-diketiminato ligand could facilitate the formation of a three-coordinate Pd(II) complex. There are not many examples of nacnac complexes of palladium in literature.[3,22,23]

This chapter deals with our attempts in synthesizing three coordinate palladium(II) complexes employing the bulky nacnac ligand **IV**.

5.2 Results and Discussion

The bulky (2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnacH ligand was prepared by the condensation of 2,6-diisopropylaniline with acetylacetone according to a literature procedure.[3] The reaction of (2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnacH with one equiv. of Pd(OAc)$_2$ in toluene affords a red solution from which red crystals of [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(μ-OAc) **11**, are isolated in 75% yield (Scheme 5-4). Complex **11** was characterized by NMR, MS and elemental analysis. To better understand the coordination environment and nuclearity of **11**, single-crystal X-ray diffraction experiments were also performed.

Scheme 5-4. Synthesis of [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(μ-OAc) **11**.



The NMR spectra of **11** are consistent with a planar structure and C_{2v} symmetry in solution. The isopropyl groups and the aromatic hydrogen atoms above and below the PdNCCCN plane are equivalent with the isopropyl methyl groups being in chemically distinct environments. The characteristic ^{1}H NMR resonance for the central CH group of the nacnac ligand in **11** is located at 4.84 ppm. The EI mass spectra show an intense molecular ion peak at *m*/*e* 582, consistent with formation of a mononuclear species.

11 co-crystallized with two molecules of dichloromethane. The crystal structure of **11** shows a mononuclear species with the Pd(II) centre adopting a typical square-planar coordination geometry with chelating nacnac and acetato ligands (Figure 5-5). The nacnac and the OAc ligands in **11** are almost exactly co-planar where the dihedral angle between the planes defined by N(1)-Pd(1)-N(2) and O(1)-Pd(1)-O(2) is only 1.4˚. The backbone of the nacnac ligand is also essentially planar as evidenced by the torsional angle defined by Pd1-Ni-C13-C14 of only 0.2˚ and a dihedral angle between the N1-Pd1-N2 and C13-C14-C15 planes of 1.3˚. This is in contrast to a previously reported structure employing less bulky unsubstituted phenyl groups which adopts a dinuclear acetato-bridged structure, $[(2,6\text{-}^{i}Pr_2C_6H_3)_2$nacnac$]Pd(\mu\text{-}OAc)]_2$, with significantly twisted nacnac ligands.[22a] An analogous structure employing an acac ligand in place of the OAc group was, however, reported to be a mononuclear species.[22d]

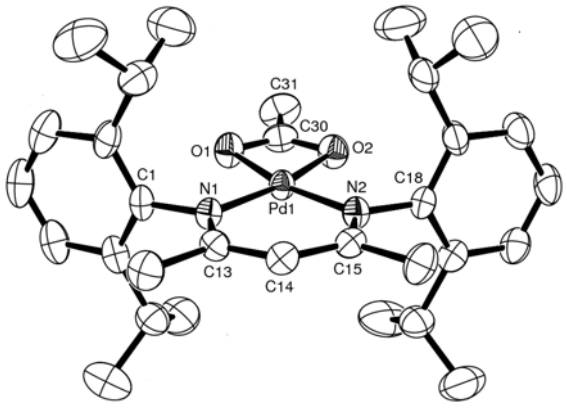
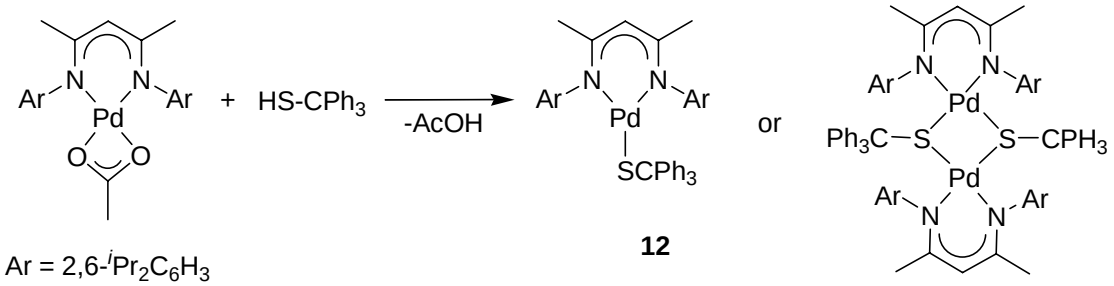


Figure 5-5. ORTEP plot of **11** at the 50% probability level. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)-N(1) = 1.961(4), Pd(1)-N(2) = 1.958(4), Pd(1)-O(1) = 2.108(4), Pd(1)-O(2) = 2.110(4), N(2)-Pd(1)-N(1) = 92.21(17), O(1)-Pd(1)-O(2) = 62.14(15).

As a first step into the synthesis of three-coordinate palladium(II) complexes [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(OAc), **11** was reacted with sterically challenging triphenyl methanethiol. The acetate ligand of the complex was expected to deprotonate the thiol liberating acetic acid and generating complex **12** (Scheme 5-5). The reaction yielded a very air-sensitive dark red compound which was characterized by NMR. The ^{1}H NMR spectrum shows the loss of the thiolate proton and the acetate signal which suggests the formation of a palladium(II) thiolate complex.

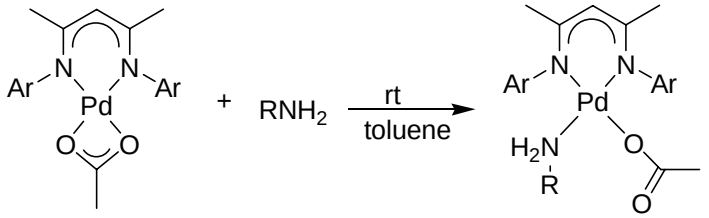
The NMR spectra of **12** are consistent with a planar structure and time-averaged C_{2v} symmetry in solution. The isopropyl groups and the aromatic hydrogen atoms above and below the PdNCCCN plane are equivalent with the isopropyl methyl groups being in chemically distinct environments. The characteristic ^{1}H NMR resonance for the central CH group of the nacnac ligand in **11** is located at 4.89 ppm. Further characterization *via* X-ray crystallography is ongoing. Unfortunately, to date, we have been unable to obtain suitable crystals for X-ray diffraction. In the absence of a crystal structure, two structures can be speculated for the thiolate complex **12**; it could either be a mononuclear three-coordinate palladium(II) thiolate complex or a dinuclear thiolate-bridged palladium(II) complex, which would be unlikely due to the steric bulk of the CPh$_3$ group (Scheme 5-5).

Scheme 5-5. Synthesis of [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(μ-OAc)(HSCPh$_3$) **12**.



As a second step into the synthesis of three-coordinate palladium(II) complexes [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(μ-OAc) **11** was reacted with sterically bulky anilines such as 2,6-diisopropylaniline and 2,6-dimethylaniline, hoping to form the three-coordinate [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(HNAr). However, no reaction was observed despite heating the reaction mixture to 120 ^{o}C. As a result we thought of employing less bulky amines such as aniline, cyclohexylamine, *tert*-butylamine and adamantylamine. The deep red solution of [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(μ-OAc) **11** immediately turned yellow on addition of aniline, cyclohexylamine and *tert*-butylamine at room temperature, while for adamantylamine stirring for two days at room temperature was needed (Scheme 5-6). The resulting complexes **13a-d** had the neutral amine coordinated to the palladium centre and a monodentate acetate ligand. The ^{1}H NMR spectra of **13a-d** gave four sets of doublets for the isopropyl methyl groups and two sets of septets for the isopropyl methylenes showing that the isopropyl groups above and below the PdNCCCN plane are equivalent with the isopropyl methyl groups being in chemically distinct environments. **13a** was crystallized from a saturated solution of dichloromethane and from the crystal structure it was confirmed that the Pd(II) was four-coordinate with a monodentate acetate and a neutral aniline ligand (Figure 5-6). Complex **13c** was interesting in that the coordinated *tert*-butylamine ligand would dissociate under vacuum resulting in the starting complex **11**, which is likely due to the volatile nature of the amine.

Scheme 5-6. Synthesis of [(2,6-$^{i}Pr_2C_6H_3)_2$nacnac]Pd(OAc)(NH_2R), **13a-d**.



Ar = 2,6-$^{i}Pr_2C_6H_3$

13a-d

13a: R = aniline
13b: R = cyclohexylamine
13c: R = *tert*-butylamine
13d: R = adamantylamine

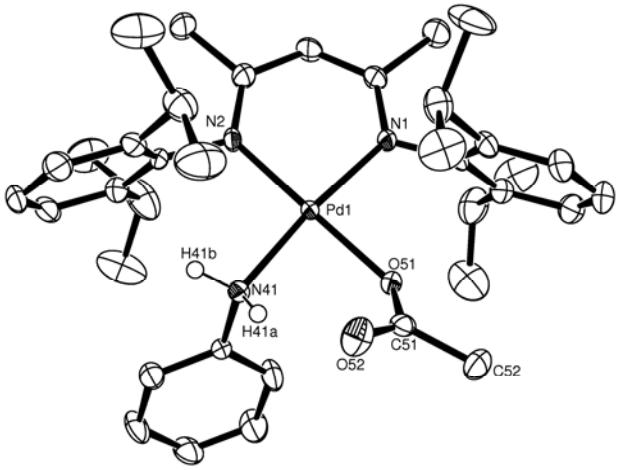
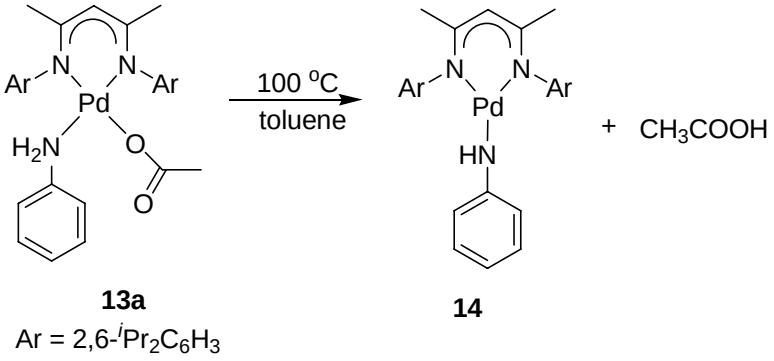


Figure 5-6. ORTEP plot of **13a** at the 50% probability level. Hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Pd(1)-N(1) = 2.017(2), Pd(1)-N(2) = 2.010(2), Pd(1)-O(51) = 2.040(2), Pd(1)-N(41) = 2.096(2), N(1)-Pd(1)-N(2) = 92.58(9), N(1)-Pd(1)-O(51) = 86.69(9), N(2)-Pd(1)-N(41) = 94.83(9), O(51)-Pd(1)-N(41) = 85.99(9).

Complex **13a** was further heated at 90 °C in toluene in an attempt to synthesize the three-coordinate palladium(II) anilido complex **14** (Scheme 5-7). However, the complex has not been well characterized.

Scheme 5-7. Attempt to synthesize [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(NHPh) **14**.

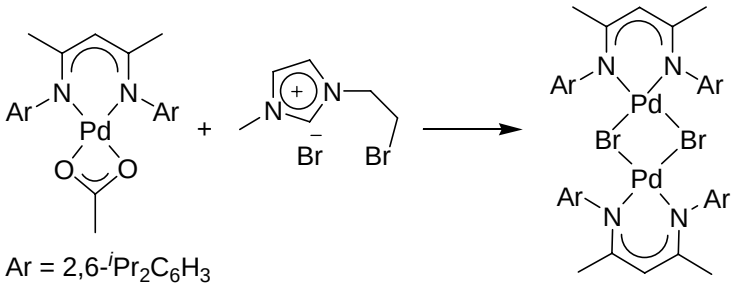


13a
Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$

14

In an effort to synthesize mixed ligand complexes with bulky β-diketiminato ligand and monodentate NHC ligands, [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(μ-OAc) **11**, was reacted with 1-(2-Bromoethyl)-3-methylimidazolium bromide, which resulted in the formation of bromide-bridged Pd(II) complex **15** (Scheme 5-8), rather than formation of an (NHC)Pd(II) complex. The fate of the NHC group was not determined.

Scheme 5-8. Synthesis of {[(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]PdBr}$_2$ **15**.



Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$

15

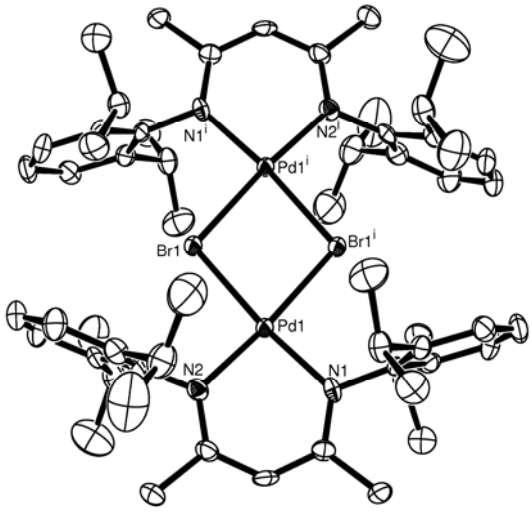
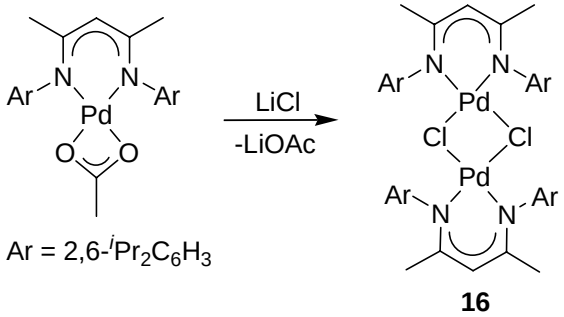


Figure 5-7. ORTEP plot of **15** at the 50% probability level. Hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Pd(1)-N(1) = 2.027(4), Pd(1)-N(2) = 2.026(4), Pd(1)-Br(1) = 2.4682(5), Pd(1)-Br(1)^{i} = 2.4780(6), N(1)-C(13) = 1.326(6), N(2)-C(15) = 1.331(6), N(1)-Pd(1)-N(2) = 91.77(15), N(2)-Pd(1)-Br(1) = 94.53(11), Br(1)-Pd(1)-Br(1)^{i} = 80.15(2).

The chloride-bridged analogue **16** was directly synthesized by reacting [(2,6-$^{i}Pr_2C_6H_3)_2$nacnac]Pd(μ-OAc) **11** with an excess of LiCl (Scheme 5-9). As with complex **15**, complex **16** was also a dinuclear species with bridging chlorides.

Scheme 5-9. Synthesis of ([($^{i}Pr_2$Ph)$_2$nacnac]PdCl)$_2$, **16**.



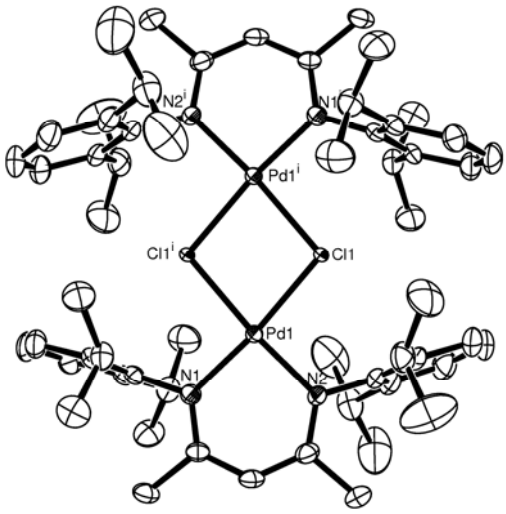


Figure 5-8. ORTEP plot of **16** at the 50% probability level. Hydrogen atoms have been removed for clarity. Selected bond lengths (Å) and angles (°): Pd(1)-N(1) = 2.009(2), Pd(1)-N(2) = 2.014(2), Pd(1)-Cl(1) = 2.3694(7), Pd(1)-Cl(1)^{i} = 2.3857(7), N(1)-C(13) = 1.331(4), N(2)-C(15) = 1.331(4), N(1)-Pd(1)-N(2) = 92.06(10), N(2)-Pd(1)-Cl(1) = 94.07(7), Cl(1)-Pd(1)-Cl(1)^{i} = 80.65(2).

Table 5-1. Crystal data and refinement parameters for compounds **11**·$2CH_2Cl_2$, **13**, **15** and **16**.

	11·$2CH_2Cl_2$	**13**	**15**	**16**
formula	$C_{33}H_{48}Cl_4N_2O_2Pd$	$C_{35}H_{51}O_2N_3Pd$	$C_{58}H_{82}Br_2N_4Pd_2$	$C_{58}H_{82}Cl_2N_4Pd_2$
formula wt	752.93	676.21	1207.90	1118.98
color	red	orange	green	yellow-green
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	14.4850(4)	12.6553(5)	9.2442(3)	9.18900(10)
b, Å	14.9227(5)	18.2267(9)	14.3104(5)	14.2584(2)
c, Å	18.0734(6)	19.8940(7)	22.7030(6)	22.5990(4)
α, deg	90	90	90	90
β, deg	105.0190(12)	124.444(3)	112.0910(19)	111.7670(5)
γ, deg	90	90	90	90
Z	4	4	2	2
ρ_{calc}, mg m^{-3}	1.325	1.187	1.442	1.351
temp, K	173(2)	173(2)	173(2)	173(2)
F(000)	540	1424	1240	1168
θ range, deg	2.98 to 25.02	1.96 to 27.10	2.40 to 26.36	2.64 to 26.73
reflns collected/unique	35015/7419	50675/8345	19242/5693	11386/5827
R_{int}	0.1142	0.1203	0.0977	0.0371
final R_1(I >2σI)	R1 = 0.0612,	R1 = 0.0447	R1 = 0.0428	R1 = 0.0376
R_1(all data)	wR2 = 0.2019	wR2 = 0.1209	wR2 = 0.0972	wR2 = 0.1012

5.3 Conclusions

In conclusion, we have synthesized a new bulky acetato-β-diketiminatopalladium(II) complex employing (2,6-$^{i}Pr_2C_6H_3)_2$nacnac as the ligand resulting in a mononuclear species with chelating monoanionic nacnac and acetato ligands. Attempts have been made to synthesize three-coordinate palladium(II) thiolate and three-coordinate palladium(II) anilido complex. The coordination environment around the metal centre is, as yet, uncertain and has to be investigated using X-ray crystallography.

Future work would include the definitive characterization of the three coordinate Pd(II) thiolate and anilido complexes, mostly by X-ray crystallography.

5.4 Experimental

General Procedures: Unless otherwise stated, all reactions were performed under N_2 using standard Schlenk techniques or in a N_2-filled drybox. Toluene was dried using a MBraun Solvent Purification System and was stored in a glovebox. All reaction temperatures for catalytic reactions refer to the temperature of pre-equilibrated sand baths. ^1H and ^{13}C $\{^1H\}$ NMR spectra were recorded on a Bruker 500 MHz Avance spectrometer. Chemical shifts for ^1H and ^{13}C NMR are reported in ppm in reference to the residual ^1H and ^{13}C resonances of $CDCl_3$ (^1H: δ 7.24; ^{13}C: δ 77.23) and C_6D_6 (^1H: δ 7.16; ^{13}C: δ 128.39). Coupling constants are given in Hz. High resolution mass spectra (HRMS) were measured on an Applied Biosystem QSTAR® XL MS/MS system (ESI-QTOF). Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. 2,6-diisopropylaniline was purchased from Alfa-Aesar Chemical Company and used as received. Aniline, cyclohexylamine, adamantylamine and *tert*-butylamine were purchased from Sigma-Aldrich Chemical Company and used as received. $Pd(OAc)_2$ and $PdCl_2$ were obtained from PMO Pty Ltd, Australia. *N,N*-(2,6-diisopropylphenyl)-2,4-pentanediimine[3] and 1-(2-Bromoethyl)-3-methylimidazolium bromide[24] were synthesized according to literature procedures.

Synthesis of [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(μ-OAc) (11): Under dinitrogen, a Schlenk flask was charged with *N,N*-(2,6-diisopropylphenyl)-2,4-pentanediimine (0.1 g, 0.24 mmol), $Pd(OAc)_2$ (54 mg, 0.24 mmol) and toluene (10mL) and stirred for 24 h at ambient

temperature. The resulting red solution was filtered and the solvent was removed under vacuum to yield a red powder. The compound was crystallized from a saturated methylene chloride solution at -20 ^{o}C (0.104 g, 75%). ^{1}H NMR (C_6D_6): δ 7.12 (t, *J* = 7.5 Hz, 2H, C*H*$_{Ar}$), 7.06 (d, *J* = 7.5 Hz, 4H, C*H*$_{Ar}$), 4.84 (s, 1H, C*H*), 3.72 (sept, 4H, CH(C*H*$_3$)$_2$), 1.72 (d, 12H, CH(C*H*$_3$)$_2$), 1.59 (s, 6H, C*H*$_3$), 1.21 (d, 12H, CH(C*H*$_3$)$_2$), 1.06 (s, 3H, C*H*$_3$CO$_2$) ppm. ^{13}C NMR (C_6D_6): δ 190.0 (CH$_3$*C*O$_2$), 156.0 (*C*=N), 144.5 (*C*H$_{Ar}$), 142.7 (*C*$_{Ar}$), 127.8 (*C*$_{Ar}$), 124.1 (*C*H$_{Ar}$), 96.0 (*C*H), 29.1 (*C*H$_3$), 24.9 (CH(*C*H$_3$)$_2$), 24.1 (CH(*C*H$_3$)$_2$), 22.6 (*C*H(CH$_3$)$_2$), 22.5 (*C*H$_3$CO$_2$). Anal. Calcd for $C_{31}H_{44}N_2O_2Pd$: C, 63.85; H, 7.61; N, 4.80. Found: C, 63.97; H, 7.79; N, 5.05. EI-MS (*m/z*): calcd for $C_{31}H_{44}N_2O_2Pd$ [M]$^{+}$: 582.2, found: 582.0.

Synthesis of [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(SCPh$_3$) (12): Under dinitrogen, a Schlenk flask was charged with [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(μ-OAc) **11** (0.1 g, 0.17 mmol), triphenylmethanethiol (95 mg, 0.34 mmol) and toluene (10mL) and stirred for 2 d at ambient temperature. The resulting dark red solution was filtered and the solvent was removed under vacuum to yield a dark red powder (0.122 g, 90%). ^{1}H NMR (C_6D_6): δ 7.12 (t, *J* = 7.5 Hz, 2H, C*H*$_{Ar}$), 7.06 (d, *J* = 7.5 Hz, 4H, C*H*$_{Ar}$), 4.89 (s, 1H, C*H*), 3.32 (sept, 4H, CH(C*H*$_3$)$_2$), 1.67 (s, 6H, C*H*$_3$), 1.22 (d, *J* = 7.1, 12H, CH(C*H*$_3$)$_2$), 1.17 (d, *J* = 6.9, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6): δ 161.88 (*C*=N), 145.34 (*C*$_{Ar}$), 144.77 (*C*$_{Ar}$), 143.15 (*C*$_{Ar}$), 141.62 (*C*$_{Ar}$), 131.84 (*C*H$_{Ar}$), 130.25 (*C*H$_{Ar}$), 128. 95 (*C*H$_{Ar}$), 127.87 (*C*H$_{Ar}$), 127.19 (*C*H$_{Ar}$), 126.90 (*C*H$_{Ar}$), 126.21 (*C*H$_{Ar}$), 123.95 (*C*H$_{Ar}$), 94.64 (*C*H), 74.85, 57.66 (*C*S), 29.0 (*C*H$_3$), 24.84 (CH(*C*H$_3$)$_2$), 23.79 (CH(*C*H$_3$)$_2$), 21.13 (*C*H(CH$_3$)$_2$).

Synthesis of [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(OAc)(NH$_2$Ph) (13a): Under dinitrogen, a Schlenk flask was charged with [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(μ-OAc) **11** (0.05 g, 0.086 mmol), aniline (16 mg, 0.17 mmol) and toluene (10mL) and stirred for 1 h at room temperature. The solvent was removed under vacuum from the resulting yellow solution to yield a yellow powder. (57 mg, 98%). ^{1}H NMR (C_6D_6): δ 7.12 (d, *J* = 7.5 Hz, 2H, C*H*$_{Ar}$), 7.03 (t, *J* = 7.7 Hz, 2H, C*H*$_{Ar}$), 6.95 (d, *J* = 7.6 Hz, 2H, C*H*$_{Ar}$), 6.88 (t, *J* = 7.6 Hz, 2H, C*H*$_{Ar}$), 6.80 (t, *J* = 7.2 Hz, 1H, C*H*$_{Ar}$), 6.58 (d, *J* = 7.9 Hz, 2H, C*H*$_{Ar}$), 4.88 (s, 1H, C*H*), 3.77 (sept, 2H, C*H*(CH$_3$)$_2$), 3.53 (sept, 2H, C*H*(CH$_3$)$_2$), 2.87 (b s, 2H, NH$_2$), 1.67 (s, 6H, *J* = 7.0, CH(C*H*$_3$)$_2$), 1.65 (s, 3H, C*H*$_3$CO$_2$), 1.49 (s, 6H, C*H*$_3$), 1.43 (s, 3H, C*H*$_3$), 1.21 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.00 (d, *J* = 6.6 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6): δ 180.61 (CH$_3$*C*O$_2$), 158.47 (*C*=N), 157.33 (*C*=N), 147.59 (*C*H$_{Ar}$), 146.58, 145.51, 144.49, 144.08, 143.86, 143.13, 141.88, 127.02, 126.56, 125.63, 125.51, 124.34, 123.73, 96.44 (*C*H), 29.08 (*C*H$_3$), 28.62 (*C*H$_3$), 24.87, 24.62, 24.56, 24.53, 24.14, 23.66, 23.35.

Synthesis of [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(OAc)(NH$_2$cyclohexyl) (13b): Under dinitrogen, a Schlenk flask was charged with [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(μ-OAc) **11** (0.05 g, 0.086 mmol), cyclohexylamine (17 mg, 0.17 mmol) and toluene (10mL) and stirred for 1 h at room temperature. The solvent was removed under vacuum from the resulting yellow solution to yield a yellow powder. (58 mg, 98%). ^{1}H NMR (C_6D_6): δ 7.18 (m, 1H, C*H*$_{Ar}$), 7.12 (d, *J* = 7.7 Hz, 2H, C*H*$_{Ar}$), 7.03-6.93 (m, 3H, C*H*$_{Ar}$), 4.89 (s, 1H, C*H*), 3.86 (b s, 2H, NH$_2$), 3.79 (sept, 2H, C*H*(CH$_3$)$_2$), 3.58 (sept, 2H, C*H*(CH$_3$)$_2$), 1.65 (s, 6H, C*H*$_3$), 1.62 (d, *J* = 6.8, 6H, CH(C*H*$_3$)$_2$), 1.55 (s, 3H, C*H*$_3$), 1.44 (s, 3H, C*H*$_3$), 1.43 (d, 6H, CH(C*H*$_3$)$_2$), 1.22 (d, *J* = 7.0, 6H, CH(C*H*$_3$)$_2$), 1.05 (d, *J* = 6.8, 6H, CH(C*H*$_3$)$_2$), 1.82-0.52

(m, 11H, cyclohexyl). ^{13}C NMR (C_6D_6): δ 179.34 (CH_3CO_2), 158.77 (*C*=N), 157.46 (*C*=N), 146.56 (C_{Ar}), 145.90 (C_{Ar}), 143.86 (CH_{Ar}), 143.80 (CH_{Ar}), 127.01 (CH_{Ar}), 126.26 (CH_{Ar}), 125.03 (CH_{Ar}), 123.61 (CH_{Ar}), 96.26 (*C*H), 52.66 (*C*H), 37.60 (CH_2), 34.28 (CH_2), 29.02 (CH_3), 28.53 (CH_3), 26.00 (CH_2), 24.95, 24.81, 24.72, 24.57, 24.53, 24.40, 24.05. HRMS (*m/z*): calcd for $C_{37}H_{57}N_3O_2Pd$ $[M\text{-}CH_3COO]^+$: 620.3352, found: 620.3348

Synthesis of [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(OAc)(NH$_2$^{t}Bu) (13c): An NMR tube was charged with [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(μ-OAc) **11** (0.025 g, 0.043 mmol), a tiny drop of *tert*-butyamine and C_6D_6 (0.5 mL). The solution immediately turned yellow. ^{1}H NMR (C_6D_6, ppm): δ 7.12 (t, *J* = 8.2 Hz, 1H, C*H*$_{Ar}$), 7.12 (d, *J* = 7.6 Hz, 2H, C*H*$_{Ar}$), 7.02-6.93 (m, 3H, C*H*$_{Ar}$), 4.89 (s, 1H, C*H*), 3.86 (b s, 2H, NH_2), 3.79 (sept, 2H, C*H*$(CH_3)_2$), 3.58 (sept, 2H, C*H*$(CH_3)_2$), 1.64 (s, 6H, C*H*$_3$), 1.63 (d, *J* = 7.0, 6H, CH(C*H*$_3)_2$), 1.53 (s, 3H, C*H*$_3$), 1.43 (d, *J* = 6.8, 6H, CH(C*H*$_3)_2$), 1.40 (s, 3H, C*H*$_3$), 1.21 (d, *J* = 6.8, 6H, CH(C*H*$_3)_2$), 1.05 (d, *J* = 6.8, 6H, CH(C*H*$_3)_2$), 0.84 (s, 9H, C(C*H*$_3)_3$) . ^{13}C NMR (C_6D_6): δ 179.24 (CH_3CO_2), 158.67 (*C*=N), 158.17 (*C*=N), 147.38 (C_{Ar}), 146.08 (C_{Ar}), 144.25 (CH_{Ar}), 144.15 (CH_{Ar}), 127.19 (CH_{Ar}), 126.22 (CH_{Ar}), 125.33 (CH_{Ar}), 123.72 (CH_{Ar}), 96.58 (*C*H), 51.08 (*C*), 31.32 (CH_3), 29.06 (CH_3), 28.67 (CH_3), 25.21 (CH_3), 24.93, 24.89, 24.79, 24.65, 23.86, 23.78.

Synthesis of [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(OAc)(NH$_2$adamantyl) (13d): Under dinitrogen, a Schlenk flask was charged with [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(μ-OAc) **11** (0.05 g, 0.086 mmol), adamantylamine (19.5 mg, 0.13 mmol) and toluene (10mL) and stirred for 2 day at room temperature. The solvent was removed under vacuum from the

resulting reddish yellow solution to yield a reddish yellow powder. (62 mg, 98%). ^{1}H NMR (C_6D_6, ppm): δ 7.23-7.09 (m, 2H, CH_{Ar}), 7.08-6.98 (m, 4H, CH_{Ar}), 4.89 (s, 1H, C*H*), 3.93 (b m, 2H, C*H*$(CH_3)_2$), 3.81(b m, 2H, C*H*$(CH_3)_2$), 1.98-1.18 (m, 44H), 1.05 (d, *J* = 6.7 Hz, 6H, CH(C$H_3)_2$). ^{13}C NMR (C_6D_6): δ 179.24 (CH_3CO_2), 158.61 (*C*=N), 158.32 (*C*=N), 144.40, 144.13, 127.83, 127.12, 126.17, 125.32, 123.94, 123.69, 96.63 (*C*H), 47.47, 47.10, 43.60, 37.05, 36.31, 30.64, 30.53, 29.09, 28.73, 25.29, 24.98, 24.92, 24.88, 24.84, 24.78, 24.73, 24.23, 24.05, 23.78.

Synthesis of ([(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]PdBr)$_2$ (15): Under dinitrogen, a Schlenk flask was charged with [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(μ-OAc) **11** (0.1 g, 0.17 mmol), 3-(2-Bromoethyl)-1-methylimidazolium bromide (69 mg, 0.26 mmol) and toluene (10mL) and stirred for 24 h at 110 ^{o}C. The resulting green solution was filtered and the solvent was removed under vacuum to yield a green powder. The compound was crystallized from a saturated methylene chloride solution (92 mg, 98%). %). ^{1}H NMR (C_6D_6): δ 7.01 (t, *J* = 8.2 Hz, 2H, CH_{Ar}), 6.94 (d, *J* = 7.7 Hz, 4H, CH_{Ar}), 4.73 (s, 1H, C*H*), 3.44 (sept, 4H, CH(C$H_3)_2$), 1.50 (s, 6H, CH_3), 1.48 (d, *J* = 7.0 Hz, 12H, CH(C$H_3)_2$), 1.11 (d, *J* = 6.8 Hz, 12H, CH(C$H_3)_2$).

Synthesis of ([(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]PdCl)$_2$ (16): Under dinitrogen, a Schlenk flask was charged with [(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$nacnac]Pd(μ-OAc) **11** (0.1 g, 0.17 mmol), LiCl (0.145 g, 3.4 mmol) and toluene (10mL) and stirred for 24 h at 110 ^{o}C. The resulting green solution was filtered and the solvent was removed under vacuum to yield a green powder. The compound was crystallized from a saturated methylene chloride solution (82 mg,

95%). ^{1}H NMR (C_6D_6): δ 7.05 (t, *J* = 7.5 Hz, 4H, C*H*$_{Ar}$), 6.90 (d, *J* = 7.5 Hz, 8H, C*H*$_{Ar}$), 4.72 (s, 2H, C*H*), 3.40 (sept, 8H, CH(C*H*$_3$)$_2$), 1.51 (d, *J* = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.45 (s, 12H, C*H*$_3$), 1.11 (d, *J* = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6): δ 156.45 (*C*=N), 146.35 (*C*H$_{Ar}$), 143.02 (*C*$_{Ar}$), 127.23 (*C*$_{Ar}$), 124.39 (*C*H$_{Ar}$), 95.05 (*C*H), 28.91 (*C*H$_3$), 25.15 (CH(*C*H$_3$)$_2$), 24.51 (CH(*C*H$_3$)$_2$), 23.93 (*C*H(CH$_3$)$_2$). HRMS (*m/z*): calcd for $C_{58}H_{82}N_4Cl_2Pd$ $[M+H]^+$: 1119.4069, found: 1119.4337.

X-ray structure determinations: Data was collected at -100 °C on a Nonius Kappa CCD diffractometer, using the COLLECT program.[25] Cell refinement and data reductions used the programs DENZO and SCALEPACK.[26] SIR97 was used to solve the structures and SHELXS-97[27] was used to refine the structures. ORTEP-3 for Windows [28] was used for molecular graphics and PLATON[29] was used to prepare material for publication. H atoms were placed in calculated positions with U_{iso} constrained to be 1.5 times U_{eq} of the carrier atom or methyl protons and 1.2 times U_{eq} of the carrier atom for all other hydrogen atoms.

5.5 References

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CHAPTER 6

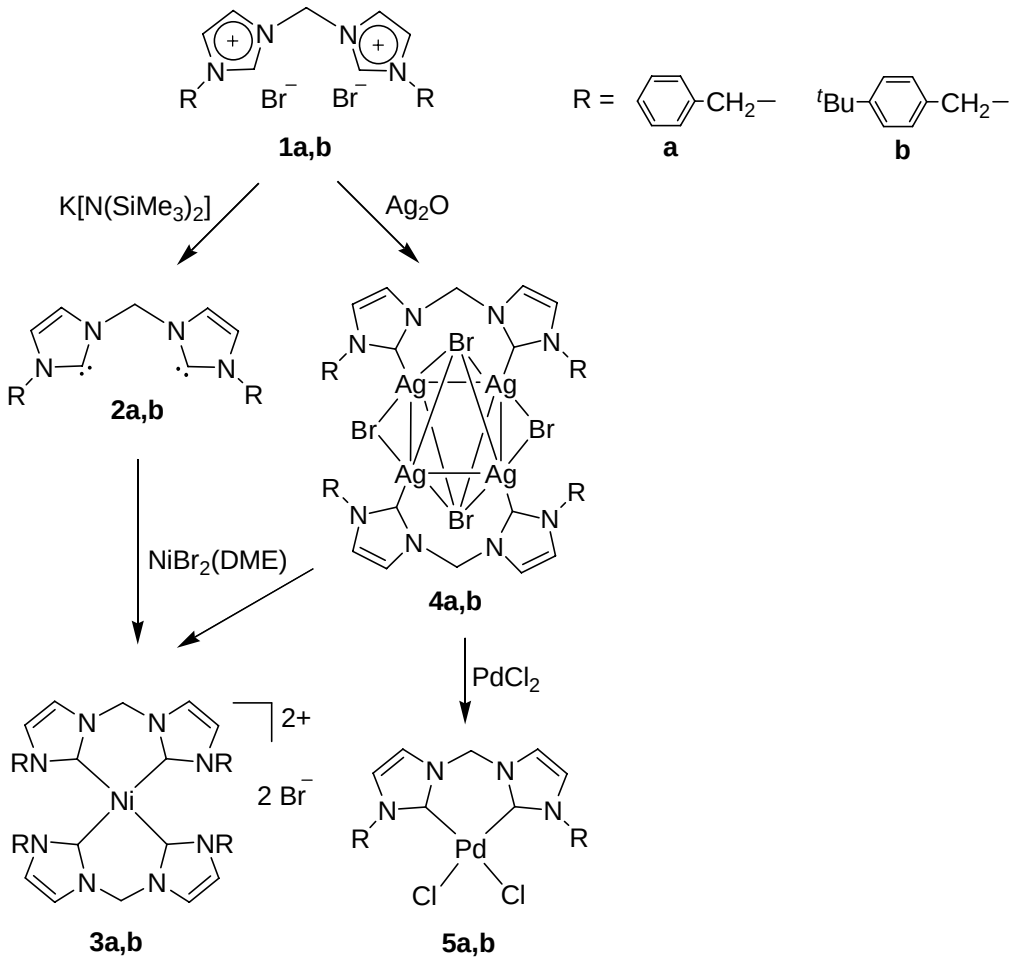
SUMMARY, CONCLUSIONS AND FUTURE WORK

The first research goal for this Ph.D. project was to investigate the catalytic potential of nickel as an alternative to the more expensive palladium systems in carbon-carbon coupling reactions. Pursuing our first research objective, we have synthesized stable diNHC complexes of Ni(II) and Pd(II) *via* both the free carbene route and the silver transmetallation route (Scheme 6-1).

There are very few examples in literature of well-defined nickel complexes that have been employed for C-C coupling reactions and they all exhibit TONs below 100. Palladium systems, in comparison, have exhibited TONs ranging from 1000 to 10^6.

The catalytic potential of the nickel(II) complex, **3a**, was investigated in Mizoroki-Heck and Suzuki-Miyaura coupling reactions (Chapter 2). The complex was found to be an active precatalyst in Mizoroki-Heck and Suzuki-Miyaura coupling reactions. However, long reaction times (2-3 days) and relatively high catalyst loadings (5 mol%) were required. A TON of 10 was obtained in the Heck coupling reaction of butyl acrylate with bromobenzene. In the Suzuki coupling reactions of phenylboronic acid, a TON of 20 was obtained with bromobenzene, 8 with 4-bromoacetophenone, 7 with chlorobenzene and 6 with 4-chloroacetophenone. The nickel precatalyst, **3a**, was also found to be active in the coupling of phenylboronic acid with aryl fluorides. The palladium analogue, **5a**, was not active for the coupling of aryl fluorides.

Scheme 6-1. Synthesis of diNHC complexes of Ag(I), Ni(II), and Pd(II).



To investigate if a nickel species was indeed the active catalyst, several control experiments were performed with butyl acrylate and iodobenzene as the coupling partners. Surprisingly, it was found that quantitative yields could be obtained with Na_2CO_3 as well as NEt_3 *in the absence* of nickel species and/or Bu_4NI. However, Na_2CO_3 was not active for Mizoroki-Heck coupling reactions with aryl bromides. Thus all investigations were carried out with aryl bromides; as aryl iodides can be easily coupled in the absence of a nickel precatalyst. For the Suzuki-Miyaura reaction, it was found that

aryl iodides and aryl bromides could be activated *in the absence* of nickel species when K_3PO_4 was used as base.

This finding emphasizes the importance of performing control reactions when assessing the catalytic activity of a potential nickel precatalyst, as the base employed, or more likely transition metal impurities in the base, can also act as a coupling agent in the absence of nickel precatalysts. The commercially obtained Na_2CO_3 and NEt_3 that were used in our experiments were analyzed for palladium and nickel content by ICP and the results indicated that Ni and Pd levels were <5 ppm (the detection limit of the ICP instrument used). The active species in these "transition metal free" experiments is most likely sub-ppm levels of palladium contaminants.

Nickel definitely appears to be a promising alternative to palladium for catalytic carbon-carbon bond forming reactions. However, further research is essential to not only improve activity at the metal center, but more importantly, to better understand the nature of the active species.

The second research goal was to synthesize non-symmetrically substituted diNHC ligands with a hemi-labile donor arm on one of the nitrogen atoms as shown in Figure 6-1.

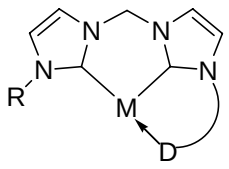


Figure 6-1. NHC complexes with hemi-labile donor arm, D.

Hemi-labile NHCs incorporate both a strongly binding NHC moiety and a hemi-labile heteroatom donor. The rationale behind the design of non-symmetrically substituted diNHC ligands with a hemi-labile functionalized neutral donor arm was that the hemi-labile arm or the weakly coordinating arm would allow the formation of a vacant coordination site which plays an important role in catalytic reactions.

While the preparation of diverse symmetrically substituted diNHC ligands have been reported, there were no examples of non-symmetrically substituted diNHC ligands in literature where R ≠ R' (Figure 6-2).

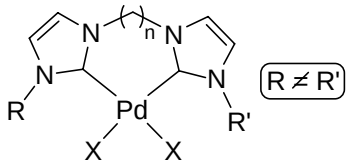
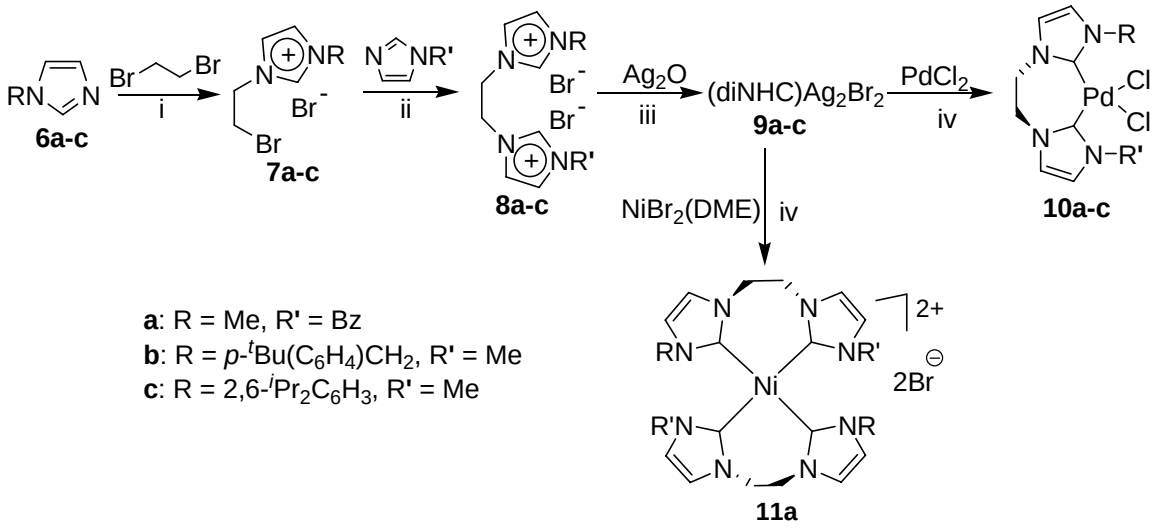


Figure 6-2. Non-symmetrically substituted (diNHC)PdX_2

Since such non-symmetrically substituted diNHCs did not exist in literature, we first set out to design a general synthetic route to non-symmetrically substituted diNHC ligands. We developed a general route into the synthesis of non-symmetrically substituted diNHC ligands, as discussed in *Chapter 3*. Non-symmetrically substituted diNHC ligands and their palladium(II) and nickel(II) complexes have been synthesized *via* the silver transmetallation route, as shown in Scheme 6-2. This synthetic route represents a general pathway into a wide variety of non-symmetrically substituted diNHC ligands. These examples of non-symmetrically substituted chelating diNHC ligand can serve in designing NHC ligands with fine-tuned steric and electronic environments around the metal centre.

Scheme 6-2. Synthesis of non-symmetric (diNHC)$PdCl_2$ complexes.



Conditions: (i) neat, 2 d, 80 °C; (ii) toluene, 3 d, 80-150 °C; (iii) dichloromethane, 2 h, rt; (iv) DMF, 24 h, 90 °C

The catalytic activity of the non-symmetrically substituted (diNHC)Pd(II) complex, **10a**, was investigated in the Suzuki-Miyaura coupling reaction of bulky substrates (Chapter 3). High to moderate yields were obtained for mono and di *ortho*-substituted biaryls provided the steric bulk was incorporated on only one of the coupling partners. No coupled product was obtained when both partners were sterically hindered.

Since we developed a general route into the synthesis of non-symmetrically substituted diNHC ligands as discussed in *Chapter 3*, our next goal was to synthesize non-symmetrically substituted diNHC ligands with a hemi-labile donor arm on one of the nitrogen atoms as shown in Figure 6-1.

Based on the available literature on NHC ligands with hemi-labile donor arms and the synthetic route we developed for non-symmetrically substituted diNHC ligand precursors, we designed two diNHC ligand precursors with a hemi-labile donor arm as

one of the nitrogen substituents; one with an imino arm and the second with a pyridine arm as shown in Figure 6-3 (Chapter 4).

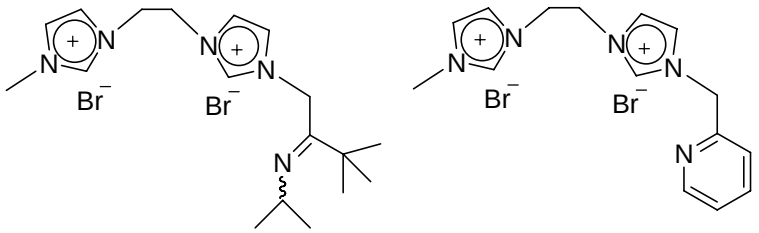
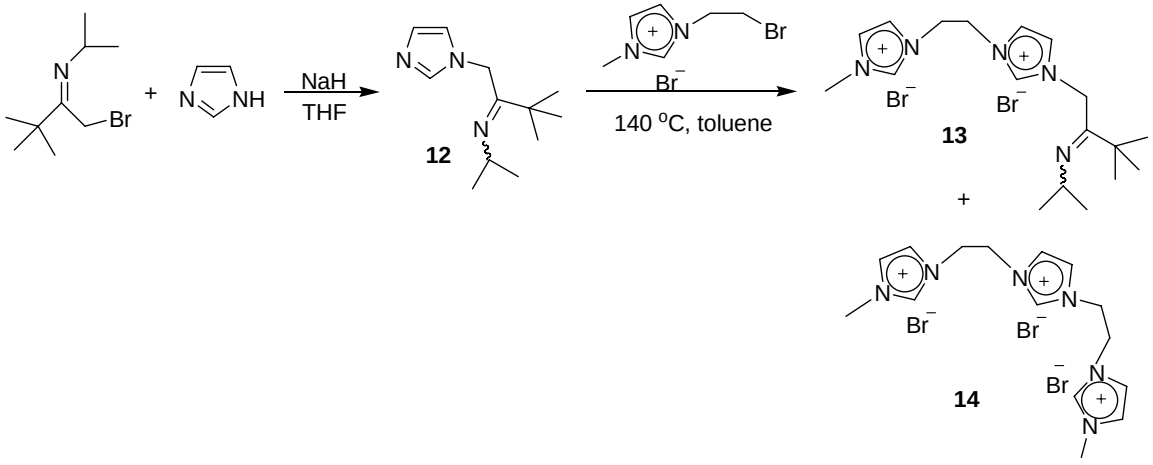


Figure 6-3. DiNHC ligand precursors with hemi-labile donor arms.

The non-symmetrically substituted diimidazolium salt with the imino arm, however, contained a triimidazolium tribromide, **14**, as a side product (Scheme 6-3).

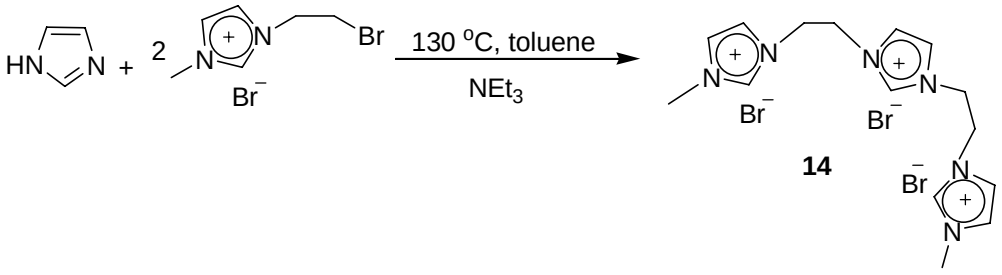
Scheme 6-3. Synthesis of non-symmetric dimidazolium salt with an imino arm.



The triimidazolium salt, **14**, was later intentionally synthesized by the reaction of two equiv. of 1-(2-Bromoethyl)-3-methylimidazolium bromide with an equiv. of imidazole in the presence of excess triethylamine (Scheme 6-4). There are very few

examples of triNHC ligands in literature. **14** can be a useful ligand precursor for synthesizing triNHC complexes.

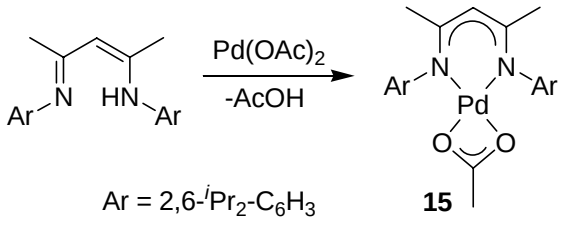
Scheme 6-4. Synthesis of of triimidazolium salt **14**.



We have also synthesized non-symmetrically substituted diNHC ligand precursor with hemi-labile pyridine arm on one of the nitrogens and their corresponding silver(I), palladium(II) and nickel(II) complexes. Although the complexes have been characterized *via* spectroscopic techniques, the coordination environment around the metal centre is, as yet, uncertain and has to be investigated using X-ray crystallography (Chapter 4). Unfortunately, to date, we have been unable to grow suitable crystals for X-ray studies.

As a side project, the synthesis of three-coordinate Pd(II) complexes using sterically bulky β-diketiminato ligand was also attempted. For this purpose, we synthesized a new bulky acetato-β-diketiminatopalladium(II) complex, **15**, employing $(2,6\text{-}^{i}Pr_2C_6H_3)_2$nacnac as the ligand resulting in a mononuclear species with chelating monoanionic nacnac and acetato ligands. (Scheme 6-5).

Scheme 6-5. Synthesis of [(2,6-$^{i}Pr_2C_6H_3)_2$nacnac]Pd(μ-OAc) **11**.



Complex **15**, was then reacted with sterically bulky triphenyl methanethiol and anilines, hoping to form the three-coordinate thiolate complex, [(2,6-$^{i}Pr_2C_6H_3)_2$nacnac]Pd($SCPh_3$), and three-coordinate anilido complex, [(2,6-$^{i}Pr_2C_6H_3)_2$nacnac]Pd(NHR). The coordination environment around the metal centre for these species is, as yet, uncertain and has to be investigated using X-ray crystallography.

In conclusion, through this Ph.D. research project we have successfully pursued the two goals that were laid out in the research objectives. We have demonstrated that nickel could be a potential alternative to palladium catalysts in C-C coupling reactions. Although the activity of the nickel complex pales in comparison to the palladium systems, better understanding of the catalytic mechanism and nature of the active species is essential to improve the catalytic activity at the metal centre.

We have also developed a general route into the synthesis of non-symmetrically substituted diNHC ligand precursors, which has opened the possibilities of designing new diNHC ligand systems. Development of non-symmetrically substituted diNHC ligand precursors with a hemi-labile donor arm has also been achieved and their corresponding Ni(II) and Pd(II) complexes have been synthesized. However, due to time constraints it was not possible to study the potential of these complexes in C-C coupling reactions for this thesis work.

As future work it will be essential to explore the activity of both the nickel and palladium complexes with hemi-labile pyridine arm in C-C coupling reactions. This work will be continued by my colleagues in the Foley group.